Organometallics **2004,** *23,* 3483−3487

Alkali-Metal Complexes of a Tetramethylcyclopentadienyl-Functionalized Pyrazolylborate Ligand. Structures of $[Li_2(THF)_3B(3\text{-}Mepz)_3(C_5Me_4)]$ and $[K_2(THF)_2B(3\text{-}Mepz)_3(C_5Me_4)]_\infty$

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Received March 10, 2004

The new dianionic ligand $[B(3\text{-}Mepz)_3(C_5Me_4)]^{2-}$ was prepared and structurally characterized as its lithium and potassium salts. In the solid state, $[Li_2(THF)_3\{B(3\text{-}Mepz)_3\}(C_5Me_4)]$ is monomeric, while $[K_2(THF)_2\{B(3\text{-}Mepz)_3\}(C_5Me_4)]_\infty$ consists of infinite puckered chains. The compounds were synthesized by reaction of $B(NMe_2)_2(C_5Me_4H)$ with 2 equiv of 3-methylpyrazole and 1 equiv of M(3-Mepz) (M = Li, K) followed by deprotonation with n-BuLi or KH. The crystal structure of the intermediate monoanion, $[Li(THF)_2\{B(3\text{-}Mepz)_3\}(C_5Me_4H)]$, is also presented.

Introduction

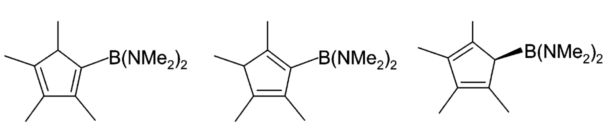
The search for new ligand frameworks is an ongoing topic of interest in organometallic chemistry. In this context, for several years we have been interested in the chemistry of f-elements with polypyrazolylborate ligands, especially hydrotris(3,5-dimethylpyrazolyl)borate (Tp^{Me_2}).[1] During our studies, we have found that thermolysis of $Sm(Tp^{Me_2})_2(Cp)$ proceeds via hydrogen abstraction from the cyclopentadienyl ring to give $Sm[HB(3,5\text{-}Me_2pz)_2(C_5H_4)](\eta^3\text{-}Tp^{Me_2})$, as a result of thermally induced and samarium-mediated intramolecular C−H activation.[2] The unexpected formation of the novel dianionic ligand $[HB(3,5\text{-}Me_2pz)_2(C_5H_4)]$ led us to develop a reliable rational synthesis to fully explore the potential offered by this type of ligand. Conceptually related ligands are the dianionic linked amido-cyclopentadienyls first introduced by Bercaw[3] that proved to be one of the most versatile ligand sets for the polymerization of α-olefins.[3,4]

Here we describe the synthesis and structural characterization of the dilithium and dipotassium salts of the $[B(3\text{-}Mepz)_3(C_5Me_4)]^{2-}$ ligand. Moreover, our synthetic strategy should allow replacement of the substituents of the pyrazolyl groups and/or cyclopentadienyl ring and hence the generation of a versatile and broad class of new, mixed pyrazolyl/cyclopentadienyl ligands.

Results and Discussion

The synthesis of the salts of $[B(3\text{-}Mepz)_3(C_5Me_4)]^{2-}$ proceeded through a stepwise protocol outlined in Scheme 1. Reaction of equimolar amounts of BCl_3 and tetramethyl(trimethylsilyl)cyclopentadiene, followed by removal of the solvent and distillation at 75−80 °C (5 mmHg), led to the air-sensitive tetramethylcyclopentadienyldichloroborane, $BCl_2(C_5Me_4H)$ (**1**). The compound was isolated as a single isomer, (1,3,4,5-tetramethyl)cyclopentadien-2-yldichloroborane, in 90% yield. The product was identified by ^1H and ^{13}C NMR spectroscopy.

Compound **1** reacts smoothly in toluene with neat dimethylamine (1:4) at 0 °C to yield $B(NMe_2)_2(C_5Me_4H)$ (**2**) as a yellow oil after separation of $(NH_2Me_2)Cl$ and removal of the solvent. The product was identified as (1,3,4,5-tetramethyl)cyclopentadien-2-yldimethylamineborane **2A** by ^1H and ^{13}C NMR spectroscopy. At room temperature **2A** slowly converts by sigmatropic rearrangements to a mixture of the three constitutional isomers (**2A**−**C**).



2A **2B** **2C**

Reaction of cyclopentadienyldimethylamineborane **2** with 2 equiv of 3-MepzH and 1 equiv of Li(3-Mepz) in THF yields $[Li(THF)_xB(3\text{-}Mepz)_3(C_5Me_4H)]$ (**3**) as a mixture of isomers. Crystallization of the mixture from a THF solution gave crystals of the isomer **3C** (the isomer in which the boron is coordinated to the C_5Me_4H ring as in configuration **2C**). Compound **3** is deprotonated by BuLi after prolonged reaction times. Crystals of $[Li_2(THF)_3B(3\text{-}Mepz)_3(C_5Me_4)]$ (**4**) suitable for X-ray diffraction analysis were grown by slow concentration of a THF solution.

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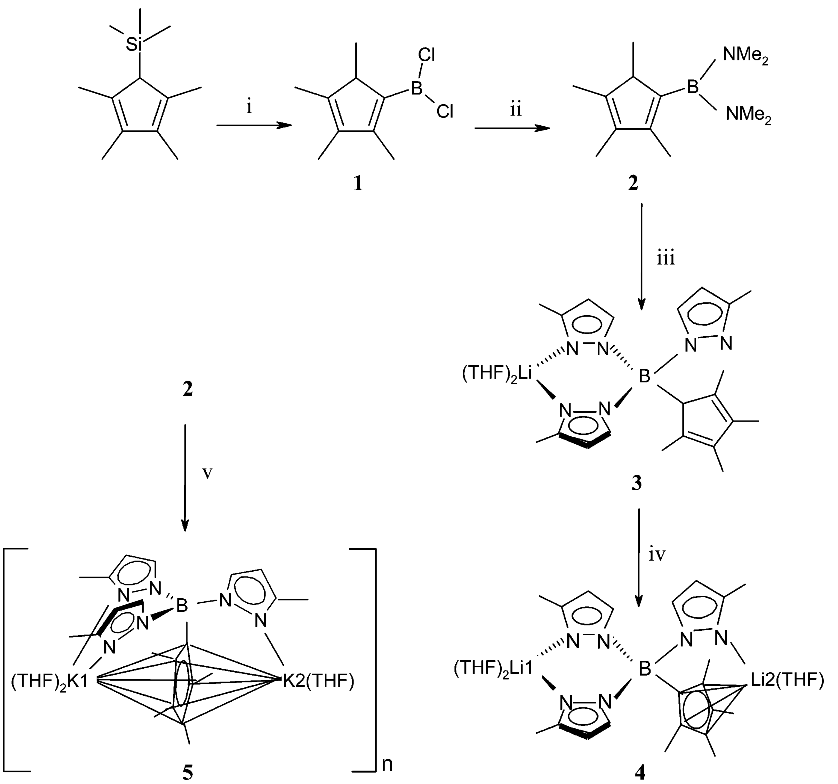
Scheme 1[a]



[a] (i) 1 M solution of BCl_3 in hexane, CH_2Cl_2, −78 °C, distallation at 75−80 °C (5 mmHg); (ii) toluene, neat $HNMe_2$, 0 °C; (iii) THF, 1 equiv of Li(3-Mepz), 2 equiv of 3-MepzH; (iv) THF, BuLi, −50 °C; (v) THF, 1 equiv of K(3-Mepz), 2 equiv of 3-MepzH, HK.

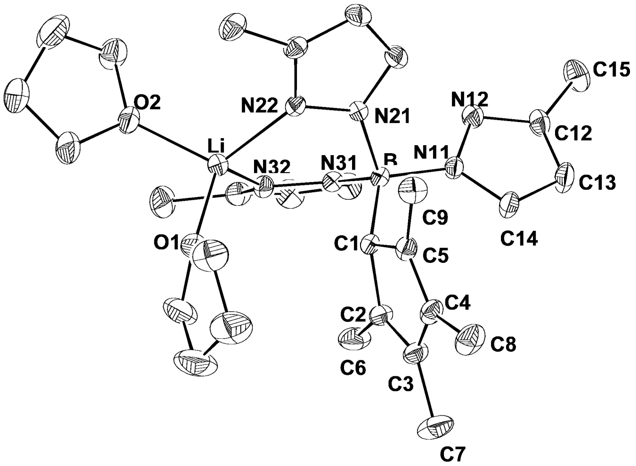


Figure 1. ORTEP diagram of [Li(THF)$_2$B(3-Mepz)$_3$(C$_5$Me$_4$H)] (**3C**), using 20% probability ellipsoids.

The potassium salt of the ligand was obtained as described for **4** by reacting **2** with 2 equiv of 3-MepzH and 1 equiv of K(3-Mepz) in THF, followed by deprotonation with KH. Slow concentration of a THF solution gave crystals of [K$_2$(THF)$_2$B(3-Mepz)$_3$(C$_5$Me$_4$)] (**5**) in a few hours.

The compounds are soluble in THF but poorly soluble in aromatic solvents. The ^{1}H NMR spectra of compounds **4** and **5** in thf-d_8 were deceptively simple. Only three peaks for the protons of the three pyrazolyl rings were observed, indicating a highly fluxional coordination sphere. In addition the spectra displayed two resonances for the methyl protons of the C_5Me_4 unit.

ORTEP views of **3C**, **4**, and **5** are presented in Figures 1−3. Selected bond lengths are given in Table 1.

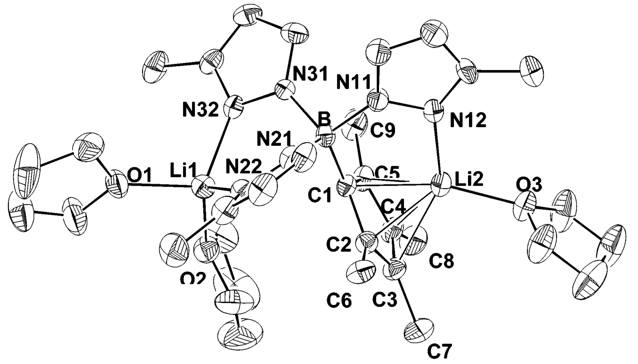


Figure 2. ORTEP diagram of [Li$_2$(THF)$_3$B(3-Mepz)$_3$(C$_5$Me$_4$)] (**4**), using 20% probability ellipsoids.

Compound **3C** is a monomer in the solid state. The molecule shows approximately a plane of symmetry containing the pyrazolyl ring N(1) and the B, Li, C(1), O(1), and O(2) atoms. This plane is almost perpendicular to the Cp plane (89.3°). The lithium center binds to two nitrogen atoms of two pyrazolyl rings and two oxygen atoms of the THF molecules. This arrangement allows for tetracoordination of the lithium ion. The Li−N bond lengths (Li−N(22) = 2.037(6) Å and Li−N(32) = 2.017(6) Å) are slightly longer than the Li−N bond lengths involving nonbridging pyrazolyl rings in [Li{FcB(pz)$_2$(μ-pz)}]$_2$ (2.007(4) Å)[5] and in [Li{HB(3,5-Me$_2$pz)$_2$(μ-3,5-Me$_2$pz)}]$_2$ (1.949(15) Å).[6] The Li−O bond distances average 1.957(6) Å, a value that compares with the corresponding distance in other complexes reported in

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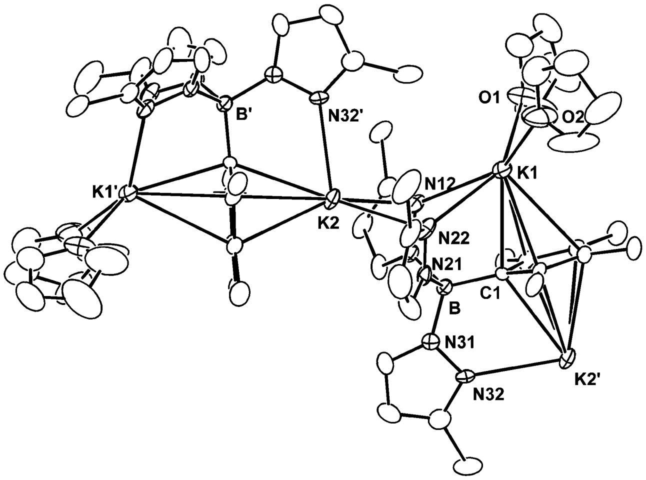

Figure 3. ORTEP diagram of a section of the infinite chain structure of [$K_2(THF)_2B(3\text{-}Mepz)_3(C_5Me_4)$] (**5**), using 20% probability ellipsoids.

Table 1. Selected Bond Distances (Å) for 3C, 4 and 5

	3C	**4**		**5**
Li(1)−N(22)	2.037(6)	2.039(10)	K(1)−N(12)	2.799(7)
Li(1)−N(32)	2.017(6)	2.018(9)	K(1)−N(22)	3.051(9)
Li(1)−O(1)	1.963(6)	2.005(9)	K(1)−O(1)	2.730(8)
Li(1)−O(2)	1.951(6)	1.947(9)	K(1)−O(2)	2.716(11)
Li(2)−N(12)		2.074(9)	K(1)−C(1)	2.830(6)
Li(2)−O(3)		1.984(9)	K(1)−C(2)	3.049(8)
Li(2)−C(1)		2.177(9)	K(1)−C(3)	3.238(8)
Li(2)−C(2)		2.222(10)	K(1)−C(4)	3.164(8)
Li(2)−C(3)		2.308(10)	K(1)−C(5)	2.919(7)
Li(2)−C(4)		2.305(10)	K(2)−N(12)	2.909(7)
Li(2)−C(5)		2.204(10)	K(2)−N(22)	2.849(7)
			K(2)−N(32)[a]	2.764(7)
			K(2)−C(1)[a]	2.896(7)
			K(2)−C(2)[a]	2.940(8)
			K(2)−C(3)[a]	2.992(9)
			K(2)−C(4)[a]	2.965(8)
			K(2)−C(5)[a]	2.883(7)
B−C(1)	1.629(5)	1.573(6)	B−C(1)	1.586(11)
C(1)−C(2)	1.511(4)	1.438(6)	C(1)−C(2)	1.429(10)
C(2)−C(3)	1.342(5)	1.408(6)	C(2)−C(3)	1.418(11)
C(3)−C(4)	1.452(6)	1.408(7)	C(3)−C(4)	1.399(12)
C(4)−C(5)	1.342(5)	1.422(6)	C(4)−C(5)	1.400(10)
C(1)−C(5)	1.509(4)	1.429(6)	C(1)−C(5)	1.410(9)

[a] Atoms related by the symmetry operation $-x-1/2$, $y-1/2$, $-z+1/2$.

the literature.[7−10] The B−C(1) bond length is 1.629(5) Å and compares with those found in [NEt_4][$C_5H_5B(C_6F_5)_3$] (1.618(3) Å)[11] and Li[($SiMe_3$)$C_5H_4B(C_6F_5)_3$] (1.625(4) Å).[12] The C−C distances of the ring shown in Table 1 indicate that the boron is bonded to the allylic carbon atom C1. This is confirmed by the sum of the angles about C(1) (342.3(3)°), considerably less than that expected for an sp^2-hybridized carbon atom. The ligand sphere of the boron ion, three nitrogen atoms of the pyrazolyl rings and one carbon atom of the C_5Me_4H ring, deviates slightly from the ideal tetrahedral geometry.

Compound **4** presents approximately a plane of symmetry containing the pyrazolyl ring N(1) and the two Li, B, O(1), and O(2) atoms. One of the lithium centers (Li(1)) is tetracoordinated by two nitrogen atoms of two pyrazolyl rings and two oxygen atoms of the THF molecules. The data of Table 1 show that the geometrical parameters for the lithium atom in **3C** and Li(1) in **4** are rather similar.

The second lithium center (Li(2)) is η^5-coordinated to the C_5Me_4 ring, to one nitrogen atom of the third pyrazolyl ring, and to the oxygen atom of the third THF molecule. The C_5Me_4 group is unsymmetrically bonded to the Li atom with Li−C bond lengths ranging from 2.177(9) to 2.308(10) Å. The Li−Cp_{cent} bond distance is 1.89(1) Å and compares with those found in other lithium cyclopentadienyl complexes structurally characterized.[8,13−15] The B−C(1) bond distance is 1.573(6) Å, slightly shorter than that found in Sm[HB(3,5-Me_2-pz)$_2$(C_5H_4)](Tp^{Me_2}) (1.595(14) Å).[2] The bulkiness of the Cp ring makes the N−B−C(1) angles bigger than those in a regular tetrahedron, with the consequent decrease in the N−B−N angles.

In contrast to **4**, the crystal structure of **5** consists of infinite puckered chains of [K(THF)$_2$[B(3-Mepz)$_3$(C_5Me_4)]] units linked to each other by a second potassium ion that coordinates one pyrazolyl and one C_5Me_4 ring of the adjacent unit. In each unit one K ion (K(1)) is bonded to two nitrogen atoms of two pyrazolyl rings (N1 and N2), η^5-coordinated to the C_5Me_4 ring and to two THF molecules.

Considering the centroid of the C_5Me_4 ring as a coodination axial site, the coordination geometry around K(1) can be described as distorted square-pyramidal. The second K ion (K(2)) is also bonded to pyrazolyl ring N(1) and N(2) and establishes the bridge with the other [B(3-Mepz)$_3$(C_5Me_4)] unit through coordination to C_5Me_4 and the pyrazolyl ring N(3). The coordination geometry for K(2) is best described as triangular pyramidal with N(32) occupying the apical position. The K(1)−O bond distances average 2.723(11) Å and compare with the value found for the corresponding distance in pentabenzylcyclopentadienylpotassium·3THF (2.735 Å).[16] The K(1)−N(12) and K(1)−N(22) bond distances are 2.799(7) and 3.051(9) Å, respectively, and are in the range reported for potassium pyrazolylborates.[17,18] The K(2)−N(12) and K(2)−N(22) bond distances (intramolecular) are 2.909(7) and 2.849 (7) Å, and the K(2)−N(32) distance to the next molecule is 2.764(7) Å; that is, the intermolecular distance is shorter than the intramolecular ones. The same situation is observed for the K−Cp distances. The potassium ion, K(1), is asymmetrically bonded to the C_5Me_4 ring (range 2.830−3.238) with a K(1)−Cp_{cent} of 2.80 Å, and K(2) is

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symmetrically bonded to the C_5Me_4 ring of the neighbor unit with a K(2)−Cp_{cent} of 2.68 Å. Both values are in the range found for other potassium cyclopentadienyls.[19,20]

Conclusions

The lithium and potassium salts of a new, mixed pyrazolyl/cyclopentadienyl ligand were prepared. The synthetic strategy described should allow replacement of the substituents of the pyrazolyl groups and/or cyclopentadienyl ring and hence the generation of a versatile and broad class of new, mixed pyrazolyl/cyclopentadienyl ligands. Metal chemistry with these ligands is under active investigation, and results will be reported in due course.

Experimental Section

General Procedures. All preparations and subsequent manipulations were carried out using standard Schlenk line and drybox techniques in an atmosphere of dinitrogen. THF, toluene, *n*-hexane, and CH_2Cl_2 were dried by standard methods and degassed prior to use. Benzene-d_6 and tetrahydrofuran-d_8 were dried over Na and distilled, and chloroform-d_1 was distilled over P_2O_5. Tetramethylcyclopentadiene, boron trichloride, and 3-methylpyrazole were purchased by Aldrich and used as received. Tetramethyl(trimethylsilyl)cyclopentadiene was prepared by a modification of the method described previously.[21] The compound was isolated by distillation at 55−65 °C (5 mmHg) with a yield of 75%. The lithium and the potassium salts of 3-methylpyrazole were synthesized by adding a stoichiometric amount of n-BuLi and KH to 3-methylpyrazole in THF. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-300 spectrometer at 300 and 75 MHz, respectively. Spectra were referenced internally using the residual proton resonances relative to tetramethylsilane. Carbon, hydrogen, and nitrogen analyses were performed in-house using a EA110 CE Instruments automatic analyzer. High-resolution electron ionization mass spectra were obtained in a Finnigan FTMS 2000-DT Fourier transform ion cyclotron resonance mass spectrometer.

$BCl_2(C_5Me_4H)$ (1). Compound **1** was obtained by a procedure similar to the one described by Jutzi for $BCl_2(C_5Me_5)$.[22] A 1 M solution of BCl_3 in hexanes (22 mL, 22 mmol) was added dropwise to 4.05 g (20.8 mmol) of $C_5Me_4H(SiMe_3)$ in CH_2Cl_2 at −78 °C. The mixture was warmed to room temperature and stirred overnight. The reaction mixture was concentrated under vacuum and transferred to a distillation apparatus. Distillation at 75−80 °C (5 mmHg) gives $BCl_2(C_5Me_4H)$ as one single isomer in 90% yield. Mass spectrum (EI 10 eV, 25 °C): found M^+ 201.05300; $^{12}C_9{}^1H_{13}{}^{10}B^{35}Cl_2$ requires M^+ 201.05182. ^1H NMR (C_6D_6): δ (ppm) 1.08 (d, 3H, (CH_3), J = 7.5 Hz), 1.39 (s, 3H, (CH_3)), 1.50 (s, 3H, (CH_3)), 2.36 (d, 3H, (CH_3), J = 2.1 Hz), 2.92 (m, 1H, C_5H). ^1H NMR ($CDCl_3$): δ (ppm) 1.20 (d, 3H, (CH_3), J = 6.2 Hz), 1.84 (s, 3H, (CH_3)), 1.95 (s, 3H, (CH_3)), 2.10 (d, 3H, (CH_3), J = 1.7 Hz), 3.12 (m, 1H, C_5H). ^{11}B NMR ($CDCl_3$): δ (ppm) 84.5. ^{13}C NMR ($CDCl_3$): δ (ppm) 10.71, 13.02, 15.27, 15.88 (CH_3 (C_5Me_4H), 53.94 (HC (C_5Me_4H)), 137.54, 158.43, 171.43 (carbons of the ring), 397.59 (C-BCl_2).

$B(NMe_2)_2(C_5Me_4H)$ (2). The compound was synthesized by a procedure similar to that used for the conversion of $C_5H_5FeC_5H_4BBr_2$ to $C_5H_5FeC_5H_4B(C_3H_3N_2)_3Li$.[23] To 2.04 g (10.04 mmol) of $BCl_2(C_5Me_4H)$ in toluene was added neat dimethylamine (1:4) at −78 °C. The reaction was immediate, as indicated by formation of a white precipitate. The temperature was raised to 0 °C, and stirring was continued for an additional 2 h. The slurry was filtered to remove the precipitate of $(NH_2Me_2)Cl$, and the toluene solution was evaporated under vacuum. The vinylic isomer **2A** was obtained as a yellow oil with a yield of 70% (1.5 g, 7.0 mmol). Mass spectrum (EI 10 eV, 25 °C): found M^+ 219.21467; $^{12}C_{13}{}^1H_{25}{}^{10}B^{14}N$ requires M^+ 219.21416. ^1H NMR (C_6D_6): δ (ppm) 1.09 (d, 3H, (CH_3), J = 6.0 Hz), 1.78 (s, 3H, (CH_3)), 1.86 (s, 3H, (CH_3)), 1.90 (d, 3H, (CH_3), J = 1.5 Hz), 2.60 (s, 6H, $N(CH_3)_2$), 2.64 (s, 6H, $N(CH_3)_2$), 2.92 (m, 1H, C_5H). ^{11}B NMR ($CDCl_3$): δ (ppm) 70.8. ^{13}C NMR (C_6D_6): δ (ppm) 11.1, 12.1, 14.5, 14.9 (CH_3, C_5Me_4H), 40.6 (CH_3, $N(CH_3)_2$), 40.9 (CH_3, $N(CH_3)_2$), 52.6 (CH, C_5Me_4H ring), 129.3, 135.0, 143.2, 146.7 (carbons of the C_5Me_4H ring). After a few hours at room temperature the three isomers were present as shown by NMR.

$[Li_2(THF)_3B(3\text{-}Mepz)_3(C_5Me_4)]$ (4). Compound **2** (1.52 g, 6.9 mmol) was stirred overnight with 3-MepzH (1.13 g, 13.8 mmol) and 3-MepzLi (0.61 g, 6.9 mmol) in THF. Removal of the solvent under vacuum gave a yellowish solid, which was washed with *n*-hexane. A white solid was obtained as a mixture of isomers. This compound could be crystallized from THF to give crystals of one of the isomers of $[Li(THF)_2B(3\text{-}Mepz)_3(C_5Me_4H)]$ (**3C**) suitable for X-ray diffraction. The crude compound was dissolved in THF, and n-BuLi was slowly added at −50 °C. Then the mixture was allowed to warm to ambient temperature. After this mixture was stirred for 48 h, the solvent was removed under reduced pressure. The resulting white solid was washed with hexane and then dissolved in THF. Concentration of the solution deposited crystals of **4** (1.25 g, 30%). Good analyses could not be obtained even for the crystals, probably due to variable amounts of THF. Anal. Calcd for $C_{21}H_{27}N_6BLi_2$·THF: C, 65.24; H, 7.66; N, 18.26. Calcd for $C_{21}H_{27}N_6BLi_2$·2THF: C, 65.43; H, 8.14; N, 15.79. Calcd for $C_{21}H_{27}N_6BLi_2$·3THF: C, 65.57; H, 8.50; N, 13.90. Found: C, 66.11; H, 7.58; N, 16.42. ^1H NMR (tetrahydrofuran-d_8): 7.31 (b, 3H, H-5(pz)), 5.89 (d, 3H, H-4(pz)), 2.16 (s, 9H, CH_3 (pz)), 1.90 (s, 6H, $CH_3(C_5Me_4)$), 0.98 (s, 6H, $CH_3(C_5Me_4)$).

$[K_2(THF)_2B(3\text{-}Mepz)_3(C_5Me_4)]$ (5). The compound was obtained as described for the dilithium salt by reacting $B(NMe_2)_2(C_5Me_4H)$ (2.06 g, 9.4 mmol) with 1.54 g (18.8 mmol) of 3-MepzH and 1.13 g (9.4 mmol) of K(3-Mepz) in THF. The clear solution was stirred for 18 h, and 400 mg (10 mmol) of KH was added. Stirring for an additional 18 h followed by separation of the excess HK and removal of the solvent under reduced pressure led to a white solid, which was washed with hexane and dried under vacuum. Yield: 70% (3.9 g, 6.6 mmol). Anal. Calcd for $C_{29}H_{43}N_6O_2K_2$: C, 58.37; H, 7.26; N, 14.08. Found: C, 56.48; H, 7.46; N, 14.31. ^1H NMR (tetrahydrofuran-d_8): 7.24 (3H, H-5(pz)), 5.80 (d, 3H, H-4(pz)), 2.18 (s, 9H, CH_3-(3) (pz)), 1.94 (s, 6H, $CH_3(C_5Me_4)$), 1.12 (s, 6H, $CH_3(C_5Me_4)$).

X-ray Crystallographic Analysis. Transparent crystals of **3C**, **4**, and **5** were grown from concentrated solutions of THF. As quality crystals of **5** could not be obtained due to the low solubility of the compound, the corresponding structural analysis is of moderate accuracy. The crystals were mounted in thin-walled glass capillaries in a nitrogen-filled glovebox. Data were collected at room temperature, for **3C** and **5** using an Enraf-Nonius CAD4-diffractometer with graphite-monochromatized Mo Kα radiation, and for **4** on an Enraf-Nonius TURBO CAD4-diffractometer with graphite-monochromatized Cu Kα radiation. The data were corrected[24] for Lorentz and

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Table 2. Crystallographic Data for Complexes 3C, 4, and 5

	3C	**4**	**5**
formula	$C_{29}H_{44}BLiN_6O_2$	$C_{33}H_{51}BLi_2N_6O_3$	$C_{29}H_{43}BK_2N_6O_2$
fw	526.45	604.49	596.70
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$
a (Å)	9.8875(10)	9.6245(11)	11.9893(15)
b (Å)	10.1790(14)	9.7384(10)	15.4349(18)
c (Å)	17.1760(15)	38.395(4)	19.073(3)
α (deg)	88.177(9)	90	90
β (deg)	85.130(8)	90	104.833(14)
γ (deg)	64.541(10)	90	90
V (Å^3)	1555.2(3)	3598.7(7)	3411.9(8)
Z	2	4	4
D_{calcd} (g cm^{-3})	1.124	1.116	1.162
no. of reflns measd	5786	4690	6121
no. of unique reflns [R(int)]	5447 (0.0142)	4422 (0.0594)	5934 (0.0668)
no. obsd [$I > 2\sigma(I)$]	3435	2617	2033
no. of params	353	407	361
R_1[a]	0.0751	0.0639	0.1192
wR_2[b]	0.1877	0.1650	0.2331

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. The values were calculated for data with $I > 2\sigma(I)$.

polarization effects, for linear decay, and empirically for absorption by Ψ scans. Table 2 summarizes the crystallographic data. Solution and refinement were made using SHELXS-97[25] and SHELXL-97.[26] All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, and the contributions of the hydrogen atoms were included in calculated positions. For **4** the absolute structure could not be determined reliably. Figures were made with ORTEP-3.[27]

Acknowledgment. Financial support from Fundação para a Ciência e Tecnologia, Portugal (POCTI/36015/QUI/1999 and POCTI/46179/QUI/2002), is gratefully acknowledged. We are grateful to NATO for the postdoctoral grant to D.R. We thank Dr. Joaquim Marçalo for the high-resolution mass spectrometric molecular weights and Prof. Josef Takats for helpful discussions.

Supporting Information Available: Listings of crystallographic files for **3C**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0498293

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