

Applications of boron–nitrogen and boron–phosphorus adducts in organometallic chemistry

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Received 5 November 2001

Dedicated to Professor Karl Wiegardt on the occasion of his 60th birthday

Abstract

Aspects of useful applications of main group Lewis acid–base pairs for the synthesis of sophisticated organometallic architectures are reviewed. Special emphasis is put on the author's own studies of boron–nitrogen and boron–phosphorus adducts and the relevance of the compounds obtained for the development of (i) organometallic materials, (ii) supramolecular entities and (iii) novel homogeneous catalysts. © 2002 Published by Elsevier Science B.V.

Keywords: Ferrocene; Lewis acid–base adducts; tris(1-pyrazolyl)borate ligands; Coordination polymers; Macrocyclic compounds

1. Introduction

The purpose of this paper is to give a review of a useful synthesis approach to organometallic compounds based on the formation of boron–nitrogen adduct bonds. Our aim is to facilitate the preparation of sophisticated molecular architectures and to generate specific materials which would be much harder to obtain using conventional organic synthesis. To illustrate applications of boron–nitrogen adducts in organometallic chemistry, examples from four different areas have been selected: (1) charge transfer polymers; (2) redox-active macrocycles; (3) switchable ansa-metallocenes and (4) redox-active tris(1-pyrazolyl)borate ligands.

The general concept is summarized in Fig. 1: Two metal complexes, M_1 and M_2 , linked by a C–C single bond or a C=C double bond (left), are put face to face to the isoelectronic boron–nitrogen bridged species (right).

Using B–N rather than C–C bonds offers several advantages. First, boron–nitrogen adducts are self-assembling. It can obviously be quite difficult to form C–C bonds in high yield, but it is generally very easy to

add a Lewis basic nitrogen-containing fragment to a Lewis acidic boron-containing fragment and to rely on Lewis acid–base pairing. Second, B–N adduct formation is reversible, and the strength of the respective bond can be influenced by choice of appropriate substituents at boron and nitrogen. It is therefore not just possible to link two fragments together, but one can also separate them again without destroying the individual components.

It is worth mentioning, that self-assembly and reversible bond formation are two key features which make hydrogen bonds so important in nature. In some way, B–N adducts behave similar to hydrogen bridges. However, in most cases they are stronger and therefore easier to control, and they are less destructive to sensitive organometallic compounds than proton donors.

2. Synthesis and physical properties of ferrocenylboranes

Various ways to synthesize borylated organometallic compounds are known to-date. Boryl substituents can be introduced conveniently into the parent complexes by electrophilic substitution with boron halides, which works particularly well in the case of ferrocene, ruthen-

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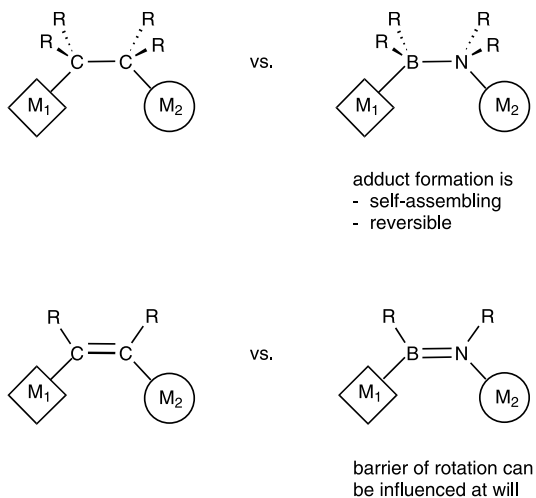


Fig. 1.

nocene and cymantrene (cyclopentadienyl manganese tricarbonyl) [1–3].

Ferrocene reacts with BBr_3 in boiling hexane cleanly and in almost quantitative yield. Depending on the stoichiometry, one or two BBr_2 substituents can be attached to the organometallic backbone to give FcBBr_2 (**1**) and $1,1'\text{-fc}(\text{BBr}_2)_2$ (**2**), respectively [$\text{Fc} = (\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$; $\text{fc} = (\text{C}_5\text{H}_4)_2\text{Fe}$; Fig. 2]. If BBr_3 is employed in large excess, the $1,1',3$ -triborylated derivative **3** and the $1,1',3,3'$ -tetraborylated ferrocene **4** are formed in the reaction mixture as well (Fig. 2).

Since the separation and isolation of these species is difficult, **4** is better synthesized by the reaction of ferrocene in neat BBr_3 , thereby ensuring exhaustive tetraborylation [4]. Only for the generation of triborylated **3** the selectivity problem has not been solved so far. It can, however, be circumvented by treating monoalkyl ferrocene (rather than ferrocene itself) with boron tribromide under the same reaction conditions as in the case of **4**. As a result, 1-alkyl- $1',3,3'$ -triboryl ferrocene **3a** is obtained in high yield [5].

The molecular structure of FcBBr_2 **1** has been investigated by X-ray crystallography (Fig. 2) [6]. The boryl substituent was found to be bent toward the iron atom by a dip angle of almost 20° . A similar structural feature has been observed for the related complexes

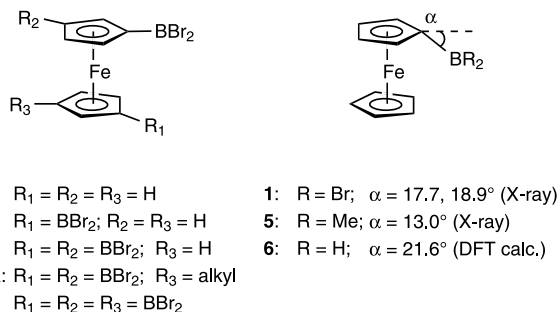


Fig. 2.

FcBMe_2 (**5**) [7] and $1,1'\text{-fc}(\text{BBr}_2)_2$ (**2**) [8]. In contrast, the diisopropylamino derivative $1,1'\text{-fc}[\text{B}(\text{N}^i\text{Pr}_2)_2]_2$ which bears boryl groups of significantly reduced Lewis acidity, shows no bending of the $\text{C}_5\text{H}_4\text{-B}(\text{N}^i\text{Pr}_2)_2$ moieties [8]. Theoretical calculations based on density functional theory (DFT) have been performed on the model system FcBH_2 (**6**) and proved to be in excellent agreement with the experimental findings (Fig. 2) [6]. According to these calculations, an interaction between filled d-type orbitals at iron and the empty p orbital of boron causes bending of the boryl substituent toward the central iron atom. Obviously, the Fe-B interaction becomes stronger with increasing Lewis acidity of the BR_2 side chain. This suggests, that the oxidation state of the iron atom might influence the Lewis acidity of the boryl substituent, and that the redox potential of the Fe(II)/Fe(III) transition should reflect the coordination state of the boron center. This assumption is in accord with cyclic voltammetric measurements: The redox potential (vs. SCE) of the Fe(II)/Fe(III) wave rises from $E^\circ = 0.44$ V in parent ferrocene to about 0.65 V in the diborylated derivative $1,1'\text{-fc}(\text{BMe}_2)_2$ (**7**) (Fig. 3) [9].

This can easily be explained by the π electron withdrawing nature of the three-coordinate boron atom. When two equiv. of γ -picoline (pic) are added, the Fe(II)/Fe(III) redox potential drops dramatically: The B-N diadduct **8** (Fig. 3) is as easy to oxidize as decamethylferrocene [E° (**8**) = -0.12 V vs. SCE; CH_2Cl_2] [9]. This is an important point, because decamethylferrocene is a widely used electron donor in organometallic charge-transfer (CT) complexes—just to mention Miller's molecular ferromagnet $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+[\text{TCNE}]^-$ [10]. The potential of FcBBr_2 to act as a one-electron donor after a Lewis base has been added is dependent on the nature of the substituents R at boron, which influence the stability of the corresponding base adducts both sterically and electronically. This has been concluded, for example, from reactions of the electron acceptor **9** with various derivatives of ferrocenylboranes.[11] In the case of FcBMe_2 **5**, no B-N adduct is formed between the boron atoms and the Lewis-basic pyrazolyl sidearms of **9**. Consequently, no electron transfer from iron to the

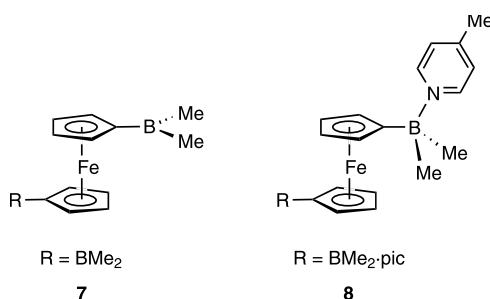
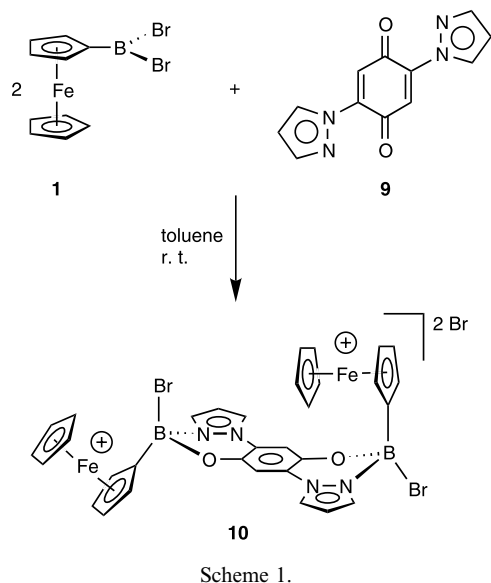


Fig. 3.



quinone ring takes place. In contrast, FcBBR_2 **1**, which tends to form strong adducts with aromatic amines, gives an immediate redox reaction with **9**, thereby generating the dinuclear complex **10** in quantitative yield (Scheme 1).

Complex **10** features ferrocene in its Fe(III) state, as well as a hydroquinone core. Given this background, ferrocenylboranes appear to be useful starting materials for the synthesis of (polymeric) CT complexes exploiting the advantages of B–N adduct formation.

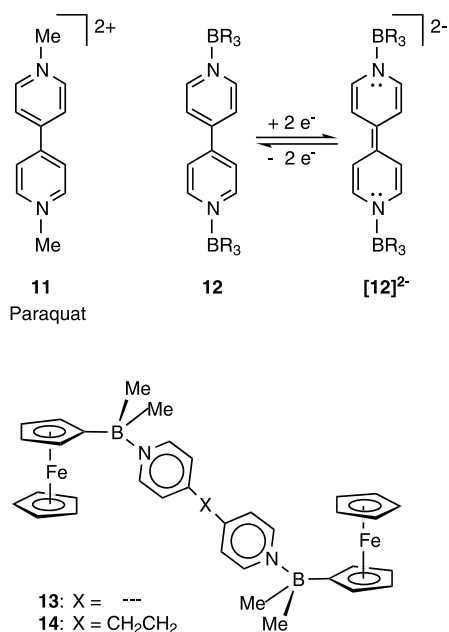


Fig. 4.

3. Ferrocene-based charge-transfer complexes with a boron–nitrogen backbone

Fig. 4 shows the well-known organic electron acceptor paraquat **11**. The molecule is able to reversibly accept two electrons and thus exists in three stable oxidation states [12]. If the $[\text{CH}_3]^+$ cations are replaced by the isoelectronic boranes, the B–N diadducts **12** are obtained, which exhibit qualitatively similar electrochemical features as paraquat [13]. Upon addition of electrons, the aromatic system **12** is first transformed into a semiquinone and then into the quinoid dianion $[\text{12}]^{2-}$ (Fig. 4).

If one of the substituents R at boron equals ferrocene, the dinuclear aggregate **13** is obtained [9]. In compound **13**, which features two ferrocene donors linked by a paraquat-type electron acceptor, the B–N adducts serve three purposes: (i) they are holding the three components together, (ii) they activate the ferrocene donor, which is oxidized at a significantly lower value than parent ferrocene (**13**: $E^{o'} = +0.17$ V; FcH: $E^{o'} = +0.49$ V; DMF vs. SCE), (iii) they activate the acceptor, which can be reduced at less negative potentials than 4,4'-bipyridine itself (**13**: $E^{o'} = -1.20, -1.75$ V; 4,4'-bipyridine: $E^{o'} = -1.84, -2.38$ V; DMF vs. SCE) [9].

Complex **13** possesses a highly unusual dark purple color indicative of charge transfer interactions within this molecule. When the extended π -electron system of bipyridine is disrupted by insertion of an ethylene spacer into its central C–C bond, the paraquat-like acceptor is destroyed. Consequently, the color of the respective dinuclear complex **14** changes to yellow (Fig. 4) [9].

Treatment of 1,1'-fc(BMe₂)₂ (**7**) with 4,4'-bipyridine yields a dark purple precipitate, which is insoluble in all common solvents [9]. Its structure in the solid state was determined by high resolution X-ray powder diffraction [14]. The material consists of polymeric chains with

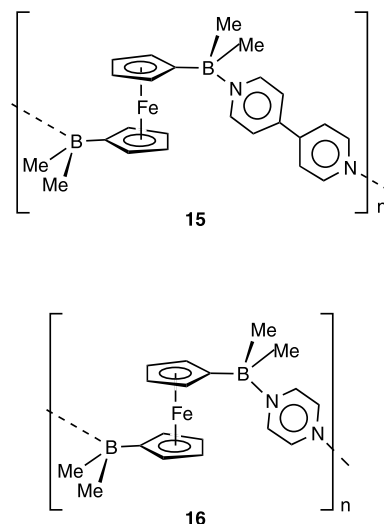


Fig. 5.

alternating ferrocene and bipyridine units (**15**; Fig. 5). Solid **15** can be handled in air without decomposition and is stable up to 240 °C as has been proven by DSC measurements [9].

An analogous green charge transfer polymer **16** (Fig. 5) has been produced from 1,1'-fc(BMe₂)₂ (**7**) and pyrazine and was structurally characterized by single crystal X-ray diffraction [15].

4. Ferrocene-based electron sponges with boron–nitrogen backbone

The two-electron acceptor diquat (**17**, Fig. 6) is chemically related to paraquat **11** (Fig. 4) and thus possesses a very similar redox behavior. As in the case of paraquat, boron analogues [18] (2,2'-bipyridylboronium cations) [16] of the diquat molecule exist, which are readily available from the reaction of halogenoboranes with 2,2'-bipyridine. Starting from **1**, **2** and **4**, straightforward high-yield syntheses of the ferrocenyl 2,2'-bipyridylboronium cations **19**, **20** and **21** have been reported (Fig. 6) [17].

The compounds are highly soluble in polar organic solvents and, except of those derivatives bearing a bromo substituent R at boron, they are stable towards air and moisture. In **19**, **20** and **21**, one, two, and four cationic [B(R)bipy]⁺ acceptors (R = Br, alkyl, OR*, NR₂*) are covalently attached to a ferrocene donor. All derivatives of these complexes exhibit a dark purple color. The extinction coefficients of the corresponding absorptions in the visible region of the electronic

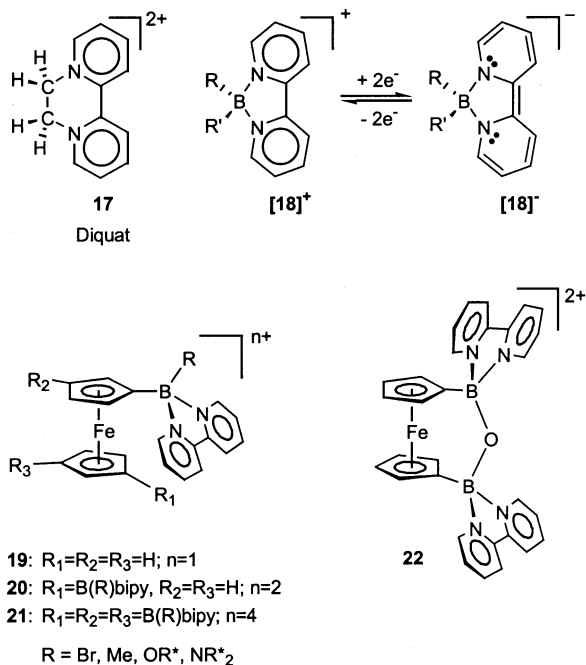


Fig. 6.

spectrum correlate with the number of pendent [B(R)bipy]⁺ units. Moreover, ESR spectra of the reduced radical species indicate admixture of Fe-d orbitals to the bipyridine π system. It has therefore been suggested, that the intense color of **19**–**21** is due to a (weak) electronic interaction between the ferrocene center and the bipyridylboronium substituents [17].

In DMF solution and under an inert atmosphere, **19**, **20** and **21** display one chemically reversible oxidation and two consecutive reversible reduction processes. They are thus capable of storing three, five and nine electrons, respectively. There is no significant electronic communication between the individual [B(R)bipy]⁺ fragments in **20** and **21** [17]. This situation changes when the boron centers of **20** are connected by an oxo bridge. The resulting ansa-ferrocene **22** (Fig. 6) shows four well-resolved one-electron reduction steps rather than the two two-electron reduction waves that had been observed in the case of **20** [18]. It can thus be concluded, that an oxygen bridge significantly promotes the electronic communication between two 2,2'-bipyridylboronium units.

Complexes **20** and **21**, being able to tolerate the loss of one electron, as well as the addition of four and eight electrons, respectively, possess a particularly high redox aptitude. Incorporation of these building blocks into linear or dendritic polymers may therefore lead to the development of efficient novel electron storage media. On principle, the aimed-for macromolecules can be generated either by connecting **20** and **21** via their boron atoms, or by treating the ferrocenylboranes **2** and **4** with ligands possessing at least two chelating Lewis basic sites.

The bromo derivatives (R = Br) of **19**, **20**, and **21** are prone to hydrolysis and alcoholysis. This has been employed for the synthesis of the oxo-bridged species **23** (Fig. 7) [19].

Attempts to apply the controlled hydrolysis of the difunctional complex **20** (R = Br) to the synthesis of linear macromolecules have not been successful so far. Treatment of **20** (R = Br) with one equivalent of water in the presence of triethylamine yields the BOB-bridged

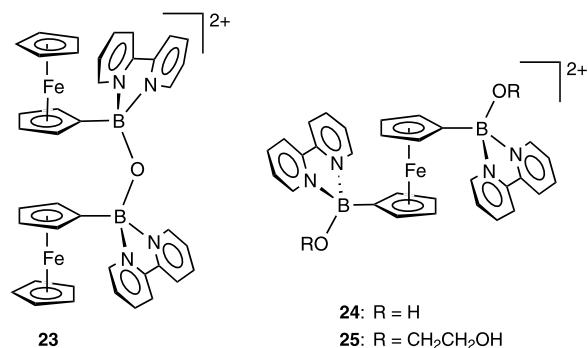


Fig. 7.

ansa-ferrocene **22** (Fig. 6) rather than the corresponding polymer [18]. When excess water is used, the reaction stops at the stage of the open-chain mononuclear hydroxy derivative **24** [19]. Glycol, which is a potential alternative to water as bridging element, has also been tried. However, the reaction rate of an equimolar mixture of **20** (R = Br) and glycol was found to be very low even after addition of excess triethylamine [20]. Only when **20** (R = Br) was dissolved in neat glycol in the presence of triethylamine, a clean and high-yield transformation could be achieved. The reaction yielded the air and water stable monomer **25**, which may be polymerized using well-established polyester and polyurethane chemistry [20].

To generate highly redox-active materials combining the polymeric nature of **15** and **16** with the high solubility and stability of **19–21**, the tetrafunctional

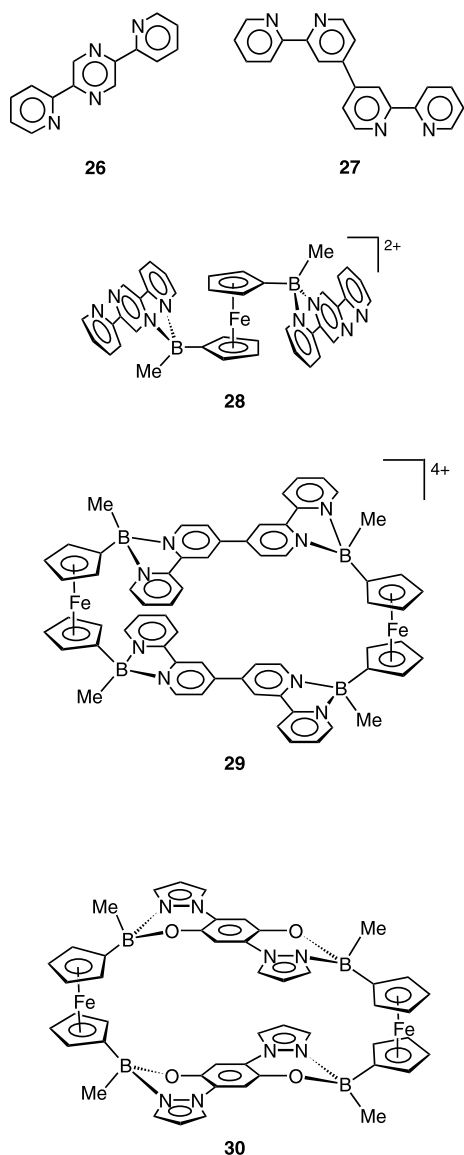


Fig. 8.

Lewis bases 2,5-bis(2-pyridyl)pyrazine (**26**) [21] and 2,2':4',4'':2'',2'''-quaterpyridine (**27**) [22] appeared to be particularly suitable ligands, since they merge 2,2'-bipyridine subunits with pyrazine and 4,4'-bipyridine functionalities, respectively (Fig. 8).

Coordination of one boron atom to **26** turned out to reduce the basicity of the second pyrazine nitrogen atom to such an extent, that a diadduct with a second boron center is not stable anymore. Thus, only mononuclear species like **28** are currently known [23]. In contrast, the 4,4'-bipyridine derivative **27** undergoes formation of stable ferrocenylborane diadducts. However, the reaction of **27** with 1,1'-fc[B(Me)Br]₂ did not lead to polymeric material, but gave the ferrocene-based macrocycle **29** [23]. This is quite a remarkable result, given the fact, that the molecule possesses four chiral boron centers. Ring closure can only occur, if all of them are in the right conformation. Complex **29** was characterized by NMR spectroscopy, ESI mass spectrometry, cyclic voltammetry and GPC measurements [23]. The structure of a related macrocycle **30**, synthesized from 1,1'-fc[B(Me)(NMe₂)₂]₂ and 2,5-di(pyrazol-1-yl)hydroquinone (**9**), was elucidated by high resolution X-ray powder diffraction (Fig. 8) [24].

The factors driving the above-mentioned reactions towards macrocycle rather than polymer formation are still under investigation.

5. Ferrocene-based redox-active macrocycles

Boron–nitrogen adduct formation has already been employed successfully for the specific synthesis of large cyclic frameworks.

Ferrocenophanes with bowl-shaped ansa-bridges like **31** [25] (Fig. 9) are promising building blocks for the generation of beltene-like receptor molecules. Various derivatives of **31** are readily accessible from pyrazoles and diborylated ferrocenes, 1,1'-fc[B(R)Br]₂, in multi-gram quantities; most of them (e.g. R = Me, R[#] = 3,4,5-H) were found to be stable toward air and moisture [26,27].

Cyclic oligomers of **31** possessing a large cavity of well-defined size can be generated by connecting the pyrazolyl rings with rigid spacers. The bridging elements are best attached to the 4-positions of the pyrazoles in order to avoid isomer formation. The reaction of the di(pyrazolyl) ligand **32** with 1,1'-fc[B(Me)Br]₂ results in a mixture of compounds possessing rather similar NMR spectra [19]. From the crude product, the cyclic dimer **33** and the macrocyclic trimer **34** were isolated by GPC separation and characterized by NMR spectroscopy and ESI mass spectrometry (Fig. 9) [19]. Other products possessing even higher molecular masses than **34** were also assembled in the course of the reaction.

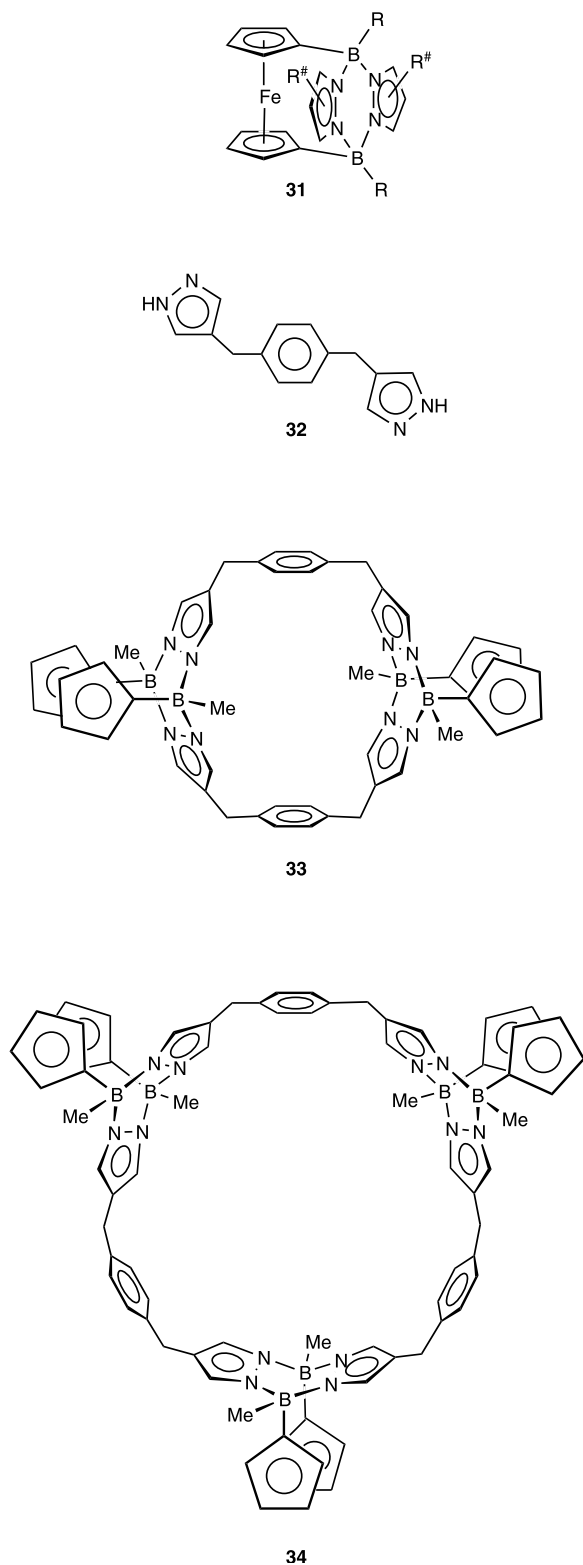


Fig. 9.

All ferrocene units in **33** and **34** have been fixed at the respective macrocyclic framework with both their cyclopentadienyl rings. Any motion of these redox-active groups relative to the main body of the molecule is

prevented. Oxidation of the ferrocene units in **33** and **34**, which is fully reversible, thus generates positive point charges at well-defined positions alongside the cavity. Moreover, derivatives of the bridging ligand **32** bearing substituents, e.g. at the 3,5-positions of the pyrazolyl rings are easily accessible. Following the general synthesis approach for **33** and **34**, it should therefore be possible to design receptor molecules offering a cavity of tailor-made charge, size, hydrophilicity and even chirality. Potential applications in the field of supramolecular chemistry, with the main focus being placed on anion recognition, are currently under investigation.

Recently, an anionic ferrocene-based macrocycle **35** was discovered, which efficiently encapsulates Li^+ cations [7]. The molecule was assembled from 1,1'- $\text{fc}(\text{BMe}_2)_2$ (**7**) and $[(\text{C}_5\text{H}_4)_2\text{Fe}]\text{Li}_2$ via B–C adduct formation (Fig. 10).

Work is currently in progress to investigate the stability of the supramolecular complex in solution, the affinity of **35** towards other metal cations and the effect of cation complexation on the ferrocene redox potential.

6. Metallocenes with switchable ansa-bridges

As has already been pointed out, B–N and B–P adducts are not only self-assembling, but can often be cleaved again without destruction of the Lewis acidic or basic components.

It has been suggested that metallocenes bearing a BR_2 substituent at one cyclopentadienyl ring and NR_2 or PR_2 substituents at the other will establish an ansa-bridge as the result of intramolecular acid–base pairing (viz. the ferrocene derivatives **36** and **37**; Fig. 11) [28]. This structural motif would give rise to a ligand sphere, whose conformational rigidity can be influenced at will: while the ansa-bridged form is preferred at low temperature, the adduct equilibrium will be shifted toward an open-chain conformation at elevated temperature.

The stability of the interannular bridge further depends on the choice of substituents at boron, as exemplified in the case of complex **37**. When $\text{R} = \text{Me}$, the most efficient way to supply the electron-deficient boron centers with additional electron density lies in the formation of interannular P–B σ -donor bonds. How-

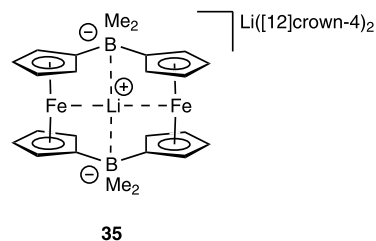


Fig. 10.

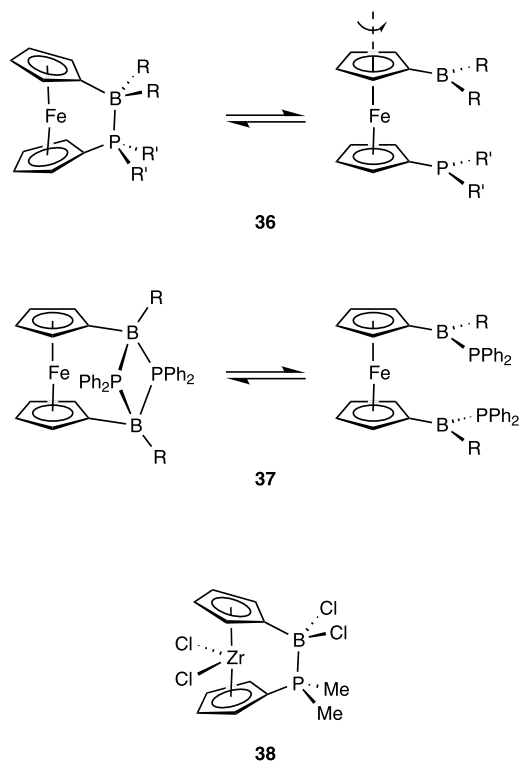


Fig. 11.

ever, **37** ($R = \text{Me}$) exhibits a remarkable dynamic behavior in its NMR spectra, which indicates a continuous and very fast breaking and re-forming of the B–P ansa-bridge [28]. When $R = \text{NR}_2^*$, N–B π -bonding leads to a significant stabilization of the three-coordinate boron centers. Thus, **37** ($R = \text{NR}_2^*$) adopts an open-chain conformation even at low temperature [28,29].

In the meantime, the concept of ‘switchable ansa-bridges’ has also been successfully applied to zirconocene chemistry (Fig. 11). Ansa-zirconocenes like **38** appear to be useful catalysts for the homogeneous polymerization of olefins [30]. Depending on the specifically optimized substitution pattern at boron and phosphorus, thermoplastics with tailor-made crystallinity, melting point or glass transition point are obtained. Some of the special properties of these catalysts, which are especially suited for making copolymers and block copolymers, can clearly be attributed to the influence of the donor–acceptor bridge.

7. Ferrocene-based tris(1-pyrazolyl)borate ligands

tris(1-Pyrazolyl)borates (‘scorpionates’) are today a well-established class of ligands (**39**; Fig. 12, substituents R^1 – R^3 at two pyrazolyl rings omitted for clarity) [31,32]. In most complexes, the monoanionic molecule acts as a tripodal six-electron donor. A huge number of

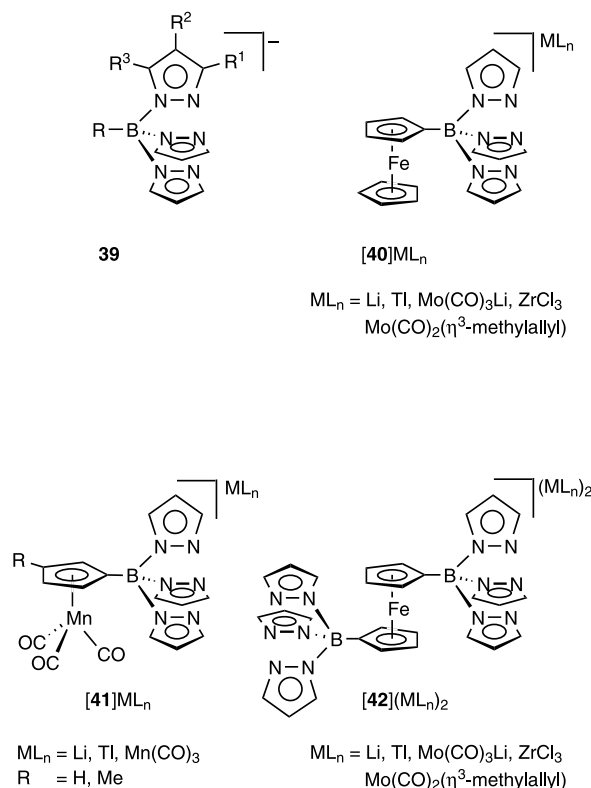


Fig. 12.

derivatives can be generated by varying the group R at boron or the substituents in the 3-, 4- and 5-position of the three pyrazolyl rings.

Scorpionate ligands with very specific steric and electronic features are thus easily accessible and have found an extraordinarily wide range of applications (e.g. analytical chemistry, catalysis and metallo-enzyme modelling, materials science) [32,33]. The synthesis of tris(1-pyrazolyl)borates is straightforward and takes advantage from the facile formation of boron nitrogen-bonds; a common procedure starts from NaBH_4 and three equivalents of an appropriate pyrazole derivative [31,32].

Recently, ferrocene- and cymantrene-based tris(1-pyrazolyl)borates **[40]**Li–**[42]**Li₂ (Fig. 12) have been developed (i) as a contribution to the rapidly growing field of redox-active ligands and (ii) for the synthesis of oligonuclear transition metal complexes [34,35]. Since neither metallocenylboranes, McBH_2 , nor metallocenylborates, $[\text{McBH}_3]^-$, are known to-date (Mc = ferrocenyl, cymantrenyl), alternative starting materials were required. For the synthesis of **[40]**Li and **[41]**Li, metallocenyl dibromoboranes FcBBR_2 (**1**) and CymBBR_2 have been applied successfully [$\text{Cym} = (\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$], while the aminoboryl derivative $1,1'\text{-fc}[\text{B}(\text{NMe}_2)_2]_2$ had to be used to obtain high yields of **[42]**Li₂ and to prevent the formation of ansa-ferrocenes **31** (Fig. 9).

A variety of metal complexes $[40]ML_n$, $[42](ML_n)_2$ [$ML_n = Li, Tl, Mo(CO)_3Li, Mo(CO)_2(\eta^3\text{-methylallyl}), ZrCl_3$] and $[41]ML_n$ [$ML_n = Li, Tl, Mn(CO)_3$] have been synthesised and many of them structurally characterised by X-ray crystallography [35,36]. Among those, the Tl(I) complexes showed interesting deviations from the common tridentate binding mode. $[40]Tl$ and $[41]Tl$ ($R = H$) are polymeric, whereas $[41]Tl$ ($R = Me$) features cyclic tetramers in the solid state. In all three cases, each scorpionate fragment binds to two different thallium atoms, thereby adopting a bridging position. According to cyclic voltammetric measurements, the Fe(II)/Fe(III) redox potential of $[40]ML_n$ and $[42](ML_n)_2$ is influenced by the chemical nature of the metal complex fragment ML_n coordinated to the scorpionate ligand.

In the (hetero)trinuclear complexes $[40]_2M$ [$M(II) = Mn, Fe, Co, Ni, Zn$; Fig. 13], the two ferrocenyl substituents are electronically non-communicating [37]. However, a striking exception was observed when Cu(II) was employed as the central metal ion. Complex $[40]_2Cu$ exhibits two well-resolved one-electron processes, corresponding to the sequential oxidation of the two Fc moieties ($\Delta E^{o'} = 130$ mV), which indicates some electronic interaction between the two iron atoms in this molecule [37].

It has also been possible to attach two different ferrocenyl scorpionate ligands to the same central metal ion (e.g. **43**, Fig. 13) [38]. When this compound is treated with the difunctional tris(1-pyrazolyl)borate $[42]Li_2$, slow ligand exchange processes take place, leading to the formation of larger oligonuclear aggregates like **44** and **45** (Fig. 13), which have been isolated from the equilibrating mixture by gel permeation chromatography.[38] In the absence of excess ligand, chloroform

solutions of **43**, **44** and **45** are apparently stable for extended periods of time.

8. Further perspectives

Numerous promising applications of B–N and B–P adducts in organometallic chemistry can be envisaged for the future.

The highly directional and self-assembling donor–acceptor bonds are an ideal tool for the crystal engineering of organometallic solids which may lead to novel materials possessing interesting electronic, magnetic or optical properties. Recently, Manners et al. developed novel strategies for the transition metal-catalyzed formation of phosphorus–boron bonds [39]. The resulting rings, chains and macromolecules may find use as precursors to boron phosphide semiconductors.

The reversible breaking and re-forming of main group Lewis acid–base pairs being incorporated into the ligand sphere of a transition metal gives access to organometallic compounds with tailor-made conformational rigidity—e.g. metallocenes with switchable ansa-bridges. As outlined above, this structural motif has already been successfully employed in olefin polymerization. It is likely to find more applications in other areas of homogeneous catalysis. In supramolecular chemistry, switchable B–N adduct bonds as integral part of a receptor framework may help to create molecular cavities whose shape and affinity to certain guest molecules can be influenced at will.

The heavier homologs of boron do not only take part in σ -adduct formation, but π adducts are known as well.

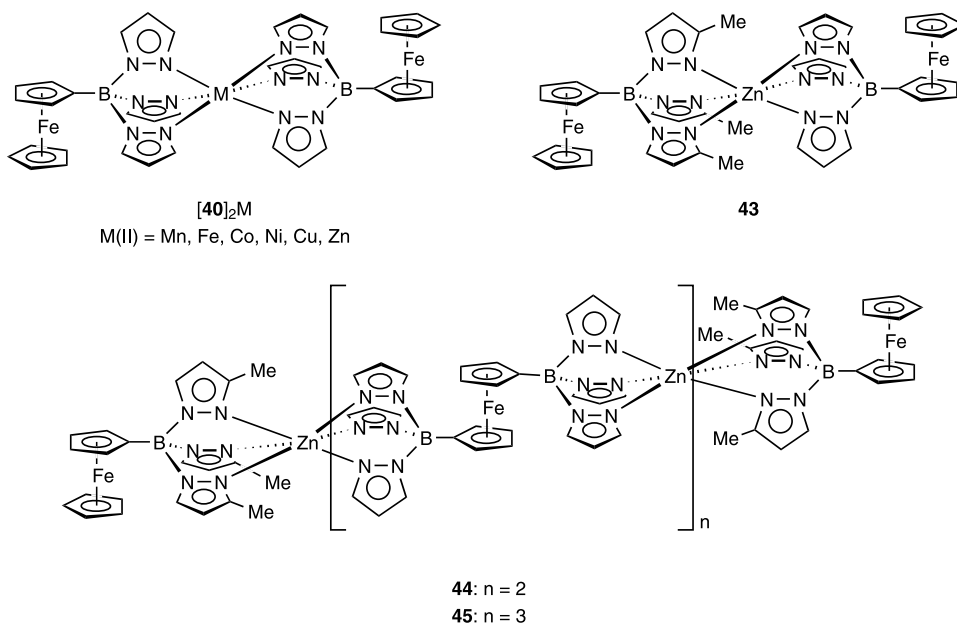
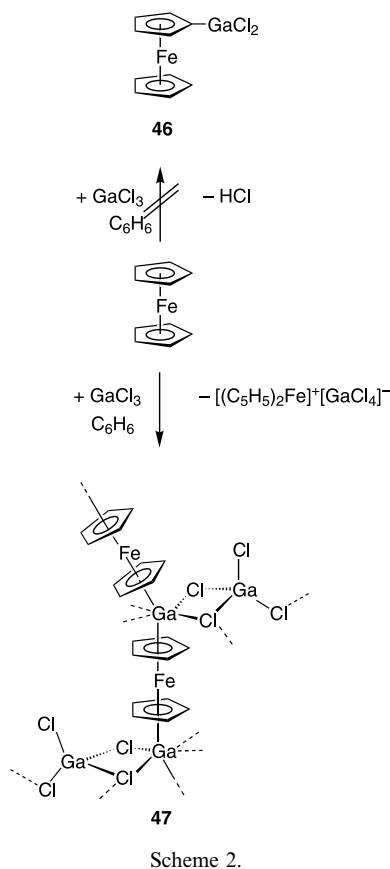


Fig. 13.



Recently, the reaction of ferrocene with gallium trichloride was found to proceed via a completely different pathway as has been observed before in the case of the boron trihalides. No FcGaCl_2 (**46**, Scheme 2) is formed, but a redox process yielding $\text{Ga}[\text{GaCl}_4]$ and ferrocenium tetrachlorogallate takes place instead. From the reaction mixture, crystals of a multidecker sandwich complex **47** featuring an array of alternating $\text{Fe}(\text{II})$ and $\text{Ga}(\text{I})$ ions were obtained [40].

It is evident, that η^5 -coordination of $\text{Ga}(\text{I})$ ions to metallocenes may not only influence the chemical behavior of the metal complex, but offers yet another way for the rational assembly of large organometallic aggregates.

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