

# Synthesis and structural characterization of ferrocene-based bis(pyrazol-1-yl)borate ligands: $\text{FcB}(\text{Me})\text{pz}_2\text{K}$ , $\text{Fc}_2\text{Bpz}_2\text{K}$ , and $1,1'\text{-fc}[\text{B}(\text{Me})\text{pz}_2]_2\text{K}_2$ (Fc: ferrocenyl, fc: ferrocenylene, pz: pyrazolyl)

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## Abstract

Reaction of the ferrocenyl(dimethylamino)boranes  $\text{FcB}(\text{Me})\text{NMe}_2$ ,  $\text{Fc}_2\text{BNMe}_2$ , and  $1,1'\text{-fc}[\text{B}(\text{Me})\text{NMe}_2]_2$  with 1:1 mixtures of pyrazole and potassium pyrazolide in refluxing THF gave the potassium salts of the ferrocene-based bis(pyrazol-1-yl)borate ligands  $\text{FcB}(\text{Me})\text{pz}_2\text{K}$ ,  $\text{Fc}_2\text{Bpz}_2\text{K}$ , and  $1,1'\text{-fc}[\text{B}(\text{Me})\text{pz}_2]_2\text{K}_2$  in good yield (Fc: ferrocenyl, fc: ferrocenylene, pz: pyrazolyl). In the solid state,  $\text{FcB}(\text{Me})\text{pz}_2\text{K}$  and  $\text{Fc}_2\text{Bpz}_2\text{K}$  form centrosymmetric dimers with short  $\text{K} \cdots \text{Cp}$  contacts suggesting an  $\eta^5$  coordination mode of the potassium ion. The crystal lattice of the ditopic ligand  $1,1'\text{-fc}[\text{B}(\text{Me})\text{pz}_2]_2\text{K}_2$  consists of coordination polymer strands featuring essentially the same structural motif that has been observed for the monotopic derivatives. All three scorpionate ligands are thus promising building blocks for the preparation of ferrocene-containing multiple-decker sandwich complexes.

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**Keywords:** Ferrocene; Nitrogen ligand; Bis(pyrazol-1-yl)borate; X-ray crystallography

## 1. Introduction

Our group is interested in the development of poly(pyrazol-1-yl)borate ligands [1] (“scorpionates”) as bridging elements for the generation of oligonuclear hybrid compounds consisting of organometallic entities (e.g., ferrocene, cymantrene) on one hand and classical Werner-type complexes on the other. For start, we prepared derivatives of the mono- and ditopic tris(pyrazol-1-yl)borates **I** and **II** (Fig. 1), which were subsequently employed for the assembly of various di- and trinuclear transition metal complexes [2–5]. Even though, in most cases, the nature of the complexed transition metal centre *M* had some influence over the redox potential of the

ferrocene iron atom, the degree of electronic communication was generally low [3,5]. We therefore decided to reduce the number of pyrazolyl substituents in **I** and **II**, assuming that a lack of  $\sigma$ -donor sites might force the complexed metal atom to bind directly to the cyclopentadienyl ring of the ferrocene backbone which could in turn lead to a more pronounced Fe/*M* interaction. The general validity of our concept was proven by an X-ray single crystal structure determination of the ditopic lithium mono(pyrazol-1-yl)borate **III** (Fig. 1) that revealed the desired multiple-decker sandwich arrangement in the solid state [6]. In order to see whether an additional chelating sidearm *per* borate unit would also lead to the aimed-for  $\eta^5 \text{M} \cdots \text{Cp}$  coordination, it appeared to be worthwhile to investigate the corresponding ferrocene-based bis(pyrazol-1-yl) borate ligands (note that an analogous bitopic ferrocenylene-linked bis(pyrazol-1-yl)methane **IV** has recently been published by Reger et al. [7]; Fig. 1). Thus, the methyl

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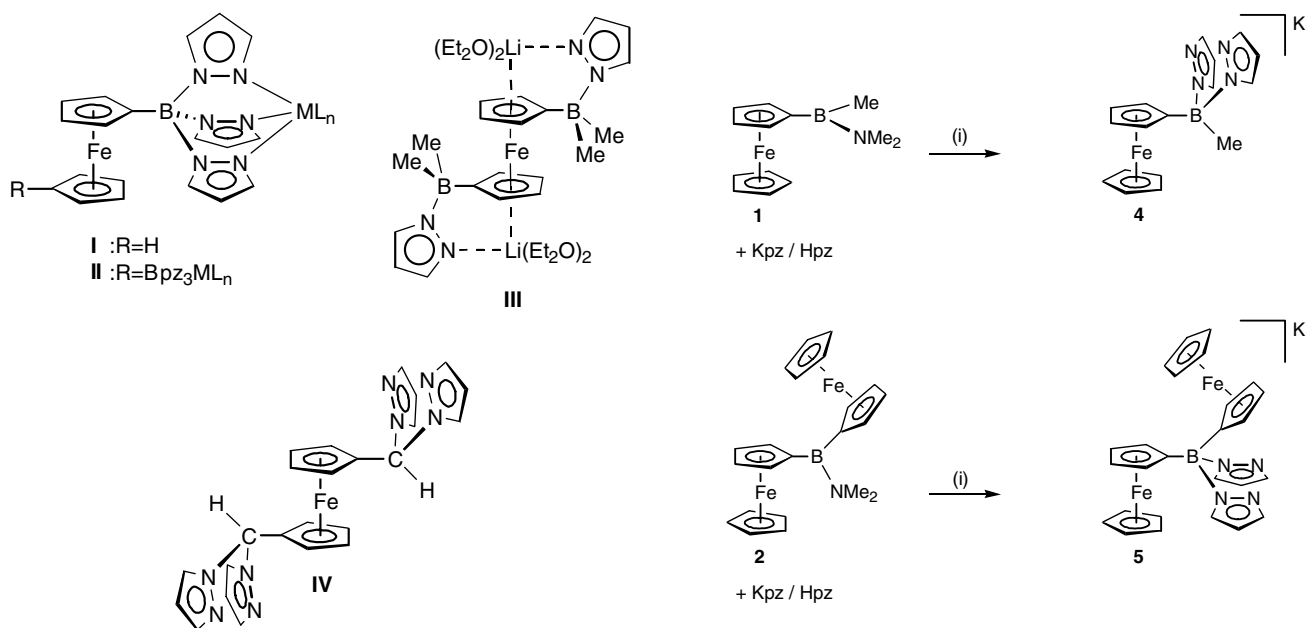


Fig. 1. Mono- and ditopic ferrocene-based tris(pyrazol-1-yl)borates **I** and **II**, the analogous lithium mono(pyrazol-1-yl)borate **III** and Reger's ferrocenylene-linked bis(pyrazol-1-yl)methane ligand **IV**.

derivatives **4** and **6** (Scheme 1) were selected as target molecules since they are closely related to **III**. In addition, the diferrocenyl ligand **5** was prepared, because the presence of *two* ferrocenyl substituents in the ligand molecule may be expected to increase the number of conformations allowing for close  $M \cdots Cp$  contacts.

## 2. Results and discussion

### 2.1. Syntheses and spectroscopy

The starting materials **1** and **3** (Scheme 1) are available by published procedures [8]. The diferrocenyl complex **2** (Scheme 1) was prepared from  $Fc_2BBr$  [8] and  $Me_3SiNMe_2$  in 86% yield (Fc: ferrocenyl). Further reaction of **1–3** with one (**1**, **2**) or two (**3**) equivalents of Kpz/Hpz in refluxing THF readily leads to the desired heteroscorpionates **4–6**. The ligands are sensitive to air; **4** and **5** are readily soluble in THF, whereas **6** is only moderately soluble in all common organic solvents.

The  $^{11}B$  NMR resonances of **4–6** appear in the range between  $-1.4$  and  $1.0$  ppm thereby testifying to the presence of four-coordinate boron nuclei. In all three cases, only one set of signals is observed for the pyrazolyl rings in the  $^1H$  as well as in the  $^{13}C$  NMR spectrum. The same is true for the ferrocenyl resonances of **5**. Thus, even though **5** and **6** are sterically quite crowded, rotation about the B–N– and the B–C bonds is obviously fast on the NMR timescale. All proton and carbon resonances appear in the usually observed region and therefore do not merit detailed discussion.

Scheme 1. Synthesis of the ferrocene-based heteroscorpionate ligands **4**, **5** and **6**. (i) THF,  $-78$  °C to reflux temperature.

### 2.2. X-ray crystallography

Crystal data and structure refinement details for **4** (monoclinic,  $P2_1/n$ ), **5** (triclinic,  $P\bar{1}$ ), and **6** (monoclinic,  $P2_1/n$ ) are compiled in Table 1.

$FcB(Me)pz_2K$ , **4**, forms centrosymmetric dimers  $(4THF)_2$  in the solid state (Fig. 2). Both pyrazolyl rings of the B(1)-scorpionate fragment bind to the potassium ion K(1) but in different manners: While the N(12)-pyrazolyl ring merely acts as a  $\sigma$ -donor ( $K(1)-N(12) = 2.806(5)$  Å), the N(22)-pyrazolyl ring coordinates in a distorted  $\eta^5$  mode ( $K(1) \cdots COG(pz) = 2.958$  Å; COG: centre of gravity). The B(1 $^\#$ )-scorpionate ligand binds to K(1) via one pyrazolyl ring ( $\eta^1$  mode;  $K(1)-N(22^\#) = 2.797(5)$  Å) and its ferrocenyl–Cp unit ( $\eta^5$  mode;  $K(1) \cdots COG(Cp^\#) = 2.942$  Å). Thus, if we just regard N(22)-pyrazolyl and C(31 $^\#$ )–Cp as pentagonal  $\pi$  electron systems, the coordination modes of both scorpionate fragments are very much alike. The ligand sphere of K(1) is completed by one THF molecule. While the N(12)-pyrazolyl ring is bonded to one potassium ion only, N(22)-pyrazolyl acts as a bridging ligand between two  $K^+$  ions. One of them is coordinated via the N(22)

Table 1

Crystal data and structure refinement details for compounds (4THF)<sub>2</sub>, [5(THF)<sub>2</sub>]<sub>2</sub> and [6(THF)<sub>4</sub>]<sub>∞</sub>

	(4THF) <sub>2</sub>	[5(THF) <sub>2</sub> ] <sub>2</sub>	[6(THF) <sub>4</sub> ] <sub>∞</sub>
Formula	C <sub>42</sub> H <sub>52</sub> B <sub>2</sub> Fe <sub>2</sub> K <sub>2</sub> N <sub>8</sub> O <sub>2</sub>	C <sub>72</sub> H <sub>88</sub> B <sub>2</sub> Fe <sub>4</sub> K <sub>2</sub> N <sub>8</sub> O <sub>5</sub>	C <sub>40</sub> H <sub>58</sub> B <sub>2</sub> FeK <sub>2</sub> N <sub>8</sub> O <sub>4</sub>
<i>F</i> <sub>w</sub>	912.44	1468.72	870.61
Colour, shape	Orange, plate	Orange, block	Orange, block
Crystal size (mm)	0.24 × 0.16 × 0.08	0.35 × 0.33 × 0.26	0.16 × 0.15 × 0.12
Temperature (K)	173(2)	173(2)	173(2)
Radiation Mo Kα (Å)	0.71073	0.71073	0.71073
Crystal syst.	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
Unit cell dimensions			
<i>a</i> (Å)	9.8960(11)	10.0893(15)	10.6714(12)
<i>b</i> (Å)	21.711(2)	13.4257(19)	15.6115(17)
<i>c</i> (Å)	10.5580(13)	13.502(2)	13.3795(17)
α (°)	90	67.942(11)	90
β (°)	107.834(9)	84.113(12)	94.535(10)
γ (°)	90	88.370(12)	90
<i>V</i> (Å <sup>3</sup> )	2159.4(4)	1686.0(4)	2222.0(4)
<i>Z</i>	2	1	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.403	1.447	1.301
μ (mm <sup>-1</sup> )	0.910	1.025	0.575
No. of reflections collected	21877	23581	18561
No. of independent reflections	4106	6390	4242
<i>R</i> <sub>int</sub>	0.0935	0.0749	0.0781
Data/restraints/parameters	4106/0/262	6390/0/433	4242/0/259
GOF	0.989	0.912	0.844
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0727, 0.1289	0.0418, 0.1024	0.0408, 0.0748
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1344, 0.1487	0.0620, 0.1105	0.0878, 0.0848
Largest differences in peak and hole (e Å <sup>-3</sup> )	0.471, -0.290	0.542, -0.381	0.309, -0.282

electron lone pair, whereas the other is embedded in the π electron cloud.

In the solid state, Fc<sub>2</sub>Bpz<sub>2</sub>K, **5**, adopts a structure very similar to (4THF)<sub>2</sub> apart from the fact that the methyl group has been replaced by a ferrocenyl substituent and that each of the two potassium ions now bears two THF ligands (i.e. [5(THF)<sub>2</sub>]<sub>2</sub>; Fig. 3). As a result of the higher coordination number, all K–N and K⋯COG values are significantly elongated in [5(THF)<sub>2</sub>]<sub>2</sub> as compared to (4THF)<sub>2</sub> (cf. [5(THF)<sub>2</sub>]<sub>2</sub>: K(1)–N(12) = 2.821(3) Å, K(1)–N(22<sup>#</sup>) = 2.871(3) Å; K(1)⋯COG(pz) = 3.168 Å, K(1)⋯COG(Cp<sup>#</sup>) = 3.171 Å). The conformation of the scorpionate ligand is such that the planes of the C(31)–Cp–, the C(51)–Cp– and the N(21)–pyrazolyl ring are all orthogonal to each other (dihedral angles: C(31)C(32)C(33)C(34)C(35)//C(51)C(52)C(53)C(54)C(55) = 82.7°, N(21)N(22)C(23)–C(24)C(25)//C(31)C(32)C(33)C(34)C(35) = 94.2°, N(21)–N(22)C(23)C(24)C(25)//C(51)C(52)C(53)C(54)C(55) = 84.2°).

The crystal lattice of the discorpionate complex 1,1'-fc[B(Me)pz<sub>2</sub>]<sub>2</sub>K<sub>2</sub>, **6**, consists of coordination polymer strands ([6(THF)<sub>4</sub>]<sub>∞</sub>; Figs. 4 and 5). Within these strands, the individual CpB(Me)pz<sub>2</sub>K fragments are again arranged into dinuclear potassium complexes giving rise to essentially the same structural motif as has already been described for (4THF)<sub>2</sub> (cf. [6(THF)<sub>4</sub>]<sub>∞</sub>: K(1)–N(12) = 2.787(3) Å, K(1)–N(22<sup>#</sup>) = 2.786(3) Å; K(1)⋯COG(pz) = 3.069 Å, K(1)⋯COG(Cp<sup>#</sup>) = 3.020

Å). Similar to [5(THF)<sub>2</sub>]<sub>2</sub>, the ligand environment of the K<sup>+</sup> ion of [6(THF)<sub>4</sub>]<sub>∞</sub> contains two THF molecules.

### 3. Conclusion

We have prepared a series of ferrocene-based bis(pyrazol-1-yl)borate ligands FcB(Me)pz<sub>2</sub>K (**4**), Fc<sub>2</sub>Bpz<sub>2</sub>K (**5**) and 1,1'-fc[B(Me)pz<sub>2</sub>]<sub>2</sub>K<sub>2</sub> (**6**; Fc: ferrocenyl, fc: ferrocenylene, pz: pyrazolyl). Single crystal X-ray structure analyses revealed **4** and **5** to exist as centrosymmetric dimers whereas **6** forms coordination polymer chains. In all three cases, each potassium ion is not only bonded to the pyrazolyl rings but also η<sup>5</sup>-coordinated to one ferrocene fragment. The respective distance between the metal atom and the centre of gravity of the cyclopentadienyl ring is 2.942 Å (**4**), 3.171 Å (**5**) and 3.020 Å (**6**). There is only one example of an η<sup>5</sup>-ferrocene–K<sup>+</sup> complex known in the literature up to now, namely [K(ferrocene)<sub>2</sub>(toluene)<sub>2</sub>]<sup>+</sup>. [9] Here, the average length of the ligand-unsupported K<sup>+</sup>⋯COG(Cp) bond equals to 2.964 Å, which is in very good agreement with our findings. This leads to the conclusion that ligands **4–6** are well-designed to promote direct bonding interactions between metal atoms and the electron π systems of the ferrocenyl substituents and thus to generate multiple-decker sandwich structures. Work is in progress to synthesize transition metal complexes of our compounds

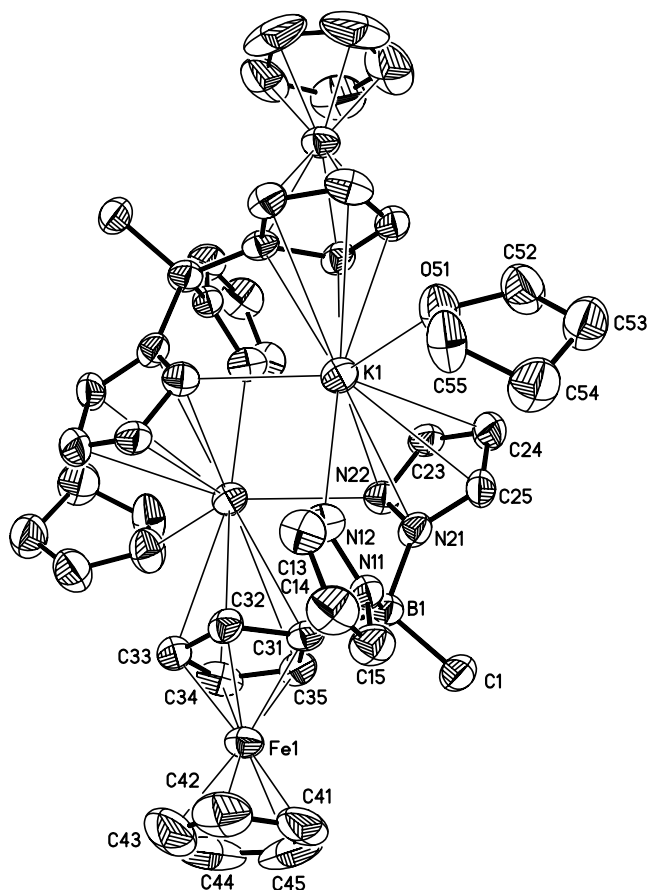


Fig. 2. Molecular structure and numbering scheme of compound  $(4\text{THF})_2$ . Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å), atom–atom distances (Å), angles ( $^\circ$ ), torsion angles ( $^\circ$ ) and dihedral angles ( $^\circ$ ): B(1)–C(31) = 1.610(9), B(1)–N(11) = 1.568(8), B(1)–N(21) = 1.583(7), K(1)–N(12) = 2.806(5), K(1)–N(22) = 3.145(5), K(1)–N(22 $^\#$ ) = 2.797(5), K(1)–COG(Cp $^\#$ ) = 2.942, K(1)–COG(pz) = 2.958, K(1)–K(1 $^\#$ ) = 4.155; N(11)–B(1)–N(21) = 106.4(4), N(12)–K(1)–N(22) = 78.4(1), N(12)–K(1)–N(22 $^\#$ ) = 91.6(1); N(11)–B(1)–C(31)–C(32) = 15.6(7), N(21)–B(1)–C(31)–C(32) = –100.3(6), N(22)–N(21)–B(1)–C(31) = –7.0(7), N(12)–N(11)–B(1)–C(31) = –72.2(6), N(12)–N(11)–B(1)–N(21) = 45.7(6); N(11)N(12)C(13)C(14)C(15)//C(31)C(32)C(33)C(34)C(35) = 104.9, N(21)N(22)C(23)C(24)C(25)//C(31)C(32)C(33)C(34)C(35) = 71.5, C(31)C(32)C(33)C(34)C(35)//C(41)C(42)C(43)C(44)C(45) = 3.6. COG(Cp $^\#$ ): centre of gravity of the C(31 $^\#$ )C(32 $^\#$ )C(33 $^\#$ )C(34 $^\#$ )C(35 $^\#$ ) ring; COG(pz): centre of gravity of the N(21)N(22)C(23)C(24)C(25) ring. Symmetry transformation used to generate equivalent atoms:  $-x + 1, -y + 1, -z + 1$  ( $^\#$ ).

and to investigate the degree of electronic metal–ferrocene communication.

## 4. Experimental

### 4.1. General remarks

All reactions and manipulations of air-sensitive compounds were carried out in dry, oxygen-free nitrogen using standard Schlenk ware. Solvents were freshly dis-

tilled under argon from Na-benzophenone (diethyl ether, THF, toluene) or dried over molecular sieves ( $\text{CDCl}_3$ ) prior to use. NMR: Bruker DPX 400, Bruker DPX 250.  $^{11}\text{B}$  NMR spectra are reported relative to external  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . All NMR spectra were run at ambient temperature; abbreviations: s = singlet, d = doublet, vtr = virtual triplet, br = broad, n.r. = multiplet expected in the NMR spectrum but not resolved, n.o. = signal not observed.  $\text{FcB}(\text{Me})\text{NMe}_2$  [8],  $1,1'$ - $\text{fc}[\text{B}(\text{Me})\text{NMe}_2]_2$  [8], and  $\text{Fc}_2\text{BBr}$  [8] were synthesized according to the literature procedures.

### 4.2. Preparation of 2

A solution of  $\text{Me}_3\text{SiNMe}_2$  (0.48 g, 4.10 mmol) in toluene (10 ml) was added dropwise with stirring at  $-78^\circ\text{C}$  to  $\text{Fc}_2\text{BBr}$  (1.89 g, 4.10 mmol) in toluene (20 ml). The mixture was slowly warmed to room temperature and stirred for 12 h. After the solvent had been removed in vacuo, the product was obtained as a dark orange solid. Yield: 1.50 g (86%).  $^{11}\text{B}$  NMR (128.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  41.0 ( $h_{1/2} = 330$  Hz).  $^1\text{H}$  NMR (250.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.22 (s, 6H,  $\text{CH}_3$ ), 4.10 (s, 10H,  $\text{C}_5\text{H}_5$ ), 4.37, 4.46 ( $2 \times$  vtr,  $2 \times$  4H,  $^3J_{\text{HH}} = ^4J_{\text{HH}} = 1.8$  Hz,  $\text{C}_5\text{H}_4$ ).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  42.5 ( $\text{CH}_3$ ), 67.7 ( $\text{C}_5\text{H}_4$ ), 68.4 ( $\text{C}_5\text{H}_5$ ), 69.8 ( $\text{C}_5\text{H}_4$ ), n.o. ( $\text{C}_5\text{H}_4$ -Cipso).

### 4.3. Preparation of 4

Kpz (0.35 g, 3.33 mmol) and Hpz (0.23 g, 3.33 mmol) were combined in THF (20 ml) and the resulting slurry added dropwise with stirring at  $-78^\circ\text{C}$  to **1** (0.85 g, 3.33 mmol) in THF (20 ml). The mixture was slowly warmed to room temperature, refluxed for 24 h and cooled to room temperature again. All volatiles were removed under reduced pressure, the solid residue washed with  $\text{Et}_2\text{O}$  (40 ml) and dried in vacuo. Yield of **4**·THF: 1.35 g (89%). X-ray quality crystals of **4**·THF gradually formed when a saturated solution of **4** in THF was stored at  $5^\circ\text{C}$  for a period of several days.  $^{11}\text{B}$  NMR (128.4 MHz,  $d_8$ -THF):  $\delta$  –1.4 ( $h_{1/2} = 150$  Hz).  $^1\text{H}$  NMR (400.1 MHz,  $d_8$ -THF):  $\delta$  0.65 (s, 3H,  $\text{CH}_3$ ), 3.84 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.99 (n.r., 4H,  $\text{C}_5\text{H}_4$ ), 5.98 (dd, 2H,  $^3J_{\text{HH}} = 2.1$  Hz,  $^3J_{\text{HH}} = 1.6$  Hz, pzH-4), 7.31\* (dd, 2H,  $^3J_{\text{HH}} = 1.6$  Hz,  $^4J_{\text{HH}} = 0.6$  Hz, pzH-3 or 5), 7.45 $^\#$  (dd, 2H,  $^3J_{\text{HH}} = 2.1$  Hz,  $^4J_{\text{HH}} = 0.6$  Hz, pzH-5 or 3).  $^{13}\text{C}$  NMR (100.6 MHz,  $d_8$ -THF):  $\delta$  10.6 (very br,  $\text{CH}_3$ ), 68.1 ( $\text{C}_5\text{H}_4$ ), 68.4 ( $\text{C}_5\text{H}_5$ ), 73.6 ( $\text{C}_5\text{H}_4$ ), 102.5 (pzC-4), 132.9 $^\#$ , 138.1\* (pzC-3,5), n.o. ( $\text{C}_5\text{H}_4$ -Cipso). The two signals (\*) on one hand and the two signals ( $^\#$ ) on the other are correlated via crosspeaks in the HSQC spectrum. The compound is sensitive to air and its crystals lose THF when isolated at ambient temperature; a decent elemental analysis was therefore not obtained.

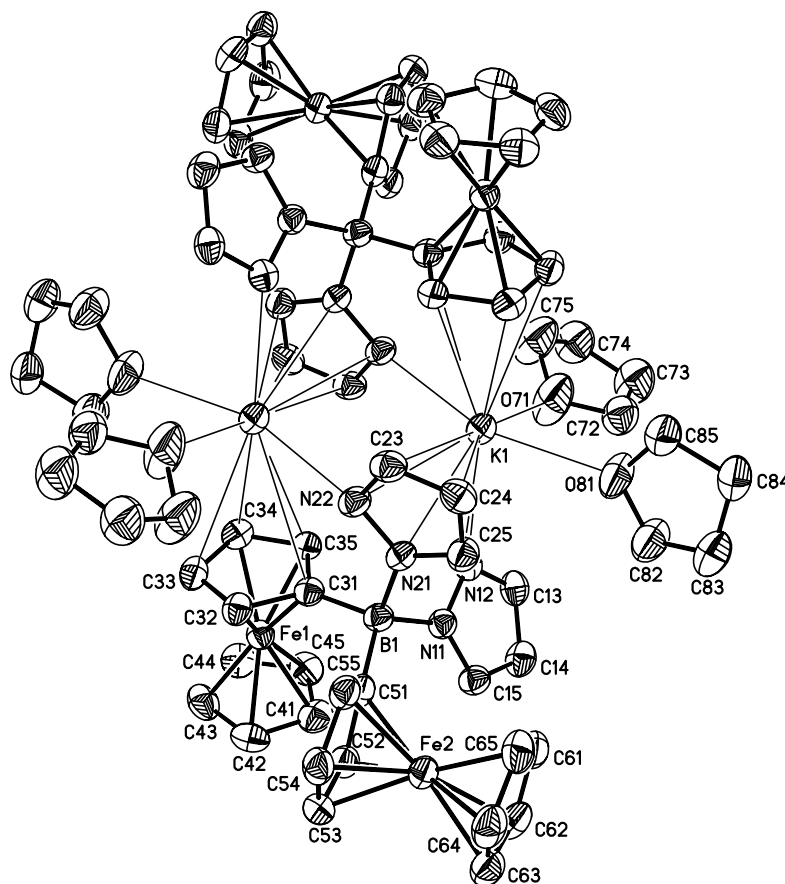


Fig. 3. Molecular structure and numbering scheme of compound  $[5(\text{THF})_2]_2$ . Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å), atom...atom distances (Å), angles (°), torsion angles (°) and dihedral angles (°): B(1)–C(31) = 1.621(4), B(1)–C(51) = 1.619(4), B(1)–N(11) = 1.563(4), B(1)–N(21) = 1.591(4), K(1)–N(12) = 2.821(3), K(1)–N(22) = 3.359(3), K(1)–N(22<sup>#</sup>) = 2.871(3), K(1)···COG(Cp<sup>#</sup>) = 3.171, K(1)···COG(pz) = 3.168, K(1)···K(1<sup>#</sup>) = 4.330; N(11)–B(1)–N(21) = 104.5(2), N(12)–K(1)–N(22) = 76.8(1), N(12)–K(1)–N(22<sup>#</sup>) = 105.4(1); N(11)–B(1)–C(31)–C(32) = 149.2(3), N(21)–B(1)–C(31)–C(32) = –96.3(3), N(22)–N(21)–B(1)–C(31) = 18.6(4), N(12)–N(11)–B(1)–C(31) = 65.9(3); N(11)N(12)C(13)C(14)C(15)//C(31)C(32)C(33)C(34)C(35) = 60.2, N(21)N(22)C(23)C(24)C(25)//C(31)C(32)C(33)C(34)C(35) = 94.2, N(21)N(22)C(23)C(24)C(25)//C(51)C(52)C(53)C(54)C(55) = 84.2, C(31)C(32)C(33)C(34)C(35)//C(41)C(42)C(43)–C(44)C(45) = 2.3, C(31)C(32)C(33)C(34)C(35)//C(51)C(52)C(53)C(54)C(55) = 82.7. COG(Cp<sup>#</sup>): centre of gravity of the C(31<sup>#</sup>)C(32<sup>#</sup>)C(33<sup>#</sup>)C(34<sup>#</sup>)C(35<sup>#</sup>) ring; COG(pz): centre of gravity of the N(21)N(22)C(23)C(24)C(25) ring. Symmetry transformation used to generate equivalent atoms:  $-x + 1, -y + 1, -z$  (#).

#### 4.4. Preparation of 5

The compound was prepared similar to **4** from Kpz (0.18 g, 1.70 mmol), Hpz (0.12 g, 1.70 mmol) and **2** (0.72 g, 1.70 mmol) in THF. Yield of **5**·2THF: 1.00 g (84%). X-ray quality crystals of  $[5(\text{THF})_2]_2$  gradually formed when a saturated solution of **5** in THF was stored at 5 °C for a period of several days. <sup>11</sup>B NMR (128.4 MHz, d<sub>8</sub>-THF): δ 1.0 (*h*<sub>1/2</sub> = 230 Hz). <sup>1</sup>H NMR (400.1 MHz, d<sub>8</sub>-THF): δ 3.69 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 4.08, 4.52 (2 × vtr, 2 × 4H, <sup>3</sup>J<sub>HH</sub> = <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, C<sub>5</sub>H<sub>4</sub>), 6.01 (vtr, 2H, <sup>3</sup>J<sub>HH</sub> = 1.7 Hz, pzH-4), 7.36 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 1.9 Hz, pzH-3 or 5), 7.41 (br, 2H, pzH-5 or 3). <sup>13</sup>C NMR (100.6 MHz, d<sub>8</sub>-THF): δ 68.4 (C<sub>5</sub>H<sub>4</sub>), 68.6 (C<sub>5</sub>H<sub>5</sub>), 74.9 (C<sub>5</sub>H<sub>4</sub>), 102.1 (pzC-4), 135.1, 138.0 (pzC-3,5), n.o. (C<sub>5</sub>H<sub>4</sub>-C<sub>ipso</sub>). The compound is sensitive to air and its crystals lose THF when isolated at ambient

temperature; a decent elemental analysis was therefore not obtained.

#### 4.5. Preparation of 6

Kpz (0.33 g, 3.08 mmol) and Hpz (0.21 g, 3.08 mmol) were combined in THF (20 ml) and the resulting slurry added with stirring at –78 °C via a dropping funnel to **3** (0.50 g, 1.54 mmol) in THF (20 ml). The mixture was slowly warmed to room temperature, stirred for 11 h, refluxed for 34 h and cooled to room temperature again. The solvent was driven off under reduced pressure, the solid residue washed with Et<sub>2</sub>O (40 ml) and dried in vacuo. Yield of **6**·4THF: 1.00 g (75%). A suspension of **6** in THF was heated at 60 °C in an ultrasonic bath. Cooling of the resulting clear solution to room temperature led to the deposition of X-ray quality crystals of

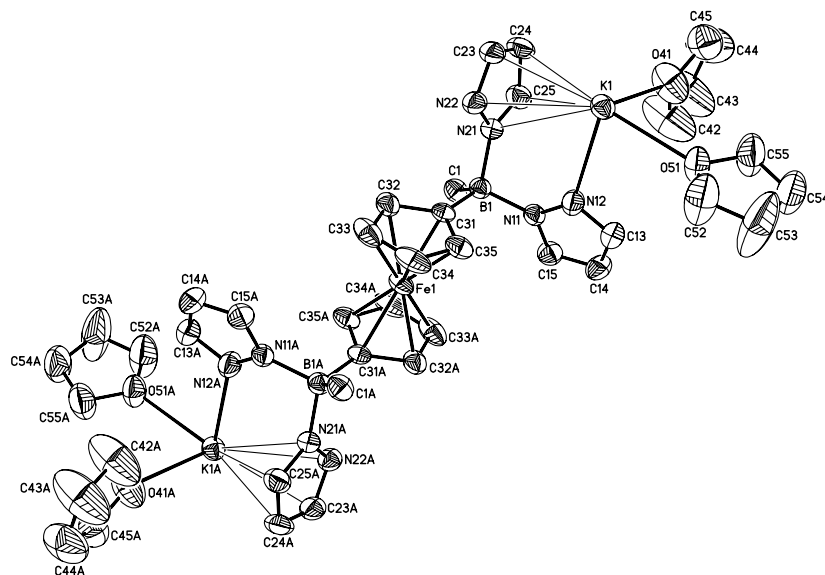


Fig. 4. Molecular structure and numbering scheme of compound  $[6(\text{THF})_4]_\infty$ . Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å), atom–atom distances (Å), angles (°), torsion angles (°), and dihedral angles (°): B(1)–C(31) = 1.606(4), B(1)–N(11) = 1.569(4), B(1)–N(21) = 1.584(4), K(1)–N(12) = 2.787(3), K(1)–N(22) = 3.243(2), K(1)–N(22<sup>#</sup>) = 2.786(3), K(1)–COG(Cp<sup>#</sup>) = 3.020, K(1)–COG(pz) = 3.069, K(1)–K(1<sup>#</sup>) = 4.558; N(11)–B(1)–N(21) = 104.8(2), N(12)–K(1)–N(22) = 72.3(1), N(12)–K(1)–N(22<sup>#</sup>) = 94.5(1); N(11)–B(1)–C(31)–C(32) = –169.7(2), N(21)–B(1)–C(31)–C(32) = 76.1(3), N(22)–N(21)–B(1)–C(31) = 2.5(4), N(12)–N(11)–B(1)–C(31) = –77.6(3); N(11)N(12)C(13)C(14)C(15)//C(31)C(32)C(33)C(34)C(35) = 104.4, N(21)N(22)C(23)C(24)C(25)//C(31)C(32)–C(33)C(34)C(35) = 102.3. COG(Cp<sup>#</sup>): centre of gravity of the C(31<sup>#</sup>)C(32<sup>#</sup>) C(33<sup>#</sup>)C(34<sup>#</sup>) C(35<sup>#</sup>) ring; COG(pz): centre of gravity of the N(21)N(22)C(23)C(24)C(25) ring. Symmetry transformation used to generate equivalent atoms:  $-x + 1, -y + 1, -z + 1$  (#).

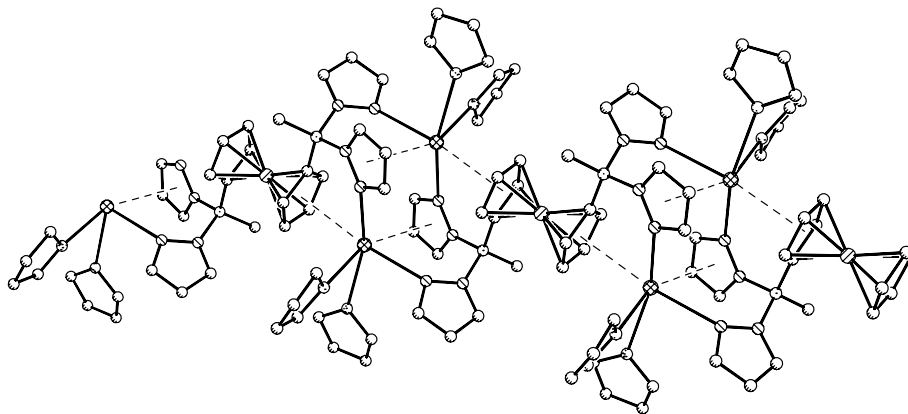


Fig. 5. View of one polymer strand of  $[6(\text{THF})_4]_\infty$ ; hydrogen atoms omitted for clarity.

$[6(\text{THF})_4]_\infty$ .  $^{11}\text{B}$  NMR (128.4 MHz,  $d_8$ -THF):  $\delta$ -1.3 ( $h_{1/2}$  = 250 Hz).  $^1\text{H}$  NMR (250.1 MHz,  $d_8$ -THF):  $\delta$  0.67 (s, 6H, CH<sub>3</sub>), 3.75, 3.80 (2 × vtr, 2 × 4H,  $^3J_{\text{HH}}$  =  $^4J_{\text{HH}}$  = 1.7 Hz, C<sub>5</sub>H<sub>4</sub>), 5.90 (dd, 4H,  $^3J_{\text{HH}}$  = 2.1 Hz,  $^3J_{\text{HH}}$  = 1.6 Hz, pzH-4), 7.21\* (dd, 4H,  $^3J_{\text{HH}}$  = 1.6 Hz,  $^4J_{\text{HH}}$  = 0.7 Hz, pzH-3 or 5) 7.47<sup>#</sup> (dd, 4H,  $^3J_{\text{HH}}$  = 2.1 Hz,  $^4J_{\text{HH}}$  = 0.7 Hz, pzH-5 or 3).  $^{13}\text{C}$  NMR (62.9 MHz,  $d_8$ -THF):  $\delta$  11 (very br, CH<sub>3</sub>), 68.9, 73.7 (C<sub>5</sub>H<sub>4</sub>), 102.0 (pz-C4), 132.3<sup>#</sup>, 137.6\* (pz-C3,5), n.o. (C<sub>5</sub>H<sub>4</sub>-C<sub>ipso</sub>). The two signals (\*) on one hand and the two signals (#) on the other are correlated via crosspeaks in the HSQC spectrum. The compound is sensitive to air and its crystals lose THF when isolated at ambient temperature; a decent elemental analysis was therefore not obtained.

## 5. X-ray crystal structure determination of (4THF)<sub>2</sub>, [5(THF)<sub>2</sub>]<sub>2</sub> and [6(THF)<sub>4</sub>]<sub>∞</sub>

Data collection for all structures was performed on a STOE-IPDS-II diffractometer with graphite-monochromated MoK<sub>α</sub>-radiation. The structures were solved with direct methods [10] and refined against  $F^2$  using full-matrix least-squares [11]. Absorption corrections were performed with the MULABS [12] option in PLATON [13]. All non-H atoms have been refined anisotropically, whereas the H atoms have been treated with a riding model, fixing their displacement parameter to 1.2 or 1.5 (for methyl groups) of the value of their parent atom. The asymmetric unit of [5(THF)<sub>2</sub>]<sub>2</sub> contains a

THF molecule which is disordered about a centre of inversion.

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 253747 ((4THF)<sub>2</sub>), 253749 ([5(THF)<sub>2</sub>]<sub>2</sub>), 253748 ([6(THF)<sub>4</sub>]<sub>∞</sub>).

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