Electronic interactions in oligoferrocenes with cationic, neutral and anionic four-coordinate boron bridges

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Dinuclear and trinuclear ferrocene complexes {[Fc₂BMe₂]Li, [Fc-BMe₂-fc-BMe₂-Fc]Li₂, Fc₂B(pyind), [Fc₂B(bipy)]PF₆, [Fc-B(bipy)-fc-B(bipy)-Fc](PF₆)₂} bearing anionic, uncharged, and cationic four-coordinate boron bridges have been synthesized (Fc: ferrocenyl; fc: 1,1'-ferrocenylene; pyind: 5-fluoro-2-(2'-pyridyl)indolyl; bipy: 2,2'-bipyridyl). The molecular structures of [Fc₂BMe₂]Li(12-crown-4)₂, [Fc-BMe₂-fc-BMe₂-Fc](Li(12-crown-4))₂, Fc₂B(pyind), and [Fc₂B(bipy)]PF₆ were determined by X-ray crystallography. The anionic aggregates [Fc₂BMe₂]⁻ and [Fc-BMe₂-fc-BMe₂-Fc]²⁻ are very sensitive to air and moisture whereas bromide salts of their cationic counterparts [Fc₂B(bipy)]⁺ and [Fc-B(bipy)-fc-B(bipy)-Fc]²⁺ may be dissolved in water without decomposition. Cyclic voltammograms of the diferrocene species show two well-resolved one-electron transitions separated by 0.21 V ([Fc₂BMe₂]Li; E^{o'} = -0.43 V, -0.64 V; vs. FcH/FcH⁺), 0.18 V (Fc₂B(pyind); E^{o'} = -0.03 V, -0.21 V), and 0.16 V ([Fc₂B(bipy)]PF₆; E^{o'} = +0.23 V, +0.07 V), which indicates electronic interactions between the two ferrocenyl substituents. Two redox waves with an intensity ratio of 1 : 2 are observed in the cyclic voltammograms of the trinuclear derivatives [Fc-BMe₂-fc-BMe₂-Fc]Li₂ and [Fc-B(bipy)-fc-B(bipy)-Fc](PF₆)₂. In the case of the BMe₂-bridged species, the electrochemically unique central ferrocenylene unit is oxidized at a much more cathodic potential value (E^{o'} = -1.21 V) than the two terminal ferrocenyl substituents (E^{o'} = -0.51 V). The opposite is true in the case of the B(bipy)-bridged trimer where oxidation of the terminal ferrocenyl groups (E^{o'} = +0.03 V) precedes oxidation of the internal iron atom (E^{o'} = +0.26 V). The Fe(II)/Fe(III) redox potentials of the mono- and dianionic species differ to a much larger extent from the redox potential of parent ferrocene (E^{o'} = 0 V) than the E^{o'} values of the corresponding mono- and dicationic derivatives. Apart from electrostatic interactions, the electrochemical properties of BMe₂- and B(bipy)-bridged oligoferrocenes are determined by the pronounced positive inductive effect of triorganoborate substituents together with positive σ/π* hyperconjugation on the one hand and ferrocene-to-B(bipy) charge transfer on the other.

Introduction

Research on metal containing polymer precursors and polymers has developed into a flourishing field of coordination chemistry because the materials created are highly interesting due to their optical, electronic or magnetic properties.^{1,2} Among all the compounds developed so far, organometallic macromolecules are receiving increasing attention since the first high molecular weight poly(ferrocenylenes) **I** (Fig. 1) with skeletal iron atoms became available *via* the ring-opening polymerisation (ROP) of strained ring-tilted [1]ferrocenophanes.³⁻⁵

Our group is particularly interested in boron-bridged oligo(ferrocenylenes) for which the ROP synthesis approach proved to be far less efficient than for the analogous silicon- or germanium-bridged derivatives **I**.^{6,7} In an alternative strategy, the facile formation of boron–nitrogen adduct bonds was exploited for the generation of polymers [-(Me₂BC₅H₄)Fe(C₅H₄BMe₂)-pyrazine-]_n and [-(Me₂BC₅H₄)Fe(C₅H₄BMe₂)-4,4'-bipyridyl-]_n.⁸⁻¹⁰ A detailed investigation of these and related materials provided strong evidence for charge transfer between the ferrocene donors and the electron-poor organic bridges.^{8,11} The polymers are insoluble in all common solvents; their structure in the solid state was determined by X-ray diffraction. In order to increase the number of iron atoms within the polymer backbone, we then attempted to replace the aromatic amine donors with 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene. However, no

Fig. 1 Poly(ferrocenylenes) **I** generated by ring opening polymerisation of ferrocenophanes, the target polymer (LiI[II])_n and its cyclic congener Li₂[III].

polymeric material was formed upon treatment of this difunctional Lewis base with 1,1'-bis(dimethylboryl)ferrocene or 1,1'-bis(dibromoboryl)ferrocene. While the methyl derivative did not

form P–B adducts at all, the bromo derivative just gave an open-chain dinuclear complex featuring only one P–B bond.¹² We therefore came to the conclusion that more strongly Lewis basic ferrocene derivatives were required. One obvious candidate was 1,1'-dilithioferrocene, which is not only easy to prepare but also able to form strong boron–carbon σ bonds. Initial efforts to prepare macromolecules (**Li**[II])_n (Fig. 1) from 1,1'-bis(dimethylboryl)ferrocene and 1,1'-dilithioferrocene resulted in a mixture of oligomeric products containing substantial amounts of the cyclic dimer **Li**₂[III] (Fig. 1), which was isolated by crystallization and turned out to be a highly efficient lithium scavenger.¹³ Work is currently in progress to separate the different linear oligomers and to determine their molecular weight by GPC techniques. During these workup and purification steps, it turned out that the compounds (**Li**[II])_n are highly sensitive to air. This is in accordance with exploratory electrochemical investigations on our product mixtures which revealed a sizable cathodic shift of the Fe(II)/Fe(III) redox transitions in these materials compared to parent ferrocene.

Since an investigation of well-defined short-chain oligomers is, by itself, already helpful for an understanding of the properties of BMe₂-bridged poly(ferrocenylene)s, we synthesized the anionic di- and triferrocene complexes **Li**[2] and **Li**₂[3] (Scheme 1) in order to study their electrochemical behaviour and to determine their molecular structure in the solid state. For comparison, we also prepared the mono- and dinuclear compounds **6** and **10** (Scheme 2) featuring four-coordinate yet uncharged boron substituents, as well as complexes **[11]PF₆** and **[14](PF₆)₂** (Scheme 3) in which two and three ferrocene moieties are linked *via* four-coordinate cationic boron bridges.

Scheme 1 Synthesis of di- and trinuclear ferrocene complexes **Li**[2] and **Li**₂[3] with anionic four-coordinate boron bridges. (i) + FcLi, THF, 0 °C to r.t.; (ii) + 1,1'-fc(Li-TMEDA)₂, THF, -78 °C to r.t.

Results and discussion

Synthesis and spectroscopy

The di- and trinuclear ferrocene complexes **Li**[2] and **Li**₂[3] were synthesized in THF *via* the reaction of FcBMe₂, **1**, with FcLi (1 equiv.) and 1,1'-fc(Li-TMEDA)₂ (0.5 equiv.), respectively [Scheme 1; Fc = (C₅H₅)Fe(C₅H₄), fc = (C₅H₄)₂Fe]. X-Ray quality crystals formed from CH₂Cl₂ (**Li**[2]) and THF/diethyl ether (**Li**₂[3]) after addition of 12-crown-4. Both compounds are highly sensitive to air and moisture. Treatment of the sodium salt **4**, prepared from 5-fluoro-2-(2'-pyridyl)indole and NaH in THF, with FcB(Me)Br, **5**, in toluene gave the monoferrocene derivative **6** in moderate yield (Scheme 2). In order to get access to the analogous diferrocenyl complex **10** (Scheme 2), we first reacted FcBBr₂, **7**, with FcSnMe₃, **8**, which yielded

Scheme 2 Synthesis of mono- and dinuclear ferrocene complexes **6** and **10** with neutral four-coordinate boron bridges. (i) toluene, -78 °C to r.t.; (ii) benzene, r.t.

the dinuclear compound **9** featuring a three-coordinate boron bridge. Subsequent addition of **4** led to the formation of **10**. Crystals of **6** and **10** suitable for X-ray crystal structure determinations were obtained from CDCl₃ and toluene, respectively. In the latter case, the crude material was contaminated with a small amount of ferrocene which could neither be fully removed by column chromatography (dichloromethane/ethyl acetate 10 : 1) nor by sublimation. Only a few single crystals of **10** were obtained and these contained 0.25 equiv. of ferrocene. Apparently, the ferrocene is necessary to stabilize the crystal packing of compound **10** since numerous attempts to grow single crystals from the ferrocene depleted mother liquor failed. The monocationic diferrocenyl complex **[11]PF₆** is readily available from **9** and 2,2'-bipyridyl (Scheme 3). Using NH₄PF₆ in water, the bromide salt of **[11]**⁺ was quantitatively transformed into the corresponding hexafluorophosphate salt which is more suitable for cyclic voltammetric measurements. Similar to the synthesis of **9**, the triferrocene species **13** was prepared from two equivs. of FcSnMe₃, **8**, and one equiv. of 1,1'-fc(BBr₂)₂, **12**, in toluene. Subsequent addition of 2,2'-bipyridyl followed by salt metathesis gave the target molecule **[14](PF₆)₂** in excellent overall yield (Scheme 3).

The ¹¹B NMR spectra of the compounds under investigation here display characteristic high-field resonances at -21.2 ppm (**Li**[2]), -19.2 ppm (**Li**₂[3]), 4.5 ppm (**6**), 4.1 ppm (**10**), 7.3 ppm (**[11]PF₆**), and 7.2 ppm (**[14](PF₆)₂**) testifying to the presence of four-coordinate boron nuclei.^{14,15} It follows from a comparison of these values that the electron density is indeed highest at the boron atoms of the negatively charged species **Li**[2] and **Li**₂[3]. Removal of the excess electron and replacement of electron releasing methyl groups by electronegative sp² hybridized nitrogen donors leads to a substantial charge depletion at boron as evidenced by a downfield shift of $\Delta(\delta(^{11}\text{B})) = 25.3$ upon going from **Li**[2] to **10**. Introduction of a positive charge, as in the case of **[11]PF₆** and **[14](PF₆)₂**, has only a minor additional effect [*cf.* $\delta(^{11}\text{B})(\text{[11]PF}_6) - \delta(^{11}\text{B})(\text{10}) = 3.2$], likely because this charge is not localized at the boron centre but efficiently

Scheme 3 Synthesis of di- and trinuclear ferrocene complexes $[\mathbf{11}]\text{PF}_6$ and $[\mathbf{14}](\text{PF}_6)_2$ with cationic four-coordinate boron bridges. (i) toluene, -78°C to r.t.; $+\text{NH}_4\text{PF}_6$, water, r.t. (ii) toluene, -78°C to r.t.

spread over the entire B(bipy) entity (bipy: 2,2'-bipyridyl). The very narrow line widths of the ^1H NMR signals of $\text{Li}[\mathbf{2}]$ ($h_1 = 10$ Hz) and $\text{Li}_2[\mathbf{3}]$ ($h_1 = 20$ Hz) are consistent with a highly symmetric BC_4 surrounding as opposed to the less symmetric BC_2N_2 substitution pattern in, for example, $\mathbf{10}$ ($h_1 = 370$ Hz) and $[\mathbf{11}]\text{PF}_6$ ($h_1 = 250$ Hz).

The methyl groups of $\text{Li}[\mathbf{2}]$ and $\text{Li}_2[\mathbf{3}]$ resonate at $\delta(^1\text{H}) = -0.12$ and -0.13 , respectively. Due to unresolved $^2J_{\text{BH}}$ coupling, both signals appear as broad multiplets. In the ^{13}C NMR spectra, the methyl substituents give rise to 1 : 1 : 1 : 1 quartets at $\delta(^{13}\text{C}) = 14.8$ ($^1J_{\text{CB}} = 41.7$ Hz; $\text{Li}[\mathbf{2}]$) and $\delta(^{13}\text{C}) = 14.6$ ($^1J_{\text{CB}} = 40.9$ Hz; $\text{Li}_2[\mathbf{3}]$). In contrast to $\text{Li}[\mathbf{2}]$, which exhibits only two ^1H and two ^{13}C NMR resonances for the substituted cyclopentadienyl rings, four C_5H_4 (each integrating 1H) and four C_5H_4 signals are found in the case of $\mathbf{6}$ (C_{ipso} is broadened beyond detection due to quadrupolar relaxation¹⁴). This observation agrees well with the molecular structure suggested for this compound (Scheme 2) since coordination of the unsymmetric 5-fluoro-2-(2'-pyridyl)indolyl ligand makes the boron atom a chiral centre and renders all C_5H_4 atoms magnetically inequivalent (similar features are observed in the ^1H and ^{13}C NMR spectrum of $\mathbf{10}$). Consistent with this view, both α and both β protons of a given C_5H_4 ring in the 2,2'-bipyridyl derivatives $[\mathbf{11}]\text{PF}_6$ and $[\mathbf{14}](\text{PF}_6)_2$ possess the same chemical shifts. As has already been

discussed in a previous paper on related ferrocene-based 2,2'-(bipyridyl)boronium salts like $[\mathbf{IV}]^+$ ¹⁶ (Fig. 2), boron chelation causes characteristic changes in the ^1H and ^{13}C NMR spectra of the 2,2'-bipyridyl ligand. The resulting shift values exhibited by $[\mathbf{11}]\text{PF}_6$ and $[\mathbf{14}](\text{PF}_6)_2$ are almost identical to those of compound $[\mathbf{IV}]^+$ and thus do not merit further discussion.

Fig. 2 The B(bipy)Me-substituted ferrocene $[\mathbf{IV}]^+$, its model system $[\mathbf{IVH}]^+$, and ferrocenyltris(ferrocenyl)borate $\mathbf{V}$.

Crystal structure determinations

Selected crystallographic data of $\text{Li}[\mathbf{2}](12\text{-crown-4})_2$, $\text{Li}_2[\mathbf{3}](12\text{-crown-4})_4$, $\mathbf{6}$, $\mathbf{10}$, and $[\mathbf{11}]\text{PF}_6$ are summarized in Table 1.

In the lithium diferrocenyldimethylborate complex $\text{Li}[\mathbf{2}](12\text{-crown-4})_2$ (monoclinic, $C2/c$), which crystallizes together with 1 equiv. of CH_2Cl_2 , the $[\text{Fc}_2\text{BMe}_2]^-$ anion possesses approximate C_{2v} symmetry (Fig. 3).

Intermolecular contacts to the $\text{Li}(12\text{-crown-4})_2^+$ counterion correspond to normal van der Waals interactions. The boron atom maintains an almost perfect tetrahedral coordination sphere [largest angular distortion from the ideal value of 109° : $\text{C}(11)\text{--B}(1)\text{--C}(21) = 105.8(1)^\circ$]. B–C bonds to the sp^3 -hybridized methyl groups [$\text{B}(1)\text{--C}(1') = 1.634(3)$ Å, $\text{B}(1)\text{--C}(1'') = 1.642(3)$ Å] possess the same length as B–C bonds involving the sp^2 -hybridized *ipso*-carbon atoms of the cyclopentadienyl rings [$\text{B}(1)\text{--C}(11) = 1.641(3)$ Å, $\text{B}(1)\text{--C}(21) = 1.638(3)$ Å], an effect which is also apparent in other ferrocenylborane adducts of the general formula $\text{FcB}(\text{Me})\text{RR}'$.^{13,16–22} Significant differences are obvious in the Fe–C distances within the ferrocenyl substituents. While the bond lengths between Fe(1) and the C(31)-cyclopentadienyl ring [Fe(2) and C(1)-cyclopentadienyl] fall in the range between 2.031(2) Å and 2.057(2) Å [2.034(2) Å and 2.052(2) Å] with a mean of 2.045 Å [2.045 Å], the distances between Fe(1) and the C(21)-cyclopentadienyl ring [Fe(2) and C(11)-cyclopentadienyl] are spread over a much broader range between 2.031(2) Å and 2.098(2) Å [2.033(2) Å and 2.102(2) Å] with a mean of 2.053 Å [2.055 Å]. By far the longest Fe–C bonds are established to the *ipso*-carbon atoms, i.e. $\text{Fe}(1)\text{--C}(21) = 2.098(2)$ Å and $\text{Fe}(2)\text{--C}(11) = 2.102(2)$ Å. If this bond stretch was simply due to steric repulsion between the BMe_2 fragment and the C_5H_5 ligands, one would also expect an elongation of the $\text{Fe}(1)\text{--C}(31)$ and the $\text{Fe}(2)\text{--C}(1)$ bond. The opposite, however, is true in that they possess the smallest values of all Fe–C bonds. It is important to note in this context that lithium ferrocenylborohydride $[\text{FcBH}_3]\text{Li}(12\text{-crown-4})$ ²² shows an even larger Fe– C_{ipso} distance (2.110(3) Å) than $\text{Li}[\mathbf{2}](12\text{-crown-4})_2$ even though any steric strain inflicted by the small BH_3 moiety is certainly negligible. This leads to the conclusion that ferrocene distortion may originate from the electronic rather than the steric properties of the strongly σ -donating borate substituent. The $\text{C}(11)\text{--B}(1)[\text{C}(21)\text{--B}(1)]$ vector is directed almost orthogonal to the C(21)-cyclopentadienyl ring [C(11)-cyclopentadienyl ring; cf. $\text{C}(11)\text{--B}(1)\text{--C}(21)\text{--C}(22) = -88.1(2)^\circ$, $\text{C}(21)\text{--B}(1)\text{--C}(11)\text{--C}(12) = 79.2(2)^\circ$; dihedral angle $\text{C}(11)\text{C}(12)\text{C}(13)\text{C}(14)\text{C}(15)/\text{C}(21)\text{C}(22)\text{C}(23)\text{C}(24)\text{C}(25) = 77.7^\circ$].

Table 1 Crystallographic data for $\text{Li}_2[\text{12-crown-4}]_2 \cdot \text{CH}_2\text{Cl}_2$, $\text{Li}_2[\text{3}](\text{12-crown-4})_4$, **6**, **10**, and $[\text{11}]\text{PF}_6$

Compound	$\text{Li}_2[\text{12-cr.-4}]_2$	$\text{Li}_2[\text{3}](\text{12-cr.-4})_4$	6	10	$[\text{11}]\text{PF}_6$
Formula	$\text{C}_{38}\text{H}_{56}\text{BF}_2\text{LiO}_8 \cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{66}\text{H}_{102}\text{B}_2\text{Fe}_3\text{Li}_2\text{O}_{16}$	$\text{C}_{24}\text{H}_{30}\text{BFFeN}_2$	$\text{C}_{33}\text{H}_{26}\text{BFFe}_2\text{N}_2 \cdot 0.5\text{C}_{10}\text{H}_8$ $0.25\text{C}_{10}\text{H}_{10}\text{Fe}$	$\text{C}_{30}\text{H}_{26}\text{BF}_6\text{Fe}_2\text{N}_2\text{P}$
<i>M</i>	855.20	1354.53	422.08	684.64	682.01
<i>T</i> /K	100(2)	173(2)	173(2)	173(2)	145(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
<i>a</i> /Å	33.7681(17)	9.7070(10)	9.7151(13)	9.1241(12)	12.1586(14)
<i>b</i> /Å	25.2931(11)	11.2570(10)	13.5859(14)	29.760(3)	21.716(4)
<i>c</i> /Å	22.5567(11)	15.763(2)	14.4080(19)	23.503(3)	15.4748(15)
<i>a</i> /°	90	79.386(8)	90	90	90
<i>β</i> /°	122.115(3)	80.220(8)	95.585(11)	101.133(10)	108.429(11)
<i>γ</i> /°	90	86.776(8)	90	90	90
<i>V</i> /Å ³	16317.7(13)	1667.8(3)	1892.7(4)	6261.7(13)	3876.4(9)
<i>Z</i>	16	1	4	8	4
<i>D_c</i> /g cm ⁻³	1.392	1.349	1.481	1.452	1.169
<i>F</i> (000)	7200	720	872	2824	1384
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.891	0.709	0.819	1.076	0.836
<i>2θ</i> _{max} /°	55.12	52.74	51.72	51.40	62.06
Measured reflections	110409	31017	9524	54585	62615
Unique reflections (<i>R</i> _{int})	18539 (0.0826)	6785 (0.0988)	3611 (0.0812)	11719 (0.2293)	11213 (0.0664)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	11675	4688	2420	4710	6713
Parameters refined	955	403	262	827	442
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0328	0.0480	0.0433	0.0620	0.1537
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0536	0.1105	0.0848	0.0959	0.4018
GOOF on <i>F</i> ²	0.885	0.934	0.902	0.740	2.362
Largest diff. peak and hole/e Å ³	0.758, −0.862	0.683, −0.521	0.548, −0.509	0.409, −0.426	3.515, −2.132

Fig. 3 Molecular structure of $\text{Li}_2[\text{12-crown-4}]_2 \cdot \text{CH}_2\text{Cl}_2$ (hydrogen atoms and $\text{Li}(\text{12-crown-4})_2$ counterion omitted for clarity; thermal ellipsoids at the 50% probability level). Selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: $\text{B}(1)–\text{C}(11) = 1.641(3)$, $\text{B}(1)–\text{C}(21) = 1.638(3)$, $\text{B}(1)–\text{C}(1') = 1.634(3)$, $\text{B}(1)–\text{C}(1'') = 1.642(3)$, $\text{Fe}(1) \cdots \text{Fe}(2) = 6.697$; $\text{C}(11)–\text{B}(1)–\text{C}(21) = 105.8(1)$, $\text{C}(11)–\text{B}(1)–\text{C}(1') = 110.3(2)$, $\text{C}(11)–\text{B}(1)–\text{C}(1'') = 109.2(2)$, $\text{C}(1')–\text{B}(1)–\text{C}(1'') = 111.0(2)$, $\text{C}(21)–\text{B}(1)–\text{C}(1') = 109.7(2)$, $\text{C}(21)–\text{B}(1)–\text{C}(1'') = 110.8(2)$, $\text{C}(11)–\text{B}(1)–\text{C}(21)–\text{C}(22) = -88.1(2)$, $\text{C}(21)–\text{B}(1)–\text{C}(11)–\text{C}(12) = 79.2(2)$, $\text{C}(1)–\text{C}(2)–\text{C}(3)–\text{C}(4)–\text{C}(5) // \text{C}(11)–\text{C}(12)–\text{C}(13)–\text{C}(14)–\text{C}(15) = 1.2$, $\text{C}(21)–\text{C}(22)–\text{C}(23)–\text{C}(24)–\text{C}(25) // \text{C}(31)–\text{C}(32)–\text{C}(33)–\text{C}(34)–\text{C}(35) = 2.3$, $\text{C}(11)–\text{C}(12)–\text{C}(13)–\text{C}(14)–\text{C}(15) // \text{C}(21)–\text{C}(22)–\text{C}(23)–\text{C}(24)–\text{C}(25) = 77.7$.

The trinuclear aggregate $\text{Li}_2[\text{3}](\text{12-crown-4})_4$ (triclinic, $P\bar{1}$; Fig. 4) lies on an inversion center and forms separated ion pairs with two $\text{Li}(\text{12-crown-4})_2^+$ complexes.

All structural parameters including torsion angles and dihedral angles of the $\text{C}(11)$ –ferrocenyl/ $\text{B}(1)\text{Me}_2$ / $\text{C}(21)$ –ferrocenyl subunit are virtually identical to those of $\text{Li}_2[\text{12-crown-4}]_2$. The molecular structure of $\text{Li}_2[\text{3}](\text{12-crown-4})_4$ has to be compared with the structure of the isoelectronic carbon-bridged species in its $\text{Fe}(\text{II})$ [$\text{Fc-CMe}_2\text{-fc-CMe}_2\text{-Fc}$]²³ and $\text{Fe}(\text{III})$ states [$\text{Fc-CMe}_2\text{-fc-CMe}_2\text{-Fc}$]³⁺.²⁴ In contrast to $\text{Li}_2[\text{3}](\text{12-crown-4})_4$, the neutral triferrocene [$\text{Fc-CMe}_2\text{-fc-CMe}_2\text{-Fc}$]⁰ (monoclinic, $P2_1/a$) adopts an unsymmetrical conformation with inequivalent $\text{Fe} \cdots \text{Fe}$ separations of 5.716 Å and 6.456 Å, both of which are significantly shorter than the $\text{Fe}(1) \cdots \text{Fe}(2)$ distance in $\text{Li}_2[\text{3}](\text{12-crown-4})_4$ (6.731 Å). Similar to $\text{Li}_2[\text{3}](\text{12-crown-4})_4$, the Fe-C_{ipso} bonds in [$\text{Fc-CMe}_2\text{-fc-CMe}_2\text{-Fc}$]⁰ are longer

Fig. 4 Molecular structure of $\text{Li}_2[\text{3}](\text{12-crown-4})_4$ (hydrogen atoms and $\text{Li}(\text{12-crown-4})_2$ counterions omitted for clarity; thermal ellipsoids at the 50% probability level). Selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: $\text{B}(1)–\text{C}(11) = 1.641(4)$, $\text{B}(1)–\text{C}(21) = 1.635(4)$, $\text{B}(1)–\text{C}(1') = 1.648(5)$, $\text{B}(1)–\text{C}(1'') = 1.655(4)$, $\text{Fe}(1) \cdots \text{Fe}(2) = 6.731$; $\text{C}(11)–\text{B}(1)–\text{C}(21) = 104.9(2)$, $\text{C}(11)–\text{B}(1)–\text{C}(1') = 109.8(2)$, $\text{C}(11)–\text{B}(1)–\text{C}(1'') = 109.8(2)$, $\text{C}(1')–\text{B}(1)–\text{C}(1'') = 111.1(3)$, $\text{C}(21)–\text{B}(1)–\text{C}(1') = 110.4(2)$, $\text{C}(21)–\text{B}(1)–\text{C}(1'') = 110.6(2)$; $\text{C}(12)–\text{C}(11)–\text{B}(1)–\text{C}(21) = 88.9(4)$, $\text{C}(22)–\text{C}(21)–\text{B}(1)–\text{C}(11) = -78.9(3)$; $\text{C}(1)–\text{C}(2)–\text{C}(3)–\text{C}(4)–\text{C}(5) // \text{C}(11)–\text{C}(12)–\text{C}(13)–\text{C}(14)–\text{C}(15) = 1.1$, $\text{C}(11)–\text{C}(12)–\text{C}(13)–\text{C}(14)–\text{C}(15) // \text{C}(21)–\text{C}(22)–\text{C}(23)–\text{C}(24)–\text{C}(25) = 99.5$. Symmetry transformation used to generate equivalent atoms: $-x, -y + 1, -z + 1$.

(2.050(2) Å, 2.056(2) Å, 2.065(2) Å, 2.067(2) Å) than the other iron–carbon bonds. This effect is, however, far less pronounced than in the case of $\text{Li}_2[\text{3}](\text{12-crown-4})_4$ [$\text{Fe}(1)–\text{C}(11) = 2.112(3)$ Å, $\text{Fe}(2)–\text{C}(21) = 2.115(2)$ Å] which lends additional support to our hypothesis that Fe-C_{ipso} bond elongation is rooted in the electronic rather than the steric properties of the BMe_2 bridge. Only negligible differences are observed in the conformation of [$\text{Fc-CMe}_2\text{-fc-CMe}_2\text{-Fc}$](O_3SCF_3)₃ (monoclinic, $C2/m$) on the one hand and $\text{Li}_2[\text{3}](\text{12-crown-4})_4$ on the other (intramolecular $\text{Fe} \cdots \text{Fe}$ distances in both molecules are 6.536 Å and 6.731 Å, respectively). The triferrocene moieties of both compounds are arranged in the stepped formation that has been predicted by MMX calculations on the related silicon-bridged [$\text{Fc-SiMe}_2\text{-fc-SiMe}_2\text{-Fc}$]⁰ to be a minimum energy conformation of such kinds of triferrocene oligomers.²⁵

The mononuclear complex **6** (Fig. 5) contains a chiral boron centre but crystallizes from CDCl_3 as a racemate in the achiral space group $P2_1/c$.

Fig. 5 Molecular structure of **6** (hydrogen atoms omitted for clarity; thermal ellipsoids at the 50% probability level). Selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)–C(1) = 1.598(5), B(1)–C(31) = 1.609(5), B(1)–N(11) = 1.633(4), B(1)–N(21) = 1.565(4), N(11)–C(12) = 1.357(4), N(21)–C(22) = 1.376(4); C(31)–B(1)–C(1) = 118.1(3), C(31)–B(1)–N(11) = 103.9(2), C(31)–B(1)–N(21) = 110.5(3), N(11)–B(1)–C(1) = 110.0(3), N(11)–B(1)–N(21) = 94.3(2), N(21)–B(1)–C(1) = 116.5(3), C(32)–C(31)–B(1)–N(11) = 86.3(3), C(32)–C(31)–B(1)–N(21) = –13.8(4), C(31)C(32)C(33)C(34)C(35)//C(41)C(42)C(43)C(44)C(45) = 1.2, B(1)N(11)C(12)C(22)N(21)//C(31)–C(32)C(33)C(34)C(35) = 86.8.

The 5-fluoro-2-(2'-pyridyl)indolyl ligand forms both a prototype dative bond [B(1)–N(11) = 1.633(4) Å] and a prototype covalent bond [B(1)–N(21) = 1.565(4) Å] to the boron atom, with the latter being shorter by 0.068(4) Å. Both B–C bonds are again equal within experimental error [B(1)–C(1) = 1.598(5) Å, B(1)–C(31) = 1.609(5) Å]. An inspection of bond angles reveals that the boron atom suffers severe distortions of the ideal tetrahedral configuration with N(11)–B(1)–N(21) = 94.3(2)° being the smallest and C(31)–B(1)–C(1) = 118.1(3)° the largest angle. The conformation of **6** is such that the boron–pyridyl bond B(1)–N(11) is directed perpendicular to the ferrocenyl substituent [C(32)–C(31)–B(1)–N(11) = 86.3(3)°] while the second B–N bond lies almost in the plane of the cyclopentadienyl ring [C(32)–C(31)–B(1)–N(21) = –13.8(4)°]. Very similar conformations have been found previously for [IV]PF₆ (monoclinic, $P2_1$; Fig. 2),¹⁶ the analogous 1,10-phenanthroline derivative (monoclinic, $P2_1/c$),²⁶ as well as for the two pseudopolymorphs of a related ferrocenylborane adduct²¹ featuring a chelating 2,5-bis(2'-pyridyl)pyrazine donor instead of the 2,2'-bipyridyl ligand (both pseudopolymorphs crystallize in the triclinic space group $P\bar{1}$). The experimentally determined conformation of [IV]⁺ was also reproduced by DFT calculations on the monocationic model system [IV^u]⁺ (Fig. 2) using B3P86/6-31G(d) for C, B, N, H and the SDD pseudopotential in combination with a DZP valence basis set for Fe.¹¹ It is important to note in this context, that the two dative boron–nitrogen bonds of [IV]⁺ are significantly different in length. The B–N bond perpendicular to the cyclopentadienyl ring, which relates to B(1)–N(11) in **6**, is 1.613(4) Å long ([IV^u]⁺: 1.596 Å), while the other possesses a length of only 1.580(4) Å ([IV^u]⁺: 1.579 Å). This correspondence between the experimentally determined and the theoretically predicted structures implies that the distortions of the N–B–N fragment are caused by internal molecular forces, as opposed to crystal packing forces. We suggest that a hyperconjugative interaction between the filled p orbital of the *ipso*-carbon atom

and the σ^* orbital of the parallel aligned B–N bond may be the reason for the elongation of this bond and provide a pathway for charge-transfer from ferrocene to the B(bipy) acceptor.

Single crystals of **10** (monoclinic, $P2_1/c$) were grown by slow evaporation of its toluene solution at room temperature. The crystal lattice contained two crystallographically independent molecules of **10**, one molecule of toluene and half a molecule of ferrocene in the asymmetric unit. Both molecules of **10** possess very similar structural features. Thus, structural parameters of only one of them are given in Fig. 6.

Fig. 6 Molecular structure of **10** (hydrogen atoms omitted for clarity; thermal ellipsoids at the 50% probability level). Selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)–C(31) = 1.629(9), B(1)–C(51) = 1.586(11), B(1)–N(11) = 1.611(9), B(1)–N(21) = 1.573(9), N(11)–C(12) = 1.349(8), N(21)–C(22) = 1.363(9), Fe(1)⋯Fe(2) = 5.711; C(31)–B(1)–C(51) = 115.0(6), C(31)–B(1)–N(11) = 109.5(5), C(31)–B(1)–N(21) = 110.0(5), N(11)–B(1)–C(51) = 112.8(5), N(11)–B(1)–N(21) = 94.7(5), N(21)–B(1)–C(51) = 113.1(5), C(32)–C(31)–B(1)–N(11) = 110.6(7), C(32)–C(31)–B(1)–N(21) = 7.8(10), C(32)–C(31)–B(1)–C(51) = –121.3(8), C(52)–C(51)–B(1)–N(11) = –117.0(7), C(52)–C(51)–B(1)–N(21) = –11.0(9), C(52)–C(51)–B(1)–C(31) = 116.4(7), C(31)C(32)C(33)C(34)C(35)//C(41)C(42)C(43)C(44)C(45) = 2.3, C(51)C(52)C(53)C(54)C(55)//C(61)C(62)C(63)C(64)C(65) = 2.7, C(31)C(32)C(33)C(34)C(35)//C(51)C(52)C(53)C(54)C(55) = 122.5, C(31)C(32)C(33)C(34)C(35)//B(1)N(11)C(12)C(22)N(21) = 68.4, C(51)C(52)C(53)C(54)C(55)//B(1)N(11)C(12)C(22)N(21) = 54.5.

The position of the C(31)-ferrocenyl group relative to the pyridylindolyl moiety is similar to **6** with torsion angles of C(32)–C(31)–B(1)–N(11) = 86.3(3)° (**6**) and 110.6(7)° (**10**). The conformation adopted by the C(51)-ferrocenyl-B(pyridylindolyl) fragment, however, is distinctly different from that of the C(31)-ferrocenyl-B(pyridylindolyl) unit, since the organometallic substituent is rotated by $\approx 180^\circ$ about its B–C bond [torsion angle C(52)–C(51)–B(1)–N(11) = –117.0(7)°]. Interestingly, the two different conformations correspond to two significantly different B–cyclopentadienyl bond lengths, which amount to 1.629(9) Å in the case of B(1)–C(31) and 1.586(11) Å in the case of B(1)–C(51). Corresponding boron–nitrogen bond lengths possess the same value within the 3σ error margin both in **6** [B(1)–N(11) = 1.633(4) Å, B(1)–N(21) = 1.565(4) Å] and in **10** [B(1)–N(11) = 1.611(9) Å, B(1)–N(21) = 1.573(9) Å].

Attempts to crystallize the B(bipy)-bridged dinuclear ferrocene complex using various different counterions resulted in single crystals of [11]Br, [11]O₃SCF₃, and [11]PF₆. In all three cases, the crystal lattices contained large amounts of solvate molecules. The structures of [11]Br and [11]O₃SCF₃ were thus seriously disordered and could not be refined. A crystal

structure determination of **[11]PF₆** (monoclinic, *P*₂/*c*) was more successful and confirmed the molecular structure already derived from NMR spectroscopy (Fig. 7).

Fig. 7 Molecular structure of **[11]PF₆** (hydrogen atoms and PF₆[−] counterion omitted for clarity; thermal ellipsoids at the 50% probability level). Selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)–C(11) = 1.599(9), B(1)–C(21) = 1.616(8), B(1)–N(1) = 1.576(8), B(1)–N(2) = 1.562(9), Fe(1)···Fe(2) = 6.600; C(11)–B(1)–N(1) = 111.1(5), C(11)–B(1)–N(2) = 112.0(5), C(21)–B(1)–N(1) = 112.2(5), C(21)–B(1)–N(2) = 112.2(5), C(11)–B(1)–C(21) = 111.6(4), N(1)–B(1)–N(2) = 97.0(4); C(11)–B(1)–C(21)–C(22) = 65.7(8), C(21)–B(1)–C(11)–C(12) = −79.9(8); C(1)C(2)C(3)C(4)–C(5)//C(11)C(12)C(13)C(14)C(15) = 5.2, C(21)C(22)C(23)C(24)C(25)//C(31)C(32)C(33)C(34)C(35) = 3.7, C(11)C(12)C(13)C(14)C(15)//C(21)C(22)C(23)C(24)C(25) = 77.3.

The conformation of **[11]PF₆** in the solid state resembles that of its BMe₂-bridged analog **Li[2]**(12-crown-4)₂ (Fig. 3) if a 2,2'-bipyridyl ligand is substituted for the two methyl groups [C(11)–B(1)–C(21)–C(22) = 65.7(8), C(21)–B(1)–C(11)–C(12) = −79.9(8)]. Bond lengths and angles of **[11]PF₆** do not depart appreciably from the values observed for other 2,2'-bipyridylboronium substituted ferrocenes.^{16,27–29}

Electrochemical investigations

Table 2 summarizes the electrochemical parameters of the redox events exhibited by compounds **Li[2]**, **Li[3]**, **6**, **10**, **[11]PF₆** and **[14](PF₆)₂**. All electrode potentials discussed in this paragraph are referenced against the ferrocene/ferrocenium couple. For review articles on metal–metal interactions in linked metallocenes see refs. 5, 30 and 31.

The electrochemical properties of the dinuclear species **Li[2]**, **10**, and **[11]PF₆**, which have been investigated in CH₂Cl₂ solutions, are considered first (Fig. 8).

Fig. 8 Cyclic voltammograms recorded at a platinum electrode on CH₂Cl₂ solutions containing [NBu₄][PF₆] (0.1 mol l^{−1}) and a) **Li[2]** (0.6 × 10^{−3} mol l^{−1}), b) **10** (0.6 × 10^{−3} mol l^{−1}), **[11]PF₆** (0.6 × 10^{−3} mol l^{−1}); only the Fe(II)/Fe(III) redox waves are shown.

Since the BMe₂ bridged **Li[2]** tends to decompose upon oxidation at room temperature, it was measured at −78 °C. Cyclic voltammograms of **10** and **[11]PF₆** were recorded at 20 °C. Under these conditions, all three compounds display chemically

Table 2 Formal electrode potentials *E*^{o'} (V vs. FcH/FcH⁺) and peak-to-peak separations ΔE_p (mV, at 0.2 Vs^{−1}) for the Fe(II)/Fe(III) redox changes exhibited by compounds **Li[2]**, **Li[3]**, **6**, **10**, **[11]PF₆** and **[14](PF₆)₂**

	<i>E</i> ^{o'} _{terminal}	$\Delta E_{p(t)}$	<i>E</i> ^{o'} _{interior}	$\Delta E_{p(i)}$	<i>T</i> /°C	Solvent	$\Delta E_{p(FeI)}$
Li[2]	−0.43/−0.64	90/100	—	—	−78	CH ₂ Cl ₂	100
Li[3]	−0.51	330	−1.21	210	−78	CH ₂ Cl ₂	250
6	−0.19	140	—	—	20	CH ₂ Cl ₂	140
10	−0.03/−0.21	80/70	—	—	20	CH ₂ Cl ₂	70
[11]PF₆ ^a	+0.23/+0.07	110/100	—	—	20	CH ₂ Cl ₂	90
	+0.13/+0.01	90/100	—	—	20	H ₃ CCN	70
[14](PF₆)₂ ^b	+0.03	100	+0.26	90	20	H ₃ CCN	80

^a Formal electrode potentials for the B(bipy)-centered reduction processes in CH₂Cl₂: *E*^{o'} = −1.29 V (ΔE_p = 90 mV), −2.35 V (peak potential value), and in H₃CCN: *E*^{o'} = −1.39 V (ΔE_p = 80 mV), −2.13 V (ΔE_p = 100 mV). ^b Formal electrode potentials for the B(bipy)-centered reduction processes: *E*^{o'} = 1.38 V (ΔE_p = 130 mV), 2.16 V (ΔE_p = 130 mV).

reversible oxidation processes as evidenced by the following criteria: where it is possible to determine them, the current ratios i_{pc}/i_{pa} are constantly equal to 1, the current functions $i_{pa}/v^{1/2}$ remain constant, and the peak-to-peak separations ($\Delta E_{p(i)}$, $\Delta E_{p(ii)}$) do not depart appreciably from the value found for the internal ferrocene standard ($\Delta E_{p(FeH)}$, Table 2; theoretically expected value for a chemically and electrochemically reversible one-electron step: 59 mV at 293 K). It should be noted that deviations from the ideal signal shape in the case of **[11]PF₆** are due to electrode adsorption of the electro-generated trication **[11]³⁺**. This effect is less pronounced at higher scan rates and absent in CH₃CN solution. All three dinuclear complexes **Li[2]**, **10**, and **[11]PF₆** exhibit two well-resolved Fe(II)/Fe(III) redox waves of relative intensity 1 : 1 (Table 2). They are assigned to successive one-electron transitions at the two ferrocenyl moieties and point to the presence of an electronic interaction between them. For obvious reasons, the anionic compound **[2]⁻** possesses the most cathodic redox potential ($E^{\circ}([2]^{-}/2) = -0.64$ V), the neutral species **10** adopts an intermediate position ($E^{\circ}(10/[10]^{+}) = -0.21$ V), and the cationic molecule **[11]⁺** is oxidized at the most anodic potential ($E^{\circ}([11]^{+}/[11]^{2+}) = +0.07$ V). On the basis of a purely electrostatic model, one would expect the difference in the redox potentials of the two Fe(II)/Fe(III) transitions to be smallest in the case of **Li[2]** and largest in the case of **[11]PF₆**, because the energy required to introduce a third positive charge into **[11]²⁺** should be disproportionately larger than the energy required to introduce a first positive charge into the neutral species **2**. The opposite trend, however, is observed in the series **Li[2]** ($E^{\circ}([2]^{-}/2) = -0.64$ V, $E^{\circ}(2/[2]^{+}) = -0.43$ V; $\Delta E^{\circ} = 0.21$ V), **10** ($E^{\circ}(10/[10]^{+}) = -0.21$ V, $E^{\circ}([10]^{+}/[10]^{2+}) = -0.03$ V; $\Delta E^{\circ} = 0.18$ V), and **[11]PF₆** ($E^{\circ}([11]^{+}/[11]^{2+}) = +0.07$ V, $E^{\circ}([11]^{2+}/[11]^{3+}) = +0.23$ V; $\Delta E^{\circ} = 0.16$ V). This leads to the conclusion that more subtle mechanisms of ferrocene-ferrocene interaction have to be taken into account including not only the influence of counterions but also some degree of charge delocalisation *via* the four-coordinate boron bridges. A comparison of the electrochemical properties of **Li[2]** and the ferricenyltris(ferrocenyl)borate zwitterion **5** (Fig. 2) furnishes further valuable information. It was anticipated that there would be little or no charge transfer through the coordinatively saturated boron atom. Cyclic voltammetry, however, revealed four reversible oxidation potentials at -0.62 V, -0.35 V, -0.15 V, and -0.03 V (*cf.* **Li[2]**: $E^{\circ} = -0.64$ V, -0.43 V). Moreover, a very broad band with a maximum near 2200 nm was detected in the electronic absorption spectrum of **5**. Both the presence of an intervalence electronic transition and the electrochemical data establish **5** as a mixed valence system and the authors suggested that electron transfer may proceed *via* a through-space mechanism. We note in passing that the ΔE° values of 0.21 V, 0.18 V, and 0.16 V determined for **Li[2]**, **10**, and **[11]PF₆**, respectively, are in the same range as the ΔE° values observed for the SiMe₂-bridged oligo(ferrocenylenes) Fc-[SiMe₂-fc]_x-SiMe₂-Fc ($x = 0-6$; $\Delta E^{\circ} = ca. 0.2$ V).³³ The two strongly cathodic redox waves of **[11]PF₆** ($E^{\circ} = -1.29$ V, -2.35 V), each representing a one-electron transition, are to be assigned to the reduction of the 2,2'-bipyridylboronium bridge, which is chemically related to the well-known two-electron acceptor diquat.³⁴ Both electrode potentials are reasonably close to those previously observed for B(bipy)-centred reductions in the case of **[IV]⁺** [$E^{\circ} = -1.43$ V, -2.23 V (peak potential value); hexafluorophosphate salt in CH₂Cl₂].¹⁶

At -78°C , the cyclic voltammogram of **Li[3]** consists of two redox waves ($E^{\circ} = -0.51$ V, -1.21 V), both of them showing features of chemical reversibility (Fig. 9).

Since the peak height of the more anodic couple is twice that of the cathodic one, the former is to be attributed to a two-electron transition and the latter to a one-electron transition. Considering the molecular structure of **[3]²⁻** which possesses (i) one electronically unique interior ferrocenylene moiety directly attached to two negatively charged $-\text{B}(\text{Fc})\text{Me}_2$ groups and (ii)

Fig. 9 Cyclic voltammogram recorded at a platinum electrode on a CH₂Cl₂ solution containing **[NBu₄][PF₆]** (0.1 mol l⁻¹) and **Li[3]** (0.5×10^{-3} mol l⁻¹).

two symmetry-related terminal ferrocenyl groups bearing only one anionic substituent, we may safely assume that the central iron atom is oxidized first and the other two subsequently. This assignment is further supported by the electrochemical data of the free macrocycle **[III]²⁻** ($E^{\circ} = -1.02$ V, -1.33 V)¹³ and of **Li[1,1'-fc(BMe₂)₂]**,²² which possesses an E° value of -1.22 V. Moreover, the formal electrode potential of the terminal ferrocenyl substituents in **Li[3]** ($E^{\circ} = -0.51$ V) agrees nicely with the mean redox potential of the diferrocenyl complex **Li[2]** ($E^{\circ} = -0.43$ V, -0.64 V). The electrochemical behaviour of **Li[3]** may be compared to that of the isoelectronic complexes Fc-EMe₂-fc-EMe₂-Fc ($E = \text{C, Si}$). In the cyclic voltammogram of the carbon-bridged derivative, three reversible redox events are resolvable at -0.14 V, 0.00 V, $+0.20$ V, ratio 1 : 1 : 1.²³ Silicon-bridged Fc-SiMe₂-fc-SiMe₂-Fc in CH₂Cl₂/CH₃CN solution shows only two redox waves with relative intensity of 2 : 1 ($E^{\circ} = -0.03$ V, $+0.23$ V).³³ In CH₂Cl₂ solution, however, the -0.03 V wave is resolved into two closely spaced one-electron waves,²⁵ indicating that the two ferrocenyl end groups are oxidized first, followed by oxidation at the interior site.^{23,33} For further in depth studies of electrochemical and structural models for poly(ferrocenylsilane) high polymers the reader is referred to refs.35,36.

The cyclic voltammogram of **[14](PF₆)₂** is characterized by four redox transitions at $E^{\circ} = +0.26$ V, $+0.03$ V, -1.38 V, and -2.16 V with relative peak heights of 1 : 2 : 2 : 2 (Fig. 10).

Fig. 10 Cyclic voltammogram recorded at a platinum electrode on a CH₂Cl₂ solution containing **[NBu₄][PF₆]** (0.1 mol l⁻¹) and **[14](PF₆)₂** (0.5×10^{-3} mol l⁻¹).

Similar to **[11]PF₆**, the two anodic processes are due to ferrocene oxidation, while the two cathodic processes are centred at the B(bipy) bridges. At difference with the trinuclear aggregate **[3]²⁻** where the interior ferrocenylene moiety is oxidized first, oxidation of the terminal ferrocenyl moieties precedes the electron transfer step at the central iron atom in **[14]²⁺**. Qualitatively, this can be explained by the fact that the central iron atom experiences twice the electronic charge of the boron substituents and this charge is of opposite sign in both molecules. At first glance we find it, however, counterintuitive that attachment of two negatively charged substituents to ferrocene leads to a huge cathodic shift of its redox potential (*cf.* the central ferrocenylene moiety in **[3]²⁻** gets oxidized at $E^{\circ} = -1.21$ V) whereas the accumulation of four positive charges in **[14]⁴⁺**

[two at the B(bipy) bridges and two more at the terminal ferrocenyl(III) groups] increases the redox potential of the interior ferrocenylene fragment by as little as +0.26 V with respect to parent ferrocene. Similarly, if we go along the series $[\text{FcB}(\text{Me})\text{bipy}]\text{PF}_6$, $[1,1'\text{-fc}(\text{B}(\text{Me})\text{bipy})_2](\text{PF}_6)_2$, and $[1,1',3,3'\text{-Fc}(\text{C}_5\text{H}_3(\text{B}(\text{Me})\text{bipy})_2)_2](\text{PF}_6)_4$, there is no concomitant increase in the values of the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox potentials ($E^\circ = -0.02$ V, -0.03 V, -0.03 V; in CH_2Cl_2) with increasing number of positively charged sidegroups.¹⁶ In this context, it is revealing to compare the influence exerted by two different kinds of negatively charged borate substituents on the ferrocene/ferrocenium couple. As mentioned above, $\text{Li}_2[1,1'\text{-fc}(\text{BMe}_3)_2]$ possesses a redox potential of $E^\circ = -1.22$ V,²² whereas $\text{Ti}[\text{FcBpz}_3]$ and $\text{Ti}_2[1,1'\text{-fc}(\text{Bpz}_3)_2]$ are oxidized at -0.01 V and -0.02 V, respectively (peak potential values; pz = pyrazol-1-yl).³⁷ This leads to the conclusion, that the negative charge of the borate substituent alone is not the determining factor for the E° value. Apart from the fact that the excess electron is spread over a larger region in the case of Bpz_3 , which may to some extent reduce its electrostatic effect on the iron atom, the group electronegativity of a Bpz_3 moiety is supposed to be considerably higher than that of a BMe_3 substituent but comparable to the group electronegativity of the B(Me)bipy fragment. Given that $[\text{FcB}(\text{Me})\text{bipy}]\text{PF}_6$ and $\text{Ti}[\text{FcBpz}_3]$ are oxidized at rather similar electrode potentials, it is tempting to speculate that electrostatic effects are of minor importance for an explanation of the electrochemical properties of $\text{Li}_2[3]$ and $[14](\text{PF}_6)_2$ and that a major contribution to the cathodic shift of the $\text{Li}_2[3]$ redox potential stems from inductive and/or hyperconjugative B(R)Me₂-to-ferrocene charge transfer (R = Me, Fc). Charge-transfer between ferrocene and its boron-containing substituent(s) is also apparent in $[11]\text{PF}_6$, $[14](\text{PF}_6)_2$, $[\text{FcB}(\text{Me})\text{bipy}]\text{PF}_6$, $[1,1'\text{-fc}(\text{B}(\text{Me})\text{bipy})_2](\text{PF}_6)_2$, and $[1,1',3,3'\text{-Fc}(\text{C}_5\text{H}_3(\text{B}(\text{Me})\text{bipy})_2)_2](\text{PF}_6)_4$, which give intensely purple-coloured solutions. In these molecules, ferrocene acts as electron donor and the B(Me)bipy substituent as the corresponding acceptor as has been found out by transient absorption measurements using femtosecond pump-probe spectroscopy¹¹ (see also the paragraph "crystal structure determination" of this paper). However, the amount of charge transferred is obviously too small to cause a significant anodic shift of the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox potential of ferrocene-based 2,2'-bipyridylboronium salts.

Apart from electron delocalization effects, possible influences of the counterions should also be considered as becomes evident from an inspection of the redox behaviour of $\text{Li}_2[III]$ (Fig. 1). The compound crystallizes from THF/diethyl ether in the presence of 12-crown-4 with one naked Li^+ ion encapsulated in the macrocyclic framework (Fig. 1). The other Li^+ ion is complexed by two molecules of crown ether. The contact ion pair $\{\text{Li}[III]\}^-$, which remains intact in THF solution (^7Li NMR spectroscopical control), is oxidized at -0.58 V (irreversible two-electron process). As a result, the Li^+ ion leaves the cage and a solvent separated species forms. Reduction of the empty macrocycle III back to its $[III]^{2-}$ state occurs in two successive one-electron steps at pronouncedly more cathodic electrode potentials ($E^\circ = -1.02$ V, -1.33 V).¹³ In $[11]\text{PF}_6$ and $[14](\text{PF}_6)_2$, the PF_6^- ion is comparatively small and thus able to approach the cationic fragment rather closely. Moreover, we are using $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte in our CV measurements, thereby causing a 200-fold increase in $[\text{PF}_6]^-$ concentration, which can be expected to further promote the formation of contact ion pairs. Thus, the fact that cationic B(bipy) entities appear to have only a small impact on the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ redox potentials may well be due to partial charge compensation. The Li^+ cations of $\text{Li}[2]$, $\text{Li}_2[3]$ and $\text{Li}_2[1,1'\text{-fc}(\text{BMe}_3)_2]$, on the other hand, are deeply embedded in ligand spheres of 12-crown-4 and THF molecules and thus kept at a large distance from the anionic part of the molecule. As a result, any effect of electrostatic forces between the boron bridges and the iron atoms is expected to be more pronounced within $[2]^-$, $[3]^{2-}$, and $[1,1'\text{-fc}(\text{BMe}_3)_2]^{2-}$ as compared to $[11]\text{PF}_6$ and $[14](\text{PF}_6)_2$.

Experimental

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 (toluene, benzene, diethyl ether, THF), Na/Pb alloy (hexane, heptane) or from CaH_2 (CH_2Cl_2 , CHCl_3 , CH_3CN) prior to use. NMR: Bruker DPX 250, AMX 250, AMX 400. ^{11}B NMR spectra are reported relative to external $\text{BF}_3 \cdot \text{Et}_2\text{O}$. All NMR spectra were run at room temperature; abbreviations: s = singlet; d = doublet; vtr = virtual triplet; q = quartet; br = broad; m = multiplet; n.r. = multiplet expected in the ^1H NMR spectrum but not resolved; n.o. = signal not observed; bipy = 2,2'-bipyridyl. FcBBr_2 ,⁴² $\text{FcB}(\text{Me})\text{Br}$,⁴² FcBMe_2 ,⁴² $1,1'\text{-fc}(\text{BBr}_2)_2$,⁴³ FcSnMe_3 ,⁴⁴ FcLi ,⁴⁵ $1,1'\text{-fc}(\text{Li-TMEDA})_2$,⁴⁶ and 5-fluoro-2-(2'-pyridyl)indole⁴⁷ were synthesized according to literature procedures.

Preparations

Synthesis of $\text{Li}[2]$. $t\text{BuLi}$ in pentane (1 mL, 1.50 mmol) was added to a solution of ferrocene (0.325 g, 1.75 mmol) in THF (5 mL) at 0°C . After the resulting mixture had been stirred for 15 min, FcBMe_2 , **1**, (0.259 g, 1.15 mmol) in THF (3 mL) was added dropwise with stirring at 0°C . The reaction mixture was stirred for one hour at room temperature, evaporated to dryness *in vacuo* and excess ferrocene was sublimed out overnight at $90^\circ\text{C}/10^{-3}$ torr. The remaining yellow microcrystalline solid was dissolved in CH_2Cl_2 (5 mL) and 12-crown-4 (0.470 g, 2.67 mmol) was added. After filtration, hexane (0.5 mL) was added to the filtrate. The clear orange solution was kept at -25°C for 24 h to give orange coloured X-ray quality crystals of $\text{Li}[2](12\text{-crown-4})_2 \cdot \text{CH}_2\text{Cl}_2$. Yield: 0.570 g (58%). ^{11}B NMR (THF-d_8 , 128.4 MHz): δ -21.2 ($h_1 = 10$ Hz). ^1H NMR (THF-d_8 , 400.0 MHz): δ -0.12 (m, 6H, CH_3), 3.64 (s, 32H, CH_2), 3.70, 3.81 (2 $\times$ vtr, 2 $\times$ 4H, $^3J_{\text{HH}} \approx ^4J_{\text{HH}} \approx 1.4$ Hz, C_5H_4), 3.84 (s, 10 H, C_5H_5). ^{13}C NMR (THF-d_8 , 100.6 MHz): δ 14.8 (q, $^1J_{\text{CB}} = 41.7$ Hz, CH_3), 66.2 (C_5H_4), 67.4 (C_5H_5), 69.6 (CH_2), 72.3 (C_5H_4), n.o. (C_{ipso}). ESI-MS: m/z 411 $[\text{M} - \text{Li}]^+$. The compound is highly sensitive to air and the crystals lose CH_2Cl_2 rapidly when isolated at room temperature; a decent elemental analysis was therefore not obtained.

Synthesis of $\text{Li}_2[3]$. FcBMe_2 , **1**, (0.107 g, 0.47 mmol) and $1,1'\text{-fc}(\text{Li-TMEDA})_2$ (0.074 g, 0.17 mmol) were dissolved in THF (3 mL) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred for 30 min. Addition of 12-crown-4 (0.326 g, 1.85 mmol) yielded a yellow precipitate. After addition of heptane (3 mL) and stirring for 30 min at room temperature, the solid material was collected on a frit, triturated with heptane (3 $\times$ 5 mL) and dried *in vacuo*. A solution of the crude product in THF was layered with diethyl ether to yield X-ray quality crystals of $\text{Li}_2[3](12\text{-crown-4})_4$ by vapour-phase diffusion. Yield: 0.182 g (79%). NMR spectra of the TMEDA adduct: ^{11}B NMR (128.4 MHz, THF-d_8): δ -19.2 ($h_1 = 20$ Hz). ^1H NMR (400.0 MHz, THF-d_8): δ -0.13 (br, 12H, CH_3), 2.14 (s, NCH₃), 2.29 (s, CH_2), 3.57, 3.63, 3.70, 3.78 (4 $\times$ n.r., 4 $\times$ 4H, C_5H_4), 3.82 (s, 10H, C_5H_5). ^{13}C NMR (100.6 MHz, THF-d_8): δ 14.6 (q, $^1J_{\text{CB}} = 40.9$ Hz, CH_3), 46.2 (NCH₃), 58.5 (CH_2), 66.0 (C_5H_4), 67.3 (C_5H_5), 67.4, 70.7, 72.1 (C_5H_4), n.o. (C_{ipso}). The compound is highly sensitive to air; a decent elemental analysis was therefore not obtained.

Synthesis of **4.** 5-Fluoro-2-(2'-pyridyl)indole was obtained following a literature procedure.⁴⁷ Since a complete assignment of its ^1H and ^{13}C NMR resonances has not been published but is helpful for an interpretation of the NMR spectra of the corresponding B-N adducts, the full NMR spectroscopic characterization of 5-fluoro-2-(2'-pyridyl)indole is given here [primed (') signals refer to the pyridyl fragment]: ^1H NMR

(DMSO- d_6 , 250.1 MHz): δ 6.93 (ddd, 1H, $^3J_{\text{HF}} = 9.6$ Hz, $^3J_{\text{HH}} = 8.9$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, H-6), 7.09 (dd, 1H, $^4J_{\text{HH}} = 2.2$ Hz, $^4J_{\text{HH}} = 0.8$ Hz, H-3), 7.24–7.32 (m, 2H, H-4, H-5'), 7.42 (dd, 1H, $^3J_{\text{HH}} = 8.9$ Hz, $^4J_{\text{HF}} = 4.7$ Hz, H-7), 7.82 (ddd, 1H, $^3J_{\text{HH}} = 8.0$ Hz, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, H-4'), 7.94 (dvtr, 1H, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} \approx ^5J_{\text{HH}} \approx 1.2$ Hz, H-3'), 8.59 (ddd, 1H, $^3J_{\text{HH}} = 4.9$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, $^5J_{\text{HH}} = 1.1$ Hz, H-6'), 11.71 (n.r., 1H, N-H). ^{13}C NMR (DMSO- d_6 , 62.9 MHz): δ 100.6 (d, $^4J_{\text{CF}} = 4.9$ Hz, C-3), 104.9 (d, $^2J_{\text{CF}} = 23.1$ Hz, C-4), 110.6 (d, $^2J_{\text{CF}} = 26.3$ Hz, C-6), 113.0 (d, $^3J_{\text{CF}} = 9.8$ Hz, C-7), 120.0 (C-3'), 122.5 (C-5'), 128.5 (d, $^3J_{\text{CF}} = 10.5$ Hz, C-9), 133.9 (C-8), 137.1 (C-4'), 138.9 (C-2), 149.2 (C-6'), 150.0 (C-2'), 157.2 (d, $^1J_{\text{CF}} = 231.9$ Hz, C-5). ^{19}F NMR (DMSO- d_6 , 235.3 MHz): δ -125.0.

For the preparation of the sodium salt **4**, a slurry of sodium hydride (0.030 g, 1.25 mmol) in THF (5 mL) was added to a solution of 5-fluoro-2-(2'-pyridyl)indole (0.200 g, 0.94 mmol) in THF (5 mL) at -78°C . After H_2 evolution had ceased, the mixture was allowed to warm to room temperature, filtered and the filtrate evaporated to dryness *in vacuo*. The off-white residue obtained was used without further purification. Yield: 0.221 g (100%).

Synthesis of 6. Compound **4** (0.221 g, 0.94 mmol) was suspended in toluene (5 mL), the resulting slurry cooled to -78°C and a solution of $\text{FcB}(\text{Me})\text{Br}$, **5**, (0.255 g, 0.88 mmol) in toluene (10 mL) added slowly with stirring. After warming to room temperature, the reaction mixture was stirred overnight. After filtration, all volatiles were removed from the filtrate under reduced pressure. The resulting solid was further purified by column chromatography (dichloromethane/ethyl acetate 10 : 1). Yield: 0.190 g (51%). Orange coloured X-ray quality crystals of **6** were grown by slow evaporation of its CDCl_3 solution at room temperature. NMR spectroscopy [primed (') signals refer to the pyridyl fragment]: ^{11}B NMR (CDCl_3 , 128.4 MHz): δ 4.5 ($h_{1/2} = 300$ Hz). ^1H NMR (CDCl_3 , 250.1 MHz): δ 3.78 (s, 5H, C_5H_5), 3.87, 3.90, 4.09, 4.11 (4 $\times$ m, 4 $\times$ 1H, C_5H_4), 6.99 (d, 1H, $^4J_{\text{HH}} = 0.8$ Hz, H-3), 7.00 (vtrd, 1H, $^3J_{\text{HF}} \approx 9.2$ Hz, $^3J_{\text{HH}} \approx 9.2$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, H-6), 7.33 (dd, 1H, $^3J_{\text{HF}} = 9.4$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, H-4), 7.36 (ddd, 1H, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 5.7$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, H-5'), 7.57 (dd, 1H, $^3J_{\text{HH}} = 9.1$ Hz, $^4J_{\text{HF}} = 4.7$ Hz, H-7), 7.85 (dvtr, 1H, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} \approx ^5J_{\text{HH}} \approx 1.1$ Hz, H-3'), 7.98 (ddd, 1H, $^3J_{\text{HH}} = 8.2$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, H-4'), 8.57 (dvtr, 1H, $^3J_{\text{HH}} = 5.7$, $^4J_{\text{HH}} \approx ^5J_{\text{HH}} \approx 1.2$ Hz, H-6'). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ 8.3 (CH_3), 68.2 (C_5H_5), 68.8, 69.0, 71.0, 71.3 (C_5H_4), n.o. (C_{ipso}), 97.5 (d, $^4J_{\text{CF}} = 5.8$ Hz, C-3), 105.9 (d, $^2J_{\text{CF}} = 22.9$ Hz, C-4), 111.9 (d, $^2J_{\text{CF}} = 26.9$ Hz, C-6), 114.6 (d, $^3J_{\text{CF}} = 9.8$ Hz, C-7), 118.5 (C-3'), 120.9 (C-5'), 132.3 (d, $^3J_{\text{CF}} = 10.4$ Hz, C-9), 135.8 (C-8), 137.6 (C-2), 140.7 (C-4'), 141.8 (C-6'), 148.8 (C-2'), 157.8 (d, $^1J_{\text{CF}} = 234.5$ Hz, C-5). ^{19}F NMR (CDCl_3 , 235.3 MHz): δ -125.3. ESI-MS: m/z 422 [M^+]. Elemental analysis: Calcd. for $\text{C}_{24}\text{H}_{20}\text{BF}_6\text{FeN}_2$ (422.08): C, 68.30; H, 4.78; N, 6.64. Found: C, 68.61; H, 4.95; N, 6.33%.

Synthesis of 9.

Method A. A solid mixture of FcBBr_2 , **7**, (0.710 g, 2.00 mmol) and FcSnMe_3 , **8**, (0.698 g, 2.00 mmol) was dissolved in 20 mL of C_6H_6 at room temperature and stirred for 8 h, whereupon a colourless precipitate (Me_3SnBr) gradually formed. After filtration and evaporation of solvent under reduced pressure, a red microcrystalline solid was obtained. Yield: 0.533 g (58%).

Method B. To FcBBr_2 , **7** (1.836 g, 5.16 mmol), in toluene (20 mL) was added neat Et_3SiH (1.321 g, 11.36 mmol) at -78°C with stirring. The resulting red solution was allowed to warm to room temperature and stirred overnight. All volatiles were driven off *in vacuo* to yield **9** as a red microcrystalline solid. Yield: 1.034 g (87%). ^{11}B NMR (CDCl_3 , 128.4 MHz): δ 54.9 ($h_{1/2} = 540$ Hz). ^1H NMR (CDCl_3 , 250.1 MHz): δ 4.08 (s, 10H, C_5H_5), 4.61, 4.64 (2 $\times$ vtr, 2 $\times$ 4H, $^3J_{\text{HH}} = ^4J_{\text{HH}} = 1.8$ Hz, C_5H_4). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ 69.8 (C_5H_5), 75.0, 76.6 (C_5H_4), n.o. (C_{ipso}).

Synthesis of 10. The compound was synthesized similar to **6** from **4** (0.165 g, 0.71 mmol) and Fc_2BBr , **9** (0.294 g, 0.64 mmol), in toluene (15 mL). Yield: 0.087 g (23%). Orange X-ray quality crystals of **10** were grown by slow evaporation of its toluene solution at room temperature. NMR spectroscopy [primed (') signals refer to the pyridyl fragment]: ^{11}B NMR (CDCl_3 , 128.4 MHz): δ 4.1 ($h_{1/2} = 370$ Hz). ^1H NMR (CDCl_3 , 250.1 MHz): δ 3.59 (s, 10 H, C_5H_5), 3.99 (m, 2H, C_5H_4), 4.09–4.13 (m, 6H, C_5H_4), 7.07 (vtrd, 1H, $^3J_{\text{HF}} \approx 9.2$ Hz, $^3J_{\text{HH}} \approx 9.2$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, H-6), 7.10 (d, 1H, $^4J_{\text{HH}} = 0.8$ Hz, H-3), 7.39 (dd, 1H, $^3J_{\text{HF}} = 9.8$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, H-4), 7.45 (ddd, 1H, $^3J_{\text{HH}} = 7.3$ Hz, $^3J_{\text{HH}} = 5.8$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, H-5'), 7.74 (dd, 1H, $^3J_{\text{HH}} = 9.0$ Hz, $^4J_{\text{HF}} = 4.8$ Hz, H-7), 7.91 (dvtr, 1H, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} \approx ^5J_{\text{HH}} \approx 1.1$ Hz, H-3'), 8.03 (ddd, 1H, $^3J_{\text{HH}} = 8.1$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, H-4'), 8.91 (dvtr, 1H, $^3J_{\text{HH}} = 5.8$ Hz, $^4J_{\text{HH}} \approx ^5J_{\text{HH}} \approx 1.2$ Hz, H-6'). ^{13}C NMR (CDCl_3 , 100.6 MHz): δ 67.7 (C_5H_5), 68.4, 68.7, 70.7, 71.5 (C_5H_4), n.o. (C_{ipso}), 98.1 (d, $^4J_{\text{CF}} = 5.7$ Hz, C-3), 106.0 (d, $^2J_{\text{CF}} = 23.0$ Hz, C-4), 112.1 (d, $^2J_{\text{CF}} = 26.8$ Hz, C-6), 115.9 (d, $^3J_{\text{CF}} = 9.7$ Hz, C-7), 118.3 (C-3'), 120.6 (C-5'), 132.4 (d, $^3J_{\text{CF}} = 10.3$ Hz, C-9), 136.4 (C-8), 138.1 (C-2), 140.9 (C-4'), 142.5 (C-6'), 148.6 (C-2'), 157.8 (d, $^1J_{\text{CF}} = 234.9$ Hz, C-5). ^{19}F NMR (CDCl_3 , 235.3 MHz): δ -125.1. ESI-MS: m/z 592 [M^+]. Calcd. for $\text{C}_{33}\text{H}_{26}\text{BF}_6\text{Fe}_2\text{N}_2$ (592.09): C, 66.94; H, 4.43; N, 4.73. Found: C, 66.45; H, 4.62; N, 4.44%.

Synthesis of [11]PF₆. To a solution of Fc_2BBr , **9** (0.265 g, 0.58 mmol), in toluene (5 mL) was added 2,2'-bipyridyl (0.128 g, 0.82 mmol) in toluene (5 mL) dropwise with stirring at -78°C . After stirring for 30 min, the solution was allowed to warm to room temperature whereupon a brown precipitate formed which was collected on a frit and triturated with toluene (10 mL). The crude product was dissolved in water and added dropwise to an aqueous solution of NH_4PF_6 (0.210 g, 1.29 mmol). The resulting PF_6 salt precipitated as a brown microcrystalline solid which was collected on a frit and dried *in vacuo*. Yield: 0.353 g (89%). Single crystals were obtained by vapour-phase diffusion of diethyl ether into an acetonitrile solution of [11]PF₆. ^{11}B NMR (CD_3CN , 128.4 MHz): δ 7.3 ($h_{1/2} = 250$ Hz). ^1H NMR (CD_3CN , 250.1 MHz): δ 3.86 (s, 10 H, C_5H_5), 4.11, 4.35 (2 $\times$ n.r., 2 $\times$ 4H, C_5H_4), 8.14 (vtr, 2H, $^3J_{\text{HH}} \approx 6.3$ Hz, bipy-5,5'), 8.64 (vtr, 2H, $^3J_{\text{HH}} \approx 7.8$ Hz, bipy-4,4'), 8.73 (dd, 2H, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, bipy-3,3'), 9.01 (d, 2H, $^3J_{\text{HH}} = 5.0$ Hz, bipy-6,6'). ^{13}C NMR (CD_3CN , 62.9 MHz): δ 70.0 (C_5H_5), 71.5, 72.4 (C_5H_4), n.o. (C_{ipso}), 123.9 (bipy-3,3'), 129.4 (bipy-5,5'), 144.7 (bipy-6,6'), 145.7 (bipy-4,4'), 145.8 (bipy-2,2'). ESI-MS: m/z 537 [$\text{M} - \text{PF}_6$] $^+$. Calcd. for $\text{C}_{30}\text{H}_{26}\text{BF}_6\text{Fe}_2\text{N}_2\text{P}$ (682.01): C, 52.83; H, 3.84; N, 4.11. Found: C, 52.43; H, 3.82; N, 3.85%.

Synthesis of [14](PF₆)₂. A toluene (10 mL) solution of FcSnMe_3 , **8** (1.080 g, 3.10 mmol), was added dropwise with stirring at -78°C to a solution of 1,1'- $\text{Fc}(\text{BBr}_2)_2$, **12** (0.781 g, 1.48 mmol), in 10 mL of toluene. The mixture was allowed to warm to room temperature and stirred for 8 h. The solvent and Me_3SnBr were removed overnight at $90^\circ\text{C}/10^{-3}$ torr. The remaining red oil was dissolved in 20 mL of toluene and 2,2'-bipyridyl (0.462 g, 2.96 mmol) in toluene (10 mL) was added dropwise at -78°C whereupon a dark brown precipitate formed. After stirring for one hour at room temperature, the solid material was collected on a frit, triturated with toluene (2 $\times$ 10 mL) and hexane (10 mL), and dried *in vacuo*. The crude product was then dissolved in 30 mL of water, filtered and the clear solution added dropwise at room temperature to an aqueous solution of NH_4PF_6 (1.630 g, 10.00 mmol). [14](PF₆)₂, which precipitated quantitatively, was isolated by filtration, triturated with diethyl ether (2 $\times$ 10 mL) and dried *in vacuo*. Yield: 1.55 g (89%). ^{11}B NMR (CD_3CN , 128.4 MHz): δ 7.2 ($h_{1/2} = 450$ Hz). ^1H NMR (CD_3CN , 400.0 MHz): δ 3.57, 3.62 (2 $\times$ n.r., 2 $\times$ 4H, C_5H_4), 3.68 (s, 10H, C_5H_5), 3.91, 4.26 (2 $\times$ n.r., 2 $\times$ 4H, C_5H_4), 8.16 (vtr, 4H, $^3J_{\text{HH}} \approx 6.4$ Hz, bipy-5,5'), 8.68 (vtr, 4H, $^3J_{\text{HH}} \approx 7.6$ Hz, bipy-4,4'), 8.75 (d, 4H, $^3J_{\text{HH}} = 8.1$ Hz, bipy-3,3'), 9.02 (d, 4H, $^3J_{\text{HH}} = 5.3$ Hz, bipy-6,6'). ^{13}C

NMR (CD₃CN, 100.6 MHz): δ 69.2 (C₅H₅), 71.0, 71.1, 71.4, 71.6 (C₅H₄), n.o. (C_{ipso}), 124.1 (bipy-3,3'), 129.6 (bipy-5,5'), 144.8 (bipy-6,6'), 145.9 (bipy-2,2'), 146.0 (bipy-4,4'). ESI-MS: m/z 444 [M – 2PF₆]²⁺. Anal. Calcd for C₅₀H₄₂B₂F₁₂Fe₃N₄P₂ (1178.00): C, 50.98; H, 3.59; N, 4.76. Found: C, 50.56; H, 3.45; N, 4.39%.

Crystal structure determinations of Li₂[(12-crown-4)₂], 6, Li₂[(12-crown-4)₄], 10, and [11]PF₆

Data collections for Li₂[(12-crown-4)₂], Li₂[(12-crown-4)₄], 6, and 10 were performed on a STOE IPDS-II two-circle diffractometer with graphite-monochromated Mo-K α -radiation (λ = 0.71073 Å). The structures were solved with direct methods⁴⁸ and refined against F^2 by full-matrix least-squares calculations.⁴⁹ Absorption corrections were performed with the MULABS⁵⁰ option in PLATON.⁵¹ 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 Li₂[(12-crown-4)₂·CH₂Cl₂] contains two anions, two Li cations (each coordinated by two crown ether rings), and two dichloromethane molecules. The anion of Li₂[(12-crown-4)₄] is located on a centre of inversion. As a result of that, there is just half an anion and one Li cation (coordinated by two crown ether rings) in the asymmetric unit. The crystals of compound 10 were all very small and weakly diffracting. As a result, the data are weak and the R -values rather high. 10 crystallizes with two crystallographically independent but rather similar molecules in the asymmetric unit. Moreover, the crystal lattice contains one molecule of toluene and half a molecule of ferrocene. The Fe atom of the ferrocene molecule is located on a centre of inversion. Consequently, the Cp rings are disordered. They simulate a hexagon in which each C atom has an occupation factor of 5/6. Distance restraints were applied to the toluene molecule. A single crystal of [11]PF₆ was measured on a SIEMENS SMART diffractometer at a temperature of about 145(2) K. Repeatedly measured reflections remained stable. An empirical absorption correction with program SADABS⁵² gave a correction factor between 0.790 and 1.000. Equivalent reflections were averaged ($R(I)_{\text{internal}}$ = 0.066). The structure was determined by direct methods using program SHELXS.⁴⁸ All hydrogen atoms were geometrically positioned and were constrained. The unit cell contains two symmetry related solvate regions of 718 Å³ each. No atoms could be located in the solvate regions. The program PLATON/SQUEEZE⁵³ was used to model the solvate density. The solvate density was estimated to contain about 405 electrons cell⁻¹. The non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined on F^2 values using program SHELXL-97.⁴⁹ The final difference density was between –2.1 and +3.5 e Å⁻³ near Fe(2). The large displacement parameters of many atoms show the structure to be partly disordered. Especially the PF₆ group is severely distorted.

CCDC reference numbers: 246197 (Li₂[(12-crown-4)₂]), 246196 (Li₂[(12-crown-4)₄]), 246198 (6), 246199 (10), and 249276 ([11]PF₆).

See <http://www.rsc.org/suppdata/dt/b4/b413581d/> for crystallographic data in CIF or other electronic format.

Electrochemical measurements

Cyclic voltammetry was performed in deaerated acetonitrile and methylene chloride solutions containing [NBu₄][PF₆] (0.1 mol l⁻¹) as the supporting electrolyte. All potential values are reported relative to the FcH/FcH⁺ redox couple. The cell for voltammetric studies was designed as detailed in ref.54. Voltammetric scans were referenced by addition of a small amount of ferrocene as internal standard at an appropriate time of the experiment.

Conclusion

In order to investigate the potential of four-coordinate boron atoms to mediate electronic communication between two ferro-

cenyl substituents, we synthesized di- and trinuclear complexes featuring negatively charged BMe₂ bridges on one hand (*i.e.* Li₂[2], Li₂[3]) and positively charged B(bipy) linkers on the other (*i.e.* [11]PF₆, [14](PF₆)₂). For comparison, we also prepared the uncharged mono- and diferrocene derivatives 6 and 10 in which the boron atom is chelated by a 2-(2'-pyridyl)indolyl ligand. Li₂[(12-crown-4)₂] (monoclinic, $C2/c$), Li₂[(12-crown-4)₄] (triclinic, $P\bar{1}$), 6 (monoclinic, $P2_1/c$), 10 (monoclinic, $P2_1/c$), and [11]PF₆ (monoclinic, $P2_1/c$) were structurally authenticated using X-ray crystallography.

As to be expected, electrostatic forces of attraction or repulsion between the boron bridges and the ferrocene moieties have an influence on the Fe(II)/Fe(III) redox potentials of Li₂[2], Li₂[3], [11]PF₆, and [14](PF₆)₂. Compared to the FcH/FcH⁺ standard, a huge cathodic shift is observed in the case of the negatively charged BMe₂-bridged species whereas the 2,2'-bipyridylboronium derivatives are oxidized at more anodic electrode potentials than parent ferrocene. It is also important to note that the cyclic voltammograms of Li₂[2], 10, and [11]PF₆ exhibit two well resolved one-electron redox waves rather than one two-electron transition (*cf.* Li₂[2]: $E^{\circ'} = -0.43$ V/–0.64 V; 10: –0.03 V/–0.21 V; [11]PF₆: $E^{\circ'} = +0.23$ V/+0.07 V; in CH₂Cl₂ vs. FcH/FcH⁺). Interestingly, the absolute shift values are significantly larger for anionic [2]⁻ than for its cationic counterpart [11]⁺ even though the amount of charge accommodated by both species is the same. Moreover, the $\Delta E^{\circ'}$ splitting between the two corresponding Fe(II)/Fe(III) redox waves decreases from 0.21 V in Li₂[2] to 0.18 V in 10 and 0.16 V in [11]PF₆, which is somewhat surprising because it should be much harder to introduce a third positive charge into [11]²⁺ than to introduce a first positive charge into the neutral species 2. This argues against mere electrostatic interactions as the only source of the redox splitting observed in Li₂[2], Li₂[3], [11]PF₆, and [14](PF₆)₂. Other factors like the positive inductive effect of B(R)Me₂ substituents (R = Fc, fc) and positive hyperconjugation from B–C σ orbitals into π^* orbitals of the C₅H₄ rings are also likely to play an important role.

Each of the trinuclear complexes Li₂[3] and [14](PF₆)₂ is characterized by one one-electron wave and one two-electron Fe(II)/Fe(III) transition (Li₂[3]: –0.51 V, –1.21 V, ratio 2 : 1; [14](PF₆)₂: +0.03 V, +0.26 V, ratio 1 : 2). Again, relative potential differences within the same cyclic voltammogram as well as absolute shifts of the redox potentials with respect to the FcH/FcH⁺ couple are most pronounced in the BMe₂-bridged aggregate. The electrochemical behaviour of Li₂[3] and [14](PF₆)₂ differs in an important aspect from the redox chemistry of the triferrocenes Fc-EMe₂-fc-EMe₂-Fc (E = C, Si)^{23,25,33}, which are uncharged isoelectronic analogues of [3]²⁻. In both these molecules, three reversible one-electron redox processes can be resolved under appropriate measurement conditions thereby indicating the degree of electronic interactions to be higher than in Li₂[3] and [14](PF₆)₂.

The basic idea behind our aim to synthesize poly(ferrocenylenes) with negatively charged borate bridges is to stabilize the Fe(III) state of the constituting ferrocenylene moieties electrostatically and to investigate the electronic and magnetic properties of the macromolecules after (partial) oxidation. Given the background that the zwitterion ferricenyltris(ferrocenyl)borate V (Fig. 2) is a mixed valence species with electronically communicating iron sites, there appears to be a realistic chance to observe electric conductivity or cooperative magnetic behaviour in related polymeric materials. In the light of our studies on short-chain model systems, however, the initial target polymer (Li[III])_n (Fig. 1) does no longer appear to be the best choice to reach our goal, given the fact that its di- and trinuclear relatives Li₂[2] and Li₂[3] (Scheme 1) are not stable upon oxidation at ambient temperature. Moreover, our simple coordination polymerization approach to (Li[III])_n, which starts from 1,1'-fc(BMe₂)₂/1,1'-fcLi₂ and relies on Lewis acid–base pairing, turned out to be less selective than expected in that it produces considerable amounts of cyclic dimer Li₂[III] (Fig. 1).

In contrast to $(\text{Li}[\text{II}])_n$, the hypothetical B(bipy)-bridged polymer $([\text{VI}]\text{PF}_6)_n$ (Fig. 11) is likely to possess much greater stability as can be deduced from the (electro)chemical properties of its oligomeric congeners $[\text{11}]\text{PF}_6$ and $[\text{14}](\text{PF}_6)_2$ (Scheme 3).

Fig. 11 The B(bipy)-bridged target polymer $([\text{VI}]\text{PF}_6)_n$.

In addition, macromolecules $([\text{VI}]\text{PF}_6)_n$ are attractive because they have the potential to act as photoswitchable materials that can be promoted from their diamagnetic ground state $[\text{Fe}(\text{II})/\text{R}_2\text{B}(\text{bipy})^+]$ into a paramagnetic excited state $[\text{Fe}(\text{III})/\text{R}_2\text{B}(\text{bipy})^*]$ upon irradiation with laser light (such a behaviour was observed when the model compound $[1,1'\text{-fc}(\text{B}(\text{Me})\text{bipy})_2](\text{PF}_6)_2$ was investigated by transient absorption measurements using femtosecond pump-probe spectroscopy).¹¹ Unfortunately, the synthesis protocol for $[\text{11}]\text{PF}_6$ and $[\text{14}](\text{PF}_6)_2$ can probably not be developed further to make $([\text{VI}]\text{PF}_6)_n$ accessible from $1,1'\text{-fc}(\text{SnMe}_3)_2/1,1'\text{-fc}(\text{BBr}_2)_2$ and 2,2'-bipyridyl. The problem lies in the fact that $1,1'\text{-fc}(\text{SnMe}_3)_2$ undergoes a unique rearrangement reaction when boron halides are added. As the result, 1-stannyl-2-borylferrocenes rather than 1,1'-diborylferrocenes are obtained as the major product.^{38,39} Thus, a completely different synthesis route is required and we suggest to employ a novel reaction which has only recently been discovered by our group: FcBBr_2 , **7**, and two equivalents of HSiEt_3 produce Fc_2BBr , **9**, in about 90% yield (Scheme 4; for details see the Experimental section of this paper).

Scheme 4 Alternative synthesis route to **9** and application of this method for the preparation of BBr-bridged oligonuclear complexes $(\text{VII})_n$. (i) toluene, -78°C to r.t.

Both in terms of starting material availability and in terms of yield, this procedure is superior to the stannyl route outlined in Scheme 2. The reaction is reminiscent of the chemical behaviour of $[\text{FcBH}_3]\text{Li}$, which, upon hydride abstraction with ClSiMe_3 , does not give the free borane but dimerizes to the BH-bridged diferrocene species Fc_2BH with concomitant liberation of B_2H_6 .⁴⁰ We have gathered considerable evidence that $1,1'\text{-fc}(\text{BBr}_2)_2$, **12**, and triethylsilane give oligomers $(\text{VII})_n$ with estimated chain lengths n ranging from 10 to 100 (Scheme 4; n was determined by GPC after $(\text{VII})_n$ had been quenched with MeOSiMe_3).⁴¹ Compounds $(\text{VII})_n$ are promising starting materials for the

preparation of B(bipy)-bridged polymers $([\text{VI}]\text{PF}_6)_n$ (Fig. 11). Moreover, they may be reacted with organolithium reagents (e.g. PhLi , FcLi) to give more stable derivatives of the initial target compound $(\text{Li}[\text{II}])_n$ (Fig. 1). These investigations are currently under way in our laboratories together with attempts to optimize the synthesis protocol for $(\text{VII})_n$ in order to obtain higher molecular weights and a smaller molecular weight distribution.

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