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DYNAMIC BEHAVIOUR OF SOME BORYL-SUBSTITUTED FERROCENES*

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Abstract—The ^{1}H, ^{13}C and ^{11}B NMR solution spectra of selected mono- and 1,1′-diborylated ferrocene derivatives, $Fe(C_5H_5)(C_5H_4BRR')$ (**3a**, **b**, **e**, **f**, **g**, **j**) and $Fe(C_5H_4BRR')_2$ (**4a–j**), have been measured [BRR′ = BBr_2 (**a**), $B(NMe_2)_2$ (**b**), $B(NPr^i_2)Br$ (**c**), B(Me)Br (**d**), $B(NMe_2)Cl$ (**e**), $B(NMe_2)Bu^t$ (**f**), $B(Bu^t)Cl$ (**g**), $B(NPr^i_2)Cl$ (**h**), $B[N(Me)CH_2]_2$ (**i**) and 9-bora-bicyclo[3.3.1]nonyl (**j**)]. Depending on the nature of the BRR′ groups, three different types of dynamic processes can be characterized: (i) All compounds containing dialkylamino-substituted boryl groups show hindered rotation about the B—N bond; the activation barrier, $\Delta G^{\#}$, is higher in the mono(dimethylamino) compounds [61.1 ± 1 (**3f**) and 62.7 ± 1 (**4f**) kJ mol^{-1}] than in the bis(dimethylamino)boryl compounds (*ca* 38.5 ± 1 kJ mol^{-1} in **3b** and **4b**). (ii) In the absence of the electron-donating dialkylamino groups, a hindered rotation about the B—C(1) bond between the boryl group and the cyclopentadienyl ring can be deduced from the temperature-dependent ^{1}H and ^{13}C NMR spectra of **4d** [$\Delta G^{\#}$ (213) = 41.2 ± 1 kJ mol^{-1}] and the 9-BBN compounds **3j** [$\Delta G^{\#}$ (213 K) = 40.5 ± 1 kJ mol^{-1}] and **4j** [$\Delta G^{\#}$ (218 K) = 42.5 ± 1 kJ mol^{-1}] (iii) Finally a low-barrier rotation of the cyclopentadienyl rings about the axis defined by the iron atom and the two ring centres becomes evident from $^{1}H/^{1}H$ NOE difference experiments. This indicates that the favoured low-temperature conformation in compounds such as **4b** and **4i** is the centrosymmetric *trans* arrangement of the ring substituents, although the limiting low-temperature spectrum could not be reached.

Boryl-substituted ferrocenes are readily obtained by electrophilic mono- or diborylation of ferrocene,[1] using boron halides such as BBr_3, and subsequent exchange of the substituents at boron (see, e.g. Schemes 1 and 2). An alternative procedure makes use of the reaction of lithioferrocene (**1**) and 1,1′-dilithioferrocene (**2**) with either alkoxyboranes[2] [see eq. (1)] or boron halides [see eq. (2)]. Boryl-substituted ferrocenes are of interest because of their synthetic potential, considering the reactivity of the various boron–element bonds. The recent synthesis and structural characterization of 1,3-dibora-[3]ferrocenophanes[3] is an example. Another point of interest is related to the influence of the boryl group on the structure of the sandwich complex: it has been demonstrated recently by X-ray structure analysis that weak bonding Fe–B interactions are present in 1,1′-bis(dibromoboryl)ferrocene[4] (**4a**), similar to Fe—C^+ bonding in α-ferrocenyl carbocations.[5] Furthermore, $(pp)\pi$-interactions between the boron p_z orbital and the cycopentadienyl π-system may result in hindered rotation about the B—C(1) bond. Thus, it has been shown that triferrocenylborane exists as a mixture of two diastereomers in solution, whereas only a single diastereomer is present in the solid state.[6] The temperature dependence of the ^{1}H NMR data of 1,1′-bis[bromo(methyl)boryl]ferrocene (**4d**) suggested the presence of dynamic processes, although these could not be defined.[1a] We have now prepared a number of monoboryl- (**3**) and 1,1′-diboryl-sub-

* Dedicated to Professor E. W. Abel, on the occasion of his retirement.

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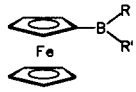
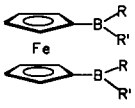
stituted ferrocenes (**4**) in order to gain better insight into the various dynamic processes which can be associated with boryl-substituted ferrocenes.



3a	b	c	d	e	f	g	h	i	j
R= Br	NMe_2	–	–	Cl	NMe_2	Cl	–	–	C_8H_{14}
R'= Br	NMe_2	–	–	NMe_2	^tBu	^tBu	–		

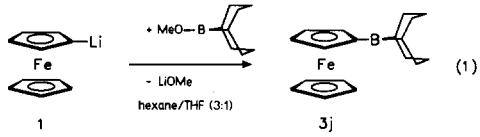


4a	b	c	d	e	f	g	h	i	j
R= Br	NMe_2	Br	Br	Cl	NMe_2	Cl	Cl	$N(Me)CH_2$	C_8H_{14}
R'= Br	NMe_2	N^iPr_2	Me	NMe_2	^tBu	^tBu	N^iPr_2	$N(Me)CH_2$	

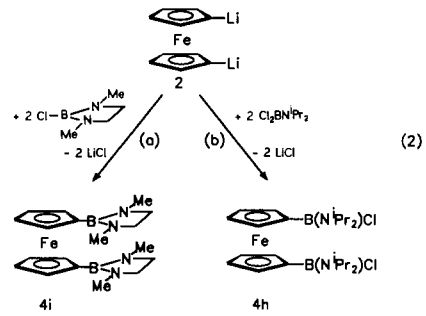
RESULTS AND DISCUSSION

Synthesis

Starting from the lithiated ferrocenes **1** and **2**, we found that boryl-substituted ferrocenes could be prepared in good yield only under certain conditions: either the boron atom must be part of a bicyclic or cyclic system [eq. (1) and eq. (2a)] or it has to bear at least one bulky dialkylamino group [eq. (2b)]. If this was not the case, side reactions took place and mixtures were obtained which could not be separated.

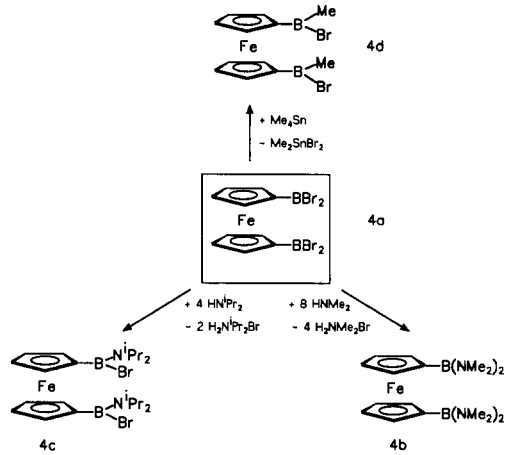


(1)

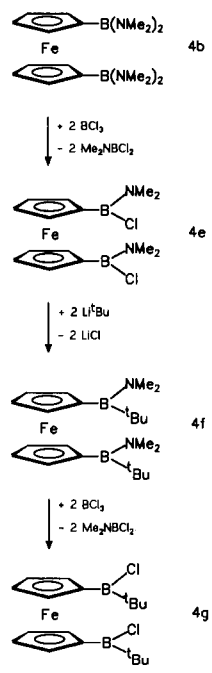


(2)

Therefore, the dibromoboryl derivatives **3a** and **4a** are more suitable starting materials for many boryl-substituted ferrocenes. This is shown for compounds **4** in Scheme 1 and it applies similarly to the analogous compounds **3**. The complexes **4b** and **4d** can be obtained as described previously,[1b] and aminolysis of **4a** with an excess of di(isopropyl)amine leads selectively to **4c**. Scheme 2 shows the route from **4b** to **4g**, and an analogous pathway leads from **3b** to **3g**. All products are sensitive towards traces of moisture, and those without B—N bonds are sensitive to oxygen.



Scheme 1.



Scheme 2.

NMR spectroscopic studies

Table 1 lists ^1H, ^{11}B and ^{13}C NMR data of the boryl-substituted ferrocenes **3** and **4**. All data are in support of the proposed structures. The assignment of ^1H and ^{13}C resonances is based on 2D $^{13}C/^1H$ heteronuclear shift correlations, on coupling

Table 1. ^{1}H, ^{11}B and ^{13}C NMR data[a] of the boryl-substituted ferrocenes **3** and **4**

	$\delta^{11}B$	$\delta^{13}C$ ($\delta^{1}H$)						
		C(1)[b]	C(2,5)	C(3,4)	C_5H_5	R		
3a	46.0	73.0	77.1	78.2	71.5			
			(4.52)	(4.92)	(4.23)			
4a	50.0	73.9	78.9	80.3				
			(4.64)	(4.86)				
3b[c]	35.4	71.3	76.2	70.3	68.8	41.4		
			(4.25)	(4.31)	(4.03)	(2.80)		
4b[c,d]	35.1	71.3	76.3	70.4		41.3		
			(4.22)	(4.34)		(2.88)		
4c[e]	35.2	73.8	76.7	73.4		52.1	47.2	23.9 22.9
			(4.31)	(4.38)		(4.28)	(3.20)	(0.90) (1.43)
4d	64.3	74.4	77.7	78.2		13.1[br]		
			(4.27)	(4.25)		(1.02)		
3e	36.2	n.o.	75.6	72.0	69.3	40.6	40.2	
			(4.23)	(4.45)	(4.06)	(2.73)	(2.57)	
4e[f]	36.7	69.7	76.2[g]	72.8		40.8	40.5	
			(4.32)	(4.50)		(2.73)	(2.58)	
3f[h]	46.4	78.1	74.8	69.0	69.1	43.9	41.6	30.2 22.7[br]
			(4.04)	(4.10)	(4.03)	(2.82)	(2.72)	(1.23)
4f	46.3	78.4	75.9[i]	69.7		44.3	42.0	30.5 22.2[br]
			(4.06)	(4.24)		(3.03)	(2.73)	(1.21)
3g	66.3	n.o.	77.3	75.9	69.9	29.6	26.8[br]	
			(4.57)	(4.35)	(3.94)	(1.24)		
4g	69.3	69.9	78.1	76.5		29.2	27.3[br]	
			(4.56)	(4.41)		(1.18)		
4h[j]	35.7	71.1	76.4[k]	73.5		51.3	46.4	23.9 21.7
			(4.53)	(4.41)		(4.35)	(3.18)	(0.93) (1.48)
4i[l]	36.2	66.5	74.0	71.0		52.4	34.6	
			(4.31)	(4.34)		(3.07)	(2.81)	
3j	76.3	71.4	75.1	74.8	68.1	34.8	29.0[br]	24.3
			(4.33)	(4.42)	(4.01)	(2.10–1.40)		
4j	77.5	71.2	75.6	74.5		34.7	29.5[br]	24.2
			(4.44)	(4.48)		(2.10–1.40)		

[a] All data for C_6D_6 solutions (≈5–15% at 25°C) if not stated otherwise; n.o. = not observed; [br] = broad.

[b] The $^{13}C(1)$ NMR signals were observed at low temperature ("quadrupolar decoupling" of ^{11}B) in toluene-d_8 at −60°C.

[c] In $CDCl_3$.

[d] $\delta^{14}N = -337$.

[e] $\delta^{14}N = -232$.

[f] $\delta^{14}N = -296$.

[g] $^{13}C/^{13}C$ INADEQUATE: $^{1}J[^{13}C(1),^{13}C(2)] = 40.0$ Hz; $^{1}J[^{13}C(2),^{13}C(3)] = 45.3$ Hz.

[h] $\delta^{14}N = -304$.

[i] $^{13}C/^{13}C$ INADEQUATE: $^{1}J[^{13}C(1),^{13}C(2)] = 38.7$ Hz; $^{1}J[^{13}C(2),^{13}C(3)] = 44.6$ Hz.

[j] $\delta^{14}N = -260$.

[k] $^{13}C/^{13}C$ INADEQUATE: $^{1}J[^{13}C(1),^{13}C(2)] = 40.8$ Hz; $^{1}J^{13}C(2),^{13}C(3)] = 45.2$ Hz.

[l] $\delta^{14}N = -318$.

constants $^{1}J(^{13}C^{13}C)$ measured via the INADEQUATE pulse sequence[7] (see Fig. 1) and also on NOE difference spectra (*vide infra*). The $^{13}C(1)$ signals are always very broad at room temperature owing to partially relaxed scalar ^{13}C–^{11}B coupling.[8] They become sharper and are more readily observed at lower temperature because of "quadrupolar decoupling". The $^{13}C(2,5)$ nuclei are coupled across one bond to $^{13}C(1)$ and to $^{13}C(3)$ or $^{13}C(4)$, respectively, in contrast to the $^{13}C(3,4)$ nuclei. This enables us to assign the cyclopentadienyl ^{13}C NMR signals unambiguously.

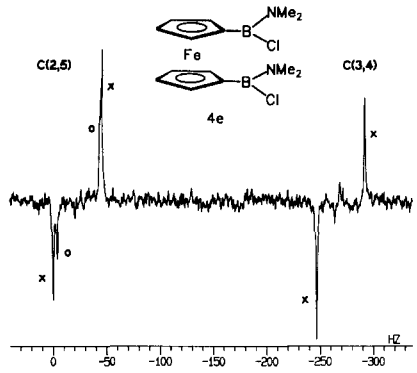


Fig. 1. 67.9 MHz INADEQUATE ^{13}C NMR spectrum of 1,1′-bis[chloro(dimethylamino)boryl]ferrocene (**4e**) in C_6D_6 at 25°C. o: $^1J[^{13}C(1), ^{13}C(2)] = 40.0$ Hz, x: $^1J[^{13}C(2), ^{13}C(3)] = 45.3$ Hz.

At least three different types of dynamic processes are important for describing the molecular structures of compounds **3** and **4** in solution: (i) hindered rotation about the B—N bond in aminoboranes is a well documented phenomenon,[9] and it was found by ^1H and ^{13}C NMR at variable temperature for all boron–nitrogen compounds studied here (**3b**, **4b**, **4c**, **3e**, **4e**, **3f**, **4f**, **4h**); (ii) as a result of BC(pp)π-interactions between the three-coordinate boron atom and the cyclopentadienyl ring, hindered rotation about the B—C(1) bond can be expected; (iii) although the low energy barrier to the rotation of the cyclopentadienyl rings about the axis passing through the iron atom and the ring centres prevents the assignment of one or more static structures of **3** or **4** in solution, the 1,1′-diborylated ferrocenes **4** should on average adopt a preferred conformation in which the boryl groups avoid mutual contacts for steric reasons.

If there is only one dialkylamino group linked to boron (**4c**, **3e**, **4e**, **3f**, **4f** and **4h**) the barrier to rotation about the B—N bond is rather high [e.g. $\Delta G^{\#} = 61.1 \pm 1$ (**3f**), 62.7 ± 1 (**4f**) kJ mol^{-1}]. For the other mono(dialkylamino)boranes **4c**, **3e**, **4e** and **4h** extensive decomposition occurs before coalescence of the relevant NMR signals can be observed (>80°C). In the bis(dimethylamino) derivatives **3b** and **4b** the activation energy of this process is much lower ($\Delta G^{\#} \approx 38.5 \pm 1$ kJ mol^{-1}), slightly less than in $PhB(NMe_2)_2$ ($\Delta G^{\#} = 42.6$ kJ mol^{-1}).[10] The dynamic behaviour of dialkylaminoboryl-substituted ferrocenes corresponds closely to that of other aminoboranes.[11]

In the absence of suitable substituents such as amino groups, the electron deficiency of the boron atom can be partially compensated by interactions with the π-system of the cyclopentadienyl ring. Any significant BC(pp)π-bonding should be evident from the ^{13}C NMR spectra of either the cyclopentadienyl carbon atoms or the carbon atoms of organo groups attached to the boron atoms. The latter is shown in Fig. 2 for the 9-BBN derivative **3j**; the same pattern is also observed for **4j**. The pairwise non-equivalence of the $^{13}C(CH_2)$ resonances at −90°C indicates the preference of the structure depicted in Fig. 2. This structure guarantees a maximum overlap of boron and carbon π-orbitals. In the case of the compounds **4d**, **3g** and **4g** one would expect two different isomers if the rotation about the B—C(1) bond becomes sufficiently slow. This can be shown for **4d** by ^1H and ^{13}C NMR at −90°C, as demonstrated by the 2D $^{13}C/^1H$ heteronuclear shift correlation in Fig. 3. In contrast, ^1H and ^{13}C NMR spectra of **3g** and **4g** are much less resolved, although the slowing down of the rotation about the B—C(1) bond is indicated by the broadening of the $^{13}C(2,5)$ and $^{13}C(3,4)$ NMR signals at low temperature. It is important to note that there is no indication at all (NMR spectra were measured at −100°C) for slow rotation about the B—C(1) bond in the compounds **3** and **4** if one or two dialkylamino groups are linked to the boron atom.

In the case of monosubstituted ferrocenes, the spatial distance between hydrogen atoms belonging to a substituent in 1-position and the hydrogen atoms in 2,5-position as well as the hydrogen atoms

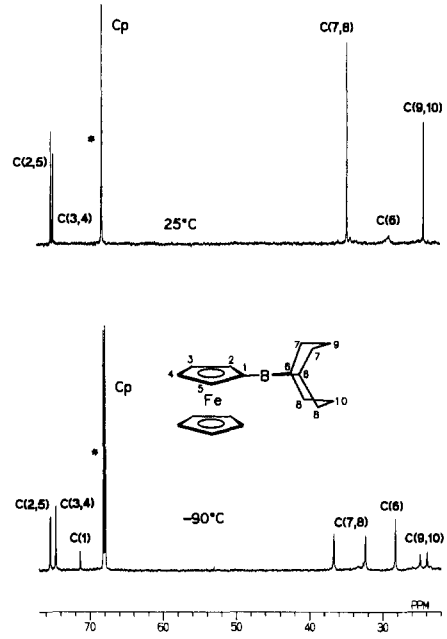


Fig. 2. ^{13}C NMR spectra of 9-(9-borabicyclo[3.3.1]-nonyl)ferrocene (**3j**) in C_6D_6 at 25°C and in toluene-d_8 at −90°C; $\Delta G^{\#}$ (213 K) = 40.5± kJ mol^{-1}. The ^{13}C NMR signal of ferrocene as an impurity is marked by an asterisk.

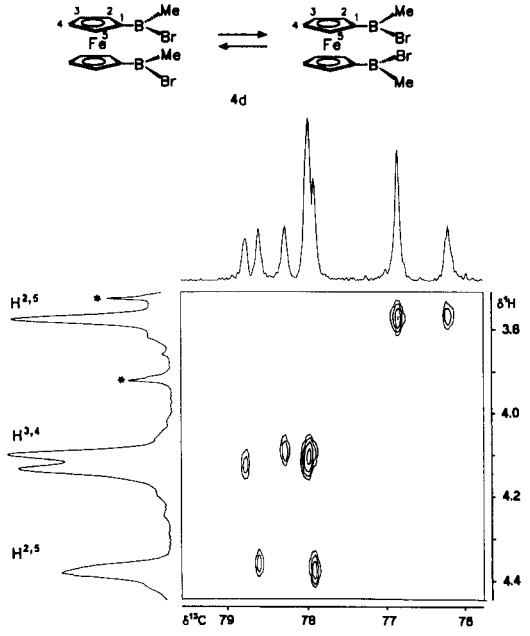
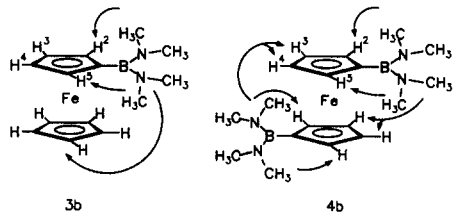


Fig. 3. Two-dimensional (67.9 MHz) $^{13}C/^{1}H$ heteronuclear shift correlation of 1,1′-bis[bromo(methyl)boryl]ferrocene (**4d**) in CD_2Cl_2 at −90°C. Impurities are marked with asterisks. $\Delta G^{\#}$(21K) 41.2 ± 1 kJ mol^{-1}.

of the Cp ring should be sufficiently short in order to carry out successful $^{1}H/^{1}H$ NOE difference experiments. As indicated by the arrows in Scheme 3, saturation of the $^{1}H(NMe_2)$ transitions in **3b** will affect the intensities of the ^{1}H(Cp) and of the $^{1}H(2,5)$ NMR signals, but not that of the $^{1}H(3,4)$ signals. In the 1,1′-diborylated ferrocenes we find, in general, a larger NOE for the $^{1}H(2,5)$ and a smaller one for the $^{1}H(3,4)$ resonance signals (see Fig. 4 with compound **4i** as a typical example). The latter NOE arises for $^{1}H(3,4)$ from saturation of ^{1}H transitions of the substituent in 1′-position and, in the same way, for $^{1}H(3',4')$ of the substituent in 1-position. This proves that the preferred conformation of the ferrocene derivatives **4** has the substituents in *trans* positions in order to minimize steric interactions.



Scheme 3. NOE difference experiments for **3b** and **4b** with saturation of ^{1}H (NMe_2) transitions. The arrows indicate the response of the other ^{1}H NMR signals.

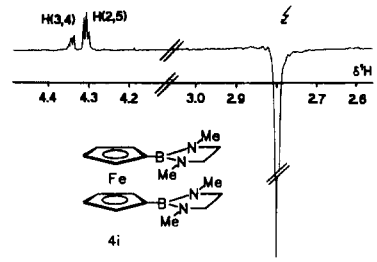


Fig. 4. 270 MHz $^{1}H/^{1}H$ NOE difference spectrum of **4i**, saturation of the ^{1}H (NMe) transition is indicated by an arrow. Response is detected for both H(2,5) and H(3,4) as shown in Scheme 3 for **3b** and **4b**.

EXPERIMENTAL

All compounds were prepared and handled under argon atmosphere, and carefully dried glassware and solvents were used. Boron halides (BBr_3 and BCl_3), di(alkyl)amines, $SnMe_4$ and $LiBu^t$ were commercial products. Lithioferrocene (**1**),[12] 1,1′-dilithioferrocene (**2**),[13] dibromoborylferrocene (**3a**),[1a] 1,1′-bis(dibromoboryl)ferrocene (**4a**),[1b,c] bis(dimethylamino)borylferrocene (**3b**),[1a] 1,1′-bis[bis(dimethylamino)boryl]ferrocene (**4b**),[1b] 1,1′-bis[bromo(methyl)boryl]ferrocene (**4d**),[1b] 9-methoxy-9-borabicyclo-[3.3.1]nonane,[14] dichloro(diisopropylamino)borane[15] and 1,3-dimethyl-2-chloro-1,3,2-diazaborolane[16] were prepared according to literature procedures.

NMR spectra were measured using JEOL FX 90Q, Bruker AC 300 (^{1}H, ^{11}B, ^{13}C, ^{14}N NMR) and JEOL EX 270 (^{1}H, ^{13}C NMR) spectrometers. Chemical shifts are given with respect to Me_4Si [$\delta^{1}H(C_6D_5H) = 7.15$; $\delta^{13}C(C_6D_6) = 128.0$] and external Et_2O–BF_3 [$\delta^{11}B = O$; $\Xi(^{11}B) = 32.083972$ MHz]; neat CH_3NO_2 [$\delta^{14}N = 0$; $\Xi(^{14}N) = 7.226455$ MHz].

1,1′-*Bis*[*bromo*(*diisopropylamino*)*boryl*]*ferrocene* (**4c**)

Diisopropylamine (2.42 g, 24.0 mmol) was added dropwise at −40°C to a solution of **4a** (1.50 g, 2.85 mmol) in toluene (30 cm^3). After warming to room temperature and stirring for 4 h, the hydrobromide was filtered off. Compound **4c** was recrystallized from hexane and isolated as a red solid (1.05 g; 65%; m.pt 80–82°C). EI-MS (70 eV): m/z = 566 (M^+, 8%); 44 ($H_2CMe_2^+$, 100%).

1,1′-*Bis*[*chloro*(*dimethylamino*)*boryl*]*ferrocene* (**4e**)

A solution of 1,1′-bis[bis(dimethylamino)boryl]-ferrocene (**4b**) (1.50 g, 3.93 mmol) in hexane (20 cm^3) was cooled to −20°C, and BCl_3/hexane

(8 cm^3, 1 M) was added dropwise. The solution was stirred for 2 h at room temperature; then the solvent and Cl_2BNMe_2 were removed *in vacuo* leaving **4e** as a red crystalline solid (1.00 g, 76%; m.pt 77–80°C). EI-MS (70 eV): $m/z = 364$ (M^+, 100%); 320 (M^+-NMe_2, 7%); 44 (NMe_2^+, 44%).

Chloro(dimethylamino)borylferrocene **(3e)**

Compound **3e** (red oil) was prepared as described above for **4e**, starting from bis(dimethylamino)borylferrocene (**3b**) (5.11 g, 18.00 mmol) and BCl_3 (2.16 g, 18.40 mmol); yield: 4.60 g (93%).

1,1′-*Bis*[*dimethylamino*(*tert-butyl*)*boryl*]*ferrocene* **(4f)**

A hexane solution of $LiBu^t$ (2 cm^3, 1 M) in hexane (10 cm^3) was added dropwise to a solution of 1,1′-bis[chloro(dimethylamino)boryl] ferrocene (**4e**) (0.36 g, 1.00 mmol) at room temperature. The mixture was stirred for 2 h at room temperature, then LiCl was filtered off and the solvent was removed to give 0.24 g (59%) of **4f** as a red oil.

Dimethylamino(*tert-butyl*)*borylferrocene* **(3f)**

Compound **3f** (red oil) was prepared as described above for **4f**, starting from chloro(dimethylamino)borylferrocene (**3e**) (0.27 g, 1.0 mmol) and a hexane solution of $LiBu^t$ (1 cm^3, 1 M); yield: 0.18 g (61%).

1,1′-*Bis*[*chloro*(*tert-butyl*)*boryl*]*ferrocene* **(4g)**

A solution of **4f** (1.71 g, 4.20 mmol) in hexane (30 cm^3) was cooled to −78°C and BCl_3 (1.00 g, 8.50 mmol) in hexane (5 cm^3) was added dropwise. The solution was stirred for 4 h at room temperature, then all volatile material was removed *in vacuo* leaving 1.18 g (72%) of **4g** as a dark red oil.

Chloro(*tert-butyl*)*borylferrocene* **(3g)**

Compound **3g** (dark-red oil) was prepared as described above for **4g**, starting from dimethylamino(tert-butylboryl)ferrocene (**3f**) (1.50 g, 5.00 mmol) and BCl_3 (0.60 g, 5.10 mmol); yield: 1.07 g (74%).

1,1′-*Bis*[*chloro*(*diisopropylamino*)*boryl*]*ferrocene* **(4h)**

Dichloro(diisopropylamino)borane (1.20 g, 6.60 mmol) was added slowly to a suspension of 1,1′-dilithioferrocene (**2**) (0.60 g, 3.03 mmol) in hexane (20 cm^3) at −78°C. After stirring for 2 h at room temperature, the precipitate of LiCl was filtered off. Removal of the solvent gave 0.94 g (65%) of **4h** as a red crystalline solid (m.pt 108°C).

1,1′-*Bis*-2-(1,3-*dimethyl*-1,3,2-*diazaborolanyl*)*ferrocene* **(4i)**

1,3 - Dimethyl - 2 - chloro - 1,3,2 - diazaborolane (0.80 g, 6.0 mmol) was added slowly to a suspension of 1,1′-dilithioferrocene (**2**) (0.60 g, 3.03 mmol) in hexane (40 cm^3) at −78°C. After stirring for 4 h at room temperature, the precipitate (LiCl) was filtered off. Removal of the solvent gave 0.5 g (46%) of **4i** as a red crystalline solid (m.pt 85–87°C). EI-MS (70 eV): $m/z = 378$ (M^+, 100%); 321 (M^+-$NMeCH_2CH_2$, 8%).

1,1′-*Bis*[9-(9-*borabicyclo*[3.3.1]*nonyl*)]*ferrocene* **(4j)**

9-Methoxy-9-borabicyclo[3.3.1]nonane (1.08 g, 7.1 mmol) was added in one portion to a suspension of 1,1′-dilithioferrocene (**2**) (0.70 g, 3.55 mmol) in hexane/THF (3:1) (20 cm^3) at −78°C. The solution was stirred for 10 min at room temperature before the solvent was removed *in vacuo*. The residue was then dissolved in hexane (20 cm^3) and LiOMe was filtered off. Evaporation of the solvent gave 1.2 g (79%) of **4j** as a yellow oil.

9-(9-*Borabicyclo*[3.3.1]*nonyl*)*ferrocene* **(3j)**

Compound **3j** (yellow oil) was prepared as described above for **4j**, from lithioferrocene (**1**) (0.40 g, 2.10 mmol) and 9-methoxy-9-borabicyclo[3.3.1]nonane (0.31 g, 2.10 mmol). A yellow oil (0.49 g, 77%) was obtained.

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