Alkali-Metal Sandwich Complexes of a 1,2-Diaza-3,5-diborolyl Ligand Featuring η^1, η^2, η^3, and η^4 Coordination Modes

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The ring closure of 1,2-diisopropylhydrazine and 1,1-bis(phenylchloroboryl)ethane produced a heterocyclic compound with a CB_2N_2 framework. Deprotonation of this precursor yielded 1,2-diisopropyl-4-methyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl, a cyclopentadienyl analogue containing only one carbon atom in the ring skeleton. Lithium, sodium, and potassium salts of the new ligand have been prepared and characterized. The structures of both monomeric and polymeric sodium metallocenes, as well as the structures of polymeric potassium metallocenes incorporating the new heterocycle, have been determined by single-crystal X-ray diffractometry. These structures reveal not only many similarities but also significant differences in the coordination behavior of the new ligand compared with that of the carbon-based analogue.

Introduction

On the quest to tune the electronic properties of the cyclopentadienyl ligand, various five-membered heterocyclic analogues have been obtained by the formal replacement of carbon atoms in the ring skeleton with isoelectronic main-group fragments. Relatively soon after the first report on sandwich compounds, metal complexes containing monoanionic ligands with C_4E skeletons were isolated. Complexes with E belonging to group 15,[1] including pyrrolyl,[2] phospholyl,[3] arsolyl,[4] stibolyl,[5] and bismolyl,[6] have been synthesized. Similar complexes incorporating the heavier group 14 elements silicon[7] and germanium[8] have been known since the mid-1990s. Anionic C_3BN, C_3BO, and C_3BS rings were obtained through the formal substitution of two carbon fragments, RC, in the cyclopentadienyl framework with the pairs (RB^-, $R'N^+$)[9] and (RB^-, O^+)[10] in the 1,2-positions, and (RB^-, S^+)[11] in the 1,2- and 1,3-positions. These rings were shown to have coordinative properties similar to those of cyclopentadienyl and proved to be feasible ancillary ligands in transition-metal catalysts.[12] Heterocyclic anionic ligands with a P_nC_{5-n} ($n = 2 - 4$) skeleton, which display a rich coordination chemistry, have been prepared through the formal substitution of RC fragments with phosphorus atoms.[13] Carbon-free cyclopentadienyl analogues of the type E_5^- have been reported for E = P, As, Sb,[14] and the coordination chemistry of the lighter derivatives has been thoroughly investigated.[15] With the exception of the group 15 derivatives described above, few cyclopentadienyl analogues containing more than two heteroelements in the ring framework have been described. Recently, Sekiguchi isolated the lithium salt of a C_2-

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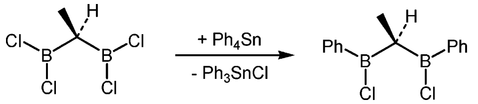
$GeSi_2$ ligand,[16] and we reported on the synthesis of lithium and zinc complexes containing a heterocycle with a CB_2N_2 skeleton.[17]

Alkali-metal salts are among the most common precursors to complexes containing cyclopentadienyl ligands,[18] and several of these salts of pnictogen-containing cyclopentadienyl analogues have been structurally characterized. For ligands incorporating boron, however, only two structures of lithium derivatives containing ligands with C_3BN[19] and CB_2N_2[17] skeletons have been reported. We were interested in developing new ligands with inorganic skeletons and investigating their coordination chemistry. Reported herein are the syntheses and structural characterization of alkali-metal salts containing a new cyclopentadienyl analogue with a CB_2N_2 framework, as well as the complete structural discussion of the recently communicated lithium 1,2-diisopropyl-4-methyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl (**2a**).[17]

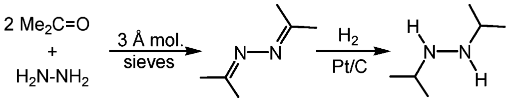
Results and Discussion

The 1,2-diaza-3,5-diborolyl ligand **1** was prepared in a fashion similar to that for its analogue featuring methyl groups on boron[17] and was preferred because of the lower solubility and better crystallization properties of its complexes. The symmetric diphenylation of $MeCH(BCl_2)_2$[17,20] with tetraphenyltin (eq 1)



(1)

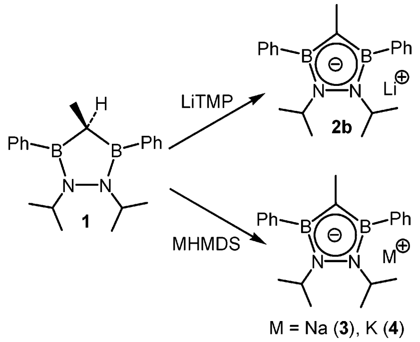
was achieved by using a variation of the method described for $H_2C(BCl_2)_2$, and the product was purified by distillation.[21] In the ^{11}B NMR spectrum, $MeCH(BPhCl)_2$ displayed a broad signal at 66.9 ppm. For the synthesis of symmetric diisopropylhydrazine, the ketazine obtained through condensation of hydrazine with acetone was hydrogenated with molecular hydrogen in the presence of platinum deposited on carbon, as shown in eq 2.[22]

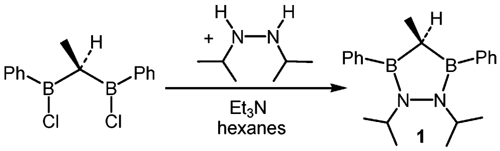


(2)

The air-sensitive product was dried on amalgamated aluminum foil. Ring closure between $MeCH(BPhCl)_2$ and diisopropylhydrazine occurred easily in hexane in presence of triethylamine (eq 3), and **1** was obtained as a colorless, viscous liquid that could not be distilled but had satisfactory purity according to NMR data.

Scheme 1





(3)

Deprotonation of **1** occurred quantitatively in THF in the presence of strong bases, yielding the salts **2b**, **3**, and **4** (Scheme 1). These salts were soluble in THF and sparingly soluble in diethyl ether but insoluble in hydrocarbons. Deprotonation resulted in a shift in the ^{11}B NMR signal from 46 ppm in **1** to 38−39 ppm in the alkali-metal salts. Additionally, a dramatic low-field shift was observed for the broad ^{13}C NMR signal corresponding to the ring carbon, from 26.8 ppm in the protonated form of the ligand, **1**, to 91.5−96.8 ppm in **2b**, **3**, and **4**. This is typical for metal cyclopentadienyl complexes with pronounced ionic character. For example, in pentamethylcyclopentadiene, deprotonation results in a shift of the analogous carbon signal from 52.2 ppm (in C_6D_6) to 105.2 ppm (Cp^*Na in THF-d_8). The ^{1}H NMR spectra of all salts described here featured only one doublet for the methyl groups of the isopropyl substituents on nitrogen, indicating that the coordination environments on both faces of the ligand are identical on the NMR time scale. This would be in agreement with a solvent-separated ion-pair structure in solution, consisting of free anionic ligands and solvated alkali-metal ions. The ^{7}Li NMR spectrum of **2b** in THF-d_8 further supports this hypothesis, featuring a chemical shift typical for $[Li(thf)_4]$ (−2.8 ppm).[17]

Structural determinations by single-crystal X-ray diffractometry have been performed for the compounds **3**, **3a** (**3**•3thf), **4a** (**4**•thf), and **4b** (**4**•2thf) (Table 1). The metric parameters of the π ligand (Table 2) display little variation among all of the structures discussed in this paper. The ring is practically planar in **2a**, with a sum of the intraannular bond angles of 539.9°. The planarity of the CB_2N_2 ring (Figure 1) is relatively good also in the structures of **3a**, **4a**, and **4b** (sum of bond angles of 539.4−539.6°). However, careful examination reveals a slight folding (6−7°) along one of the transannular B−N axes, resulting in an envelope conformation. The substituents on the ring carbon and boron atoms lie in the plane of the ring, with the extraannular C−C and B−C bonds forming angles of less than 4° with the ring plane. The isopropyl groups in structures **3a**, **4a**, and **4b** lie noticeably above and below the ligand plane, with the extraannular N−C bonds forming angles of 26−33° with the plane of the ring. The ligand geometry in **3** deviates slightly from this generalization, with the sum of the intraannular bond angles being 539.2°, a folding angle of the envelope conformation of 8.5°, and the B(2)−C(15) and N(1)−C(3) bonds forming angles of 6.1 and 12.5°, respectively, with the best plane of the CB_2N_2 ring. In **2a**, only one of the isopropyl groups lies outside the ligand plane, which forms angles of 2.4 and 23.2° with the two N−C bonds.

At 1.50 Å, the intraannular B−C bonds are 0.1 Å shorter than the corresponding extraannular bonds and comparable to

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Table 1. Selected Data and Structure Refinement Details for 3, 3a, 4a, and 4b

	3	**3a**	**4a**	**4b**
empirical formula	$C_{20}H_{27}B_2N_2Na$	$C_{32}H_{51}B_2N_2NaO_3$	$C_{24}H_{35}B_2KN_2O$	$C_{28}H_{43}B_2KN_2O_2$
formula wt	340.05	556.36	428.26	500.36
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	Cc	Pn
a (Å)	11.711(2)	17.466(4)	6.055(1)	11.852(7)
b (Å)	10.170(2)	9.358(2)	17.628(5)	6.165(2)
c (Å)	17.149(3)	20.269(4)	22.867(6)	20.203(1)
β (deg)	106.34(3)	90.48(3)	96.50(2)	96.06(2)
V (Å^3)	1959.8(7)	3313(1)	2425(1)	1468(1)
Z	4	4	4	2
d_{calcd} (g cm^{-3})	1.152	1.116	1.173	1.132
μ (mm^{-1})	0.085	0.080	0.236	0.207
θ range (deg)	2.35−25.03	3.19−27.49	3.5−27.5	3.5−27.5
no. of indep rflns	3418 ($R_{int} = 0.027$)	7579 ($R_{int} = 0.061$)	2759 ($R_{int} = 0.023$)	3335 ($R_{int} = 0.043$)
no. of data/restraints/params	3431/0/230	7579/0/366	2759/2/271	3335/2/316
GOF on F^2	1.070	1.016	1.05	1.03
R1 ($I > 2\sigma(I)$)	0.0528	0.0593	0.036	0.053
wR2 ($I > 2\sigma(I)$)	0.1274	0.138	0.090	0.122

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

	2a (M = Li)	**3** (M = Na)[a]	**3a** (M = Na)	**4a** (M = K)	**4b** (M = K)
C(1)−B(1)	1.513(4)	1.514(3)	1.494(3)	1.503(4)	1.491(7)
C(1)−B(2)	1.498(4)	1.496(3)	1.498(3)	1.506(3)	1.486(6)
B(1)−N(1)	1.457(4)	1.452(3)	1.460(3)	1.458(4)	1.465(6)
B(2)−N(2)	1.479(4)	1.481(3)	1.453(3)	1.459(3)	1.465(6)
N(1)−N(2)	1.466(3)	1.449(2)	1.460(3)	1.444(3)	1.456(5)
C(1)−C(2)	1.519(4)	1.526(3)	1.521(3)	1.516(3)	1.530(6)
B(1)−C(9)	1.589(4)	1.581(3)	1.589(3)	1.595(4)	1.579(7)
B(2)−C(15)	1.593(4)	1.590(3)	1.586(3)	1.589(4)	1.584(6)
N(1)−C(3)	1.485(3)	1.482(3)	1.479(3)	1.481(3)	1.476(5)
N(2)−C(6)	1.481(3)	1.489(3)	1.471(3)	1.473(3)	1.472(5)
M(1)−C(1)	2.225(6)	2.801(2)	2.616(2)	3.058(2)	3.127(4)
M(1a)[a]−C(1)	2.480(6)	2.624(5)−2.755(5)		3.033(2)	3.156(4)
M(1)···C(2)	2.786(6)	3.744(4)	3.139(3)	3.321(3)	3.247(4)
M(1a)···C(2)	3.622(6)	3.296(5)−3.644(5)		3.331(3)	3.203(4)
M(1)−B(1)	2.543(6)	2.884(2)	2.874(2)	3.211(3)	3.802(4)
M(1)−B(2)	2.750(6)	2.629(2)	3.101(3)	3.752(3)	3.425(4)
M(1a)−B(1)	2.370(6)	2.517(5)−2.654(5)		3.477(3)	3.364(4)
M(1a)−B(2)	2.354(6)	3.971(5)−3.399(5)		3.315(3)	3.895(4)
M(1)−N(1)	2.075(5)	2.872(2)	3.351(2)	3.898(3)	4.419(4)
M(1)−N(2)	2.112(5)	2.610(2)	3.540(2)	4.256(2)	4.143(4)
M(1a)−N(1)	3.313(6)	2.766(5)−3.144(5)		3.992(3)	4.131(4)
M(1a)−N(2)	3.179(6)	3.077(5)−3.695(6)		3.832(3)	4.483(4)
M(1)−O(1)			2.333(2)−2.344(2)	2.733(2)	2.726(4), 2.816(4)
M(1)···M(1a)	4.381(8)	5.01(1)−5.21(1)		6.055(3)	6.165(4)
B(1)−C(1)−B(2)	106.9(3)	104.9(2)	103.7(2)	103.3(2)	104.2(4)
C(2)−C(1)−B(1)	126.4(3)	128.5(2)	129.7(2)	129.6(2)	128.8(4)
C(2)−C(1)−B(2)	126.6(3)	126.6(2)	126.5(2)	127.1(2)	126.9(4)
C(1)−B(1)−N(1)	107.5(3)	108.3(2)	110.0(2)	109.8(2)	110.1(4)
C(1)−B(1)−C(9)	128.3(3)	129.2(2)	128.0(2)	126.7(2)	127.4(4)
C(9)−B(1)−N(1)	124.2(3)	122.5(2)	121.9(2)	123.5(2)	122.5(4)
C(1)−B(2)−N(2)	107.6(2)	109.2(2)	109.8(2)	110.1(2)	110.0(4)
C(1)−B(2)−C(15)	128.8(3)	126.3(2)	126.2(2)	126.0(2)	127.6(4)
C(15)−B(2)−N(2)	123.4(3)	123.5(2)	124.0(2)	123.8(2)	122.4(4)
B(1)−N(1)−N(2)	109.6(2)	109.8(2)	107.5(2)	108.5(2)	107.4(3)
B(1)−N(1)−C(3)	123.4(3)	125.7(2)	121.6(2)	126.0(2)	125.3(3)
C(3)−N(1)−N(2)	119.0(2)	120.3(2)	116.3(2)	112.8(2)	112.2(3)
B(2)−N(2)−N(1)	108.3(2)	107.1(2)	108.5(2)	107.9(2)	107.7(3)
B(2)−N(2)−C(6)	125.1(2)	124.4(2)	126.9(2)	124.6(2)	123.9(3)
C(6)−N(2)−N(1)	118.7(2)	114.7(2)	113.9(2)	111.3(2)	112.0(3)
$\Sigma_{pentagon\ angles}$	539.9	539.2	539.5	539.6	539.4

[a] In complex **3**, M(1a) is M(2), as shown in Figure 3.

the B−C bonds featured by 1,2-azaborolinyl[9] and boratabenzene[23] complexes (1.48−1.53 and 1.50−1.55 Å, respectively). The B−N bonds (1.46 Å) are intermediate in length between the B−N bonds observed in borazines (1.42−1.44 Å)[24] and 1,2-azaborolinyl complexes (1.46−1.50 Å),[9] indicating partial multiple-bond character. At 1.45−1.46 Å, the N−N bonds are much closer in length to a single bond (1.45 Å in hydrazine)[25] than to a double bond (1.34 Å in pyridazine).[26] For comparison, the N−N bonds in η^5-pyrazolato ligands measure 1.38−1.40 Å.[27] It appears, therefore, that the electron delocalization on the N−B−C−B−N skeleton does not extend over the N−N bond. The pyramidal arrangement at the nitrogen centers is nevertheless puzzling, given the multiple-bond character of the B−N bonds; one contributing cause to this geometry could be the steric strain between the bulky isopropyl substituents.

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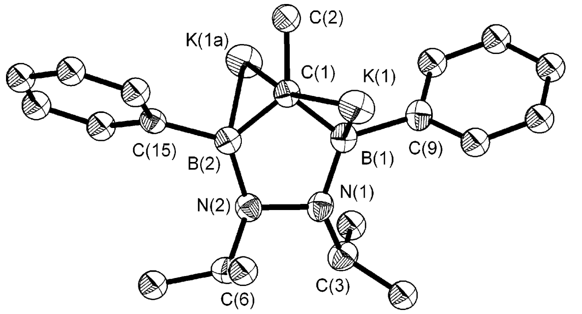

Figure 1. Fragment from the polymeric structure of **4a**, showing the structure of the ligand and the relative position of the coordinated metal centers. The thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms have been omitted for clarity.

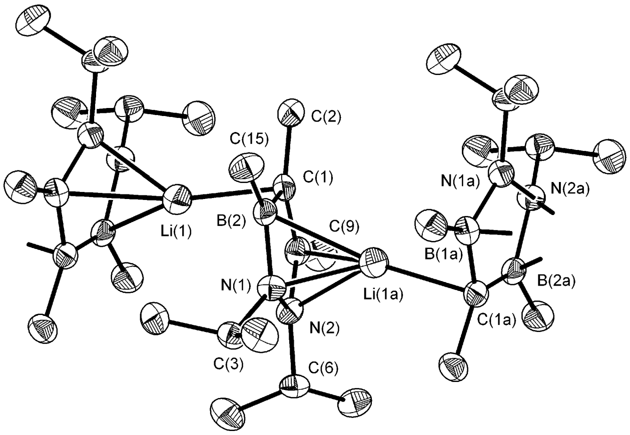

Figure 2. Structure of the polymeric chain of **2a** in the solid state. The hydrogen atoms have been omitted for clarity.

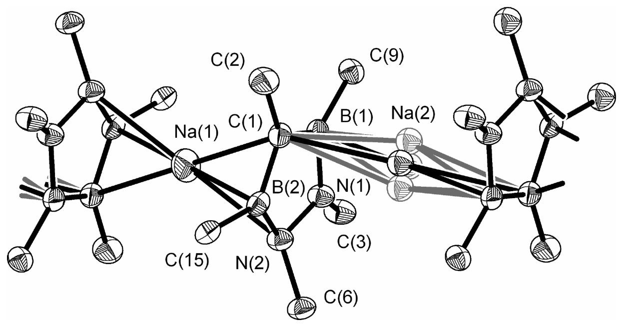

Figure 3. Structure of a fragment of the polymeric chain of **3**, with thermal ellipsoids drawn at the 50% probability level. For clarity, only the α-carbon atoms in the organic substituents are represented and all hydrogen atoms have been omitted.

In a previous communication we reported the crystallographic structural determination of **2a** (Figure 2),[17] which revealed a polydecker sandwich structure with a bifacially coordinating ligand, typical for solid, base-free alkali-metal cyclopentadienyls.[18] Atypically for cyclopentadienyls, though, the bridging ligand coordinates to lithium in an η^1 fashion with one face and an η^4 fashion with the other face. The η^1 coordination of the lithium ion involves a short bond to carbon (2.225(6) Å), while the η^4 coordination is comprised of two short bonds to nitrogen (2.075(5) and 2.112(5) Å) and two bonds to boron (2.354(6) and 2.369(6) Å). The Li−N bond lengths are shorter than those observed in lithium complexes containing η^5-coordinating 1,2-azaboryl (2.142(7) Å)[19] and pyrrolyl type ligands (2.161(4), 2.185(1) Å).[28] In polymeric lithium cyclopentadienyls, the Li−C bond distances range from 2.22 to 2.37 Å,[29] while the Li−B and Li−C bond distances in sandwich complexes containing η^5-coordinated five-membered boron heterocycles are in the ranges 2.18−2.42 and 2.05−2.41 Å, respectively.[30] In lithium boratabenzene sandwiches, the Li−B and Li−C bonds are somewhat longer, usually in the ranges 2.45−2.58 and 2.30−2.56 Å, respectively.[31] Although the coordination mode in **2a** has been described as $\mu,\eta^3:\eta^4$,[17] the Li(1)−B(1) and Li(1)−B(2) distances (2.543(6) and 2.751(6) Å) are situated outside the typical range observed for Li−B bonds in related compounds, and the binding mode is more accurately described as $\mu,\eta^1:\eta^4$ (Figure 7). At 2.480(6) Å, the Li(1a)−C(1) separation is greater than all Li−C distances observed in polymeric lithiocenes containing carbon-based ligands. The alternating ligand planes form angles of 21.4° with each other, and the consecutive rings are staggered at an angle of 180°. The distance between neighboring lithium ions (4.381(8) Å) is larger than in polymeric lithiocenes incorporating carbon-based ligands (3.9−4.0 Å),[29] and the lithium ions are closer to the plane of the η^4 face (1.861(5) Å) than to the plane of the η^1 face (2.196(5) Å).

A polydecker sandwich structure in the solid state is found also for the solvent-free sodocene **3** (Figure 3). The structure is slightly disordered, with one of the two independent sodium ions, Na(2), occupying several different positions in relation to the anion. This sodium ion was modeled as a 27:23 isotropic mixture; the remaining two positions are generated by symmetry. While Na(1) is symmetrically coordinated between the η^3 faces of the perfectly parallel ligands, Na(2) is disordered around an η^2 position with respect to the other face of the ligands, resulting in an $\mu,\eta^2:\eta^3$ coordination mode (Figure 7). The separation between neighboring metals is 5.01(1)−5.21(1) Å; for comparison, in reported polymeric sodium cyclopentadienyls, the Na···Na distance is between 4.61 and 4.86 Å for solvent-free

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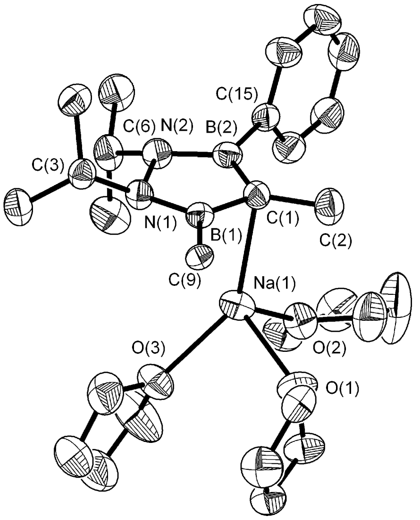

Figure 4. Molecular structure of **3a**, with thermal ellipsoids drawn at the 50% probability level. For clarity, in one of the phenyl substituents only the ipso carbon atom is represented, and all hydrogen atoms have been omitted.

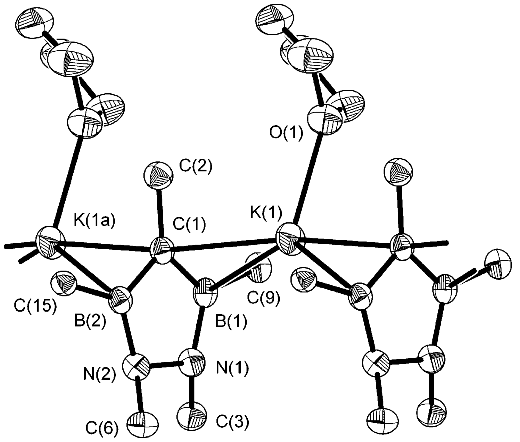

Figure 5. Structure of the polymeric chain of **4a** in the solid state, with thermal ellipsoids drawn at the 50% probability level. For clarity, only the α-carbon atoms in the organic substituents are represented and all hydrogen atoms have been omitted.

structures[29b,c,32g] and between 4.89 and 5.21 Å for structures containing solvated sodium.[32] The disorder of the metal ion prevents a detailed discussion of the η^2 coordination of Na(2) in **3**. The η^3 coordination of Na(1) is comprised of one short bond to nitrogen (2.612(2) Å), one bond to carbon (2.801(2) Å), and one relatively short bond to boron (2.631(2) Å). The Na−C distances in sodium cyclopentadienyls typically range from 2.60 Å to over 3.20 Å, with the shortest Na−C bond in each complex being between 2.616(9) and 2.795(2) Å.[29b,32] Sodocenes featuring five-membered, boron-containing π ligands have not been structurally characterized to date; however, a couple of sodium boratabenzene structures are available for comparison.[33a,b] In the latter complexes, the Na−B distances are much longer than in **3**, being 2.910(6) and 2.976(2) Å, while the Na−C distances range between 2.732(2) and 3.000(2) Å. The Na−B distances are significantly longer (2.896(3) and 3.130(3) Å) also in a dimeric Na salt featuring the $Et_6C_2B_4H^-$ ligand.[33c] In a complex featuring π-coordinating pyrazolyl ligands, the Na−N distances are 2.494(2)−2.638(2) Å, and in a complex containing π coordinating pyrrolyl ligands the Na−N separation is 2.694(1) Å.[34] The Na(1)−N(1) and Na(1)−B(1) distances (2.872(2) and 2.884(2) Å, respectively) are substantially longer than the bonding interactions described above, and therefore the bonding mode of the ligand is best described as η^3 (Figure 7).

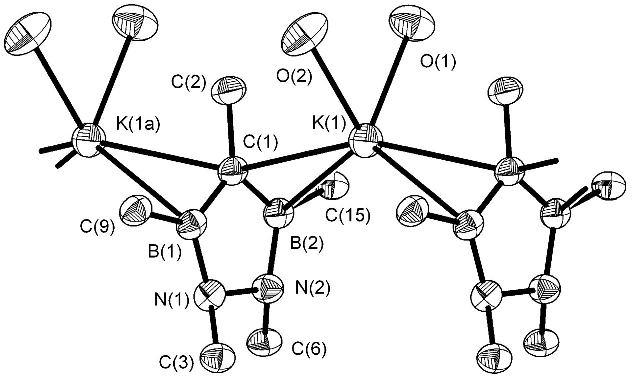

Figure 6. Structure of the polymeric chain of **4b** in the solid state, with thermal ellipsoids drawn at the 50% probability level. For clarity, only the α-carbon atoms in the organic substituents are represented and all hydrogen atoms, as well as the methylene groups in THF, have been omitted.

In contrast to **2a** and **3**, **3a** is monomeric in the solid state and features a piano-stool structure, with the sodium cation being coordinated by the π ligand and three tetrahydrofuran molecules (Figure 4). The Na−O bonds (2.333(2)−2.344(2) Å) and O−Na−O angles (87−100°) fall in the typical ranges for solvated sodium cations. At 2.616(2) Å, the Na−C bond is comparatively short,[32] and in fact shorter bonds (2.544(3)−2.575(6) Å) have been observed only for dicyclopentadienylsodium anions, a solvent-free cyclopentadienylsodium derivative, and a strained-geometry cyclopentadienylsodium species featuring a pendant aza macrocycle.[35] The sodium atom in **3a** is positioned above the B(1)−C(1) bond (Figure 4), and therefore the Na(1)−B(2) distance is considerably longer than the Na(1)−B(1) distance (3.101(3) vs 2.874(2) Å). Both distances, however, are more than 0.3 Å longer than the Na(2)−B(1) bond in **3**, and therefore the binding mode of the heterocyclic ligand in **3a** is best described as η^1. The shortest Na−N distance is more than 3.35 Å, and the distance of the metal to the ligand plane is 2.609(2) Å.

Compounds **4a** and **4b** are polymeric in the solid state, featuring polydecker sandwich structures containing potassium ions intercalated with parallel, π-coordinating diazadiborolidine

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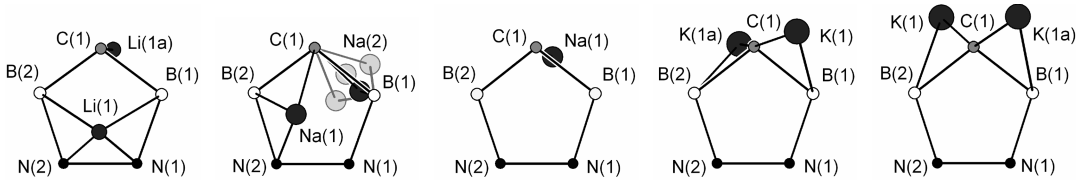

Figure 7. Perpendicular projections onto the CB_2N_2 plane, revealing the hapticities of the ligands (from left to right): **2a** ($\mu,\eta^1{:}\eta^4$), **3** ($\mu,\eta^2{:}\eta^3$), **3a** (η^1), **4a** ($\mu,\eta^2{:}\eta^2$), and **4b** ($\mu,\eta^2{:}\eta^2$).

ligands (Figures 5 and 6). This is not typical for polymeric potassium cyclopentadienyls, which usually display bent geometries with nonparallel ligands.[18] The main difference between the two structures is the number of tetrahydrofuran molecules completing the coordination sphere of each of the potassium ions: one in **4a** and two in **4b**. With lengths between 2.723(2) and 2.816(4) Å, the K−O bonds fall in the usual range. The multidecker sandwich structure in **4a**, where potassium ions have a lower coordination number, is more compact, with a K···K separation of 6.055(3) Å versus 6.165(4) Å in **4b**. For comparison, the K···K distance in bent, polymeric potassium cyclopentadienyls is between 5.52 and 5.85 Å.[29b,32c,h,35b,36]

Uncharacteristic for alkali-metal cyclopentadienyls, the potassium ions in **4a** and **4b** are not contained between the ligands but are instead situated outside of the columns formed by the parallel CB_2N_2 rings, alternating on both sides in the vicinity of the two endocyclic C−B bonds (Figure 7). The K−C bond distances are 3.033(2) and 3.058(2) Å in **4a** and 3.127(4) and 3.156(4) Å in **4b**. In polymeric potassium cyclopentadienyls, the K−C distances range from 2.95 to over 3.30 Å, with the shortest K−C bond in each complex being between 2.952(2) and 3.074(7) Å.[29b,32c,h,35b,36] The potassium ions are closer to one of the boron atoms of each of the coordinating ligands. The two shorter K−B distances are 3.211(3) and 3.315(3) Å in **4a** and 3.364(4) and 3.425(4) Å in **4b**, while the longer K−B distances are 3.477(3) and 3.752(3) Å in **4a** and 3.802(4) and 3.895(4) Å in **4b**. Potassium borole salts have not been structurally characterized, but a few potassium borata- and diboratabenzene complexes displaying monomeric and polymeric sandwich structures have been reported. The K−B distances in these complexes fall between 3.062(13) and 3.686(6) Å, while the K−C distances are situated between 2.952(3) and 3.572(5) Å.[37] Taking into account the geometry and bond distances, it appears that the best description for the bonding of the diazadiborolidine ligands in **4a** and **4b** is $\mu,\eta^2{:}\eta^2$. The K−N distances are greater than 3.8 Å.

The distances between potassium and the methyl substituents of the ring carbon are quite short as a result of the unusual position of the potassium ions, on the outside of the columns formed by the CB_2N_2 rings (Figure 5 and 6). The K−C(2) distances range between 3.203(4) and 3.331(3) Å, only 0.05−0.30 Å longer than the K−C(1) bonds and shorter than some of the distances between potassium and the ring carbon in polymeric potassium cyclopentadienyls (2.95 Å to over 3.30 Å).[29b,32c,h,35b,36] This geometry is not observed in any of the other compounds described in this paper or in other reported potassium sandwich compounds.

Conclusion

Two cyclopentadienyl analogues with a CB_2N_2 framework, 1,2-diisopropyl-4-methyl-3,5-dimethyl-1,2-diaza-3,5-diborolyl and 1,2-diisopropyl-4-methyl-3,5-diphenyl-1,2-diaza-3,5-diborolyl, have been synthesized, and their coordination chemistry toward alkali metals was investigated. The results reveal substantial similarities but also important differences with respect to the all-carbon analogues. In agreement with the ^{13}C NMR data, the structural analyses indicate electron delocalization over the NBCBN skeleton. The intraannular B−C and B−N distances are intermediate in length between those corresponding to single and double bonds; however, the N−N bond lengths are typical for single bonds. The latter observation, together with the fact that the substituents on nitrogen feature significant deviations from the ring plane, implies that the electron delocalization over the ring framework does not extend over the N−N bond. Similar to cyclopentadienyl, the new π ligands coordinate face-on, forming monomeric (**3a**) and polymeric (**2a**, **3**, **4a**, **4b**) sandwich complexes. The distances separating the metal ions are systematically larger in the compounds described herein than in the polymeric cyclopentadienyl analogues, indicating the lower coordinating ability of the new ligands. These ligands nevertheless exhibit a remarkable variability in their coordination manner, and because the ring atoms have different radii, the assignment of the coordination mode is not unequivocal. Taking into account the geometry and bond distances reported in the literature, η^1 (C), η^2 (BC), η^3 (NBC), and η^4 (BNNB) coordination modes have been assigned. Relatively short bonding distances between the metal and the ring carbon are present in all compounds, while only some of the complexes feature short distances between the metal and boron or nitrogen. By comparison, the cyclopentadienyl ligand displays almost exclusively the η^5 coordination in alkali-metal sandwich complexes. No trends regarding the preference of the ligand for a specific coordination mode can be formulated at this point, but it appears obvious that the energetic differences between various coordination modes are small. This is not unexpected, given the predominantly ionic character of the bonding in the complexes described herein. The coordination ability of the new ligands toward main-group and transition metals is currently under investigation.

Experimental Section

General Considerations. All operations were performed under an argon atmosphere using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated prior to use. Starting materials were prepared according to reported procedures or purchased from commercial suppliers. 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), C_6D_6 (^{13}C, 128.39 ppm), THF-d_8 (^{13}C, 67.57 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. Elemental analyses of compounds **1**−**4** failed to produce satisfactory results, potentially due to boron carbide formation under the sample burning conditions.

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Synthesis of 1,1-Bis(chlorophenylboryl)ethane. Bis(chloroboryl)ethane[17,20] (5.31 g, 27.7 mmol) was added to Ph_4Sn (7.90 g, 18.5 mmol), and the neat mixture was stirred at ambient temperature for 2 h. Subsequently, the colorless suspension was heated and maintained at 80 °C overnight. Vacuum distillation yielded $PhSnCl_3$ at 60−80 °C/0.1 Torr and the desired product at 100−115 °C/0.10 Torr, as a colorless liquid (6.50 g, 85%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 1.51 (d, 3H, $^3J_{HH}$ = 6.6 Hz, $HCCH_3$), 3.22 (q, 1H, $^3J_{HH}$ = 6.6 Hz, $HCCH_3$), 7.01−7.16 (m, 6H, *m*-, *p*-C_6H_5), 7.98 (d, 4H, *o*-C_6H_5). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ 66.9 (s, br, $LW_{1/2}$ = 454 Hz).

Synthesis of $Me_2C{=}NN{=}CMe_2$. Hydrazine (10 g, 0.312 mol) was slowly mixed with acetone (100 mL) under external cooling, in a flask containing molecular sieves (3 Å, 100 g). The mixture was left sitting at ambient temperature for 24 h, and then the solution was decanted and distilled at atmospheric pressure. The product was collected as a clear colorless liquid at 134 °C (26.7 g, 74%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 1.80 (d, 12H, CCH_3).

Synthesis of 1,2-Diisopropylhydrazine. A Parr hydrogenation apparatus was loaded with $Me_2C{=}NN{=}CMe_2$ (26.7 g, 0.238 mol), ethanol (36 mL), acetic acid (5.35 mL), and the Pt/C catalyst (10%, 100 mg). The apparatus was deoxygenated and stirred under 5 bar of H_2 for 24 h. The resulting mixture was filtered, and the filtrate was decomposed with HCl solution (12.1 M, 50 mL). Volatiles were removed in vacuo, and the residue was dissolved in water (60 mL) and treated with solid KOH (34.0 g, 0.606 mol). The product was extracted with diethyl ether (3 × 50 mL), and the united extracts were dried over amalgamated aluminum foil and distilled at atmospheric pressure, yielding an air-sensitive colorless liquid boiling at 124 °C (16.4 g, 59%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 0.97 (d, 12H, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$), 2.34 (s, br, 2H, NH), 2.74 (sep, 2H, $^3J_{HH}$ = 6.2 Hz, $CH(CH_3)_2$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ 21.6 (s, $CH(CH_3)_2$), 50.9 (s, $CH(CH_3)_2$). The NMR data correlate with the reported values.[38]

Synthesis of 1,2-Diisopropyl-1,2-diaza-3,5-diphenyldiborolidine (1). A solution of 1,1-diisopropylhydrazine (1.27 g, 10.9 mmol) and triethylamine (2.21 g, 21.8 mmol) in hexane (30 mL) was slowly added to a stirred solution of 1,1-bis(chlorophenylboryl)ethane (3.00 g, 10.9 mmol) in hexane (20 mL). The mixture was stirred at ambient temperature for 12 h, and the white precipitate was filtered off. Volatiles were removed under full vacuum, leaving behind the product as a thick colorless liquid (2.46 g, 71%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 1.12 (d, 3H, $^3J_{HH}$ = 6.8 Hz, $HCCH_3$), 1.13 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 1.14 (d, 6H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 3.91 (sep, 2H, $^3J_{HH}$ = 6.9 Hz, $CH(CH_3)_2$), 7.20−7.31 (m, 6H, *m*-, *p*-C_6H_5), 7.46 (d, 4H, *o*-C_6H_5). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 9.32 (s, CCH_3), 24.0, 24.2 (s, $CH(CH_3)_2$), 26.8 (s, br, CCH_3), 49.4 (s, $CH(CH_3)_2$), 127.9 (s, *p*-C_6H_5), 128.2 (s, *m*-C_6H_5), 133.0 (s, *o*-C_6H_5), 141.8 (s, br, *i*-C_6H_5). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): δ 46.0 (s, br, $LW_{1/2}$ = 552 Hz). MS (EI+, 70 eV; *m/z* (%)): 318 (100) $[M]^+$, 303 (88) $[M-Me]^+$, 190 (48) $[M - (iPrN)_2Me + H]^+$.

Synthesis of (1,2-Diisopropyl-1,2-diaza-3,5-diphenyldiborolyl)lithium (2b). A yellow solution of lithium 2,2,6,6-tetramethylpiperidide (LiTMP), formed in situ from 1.6 M *n*-butyllithium in hexane (3.20 mL, 5.12 mmol) and tetramethylpiperidine (TMP; 0.724 g, 5.12 mmol) in THF (3 mL), and a solution of **1** (1.63 g, 5.12 mmol) in THF (20 mL) were precooled to −35 °C for 1 h. The precooled solutions of **1** and LiTMP were mixed and kept at −35 °C for 12 h. The solvent was removed under vacuum, producing a pale yellow residue, which was washed several times with hexane (30 mL) and dried under vacuum. The product was obtained as an off-white powder (680 mg, 41%). ^1H NMR (400 MHz, THF-d_8, 25 °C): δ 1.07 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.72 (s, 3H, CCH_3), 3.80 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 6.90 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-C_6H_5), 7.06 (t, 4H, $^3J_{HH}$ = 7.3 Hz, *m*-C_6H_5), 7.45 (d, 4H, $^3J_{HH}$ = 7.3 Hz, *o*-C_6H_5). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 14.7 (s, CCH_3), 23.9 (s, $CH(CH_3)_2$), 50.7 (s, $CH(CH_3)_2$), 94.8 (s, br, CCH_3), 124.1 (s, *p*-C_6H_5), 126.6 (s, *m*-C_6H_5), 135.1 (s, *o*-C_6H_5), 151.2 (s, br, *i*-C_6H_5). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 37.9 (s, br, $LW_{1/2}$ = 600 Hz). ^7Li NMR (155 MHz, THF-d_8, 25 °C): δ −2.8 (s, $LW_{1/2}$ = 14 Hz).

Synthesis of (1,2-Diisopropyl-1,2-diaza-3,5-diphenyldiborolyl)sodium (3). A solution of **1** (200 mg, 0.629 mmol) in THF (20 mL) was added to a stirred solution of sodium bis(trimethylsilyl)amide (NaHMDS; 115 mg, 0.629 mmol) in THF (15 mL), forming a yellow mixture, which was stirred at ambient temperature for 1 day to ensure the reaction had completed. The volatiles were removed under vacuum, producing a colorless solid, which was washed twice with hexane (30 mL) and dried under vacuum. The product was obtained as a colorless powder (159 mg, 75%). ^1H NMR (400 MHz, THF-d_8, 25 °C): δ 1.12 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.75 (s, 3H, CCH_3), 3.90 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 6.98 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-C_6H_5), 7.13 (t, 4H, $^3J_{HH}$ = 7.3 Hz, *m*-C_6H_5), 7.46 (d, 4H, $^3J_{HH}$ = 7.3 Hz, *o*-C_6H_5). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 13.9 (s, CCH_3), 23.9 (s, $CH(CH_3)_2$), 50.5 (s, $CH(CH_3)_2$), 91.5 (s, br, CCH_3), 125.0 (s, *p*-C_6H_5), 127.1 (s, *m*-C_6H_5), 135.0 (s, *o*-C_6H_5), 149.2 (s, br, *i*-C_6H_5). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 39.1 (s, br, $LW_{1/2}$ = 667 Hz).

Colorless block crystals of **3a** that were suitable for X-ray diffraction analysis were obtained by storing a concentrated solution of **3** in THF/hexane at −35 °C for a few days. Colorless thin plates of **3** were obtained by slow room-temperature evaporation from a solution of **3** in C_6H_6/THF.

Synthesis of (1,2-Diisopropyl-1,2-diaza-3,5-diphenyldiborolyl)potassium (4). A solution of **1** (1.35 g, 4.24 mmol) in THF (20 mL) was added to a stirred solution of potassium bis(trimethylsilyl)amide (KHMDS; 0.950 g, 4.24 mmol) in THF (15 mL), forming a yellow mixture. The mixture was stirred at ambient temperature for 12 h, and the volatiles were removed under vacuum, producing a colorless solid, which was washed twice with hexane (30 mL) and dried under vacuum. The product was obtained as a colorless powder (1.41 g, 93%). ^1H NMR (400 MHz, THF-d_8, 25 °C): δ 1.12 (d, 12H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.73 (s, 3H, CCH_3), 3.89 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 6.97 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-C_6H_5), 7.13 (t, 4H, $^3J_{HH}$ = 7.3 Hz, *m*-C_6H_5), 7.43 (d, 4H, $^3J_{HH}$ = 7.3 Hz, *o*-C_6H_5). ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ 14.3 (s, CCH_3), 23.9 (s, $CH(CH_3)_2$), 50.3 (s, $CH(CH_3)_2$), 96.8 (s, br, CCH_3), 124.7 (s, *p*-C_6H_5), 127.1 (s, *m*-C_6H_5), 134.6 (s, *o*-C_6H_5), 149.9 (s, br, *i*-C_6H_5). ^{11}B NMR (128 MHz, THF-d_8, 25 °C): δ 38.6 (s, br, $LW_{1/2}$ = 560 Hz). Colorless crystals that were suitable for X-ray diffraction analysis were obtained by either storing a concentrated solution of **4** in THF/hexane at −35 °C (**4b**) or by slow diffusion of hexane into a THF solution of the salt (**4a**).

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Supporting Information Available: Figures giving NMR spectra for all new compounds, as well as complete crystallographic data in CIF and table formats. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files are also available online from the Cambridge Crystallographic Data Centre (CCDC Nos. 629092 (**3**), 629093 (**3a**), 629094 (**4a**), and 629095 (**4b**)).

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