# A Manganese(II) Coordination Polymer with Ditopic Bis(pyrazol-1-yl)borate Bridges

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Dedicated to Professor Heinrich Nöth on the Occasion of his 80<sup>th</sup> Birthday

**Abstract.** The synthesis and characterization of the ditopic bis(pyrazol-1-yl)borate ligand  $\text{Li}_2[p-\text{C}_6\text{H}_4(B(\text{C}_6\text{F}_5)\text{pz}_2)_2]$  is reported (pz = pyrazol-1-yl). Compared to the corresponding *t*-butyl derivative  $\text{Li}_2[p-\text{C}_6\text{H}_4(B(t-\text{Bu})\text{pz}_2)_2]$ , the  $\text{C}_6\text{F}_5$ -substituted scorpionate is significantly more stable towards hydrolysis. Reaction of  $\text{Li}_2[p-\text{C}_6\text{H}_4(B(\text{C}_6\text{F}_5)\text{pz}_2)_2]$  with two equivalents of  $\text{MnCl}_2$  leads to the formation of coordination polymers  $\{(\text{MnCl}_2)_2(\text{Li}(\text{THF})_3)_2[p-\text{C}_6\text{H}_4(B(\text{C}_6\text{F}_5)\text{pz}_2)_2]\}_\infty$  featuring penta-coordinate  $\text{Mn}^{II}$  ions che-

lated by one bis(pyrazol-1-yl)borate fragment and further bonded to three chloride ions. Two of the three chloride ions are also coordinated to a neighbouring  $Mn^{II}$  ion; the third chloro ligand is shared between the  $Mn^{II}$  centre and a Li(THF)<sub>3</sub> moiety.

**Keywords:** Manganese; Poly(pyrazol-1-yl)borate; Scorpionate ligand; Crystal structures; Coordination polymer

#### **1** Introduction

The presence of two or more metal ions in the same molecule can lead to synergistic effects that profoundly influence both the chemical and the physical properties of the molecule. In the context of homogeneous catalysis, the possibility of more efficient catalytic transformations based on the cooperative reactivity of active centres in multinuclear complexes is therefore being intensively investigated [1]. Similarly, in the field of materials science, great attention is currently paid to the development of metal-containing polymers in which metal-metal interactions bring about useful magnetic, optical or electronic behaviour [2]. For both applications, the design of the bridging ligands is of crucial importance, because they not only form the backbones of the oligometallic aggregates, but can also act as transmitters of metal-metal communication. Ditopic poly-(pyrazol-1-yl)borate ("scorpionate") ligands [3, 4] are particularly well-suited to stabilize oligonuclear complexes due to the fact that their steric and electronic properties can easily be modified over a wide range to identify the optimal derivative for a specific purpose. So far, ditopic scorpionates containing a B-B bond (A; Figure 1) [5], a 1,1'-ferrocenylene bridge (**B**) [6-10], or *meta-/ para-*phenylene linkers

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(C) [11–14], have been synthesized and used for the preparation of oligonuclear transition metal compounds (A; B, x = 0; C, x = 0, 1) [5, 7, 9, 13–16], and multiple-decker sandwich complexes (B, x = 1, 2) [10, 17, 18].



Figure 1 Three classes of ditopic scorpionate ligands A - C; the dinuclear  $Mn^{II}$  complex D featuring a C-type bridge.



Using a *t*-butyl-substituted *p*-**C**-type heteroscorpionate ligand, we have recently synthesized complex **D** featuring two Mn<sup>II</sup> ions bridged by two chloride ions (Figure 1) [13]. This molecule provided an important proof-of-principle, because it showed that the ligand is indeed apt to bring two metal ions into close proximity so that they can act on a common substrate. One shortcoming, however, is the sensitivity of the ligand towards water and strong Lewis acids which induce B-N bond rupture. The fact that tris(pyrazol-1-yl)borates are usually less prone to hydrolysis and loss of pyrazolyl substituents than bis(pyrazol-1-yl)borates, led us to the conclusion that most of the problem was caused by the t-butyl-group that had initially been introduced for solubility reasons. Due to its positive inductive effect and high steric demand, the *t*-butyl-substituent has the disadvantage that it stabilizes three-coordinate boron atoms and thereby promotes the degradation of the scorpionate moiety. We therefore decided to replace the *t*-butyl-group by a smaller substituent with higher group electronegativity and selected the  $C_6F_5$ -moiety as promising alternative. The purpose of this paper is to describe the synthesis of the ditopic  $C_6F_5$ substituted scorpionate 4 (Scheme 1) and its reaction with MnCl<sub>2</sub>.

### 2 Results and Discussion

# 2.1 Synthesis and Spectroscopy

 $C_6F_5$ -substituted poly(pyrazol-1-yl)borates have not been reported in the literature so far. Our synthesis sequence to scorpionate **4** is outlined in Scheme 1.

Starting from readily available p-bis(dibromoboryl)benzene (1) [19], we first prepared the aminoborane 2 by treatment of 1 with 2 equivalents of Me<sub>3</sub>SiNMe<sub>2</sub> at low temperatures. This transformation is important in order to reduce the Lewis acidity of the boron centres so that no ether cleavage takes place during the subsequent synthesis step. To generate 3, the two remaining bromine atoms of 2 were replaced by  $C_6F_5$ -groups using freshly prepared  $C_6F_5MgBr$ [20] in Et<sub>2</sub>O. For the preparation of the lithium heteroscorpionate ligand 4, 3 was treated with 2 equivalents of Lipz and 2 equivalents of Hpz in toluene (pz = pyrazol-1-yl). In our first synthesis attempt, the toluene suspension was heated to reflux for 1 h, which led to the formation of a complex mixture of products, even though a similar protocol had successfully been applied for the preparation of the corresponding t-butyl-substituted heteroscorpionate ligand [11]. Transamination of 3 to 4 was finally achieved by stirring the reaction mixture for 3 days at room temperature. To investigate the sensitivity of 4 towards moisture, a solution of this compound in THF was stirred in an open vessel at room temperature. The progress of the hydrolytic decay was monitored by <sup>1</sup>H NMR spectroscopy. After 1 h, the sample was found to be virtually unchanged, also after 12 h only little decomposition could be observed. After 3 d, however, the solution contained mainly free pyrazole and almost no (pyrazol-1-yl)borate was left. Under the same



Scheme 1 Synthesis of the ditopic scorpionate ligand 4 and the Mn<sup>II</sup> coordination polymer 5. (i) toluene, -78 °C to r.t.; (ii) toluene / Et<sub>2</sub>O, -78 °C to r.t.; (iii) toluene, r.t.; (iv) THF, r.t.

conditions, the corresponding *t*-butyl-substituted ligand  $\text{Li}_2[p-\text{C}_6\text{H}_4(\text{B}(t-\text{Bu})\text{pz}_2)_2]$  showed about 50 % decomposition already after 1 h and was fully degraded after 12 h (cf. also refs. [11, 14]).

Coordination polymer **5** was prepared by stirring a mixture of **4** and  $MnCl_2$  (molar ratio 1:2) in THF for 12 h. Single crystals suitable for X-ray diffraction were grown by gas-phase diffusion of hexane into a THF solution of **5**.

The most revealing NMR data of **2** and **3** are their <sup>11</sup>B NMR shift values of 36.5 ppm and 38.3 ppm, respectively, which point to the presence of three-coordinate boron atoms [21]. The <sup>1</sup>H NMR spectrum of **2** is characterized by three singlets at  $\delta(^{1}H) = 2.94$ , 3.15, and 7.49 with an integral ratio of 6:6:4. Compound **3** gives rise to a qualitatively similar signal pattern ( $\delta(^{1}H) = 2.33$ , 2.47, 7.46). In both cases, the two resonances at higher field correspond to the dimethylamino moieties, and the third signal has to be assigned to the phenylene bridge. The <sup>11</sup>B and <sup>1</sup>H NMR data confirm the proposed molecular structures of **2** and **3** with chemically equivalent [B(R)(NMe<sub>2</sub>)] fragments (Scheme 1). The two signals for the dimethylamino groups are caused by hindered rotation about the B-N axes resulting from a

 Table 1
 Crystallographic data of the compounds 2 and 3 a)

	2	3
formula	$C_{10}H_{16}B_2Br_2N_2$	$C_{22}H_{16}B_2F_{10}N_2$
fw	345.69	519.99
colour, shape	colourless, block	colourless, block
temp /K	173(2)	173(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	ΡĪ
a /Å	7.9507(13)	9.7713(14)
b /Å	7.3059(8)	10.4624(14)
c /Å	12.495(2)	12.8142(18)
α /°	90	104.258(11)
βΙ°	99.162(13)	94.947(11)
y /°	90	114.368(10)
$V/Å^3$	716.52(18)	1130.1(3)
Ζ	2	2
$D_{\rm calcd}$ /g cm <sup>-3</sup>	1.602	1.528
F(000)	340	524
$\mu$ /mm <sup>-1</sup>	5.632	0.147
crystal size /mm	$0.35 \times 0.33 \times 0.26$	$0.22 \times 0.14 \times 0.11$
Θ <sub>min max</sub> /°	3.81, 27.31	3.66, 26.25
no. of rflns collected	4443	14055
no. of indep rflns $(R_{int})$	1597 (0.0670)	4255 (0.0978)
R flns with $I > 2\sigma(I)$	1423	3115
data/restraints/parameters	1597 / 0 / 76	4255 / 0 / 331
$GOOF$ on $F^2$	1.056	1.104
R1, wR2 $(I>2\sigma(I))$	0.0445, 0.1150	0.1240, 0.3253
R1, wR2 (all data)	0.0502, 0.1185	0.1510, 0.3451
largest diff peak and hole /e $Å^{-3}$	1.453 , -1.293	0.622, -0.509

<sup>*a*)</sup> Crystallographic data of the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 677199 (2), 677200 (3). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

significant degree of B-N double bond character. All <sup>13</sup>C NMR signals of **2** and **3** appear in the expected regions of the spectra and therefore do not merit further discussion; no <sup>13</sup>C NMR resonances have been observed for the C<sub>6</sub>F<sub>5</sub>-substituents due to extensive <sup>13</sup>C-<sup>19</sup>F coupling (C-*o*, *m*, *p*) and quadrupolar broadening (C-*i*). Nevertheless, the successful introduction of C<sub>6</sub>F<sub>5</sub> groups is documented by three signals in the <sup>19</sup>F NMR spectrum of **3** ( $\delta$ (<sup>19</sup>F) = -161.7, -155.0, -133.4).

The <sup>11</sup>B NMR spectrum of **4** features one signal at 0.0 ppm, testifying to the presence of chemically equivalent, tetra-coordinate boron centres [21]. The pyrazolyl protons give rise to one multiplet at  $\delta(^{1}\text{H}) = 6.06$  and two doublets at  $\delta(^{1}\text{H}) = 7.46$  and 7.52. A singlet at  $\delta(^{1}\text{H}) = 7.19$  has to be assigned to the *p*-disubstituted phenylene bridge. The relative integral values of the four observed proton signals (4:4:4:4) are in accordance with the assumption that **4** contains two bis(pyrazol-1-yl)borate moieties. Similar to **3**, no  $^{13}C_{6}F_{5}$ -signals could be detected; all  $^{13}$ C NMR data of **4** are unexceptional. The  $^{19}$ F NMR spectrum of **4** reveals three signals ( $\delta(^{19}\text{F}) = -167.9, -163.3, -135.8$ ) from which the first two (F-*m*, *p*) are considerably more shielded than in the precursor compound **3**.

### 2.2 X-ray Crystallography

Crystallographic data of the compounds 2-5 are compiled in Tables 1 and 2. All four molecules have a centre of inver-

**Table 2** Crystallographic data of the compounds  $4([12]crown-4)_2$  and  $5^{a_j}$ 

	<b>4</b> ([12]crown-4) <sub>2</sub>	5
formula	C46H48B2F10Li2N8O8	C54H64B2Cl4F10Li2Mn2N8O6
fw	1066.42	1398.31
colour, shape	colourless, block	colourless, plate
temp /K	173(2)	173(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	PĪ
a /Å	8.8011(10)	11.2963(19)
b /Å	15.1808(11)	12.936(2)
c /Å	18.877(2)	16.593(3)
$\alpha /^{\circ}$	90	110.068(12)
βΙ°	100.256(9)	98.677(13)
y /°	90	99.317(13)
$V/Å^3$	2481.8(4)	2191.0(6)
Ζ	2	1
$D_{\rm calcd.}$ /g cm <sup>-3</sup>	1.427	1.060
F(000)	1100	716
$\mu / \text{mm}^{-1}$	0.122	0.470
crystal size /mm	0.21  imes 0.16  imes 0.14	$0.36 \times 0.19 \times 0.09$
$\Theta_{\min,\max}$ /°	3.47, 25.70	3.48, 25.03
no. of rflns collected	19962	25784
no. of indep rflns $(R_{int})$	4673 (0.0828)	7722 (0.1208)
Rflns with $I > 2\sigma(I)$	3100	3681
data/restraints/parameters	4673 / 0 / 344	7722 / 0 / 397
$GOOF$ on $F^2$	1.021	1.273
R1, wR2 $(I \ge 2\sigma(I))$	0.0600, 0.1350	0.1200, 0.2677
R1, wR2 (all data)	0.0995, 0.1531	0.2054, 0.3028
largest diff peak and	0.300, -0.268	0.687, -0.517
hole /e $Å^{-3}$		

<sup>*a*)</sup> Crystallographic data of the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 677201 ( $4([12]crown-4)_2)$ , 677202 (5). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

sion located at the centroid of the respective phenylene spacer; compound 5 has a second inversion centre at the midpoint of the four-membered  $Mn_2Cl_2$  ring (Figure 5). The C<sub>6</sub>F<sub>5</sub>-substituted borane 3 crystallizes from toluene with two crystallographically independent molecules (3<sub>A</sub>, 3<sub>B</sub>) in the asymmetric unit. Since the key structural parameters of 3<sub>A</sub> and 3<sub>B</sub> are the same within experimental error, only the bond lengths and angles of 3<sub>A</sub> are considered here.

The molecular structures of the mono(amino)boranes 2 and 3 have been determined in order to find out whether replacement of a bromine atom by the highly electronegative  $C_6F_5$ -fragment has a visible impact on the B-N bond length, which in turn could be interpreted as a change in the degree of N-B  $\pi$ -bonding. As evidenced by the very similar values of B(1)-N(1) = 1.388(5) Å in 2 (Figure 2) and 1.395(11) Å in 3<sub>A</sub> (Figure 3), no such effect is apparent. The B-N bond of 3<sub>A</sub> is, however, slightly longer than the corresponding bond in the related aminoborane (CH<sub>2</sub>)<sub>4</sub>N-B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1.366(3) Å) [22] bearing *two* electronwithdrawing C<sub>6</sub>F<sub>5</sub>-substituents.

As to be expected, the boron as well as the nitrogen atoms of 2 and  $3_A$  adopt perfectly planar configurations (sums of the bond angles about these atoms:  $360^\circ$ ). We also observe almost identical conformations of the [(N)(R)B-C<sub>6</sub>H<sub>4</sub>-B(R)(N)] cores in 2 and  $3_A$  with dihedral angles



Figure 2 Structure of 2 in the crystal. Displacement ellipsoids are drawn at the 50 % probability level.



Figure 3 Structure of  $3_A$  in the crystal. Displacement ellipsoids are drawn at the 50 % probability level.

Selected bond lengths/Å, bond angles/°, and dihedral angles/°: B(1)-N(1) = 1.395(11), B(1)-C(11) = 1.584(11), B(1)-C(21) = 1.610(11), N(1)-C(2) = 1.475(9), N(1)-C(3) = 1.466(9); N(1)-B(1)-C(11) = 123.4(7), N(1)-B(1)-C(21) = 120.4(7), C(11)-B(1)-C(21) = 116.2(6), B(1)-N(1)-C(2) = 122.9(7), B(1)-N(1)-C(3) = 124.4(6), C(2)-N(1)-C(3) = 112.3(6);  $N(1)B(1)C(21)//C_6H_4 = 58.2^\circ$ .

 $N(1)B(1)Br(1)//C_6H_4 = 58.4^{\circ}$  (2) and  $N(1)B(1)C(21)//C_6H_4 = 58.2^{\circ}$  (3<sub>A</sub>). With regard to the crystal packing of 3, intermolecular edge-to-face interactions between phenylene spacers and C<sub>6</sub>F<sub>5</sub>-rings appear to play a prominent role (CH···COG(C<sub>6</sub>F<sub>5</sub>) = 3.039 Å, 3.052 Å; COG: ring centroid).

In the solid state structure of the lithium scorpionate 4, each Li<sup>+</sup> ion is coordinated to one molecule of [12]crown-4 (4([12]crown-4)<sub>2</sub>; Figure 4) and to two pyrazolyl rings (N(12)-Li(1) = 2.123(5) Å, N(22)-Li(1) = 2.109(5) Å; N(12)-Li(1)-N(22) = 87.6(2)°). The phenylene spacer is located in the plane bisecting the N-B-N angles, while the  $C_6F_5$ -rings are oriented almost perpendicular to it (dihedral angle  $C_6H_4//C_6F_5 = 74.1^\circ$ ). The overall structure of  $4([12]crown-4)_2$  closely resembles that of the Li<sup>+</sup> salt of the *t*-butyl derivative (Li(THF)<sub>2</sub>)<sub>2</sub>[*p*-C] [13] (Figure 1).



Figure 4 Structure of  $4([12]crown-4)_2$  in the crystal. H atoms are omitted for clarity, displacement ellipsoids are drawn at the 50 % probability level.

Selected bond lengths/Å, bond angles/°, and torsion angles/°: B(1)-N(11) = 1.564(3), B(1)-N(21) = 1.580(4), B(1)-C(31) = 1.659(4), B(1)-C(41) = 1.633(4), N(12)-Li(1) = 2.123(5), N(22)-Li(1) = 2.109(5); N(11)-B(1)-N(21) = 108.0(2), N(12)-Li(1)-N(22) = 87.6(2); C(42)-C(41)-B(1)-C(31) = -178.5(2), C(42)-C(41)-B(1)-N(11) = -55.7(3), C(42)-C(41)-B(1)-N(21) = 61.6(3).

The scorpionate ligand in the solid state structure of the  $Mn^{II}$  complex 5 (Figure 5) adopts the same conformation as in the Li<sup>+</sup> salt 4([12]crown-4)<sub>2</sub>.

Each Mn<sup>II</sup> ion is chelated by one bis(pyrazol-1-yl)borate unit (N(12)-Mn(1) = 2.174(6) Å, N(22)-Mn(1) =2.223(6) Å) and further bonded to three chloro ligands. The resulting coordination polyhedron is intermediate between a distorted square pyramid and a trigonal bipyramid (trigonality index  $\tau$  [23] = 0.48). Two of the three chloride ions act as bridges to a neighbouring Mn<sup>II</sup> ion so that a coordination polymer is formed (Cl(1)-Mn(1))2.501(3) Å, Cl(1B)-Mn(1) = 2.578(2) Å) [24]. The apical chloride ion is also a bridging ligand, because it coordinates not only to the Mn<sup>II</sup> centre but also to a Li(THF)<sub>3</sub> fragment (Cl(2)-Mn(1) = 2.396(3) Å). It is revealing to compare the structure of coordination polymer 5 with that of the dinuclear complex **D** (Figure 1). In **D** [13], the two  $Mn^{II}$ ions are also penta-coordinate and we observe a similar  $[R_2Bpz_2Mn(\mu-Cl)_2Mnpz_2BR_2]$  core as in the case of 5 (D: Cl-Mn = 2.516(2) Å; N-Mn = 2.175(5) Å). However, the fifth ligand in **D** is a THF molecule and the coordination polyhedron of  $Mn^{II}$  is an ideal square-pyramid ( $\tau = 0$ ).

#### **3** Conclusion

Replacement of the *t*-butyl-substituents in the ditopic bis(pyrazol-1-yl)borate ligand  $[p-C_6H_4(B(t-Bu)pz_2)_2]^{2-}$  by  $C_6F_5$ -rings leads to a significantly enhanced stability of the resulting scorpionate  $[p-C_6H_4(B(C_6F_5)pz_2)_2]^{2-}$  towards air and moisture. The seemingly innocent spectator group has



Figure 5 a) Structure of 5 in the crystal. b) Ball-and-stick model of the polymer chain of 5. H atoms are omitted for clarity, displacement ellipsoids are drawn at the 30 % probability level.

Selected bond lengths/Å, bond angles/°, and torsion angles/°: B(1)-N(11) =2.223(6). Cl(1)-Mn(1) = 2.501(3), Cl(1B)-Mn(1) = 2.578(2), Cl(2)-Mn(1)2.34(2); N(12)-Mn(1)-N(22) =2.396(3), Cl(2)-Li(1) =84.0(2). Cl(1)-Mn(1)-N(12) = 131.8(2), Cl(1B)-Mn(1)-N(22) 160.8(2). Cl(1)-Mn(1)-Cl(1B) = 82.2(1), Cl(1)-Mn(1)-Cl(2)111.2(1), Cl(1B)-Mn(1)-Cl(2) = 95.7(1), Mn(1)-Cl(1)-Mn(1B) =97.8(1), Mn(1)-Cl(2)-Li(1) 118.5(5); C(42)-C(41)-B(1)-C(31)3.8(10), C(42)-C(41)-B(1)-N(11) = -116.9(8), C(42)-C(41)-B(1)-N(21) =124.0(8). Symmetry transformation used to generate equivalent atoms: B = -x+2, -y+1, -z+1.

also considerable impact on the molecular structures of corresponding  $Mn^{II}$  complexes. From 2 : 1 mixtures of  $MnCl_2$ with  $Li_2[p-C_6H_4(B(t-Bu)pz_2)_2]$  or  $Li_2[p-C_6H_4(B(C_6F_5)pz_2)_2]$ in THF/hexane we isolated single crystals consisting of discrete dinuclear metallomacrocycles in the case of the *t*-butyl-derivative (**D**; Figure 1) and coordination polymers in the case of the  $C_6F_5$  analogue (**5**, Figure 5). Detailed investigations into the magnetic properties of both species are currently underway in our laboratory.

# 4 Experimental Section

#### **General Considerations**

All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free argon using standard Schlenk ware.  $CH_2Cl_2$  and  $CDCl_3$  were passed through a 4 Å molecular sieves column prior to use. All other solvents were freshly distilled under argon from Na/benzophenone. p-C<sub>6</sub>H<sub>4</sub>(BBr<sub>2</sub>)<sub>2</sub> (1) [19] and C<sub>6</sub>F<sub>5</sub>MgBr [20] were prepared following literature procedures. NMR: Bruker AMX 250, AMX 300, AMX 400, Bruker DPX 250 spectrometers. <sup>1</sup>H- and <sup>13</sup>C NMR spectra are calibrated against residual solvent signals. <sup>11</sup>B NMR spectra were reported relative to external BF<sub>3</sub>·Et<sub>2</sub>O. All NMR spectra were run at room temperature. Abbreviations: s = singlet, d = doublet, m = multiplet, n.o. = signal not observed, pz = pyrazol-1-yl. Elemental analyses were performed by the microanalytical laboratory of the University of Frankfurt.

Synthesis of 2. A solution of Me<sub>3</sub>SiNMe<sub>2</sub> (3.05 g, 26.02 mmol) in toluene (20 mL) was added dropwise with stirring at -78 °C to 1 (5.43 g, 13.01 mmol) in toluene (40 mL). The clear solution was slowly allowed to warm to room temperature, stirred for 12 h and evaporated to dryness in vacuo. Yield: 4.05 g (90 %). Colourless crystals of 2 were grown by slow evaporation of a toluene solution at ambient temperature.

<sup>11</sup>**B** NMR (128.4 MHz, CDCl<sub>3</sub>): 36.5 ( $h_{1/2}$  = 280 Hz). <sup>1</sup>**H** NMR (300.0 MHz, CDCl<sub>3</sub>): 2.94, 3.15 (2 × s, 2 × 6H, NCH<sub>3</sub>), 7.49 (s, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>**C** NMR (75.5 MHz, CDCl<sub>3</sub>): 41.1, 42.5 (NCH<sub>3</sub>), 131.6 (C<sub>6</sub>H<sub>4</sub>), n.o. (CB).

Synthesis of 3. A solution of  $C_6F_5MgBr$  in Et<sub>2</sub>O (2.2 M, 4.25 mL, 9.35 mmol) was added dropwise under vigorous stirring at -78 °C to a solution of 2 (1.62 g, 4.68 mmol) in toluene (30 mL). The resulting light brown mixture was allowed to warm to room temperature and all volatiles were removed in vacuo. The solid product was extracted into hexane (2 × 50 mL) and the extract evaporated to dryness in vacuo. Yield: 1.80 g (74 %). Crystals suitable for X-ray diffraction were grown by recrystallization of the crude material from toluene.

<sup>11</sup>**B** NMR (96.3 MHz,  $C_6D_6$ ): 38.3 ( $h_{1/2} = 490$  Hz). <sup>1</sup>H NMR (300.0 MHz,  $C_6D_6$ ): 2.33, 2.47 (2 × s, 2 × 6H, NCH<sub>3</sub>), 7.46 (s, 4H,  $C_6H_4$ ). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): 40.9, 41.7 (NCH<sub>3</sub>), 131.3 ( $C_6H_4$ ), n.o. (CB, CF). <sup>19</sup>F NMR (282.3 MHz,  $C_6D_6$ ): -161.7 (m, 4F, F-m), -155.0 (m, 2F, F-p), -133.4 (m, 4F, F-o).

Synthesis of 4. A mixture of neat Lipz (0.115 g, 1.55 mmol) and neat Hpz (0.106 g, 1.56 mmol) was added to a solution of 3 (0.410 g, 0.78 mmol) in toluene (50 mL) at room temperature. The suspension was stirred for 72 h and then evaporated to dryness in vacuo. Yield: 0.440 g (79 %). X-ray quality crystals of 4([12]crown-4)<sub>2</sub> were grown by gas-phase diffusion of hexane into a saturated solution of 1 equivalent of 4 and 2 equivalents of [12]crown-4 in THF at room temperature. Anal. Calcd. for  $C_{46}H_{48}B_2F_{10}Li_2N_8O_8$ (1066.42) × 2 H<sub>2</sub>O (18.02): C, 50.12; H, 4.75; N, 10.16. Found: C, 50.30; H, 4.82; N, 9.89 %.

<sup>11</sup>**B** NMR (96.3 MHz, THF-d<sub>8</sub>): 0.0 ( $h_{1/2}$  = 340 Hz). <sup>1</sup>**H** NMR (400.1 MHz, THF-d<sub>8</sub>): 6.06 (m, 4H, pzH-4), 7.19 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 7.46, 7.52 (2 × d, 2 × 4H, <sup>3</sup>J<sub>HH</sub> = 2.0 Hz, 1.4 Hz, pzH-3/5). <sup>13</sup>C NMR (75.4 MHz, THF-d<sub>8</sub>): 103.3 (pzC-4), 134.7 (pzC-3/5), 137.1 (C<sub>6</sub>H<sub>4</sub>), 140.1 (pzC-3/5), n.o. (CB, CF). <sup>19</sup>F NMR (282.3 MHz, THF-d<sub>8</sub>): -167.9 (m, 4F, F-*m*), -163.3 (m, 2F, F-*p*), -135.8 (m, 4F, F-*o*).

Synthesis of 5. A solution of 4 (0.243 g, 0.34 mmol) in THF (20 mL) was added to neat MnCl<sub>2</sub> (0.086 g, 0.68 mmol). The suspension was stirred at room temperature for 12 h to give a clear light brown solution. After the solvent had been removed in vacuo the product was extracted into CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The extract was evaporated to dryness in vacuo to give a pale brown solid. Yield: 0.400 g. Few crystals suitable for X-ray analysis were grown by gasphase diffusion of hexane into a saturated THF solution of the product at room temperature.

#### X-ray Crystal Structure Determinations of 2-5

Data collection was performed on a Stoe-IPDS-II two-circle-diffractometer with graphite-monochromated MoK<sub> $\alpha$ </sub> radiation (0.71073 Å). Empirical absorption corrections with the MULABS option in the program PLATON [25] were performed for **2** and **5**. The structures were solved by direct methods [26] and refined with full-matrix least-squares on  $F^2$  using the program SHELXL97 [27]. Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. CCDC reference numbers: 677199 (**2**), 677200 (**3**), 677201 (**4**([12]crown-4)<sub>2</sub>), 677202 (**5**). Acknowledgement. The authors are grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial funding. T. M. wishes to thank the Fonds der Chemischen Industrie (FCI) for a Ph. D. grant.

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