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Bitopic Bis- and Tris(1-pyrazolyl)borate Ligands: Syntheses and Structural Characterization

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Starting from 1,4- and 1,3-diborylated benzene derivatives, bitopic bis(1-pyrazolyl)borates ($K_2[1,4\text{-}(t\mathrm{BuBpz}_2)_2C_6H_4]$; $(Li,K)_2[1,3\text{-}(t\mathrm{BuBpz}_2)_2C_6H_4]$) and tris(1-pyrazolyl)borates ($K_2[1,4\text{-}(\mathrm{Bpz}_3)_2C_6H_4]$) have been synthesized (pz = pyrazolyl). X-ray single-crystal structure analyses revealed $K_2[1,3\text{-}(t\mathrm{BuBpz}_2)_2C_6H_4]$ to establish a polymeric structure in the solid state. In contrast, the unsymmetrically substituted hydrolysis product $Li_2[1,3\text{-}(t\mathrm{BuBpz}_2)(t\mathrm{BuB(OH)pz})C_6H_4]$ forms discrete dimers in which four lithium cations are encapsulated by their organic ligands. As a representative of bitopic 1,2-diboryl benzene-based scorpionates, the 9,10-dihydro-9,10-diboraanthracene derivative $K_2[(\mathrm{Bpz}_2)_2(C_6H_4)_2]$ is described, which bears two pyrazolyl substituents at each of its boron atoms and stands out due to its stereorigidity.

Introduction

Poly(1-pyrazolyl)borates ("scorpionates") are well established, versatile, and easily accessible ligands in coordination chemistry, which have found widespread applications ranging from analytical chemistry to homogeneous catalysis and materials science.[1] Considering the fact that increasing interest exists in the development of ligands able to bind more than one transition metal ion, surprisingly few examples of oligotopic scorpionates are known to date. Depending on their specific geometries, either these species might serve as rigid linkers in the synthesis of coordination polymer networks or they could be used to bring about cooperative effects between different transition metal ions by forcing them into close proximity.

The first example, **A** (Figure 1), of a discorpionate ligand was reported by Niedenzu et al. in 1988.[2] Our group has synthesized the ferrocene-based tris(1-pyrazolyl)borate **B**,[3] which was successfully employed for the generation of heterotrimetallic complexes.[4,5] Reger et al. recently published the related bis(1-pyrazolyl)methane system **C** and several silver(I) coordination polymers thereof.[6]

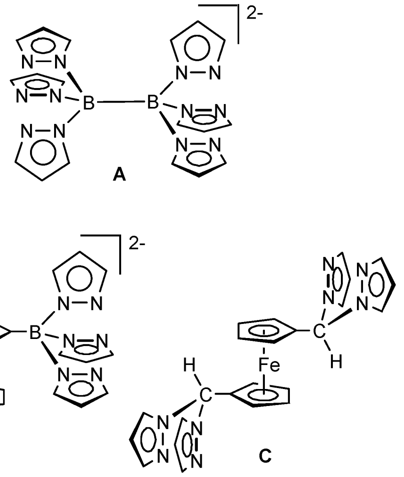

Figure 1. Bitopic scorpionate ligands **A**, **B**, and **C**.

The purpose of this paper is to describe a convenient route from 1,4-, 1,3-, and 1,2-diborylated benzene derivatives to bitopic homo- and heteroscorpionates with potential applications both in materials science and in homogeneous catalysis.

Results and Discussion

Selection of Ligand Systems. In most cases, tris(1-pyrazolyl)borates act as tripodal six-electron donors toward transition metal ions. Thus, if we consider dinuclear metal complexes of homoscorpionate ligands featuring two $[\mathrm{Bpz}_3]^-$ substituents (pz = pyrazolyl) at the same benzene ring (e.g., $[1,4\text{-}(\mathrm{Bpz}_3)_2C_6H_4]^{2-}$, **[3]**$^{2-}$; Scheme 1), both angles metal···B−C(ipso) will normally be close to 180°. The two metal ions are therefore not only sterically shielded but always kept at the same distance from each other. Given this background, the conformationally rigid bitopic homoscorpionate ligand

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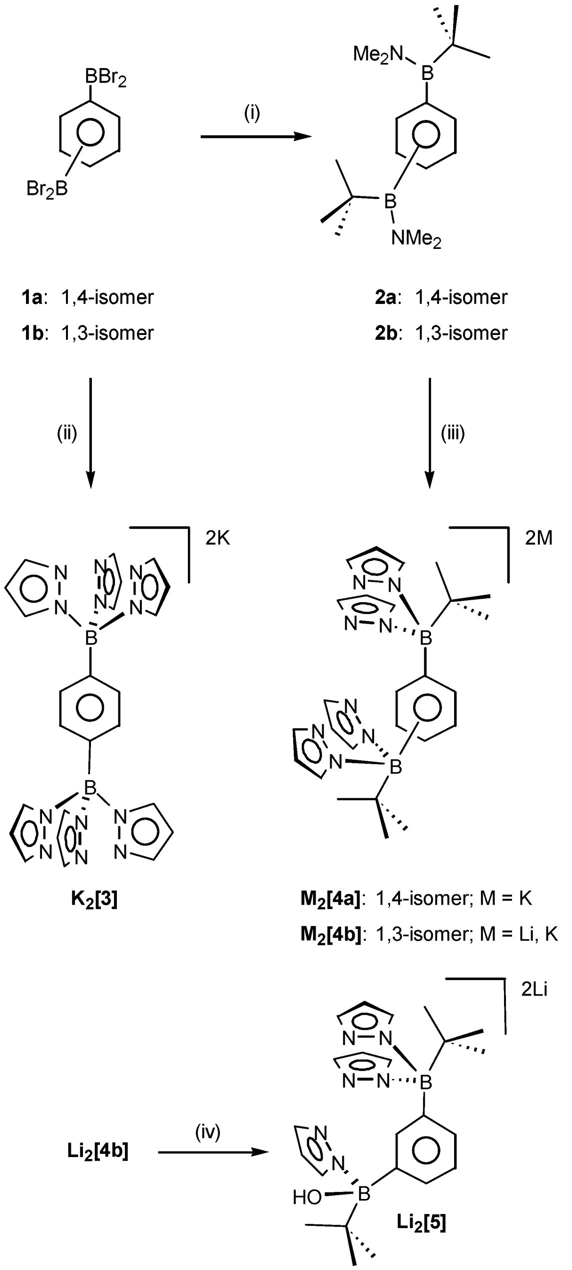
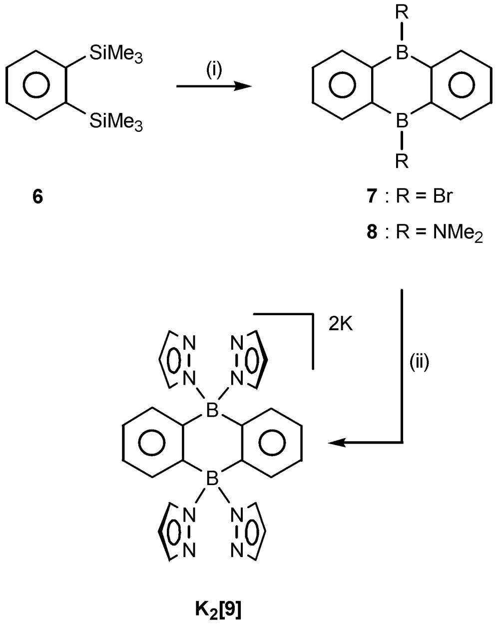
Scheme 1. Syntheses of the Bitopic Bis- and Tris(1-pyrazolyl)borate Ligands $K_2[3]$, $K_2[4a]$, $M_2[4b]$ ($M = Li^+$, K^+), and $Li_2[5]$[a]



[a] (i) + 10 equiv of $HNMe_2$, toluene, −78 to +80 °C; + 2 equiv of BCl_3, toluene/heptane, −78 °C to r.t.; + 2 equiv of *t*BuLi, toluene, −78 °C to r.t. (ii) **1a** + 10 equiv of $HNMe_2$, toluene, −78 to +80 °C; + 2 equiv of Kpz/4 equiv of Hpz, toluene, reflux. (iii) + 2 equiv of Mpz/2 equiv of Hpz, toluene, reflux. (iv) $+H_2O$, THF, r.t.

Scheme 2. Synthesis of $K_2[9]$[a]



[a] (i) **6** + exc BBr_3, toluene, r.t.; **7** + 2 equiv of Me_3SiNMe_2, toluene, −30 °C to r.t. (ii) **8** + 2 equiv of Kpz/2 equiv of Hpz, toluene, reflux.

[3]$^{2-}$ appears to be a well-suited building block for the generation of strictly one-dimensional, rodlike coordination polymer chains. The related heteroscorpionate ligands, however, in which dipodal four-electron donors $[RBpz_2]^-$ are connected via a C_6H_4 backbone (e.g., $[1,4\text{-}(RBpz_2)_2C_6H_4]^{2-}$, $[1,3\text{-}(RBpz_2)_2C_6H_4]^{2-}$, **[4a,b]**$^{2-}$, R = *t*Bu; Scheme 1) will give rise to metal complexes with metal···B−C(ipso) angles of about 90°. As a consequence, these aggregates can easily adopt conformations that bring both metal atoms in sufficiently close proximity to facilitate their simultaneous action on the same substrate molecule. To give access to dinuclear complexes with different average metal···metal distances, we have synthesized both the 1,4-isomer **[4a]**$^{2-}$ and the 1,3-isomer **[4b]**$^{2-}$. *tert*-Butyl groups were chosen as the innocent spectator substituents to give the boron atoms maximum protection from nucleophilic attack and to increase the ligands' solubility in less polar solvents. Simultaneous introduction of $[RBpz_2]^-$ moieties (R = pz, *t*Bu) into the positions 1 and 2 of a benzene ring would result in severe steric congestion. Overcrowding in hypothetical $[1,2\text{-}(RBpz_2)_2C_6H_4]^{2-}$ ligands can, however, be avoided when the two substituents R are replaced by a second bridging 1,2-phenylene bridge as in the 9,10-dihydro-9,10-diboraanthracene-based system $K_2[(Bpz_2)_2(C_6H_4)_2]$, **K$_2$[9]** (Scheme 2).

Syntheses and Spectroscopy: K$_2$[3], M$_2$[4a] ($M = K^+$), and **M$_2$[4b]** ($M = Li^+$, K^+) are obtained from readily available 1,4-bis(dibromoboryl)benzene, **1a**,[7] and 1,3-bis(dibromoboryl)benzene, **1b**,[7] respectively (Scheme 1). For the synthesis of **K$_2$[3]**, $1,4\text{-}[(Me_2N)_2B]_2C_6H_4$[8] is prepared from **1a** and $HNMe_2$ and then treated with 2 equiv of Kpz and 4 equiv of Hpz (pz = pyrazolyl) in toluene solution. Since the introduction of *tert*-butyl substituents at the boron centers via direct reaction of **1a** and **1b** with *t*BuLi suffers from side product formation, both dibromoboranes are first transformed into the corresponding aminochloroborane derivatives $1,4\text{-}[(Me_2N)ClB]_2C_6H_4$ and $1,3\text{-}[(Me_2N)ClB]_2C_6H_4$.[9] Subsequent addition of 2 equiv of *t*BuLi generates **2a** and **2b**. Further reaction of **2a** and **2b** with 2 equiv of Mpz (M: Li^+, K^+) and 2 equiv of Hpz in toluene at reflux temperature gives **K$_2$[4a]**, **Li$_2$[4b]**, and **K$_2$[4b]** in excellent yields. While the potassium salts proved to be rather stable toward hydrolysis, stirring of a THF

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[9] $1,4\text{-}[(Me_2N)BrB]_2C_6H_4$ and $1,3\text{-}[(Me_2N)BrB]_2C_6H_4$, which are directly accessible from **1a**/**1b** and 2 equiv of Me_3SiNMe_2 in toluene, may also be employed for the synthesis of **2a** and **2b**.

solution of **Li_2[4b]** in an open vessel for several days resulted in the complete breakdown of all boron−nitrogen bonds (NMR spectroscopical control). In contrast, single crystals of $Li_2[1,3\text{-}(t\text{BuBpz}_2)(t\text{BuB(OH)pz})\text{-}C_6H_4]$, **$Li_2$[5]**, which represents one of the earliest hydrolysis products, could be isolated in about 80% yield after **Li_2[4b]** in THF had been exposed to air *without* stirring (Scheme 1). Thus, careful hydrolysis of **Li_2[4b]** offers a convenient way to generate the unsymmetrically substituted bitopic ligand **Li_2[5]**. The 9,10-dihydro-9,-10-diboraanthracene scaffold underlying **K_2[9]** (Scheme 2) is accessible from 1,2-bis(trimethylsilyl)benzene, **6**, and 3 equiv of BBr_3. Treatment of the resulting bromo derivative **7**[10] with Me_3SiNMe_2 leads to the aminoborane **8**, which readily reacts with 2 equiv of Kpz and 2 equiv of Hpz in toluene to give the discorpionate ligand **K_2[9]** in about 70% yield.

The ^{11}B NMR spectrum of **K_2[3]** reveals one signal at 1.0 ppm, thereby testifying to the presence of magnetically equivalent, tetracoordinated boron atoms.[11] In the ^{1}H and ^{13}C NMR spectra, a singlet resonance at $\delta(^1H) = 6.93$ and a signal at $\delta(^{13}C) = 130.9$ have to be assigned to the 1,4-disubstituted benzene ring. The pyrazolyl groups give rise to three doublets of doublets at $\delta(^1H) = 6.00$, 7.15, and 7.39. The relative integral values of all four proton signals (4:6:6:6) are in accord with the assumption that **K_2[3]** contains two tris(1-pyrazolyl)borate functionalities *per* molecule. The NMR spectra of **K_2[4a]** resemble those of **K_2[3]** apart from the fact that an additional signal appears at $\delta(^1H) = 0.90$ [$\delta(^{13}C) = 31.3$], which is due to the two *tert*-butyl groups. Moreover, the integral ratios of the proton resonances indicate each boron atom of **K_2[4a]** to bear only two (rather than three) pyrazolyl substituents. The only important difference between the NMR spectra of **K_2[4a]** and **K_2[4b]** comes from the C_6H_4 fragment, since three resonances, characteristic of a 1,3-disubstituted benzene ring, are visible both in the ^{1}H NMR spectrum [$\delta = 6.91$ (tr, 1H), 7.11 (d, 2H), 7.25 (s, 1H)] and in the ^{13}C NMR spectrum of **K_2[4b]** (the signal of the ipso-^{13}C atoms is broadened beyond detection, which has to be attributed to the quadrupolar relaxation of the adjacent boron nucleus[11]). Exchange of K^+ for Li^+ has no significant effect on the NMR parameters of **[4b]**$^{2-}$. Two partially overlapping resonances are observed in the ^{11}B NMR spectrum of **Li_2[5]** ($\delta = 1.6$, 2.5). In addition, two sets of pyrazolyl proton signals can be identified. A comparison of the respective integral values with the integrals of the C_6H_4 proton signals leads to the conclusion that the first set of resonances at $\delta(^1H) = 6.00$ (virtual tr), 7.25 (d), and 7.63 (d) represents one pyrazolyl ring. The second set features a pattern of five signals at $\delta(^1H) = 5.89$, 5.90 (2 × virtual tr, 2 × 1H), 6.96, 6.98 (2 × d, 2 × 1H), and 7.42 (d, 2H) assignable to two pyrazolyl moieties which are placed in a very similar—but not quite the same—chemical environment. Considering the fact that **Li_2[5]** was formed upon exposure of **Li_2[4b]** to air and moisture, these NMR features can be explained in the following way: As a result of partial hydrolysis, one boron atom of **Li_2[5]** bears a pyrazolyl ring and a *tert*-butyl- and a hydroxy group and thus has a chiral configuration. The other boron atom is still substituted by two pyrazolyl rings, which exhibit slightly different proton shift values due to the presence of a chiral center in the *meta* position of the C_6H_4 bridge. The conclusion that **Li_2[5]** possesses two different boryl groups is supported by the observation of two singlets for the *tert*-butyl substituents [$\delta(^1H) = 0.66$, 0.67] and two multiplets for the protons in positions 4 and 6 of the central benzene ring [$\delta(^1H) = 7.07$, 7.17]. All general features outlined for the ^{1}H NMR spectrum of **Li_2[5]** are also reflected by its ^{13}C NMR spectrum, which therefore does not merit further discussion. The most revealing NMR data of **K_2[9]** are its ^{11}B NMR shift value of 0.0 ppm, the presence of two doublets of doublets at $\delta(^1H) = 6.77$ and 6.87, indicative of 1,2-disubstituted benzene moieties, and an integral ratio of C_6H_4 to pyrazolyl proton signals of 2:3, which is in accord with the molecular structure suggested in Scheme 2.

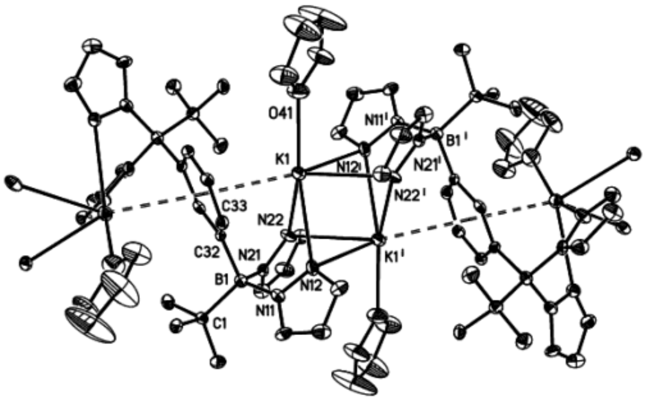

Figure 2. Structure of **K_2[4b]** in the crystal. Selected bond lengths (Å), atom···atom distances (Å), bond angles (deg), and torsion angles (deg); H atoms omitted for clarity: K(1)−O(41) = 2.676(2), K(1)−N(12) = 3.018(2), K(1)−N(12)^i = 2.884(2), K(1)−N(22) = 2.859(2), K(1)−N(22)^i = 2.987(3), K(1)−C(32) = 3.061(3), K(1)−C(33) = 3.060(3), K(1)···K(1)^i = 3.426(1), B(1)−N(11) = 1.588(4), B(1)−N(21) = 1.583(4), B(1)−C(1) = 1.657(4), B(1)−C(32) = 1.634(4); N(12)−K(1)−N(22) = 62.6(1), N(12)^i−K(1)−N(22)^i = 62.7(1), N(12)−K(1)−N(12)^i = 109.1(1), N(22)−K(1)−N(22)^i = 108.3(1), N(12)−K(1)−N(22)^i = 75.3(1), N(22)−K(1)−N(12)^i = 79.4(1), K(1)−N(12)−K(1)^i = 70.9(1), K(1)−N(22)−K(1)^i = 71.7(1); C(1)−B(1)−C(32)−C(33) = 99.0(3), B(1)−N(11)−N(12)−K(1) = 15.0(3), B(1)^i−N(11)^i−N(12)^i−K(1) = 70.8(3), B(1)−N(21)−N(22)−K(1) = −6.4(3), B(1)^i−N(21)^i−N(22)^i−K(1) = −78.6(3). i: symmetry transformation $^1/_2-x$, $^1/_2-y$, $1-z$.

Crystal Structure Determinations

K_2[4b] crystallizes from THF/Et_2O (1:2) in the monoclinic space group $C2/c$ (Figure 2). Crystal data and structure refinement details for **K_2[4b]** are compiled in Table 1. The molecule consists of a central benzene ring bearing two $[t\text{BuBpz}_2]^-$ substituents in its 1 and 3 positions. The two symmetry-related *t*Bu groups adopt a *trans* configuration with respect to the plane of the six-membered ring [torsion angle C(1)−B(1)−C(32)−C(33) = 99.0(3)°]. The bond angles around boron fall in the interval between 106.1(2)° [N(11)−B(1)−N(21)] and 112.3(2)° [C(1)−B(1)−N(21)]. Deviations from the value

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[10] For syntheses of the corresponding chloro and iodo derivatives, see: Eisch, J. J.; Kotowicz, B. W. *Eur J. Inorg. Chem.* **1998**, 761−769 and Siebert, W.; Schmidt, M.; Gast, E. *J. Organomet. Chem.* **1969**, *20*, 29−33, respectively.

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Table 1. Crystal Data and Structure Refinement Details for K_2[4b] and {Li_2[5]}$_2$

	K_2[4b]	{Li_2[5]}$_2$
formula	$C_{26}H_{34}B_2K_2N_8 \times 2\ C_4H_8O$	$C_{46}H_{64}B_4Li_4N_{12}O_2 \times 2\ C_4H_8O \times C_6H_{14}$
fw	702.64	1118.47
color, shape	colorless, block	colorless, rod
temp (K)	173(2)	154(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
a (Å)	19.652(3)	9.2660(16)
b (Å)	18.294(2)	18.810(5)
c (Å)	11.9262(17)	37.439(7)
α (deg)	90	90
β (deg)	120.552(10)	93.209(13)
γ (deg)	90	90
V (Å^3)	3692.4(9)	6515(2)
Z	4	4
D_{calcd} (g cm^{-3})	1.264	1.140
F(000)	1496	2408
μ (mm^{-1})	0.299	0.071
cryst size (mm)	0.23 × 0.22 × 0.12	0.16 × 0.18 × 0.70
no. of rflns collected	18 391	72 476
no. of indep rflns (R_{int})	3536 (0.0854)	17 335 (0.0710)
no. of data/restraints/params	3536/0/218	17 335/0/766
GOOF on F^2	0.814	1.092
R1, wR2 ($I > 2\sigma(I)$)	0.0451, 0.0812	0.1121, 0.1813
R1, wR2 (all data)	0.1003, 0.0907	0.1926, 0.2093
largest diff peak and hole (e Å^{-3})	0.354, −0.312	0.460, −0.465

of 109.3° expected for an ideal tetrahedron are due to the steric requirements of the *t*Bu substituent. Each potassium ion is coordinated by four pyrazolyl rings of two different **[4b]**$^{2-}$ ligands, thereby creating a polymeric structure in the solid state. All K−N bond lengths [K(1)−N(12) = 3.018(2) Å, K(1)−N(22) = 2.859(2) Å; K(1)−N(12)^{i} = 2.884(2) Å, K(1)−N(22)^{i} = 2.987(3) Å; i: symmetry transformation $^1/_2-x$, $^1/_2-y$, $1-z$] as well as the corresponding N−K−N bond angles [N(12)−K(1)−N(22) = 62.6(1)°, N(12)^{i}−K(1)−N(22)^{i} = 62.7(1)°] are rather similar. In contrast, substantial differences are observed in the torsion angles B(1)−N(11)−N(12)−K(1) = 15.0(3)° and B(1)−N(21)−N(22)−K(1) = −6.4(3)° on one hand, compared to B(1)^{i}−N(11)^{i}−N(12)^{i}−K(1) = 70.8(3)° and B(1)^{i}−N(21)^{i}−N(22)^{i}−K(1) = −78.6(3)° on the other. It may therefore be concluded that the interaction of K(1)$^+$ with the first chelating [*t*BuBpz$_2$]$^-$ moiety occurs via filled sp^2-type orbitals on the nitrogen atoms N(12) and N(22), whereas the second chelating [*t*BuBpz$_2$]$^-$ ligand binds mainly via p-type orbitals on N(12)^{i} and N(22)^{i}. The coordination sphere of each potassium cation is completed by one THF molecule [K(1)−O(41) = 2.676(2) Å] and the C_6H_4 ring [two short contacts: K(1)−C(32) = 3.061(3) Å, K(1)−C(33) = 3.060(3) Å], which results in an overall coordination number of six. The potassium ions in polymeric **K_2[4b]** are grouped into dinuclear aggregates [interatomic distances K(1)···K(1)^{i} = 3.426(1) Å] held together by four bridging pyrazolyl rings with angles K(1)−N(12)−K(1)^{i} = 70.9(1)° and K(1)−N(22)−K(1)^{i} = 71.7(1)°. **K_2[4b]** forms parallel chains running along the face-diagonal of the *ac*-plane.

Li_2[5] features two different coordination sites, a [*t*BuBpz$_2$]$^-$ and a [*t*BuB(OH)pz]$^-$ group, in the bitopic ligand molecule (Figure 3). Contrary to polymeric **K_2[4b]**, **Li_2[5]** forms discrete dimers {**Li_2[5]**}$_2$ of approximate C_2 symmetry in the solid state (monoclinic space group $P2_1/c$; Table 1), which are composed of two **[5a]**$^{2-}$ anions connected by four lithium atoms. Moreover, the two *t*Bu substituents are now placed at the same side of the bridging benzene ring with torsion angles (H_3C)$_3$*C*−B−C(*ipso*)−C(*ortho*) ranging from 63.8(4)° to 80.3(3)°. The cations Li(1) and Li(4) are each coordinated by a chelating [*t*BuBpz$_2$]$^-$ moiety, giving rise to obtuse N−Li−N angles of 96.7(2)° and 98.6(3)°, respectively. In contrast, acute N−K−N angles of 62.6(1)° [N(12)−K(1)−N(22)] and 62.7(1)° [N(12)^{i}−K(1)−N(22)^{i}] are found in **K_2[4b]**, which has to be attributed to the larger ionic radius of K$^+$ compared to Li$^+$. Li(2) and Li(3) bind to [*t*BuB(OH)pz]$^-$ groups in an η^2 fashion. Most interestingly, these two lithium cations are also chelated by two pyrazolyl rings belonging to different boron atoms [i.e., Li(2) to N(10), N(12); Li(3) to N(4), N(6)]. As to be expected, the Li−N bond lengths to terminal pyrazolyl rings are shorter [Li(1)−N(8) = 1.997(6) Å, Li(4)−N(2) = 2.012(6) Å] and the Li−N−N−B torsion angles are smaller [B(3)−N(7)−N(8)−Li(1) = 6.9(4)°, B(1)−N(1)−N(2)−Li(4) = 10.1(4)°] than the corresponding bonds and torsion angles at bridging pyrazolyl ligands [e.g., Li(1)−N(10) = 2.129(6) Å, Li(4)−N(4) = 2.205(6) Å; B(3)−N(9)−N(10)−Li(1) = −46.8(3)°, B(1)−N(3)−N(4)−Li(4) = −56.1(3)°]. Along the pathways N(8)−Li(1)−N(10)−Li(2)−N(12)−Li(3) and N(2)−Li(4)−N(4)−Li(3)−N(6)−Li(2), alternating shorter and longer Li−N bonds are observed, the shorter bonds generally being associated with smaller B−N−N−Li torsion angles. Each of the two outer Li$^+$ cations, Li(1) and Li(4), is bonded to two oxygen (B*O*H, THF) and two pyrazolyl nitrogen atoms in a distorted tetrahedral geometry. The two inner Li$^+$ cations, Li(2) and Li(3), both have a coordination number of five and bind to one hydroxy group (B*O*H), three pyrazolyl nitrogen atoms, and the central benzene ring [Li(2)−C(35) = 2.494(6) Å; Li(3)−C(12) = 2.387(6) Å]. Li(1) and Li(2), as well as Li(3) and Li(4), are doubly bridged by a pyrazolyl ring and a B*O*H ligand with Li$^+$···Li$^+$ distances of 2.594(7) and 2.649(8) Å, respectively. Li(2) and Li(3) are connected at a distance of 2.714(7) Å by two μ^2-pyrazolyl ligands. The BOH hydroxyl groups show an intramolecular O−H···π(benzene) contact with H···Cg distances

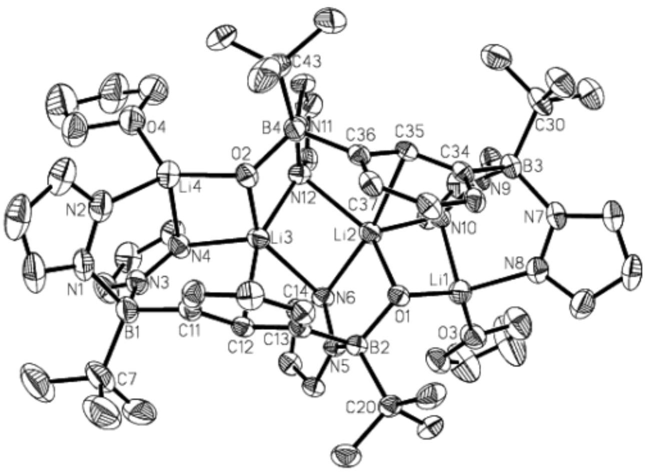

Figure 3. Structure of $\{\mathbf{Li_2[5]}\}_2$ in the crystal. Selected bond lengths (Å), atom⋯atom distances (Å), bond angles (deg), and torsion angles (deg); H atoms omitted for clarity: Li(1)−O(1) = 1.987(6), Li(1)−O(3) = 1.987(6), Li(2)−O(1) = 1.994(5), Li(3)−O(2) = 2.051(6), Li(4)−O(2) = 1.977(6), Li(4)−O(4) = 1.980(6), Li(1)−N(8) = 1.997(6), Li(1)−N(10) = 2.129(6), Li(2)−N(6) = 2.106(6), Li(2)−N(10) = 2.086(6), Li(2)−N(12) = 2.283(6), Li(3)−N(4) = 2.049(6), Li(3)−N(6) = 2.481(6), Li(3)−N(12) = 2.080(6), Li(4)−N(2) = 2.012(6), Li(4)−N(4) = 2.205(6), Li(2)−C(35) = 2.494(6), Li(3)−C(12) = 2.387(6), Li(1)⋯Li(2) = 2.594(7), Li(2)⋯Li(3) = 2.714(7), Li(3)⋯Li(4) = 2.649(8), B(1)−N(1) = 1.593(5), B(1)−N(3) = 1.588(5), B(2)−N(5) = 1.590(4), B(2)−O(1) = 1.521(4), B(3)−N(7) = 1.588(4), B(3)−N(9) = 1.595(4), B(4)−N(11) = 1.593(4), B(4)−O(2) = 1.530(4); N(8)−Li(1)−N(10) = 96.7(2), N(6)−Li(2)−O(1) = 80.7(2), N(10)−Li(2)−N(12) = 113.2(2), N(12)−Li(3)−O(2) = 81.8(2), N(4)−Li(3)−N(6) = 111.1(2), N(2)−Li(4)−N(4) = 98.6(3), Li(1)−N(10)−Li(2) = 76.0(2), Li(1)−O(1)−Li(2) = 81.3(2), Li(2)−N(6)−Li(3) = 72.0(2), Li(2)−N(12)−Li(3) = 76.8(2), Li(3)−N(4)−Li(4) = 76.9(2), Li(3)−O(2)−Li(4) = 82.2(2); C(7)−B(1)−C(11)−C(12) = 78.0(4), C(20)−B(2)−C(13)−C(14) = 63.8(4), C(30)−B(3)−C(34)−C(35) = 80.3(3), C(43)−B(4)−C(36)−C(37) = 74.9(4), B(1)−N(1)−N(2)−Li(4) = 10.1(4), B(1)−N(3)−N(4)−Li(4) = −56.1(3), B(1)−N(3)−N(4)−Li(3) = 28.3(5), B(2)−N(5)−N(6)−Li(2) = 26.7(3), B(2)−N(5)−N(6)−Li(3) = −51.6(3), B(3)−N(7)−N(8)−Li(1) = 6.9(4), B(3)−N(9)−N(10)−Li(1) = −46.8(3), B(3)−N(9)−N(10)−Li(2) = 42.4(4), B(4)−N(11)−N(12)−Li(2) = −53.6(3), B(4)−N(11)−N(12)−Li(3) = 31.2(3).

of 2.49 and 2.65 Å and O−H⋯Cg angles of 131° and 127° (Cg is the centroid of a benzene ring).

Conclusion

Bitopic bis- and tris(1-pyrazolyl)borate ligands have been synthesized from 1,4-, 1,3-, and 1,2-diborylated benzene derivatives. X-ray single-crystal structure analyses revealed $K_2[1,3\text{-}(t\text{BuBpz}_2)_2C_6H_4]$, $\mathbf{K_2[4b]}$, and the unsymmetrically substituted compound $Li_2[1,3\text{-}(t\text{BuBpz}_2)(t\text{BuB(OH)pz})C_6H_4]$, $\mathbf{Li_2[5]}$, to form complex supramolecular aggregates in the solid state. $\mathbf{K_2[4b]}$ has its two *tert*-butyl substituents in a transoid conformation with respect to the central C_6H_4 ring and thus establishes a polymeric structure $\{\mathbf{K_2[4b]}\}_n$. In contrast, a cisoid conformation is adopted by the *tert*-butyl groups of $\mathbf{Li_2[5]}$, giving rise to a dimeric structure $\{\mathbf{Li_2[5]}\}_2$ in which four lithium cations are encapsulated by their organic ligands. $\mathbf{[5]}^{2-}$ is capable of chelating lithium cations not only via pyrazolyl rings attached to the *same* boron atom but also via pyrazolyl rings belonging to the two *different* boron atoms of the ligand molecule. Thus, $\mathbf{[5]}^{2-}$ apparently possesses a higher degree of structural flexibility than we had initially expected. Our findings clearly demonstrate the promising potential of our ligand system for the development of coordination network solids on one hand and for the stabilization of oligometallic cluster cores on the other.

Experimental Section

General Considerations. All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon using standard Schlenk ware. Solvents were freshly distilled under argon from Na/benzophenone prior to use. NMR: Bruker AMX 250, AMX 400, Bruker DPX 250. ^{11}B NMR spectra were reported relative to external $BF_3{\cdot}Et_2O$. Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, tr = triplet, vtr = virtual triplet, mult = multiplet, br = broad, n.r. = multiplet expected in the ^{1}H NMR spectrum but not resolved, n.o. = signal not observed, pz = pyrazolide. Elemental analyses were performed by the microanalytical laboratory of the University of Frankfurt. Compound **6** was synthesized according to a literature procedure.[12]

Synthesis of 2a. Step 1. First, **1a** was transformed into $1,4\text{-}[(Me_2N)_2B]_2C_6H_4$ following a literature procedure.[8] A solution of BCl_3 in heptane (1 M, 5.20 mL, 5.20 mmol) was added dropwise with stirring to $1,4\text{-}[(Me_2N)_2B]_2C_6H_4$ (0.70 g, 2.56 mmol) in toluene (15 mL) at −78 °C. The clear solution was allowed to warm to room temperature and stirred for 2 h. All volatiles were removed in vacuo to leave behind a colorless solid residue, which was used for the subsequent reaction without further purification. Yield: 0.62 g (94%). ^{11}B NMR (128.4 MHz, C_6D_6): 36.8 ($h_{1/2}$ = 250 Hz). ^{1}H NMR (250.1 MHz, C_6D_6): 2.43, 2.69 (2 × s, 2 × 6H, NCH_3), 7.56 (s, 4H, C_6H_4). ^{13}C NMR (62.9 MHz, C_6D_6): 39.8, 40.3 (NCH_3), 132.4 (C_6H_4), n.o. (CB).

Step 2. *t*BuLi (1.6 M, 0.94 mL, 1.50 mmol) in pentane was added dropwise with stirring to a solution of $1,4\text{-}[(Me_2N)ClB]_2C_6H_4$ (0.19 g, 0.74 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for 3 h, whereupon a colorless precipitate formed. After filtration, the solvent was removed from the filtrate in vacuo to give **2a** as colorless microcrystalline solid. Yield: 0.20 g (90%). ^{11}B NMR (128.4 MHz, C_6D_6): 45.6 ($h_{1/2}$ = 450 Hz). ^{1}H NMR (250.1 MHz, C_6D_6): 1.25 (s, 18H, CH_3), 2.46, 2.68 (2 × s, 2 × 6H, NCH_3), 7.21 (s, 4H, C_6H_4). ^{13}C NMR (62.9 MHz, C_6D_6): 30.4 (CH_3), 40.3, 43.8 (NCH_3), 128.7 (C_6H_4), n.o. (CB). **2a** is extremely moisture sensitive; a decent elemental analysis was not obtained.

Synthesis of 2b. Step 1. $HNMe_2$ (12.20 g, 270.60 mmol) was condensed at −78 °C into a solution of **1b** (11.20 g, 26.84 mmol) in toluene (100 mL). The resulting mixture was slowly warmed to room temperature, heated at 80 °C for 2 h, and cooled to room temperature again. After filtration, the solvent was removed from the filtrate in vacuo and the solid crude product distilled under reduced pressure to give colorless crystals of $1,3\text{-}[(Me_2N)_2B]_2C_6H_4$. Yield: 6.34 g (86%). ^{11}B NMR (128.4 MHz, C_6D_6): 33.4 ($h_{1/2}$ = 240 Hz). ^{1}H NMR (400.0 MHz, C_6D_6): 2.65 (s, 24H, NCH_3), 7.41 (mult, 1H, H-5), 7.50 (mult, 2H, H-4,6), 7.69 (br, 1H, H-2). ^{13}C NMR (62.9 MHz, C_6D_6): 40.7 (NCH_3), 128.3 (CH-5), 133.3 (CH-4,6), 139.5 (CH-2), n.o. (CB).

Step 2. A solution of BCl_3 in heptane (1M, 26.00 mL, 26.00 mmol) was added dropwise with stirring to $1,3\text{-}[(Me_2N)_2B]_2C_6H_4$ (3.57 g, 13.03 mmol) in toluene (40 mL) at −78 °C. The clear solution was allowed to warm to room temperature and stirred for 3 h. All volatiles were removed in vacuo and the oily residue

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(12) Kitamura, T.; Todaka, M.; Fujiwara, Y. *Org. Synth.* **2002**, *78*, 104−112.

of 1,3-[$(Me_2N)ClB]_2C_6H_4$ distilled under reduced pressure. Yield: 3.12 g (93%). ^{11}B NMR (128.4 MHz, C_6D_6): 36.7 ($h_{1/2}$ = 240 Hz). ^{1}H NMR (250.1 MHz, $CDCl_3$): 2.85, 2.98 (2 × s, 2 × 6H, NCH_3), 7.32 (tr, 1H, $^3J_{HH}$ = 7.4 Hz, H-5), 7.50 (d, 2H, $^3J_{HH}$ = 7.4 Hz, H-4,6), 7.67 (s, 1H, H-2). ^{13}C NMR (62.9 MHz, C_6D_6): 39.8, 40.3 (NCH_3), 127.2 (CH-5), 134.0 (CH-4,6), 137.7 (CH-2), n.o. (CB).

Step 3. *t*BuLi (1.6 M, 3.90 mL, 6.24 mmol) in pentane was added dropwise with stirring to a solution of 1,3-[$(Me_2N)ClB]_2C_6H_4$ (0.77 g, 3.00 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 10 h, whereupon a colorless precipitate formed. After filtration, the solvent was removed from the filtrate in vacuo and the oily crude product distilled under reduced pressure to give **2b** as a colorless viscous liquid. Yield: 0.81 g (90%). ^{11}B NMR (128.4 MHz, C_6D_6): 45.4 ($h_{1/2}$ = 330 Hz). ^{1}H NMR (250.1 MHz, $CDCl_3$): 0.92 (s, 18H, CH_3), 2.52, 2.97 (2 × s, 2 × 6H, NCH_3), 6.82 (s, 1H, H-2), 6.90 (d, 2H, $^3J_{HH}$ = 7.4 Hz, H-4,6), 7.14 (tr, 1H, $^3J_{HH}$= 7.4 Hz, H-5). ^{13}C NMR (62.9 MHz, $CDCl_3$): 30.1 (CCH_3), 40.5, 43.7 (NCH_3), 125.9 (CH-5), 126.5 (CH-4,6), 129.9 (CH-2), n.o. (CB). **2b** is extremely moisture sensitive; a decent elemental analysis was not obtained.

Synthesis of K_2[3]. First, **1a** was transformed into 1,4-[$(Me_2N)_2B]_2C_6H_4$ following a literature procedure.[8] To a stirred solution of 1,4-[$(Me_2N)_2B]_2C_6H_4$ (1.00 g, 3.65 mmol) in toluene (15 mL) was added at ambient temperature 0.80 g (7.54 mmol) of neat Kpz and 0.99 g (14.54 mmol) of neat Hpz. After the resulting suspension had been heated to reflux for 24 h, the insolubles were collected on a frit, washed with toluene (2 × 5 mL) and pentane (5 mL), and dried in vacuo. Yield: 1.75 g (83%). ^{11}B NMR (128.4 MHz, d_6-DMSO): 1.0 ($h_{1/2}$ = 450 Hz). ^{1}H NMR (250.1 MHz, d_6-DMSO): 6.00 (dd, 6H, $^3J_{HH}$ = 2.1 Hz, 1.5 Hz, pzH-4), 6.93 (s, 4H, C_6H_4), 7.15 (dd, 6H, $^3J_{HH}$ = 2.1 Hz, $^4J_{HH}$ = 0.6 Hz, pzH-3 or 5), 7.39 (dd, 6H, $^3J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 0.6 Hz, pzH-5 or 3). ^{13}C NMR (62.9 MHz, d_6-DMSO): 101.5 (pzC-4), 130.9 (C_6H_4), 132.3, 137.3 (pzC-3,5), n.o. (CB). Anal. Calcd for $C_{24}H_{22}B_2K_2N_{12}$ (578.34): C, 49.84; H, 3.83; N, 29.06. Found: C, 49.59; H, 3.75; N, 28.77.

Synthesis of K_2[4a]. To a stirred solution of **2a** (0.22 g, 0.73 mmol) in toluene (15 mL) was added at ambient temperature 0.16 g (1.51 mmol) of neat Kpz and 0.10 g (1.46 mmol) of neat Hpz. After the resulting suspension had been heated to reflux for 24 h, the insolubles were collected on a frit, washed with toluene (2 × 5 mL) and pentane (5 mL), and dried in vacuo. Yield: 0.35 g (86%). ^{11}B NMR (128.4 MHz, CD_3CN): 2.5 ($h_{1/2}$ = 210 Hz). ^{1}H NMR (250.1 MHz, CD_3CN): 0.90 (s, 18H, CH_3), 6.00 (vtr, 4H, $^3J_{HH}$ = 1.7 Hz, pzH-4), 6.94 (s, 4H, C_6H_4), 7.22, 7.34 (d, n.r., 2 × 4H, $^3J_{HH}$ = 1.7 Hz, pzH-3,5). ^{13}C NMR (62.9 MHz, CD_3CN): 31.3 (CH_3), 102.4 (pzC-4), 133.4 (C_6H_4), 135.0, 137.9 (pzC-3,5), n.o. (CB). Anal. Calcd for $C_{26}H_{34}B_2K_2N_8$ (558.43): C, 55.92; H, 6.14; N, 20.07. Found: C, 55.76; H, 6.46; N, 19.79.

Synthesis of Li_2[4b]. To a stirred solution of **2b** (0.81 g, 2.70 mmol) in toluene (60 mL) was added at ambient temperature 0.41 g (5.54 mmol) of neat Lipz and 0.39 g (5.73 mmol) of neat Hpz. After the resulting suspension had been heated to reflux for 24 h, the solvent was evaporated and the solid residue dried in vacuo at 60−80 °C for 2 h to remove unreacted pyrazole. **Li_2[4b]** was recrystallized by layering its toluene solution with hexane. Yield: 1.17 g (88%). ^{11}B NMR (128.4 MHz, d_8-THF): 1.2 ($h_{1/2}$ = 380 Hz). ^{1}H NMR (250.1 MHz, d_8-THF): 0.58 (s, 18H, CH_3), 5.94 (vtr, 4H, $^3J_{HH}$ = 1.8 Hz, pzH-4), 6.94 (tr, 1H, $^3J_{HH}$ = 7.5 Hz, H-5), 7.08 (d, 4H, $^3J_{HH}$ = 1.8 Hz, pzH-3 or 5), 7.23 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H-4,6), 7.45 (d, 4H, $^3J_{HH}$ = 1.8 Hz, pzH-5 or 3), 7.92 (s, 1H, H-2). ^{13}C NMR (62.9 MHz, d_8-THF): 30.4 (CH_3), 102.0 (pzC-4), 125.4 (C-5), 133.7 (C-4,6), 137.5, 137.9 (pzC-3,5), 144.6 (C-2), n.o. (CB). Anal. Calcd for $C_{26}H_{34}B_2Li_2N_8$ (494.12): C, 63.20; H, 6.94; N, 22.68. Found: C, 63.55; H, 6.99; N, 22.28.

Synthesis of K_2[4b]. The preparation was carried out similar to the synthesis of **K_2[4a]** using 0.42 g (1.40 mmol) of **2b**, 0.30 g (2.83 mmol) of neat Kpz, and 0.19 g (2.79 mmol) of neat Hpz in 40 mL of toluene. Yield: 0.71 g (91%). X-ray quality crystals were grown from THF/Et_2O (1:2) at −20 °C. ^{11}B NMR (128.4 MHz, d_8-THF): 0.8 ($h_{1/2}$ = 290 Hz). ^{1}H NMR (250.1 MHz, d_8-THF): 0.87 (s, 18H, CH_3), 5.97 (vtr, 4H, $^3J_{HH}$ = 2.0 Hz, pzH-4), 6.91 (tr, 1H, $^3J_{HH}$ = 7.3 Hz, H-5), 7.11 (d, 2H, $^3J_{HH}$ = 7.3 Hz, H-4,6), 7.25 (s, 1H, H-2), 7.29 (d, 8H, $^3J_{HH}$ = 2.0 Hz, pzH-3,5). ^{13}C NMR (62.9 MHz, d_8-THF): 31.3 (CH_3), 102.5 (pzC-4), 125.2 (C-5), 132.3 (C-4,6), 134.3, 137.6 (pzC-3,5), 139.9 (C-2), n.o. (CB). Anal. Calcd for $C_{26}H_{34}B_2K_2N_8$ (558.43) × 2 C_4H_8O (72.11): C, 58.12; H, 7.17; N, 15.95. Found: C, 57.82; H, 7.15; N, 15.65.

Synthesis of Li_2[5]. X-ray quality crystals of {**Li_2[5]**}$_2$ × 2 THF × 1 hexane were obtained after a solution of **Li_2[4b]** × 0.5 hexane (0.82 g, 1.52 mmol) in THF had been exposed to air for a prolonged time without stirring. Yield: 0.67 g (79%). The crystals contain hexane, which was previously used in the workup of **Li_2[4b]** (see above). ^{11}B NMR (128.4 MHz, d_8-THF, 330 K): 1.6, 2.5 (both resonances are overlapping; reliable $h_{1/2}$ values could not be determined). ^{1}H NMR (250.1 MHz, d_8-THF): 0.66, 0.67 (2 × s, 2 × 9H, CH_3), 5.89, 5.90 (2 × vtr, 2 × 1H, $^3J_{HH}$ = 2.1 Hz, pzH-4), 6.00 (vtr, 1H, $^3J_{HH}$ = 1.9 Hz, pzH-4*), 6.85 (vtr, 1H, $^3J_{HH}$ = 7.4 Hz, H-5), 6.96, 6.98 (2 × d, 2 × 1H, $^3J_{HH}$ = 2.1 Hz, pzH-3 or 5), 7.07, 7.17 (2 × mult, 2 × 1H, H-4,6), 7.25 (d, 1H, $^3J_{HH}$ = 1.9 Hz, pzH-3* or 5*), 7.42 (d, 2H, $^3J_{HH}$ = 2.1 Hz, pzH-5 or 3), 7.63 (d, 1H, $^3J_{HH}$ = 1.9 Hz, pzH-5* or 3*), 7.79 (s, 1H, H-2). ^{13}C NMR (62.9 MHz, d_8-THF): 29.8, 30.5 (CH_3), 101.8 (pzC-4), 103.0 (pzC-4*), 125.1 (C-5), 130.0, 132.8 (C-4,6), 133.2, 135.5 (pzC-3*,5*), 137.5, 138.0 (pzC-3,5), 140.7 (C-2). Note: chemical shift values marked with (*) are assigned to the pyrazolyl ring of the B*pz*(*t*Bu)OH moiety. Anal. Calcd for $C_{23}H_{32}B_2Li_2N_6O$ (444.04) × 1 C_4H_8O (72.11) × 0.5 C_6H_{14} (86.18): C, 64.43; H, 8.47; N, 15.03. Found: C, 64.78; H, 8.53; N, 15.37.

Synthesis of 7. To a solution of **6** (2.42 g, 10.89 mmol) in 10 mL of toluene was added BBr_3 (7.64 g, 30.50 mmol) with stirring at ambient temperature. After the mixture had been refluxed overnight, all volatiles were removed in vacuo and the solid residue was washed with pentane (5 mL) and recrystallized from toluene (10 mL). Yield: 1.05 g (58%). ^{11}B NMR (128.4 MHz, C_6D_6): 41.8 ($h_{1/2}$ = 250 Hz). ^{1}H NMR (250.1 MHz, C_6D_6): 7.27, 7.67 (2 × dd, 2 × 4H, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 3.3 Hz, C_6H_4). ^{13}C NMR (100.6 MHz, C_6D_6): 131.3, 131.7 (C_6H_4), n.o. (CB). **7** is extremely moisture sensitive; a decent elemental analysis was not obtained.

Synthesis of 8. A solution of Me_3SiNMe_2 (0.74 g, 6.30 mmol) in toluene (5 mL) was added dropwise with stirring to **7** (1.05 g, 3.15 mmol) in toluene (10 mL) at −30 °C. The resulting colorless solution was slowly allowed to warm to room temperature and stirred overnight. After all volatiles had been removed in vacuo, the colorless solid residue was used for the subsequent reaction without further purification. Yield: 0.77 g (93%). ^{11}B NMR (128.4 MHz, C_6D_6): 32.5 ($h_{1/2}$ = 230 Hz). ^{1}H NMR (250.1 MHz, C_6D_6): 2.84 (s, 12H, NCH_3), 7.24, 7.61 (2 × dd, 2 × 4H, $^3J_{HH}$ = 5.4 Hz, $^4J_{HH}$ = 3.2 Hz, C_6H_4). ^{13}C NMR (62.9 MHz, C_6D_6): 41.3 (NCH_3), 126.6, 131.7 (C_6H_4), n.o. (CB). **8** is moisture sensitive; a decent elemental analysis was not obtained.

Synthesis of K_2[9]. The preparation was carried out similar to the synthesis of **K_2[4a]** using 0.77 g (2.93 mmol) of **8**, 0.63 g (5.93 mmol) of neat Kpz, and 0.40 g (5.88 mmol) of neat Hpz in 15 mL of toluene. Yield: 1.03 g (68%). ^{11}B NMR (128.4 MHz, CD_3CN): 0.0 ($h_{1/2}$ = 230 Hz). ^{1}H NMR (250.1 MHz, d_6-DMSO): 5.79 (dd, 4H, $^3J_{HH}$ = 2.2 Hz, 1.6 Hz, pzH-4), 6.77, 6.87 (2 × dd, 2 × 4H, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 3.3 Hz, C_6H_4), 6.92, 7.17 (2 × d, 2 × 4H, $^3J_{HH}$ = 2.2 Hz, 1.6 Hz, pzH-3,5). ^{13}C NMR (62.9 MHz, d_6-DMSO): 100.7 (pzC-4), 123.1, 132.4

(C_6H_4), 133.2, 137.3 (pzC-3,5). Anal. Calcd for $C_{24}H_{20}B_2K_2N_8$ (520.30): C, 55.40; H, 3.87; N 21.54. Found: C, 55.06; H, 3.99; N, 21.27.

Crystal Structure Determinations of K_2[4b] and {Li_2[5]}$_2$. K_2[4b]. Data collection was performed on a Stoe-IPDS-II two-circle diffractometer with graphite-monochromated Mo Kα radiation. An empirical absorption correction with the MULABS option[13] in the program PLATON[14] gave a correction factor between 0.935 and 0.965. Equivalent reflections were averaged [$R(I)_{\mathrm{int}} = 0.085$]. The structure was solved by direct methods[15] and refined with full-matrix least-squares on F^2 using the program SHELXL-97.[16] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model.

{Li_2[5]}$_2$. Data collection was performed on a SIEMENS SMART diffractometer with graphite-monochromated Mo Kα radiation. Repeatedly measured reflections remained stable. An empirical absorption correction with the program SADABS[17] gave a correction factor between 0.951 and 1.000. Equivalent reflections were averaged [$R(I)_{\mathrm{int}} = 0.071$]. The structure was determined by direct methods using the program SHELXS.[15] All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms at the hydroxyl groups were taken from a difference Fourier synthesis and were refined with individual isotropic thermal parameters. All other H atoms were geometrically positioned and treated as riding atoms. The structure was refined on F^2 values using the program SHELXL-97.[16] {**Li_2[5]**}$_2$ crystallizes together with 1 equiv of hexane, which is disordered. The C atoms of the THF groups also possess rather large displacement parameters.

CCDC reference numbers: 228437 (**K_2[4b]**), 228438 ({**Li_2[5]**}$_2$).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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