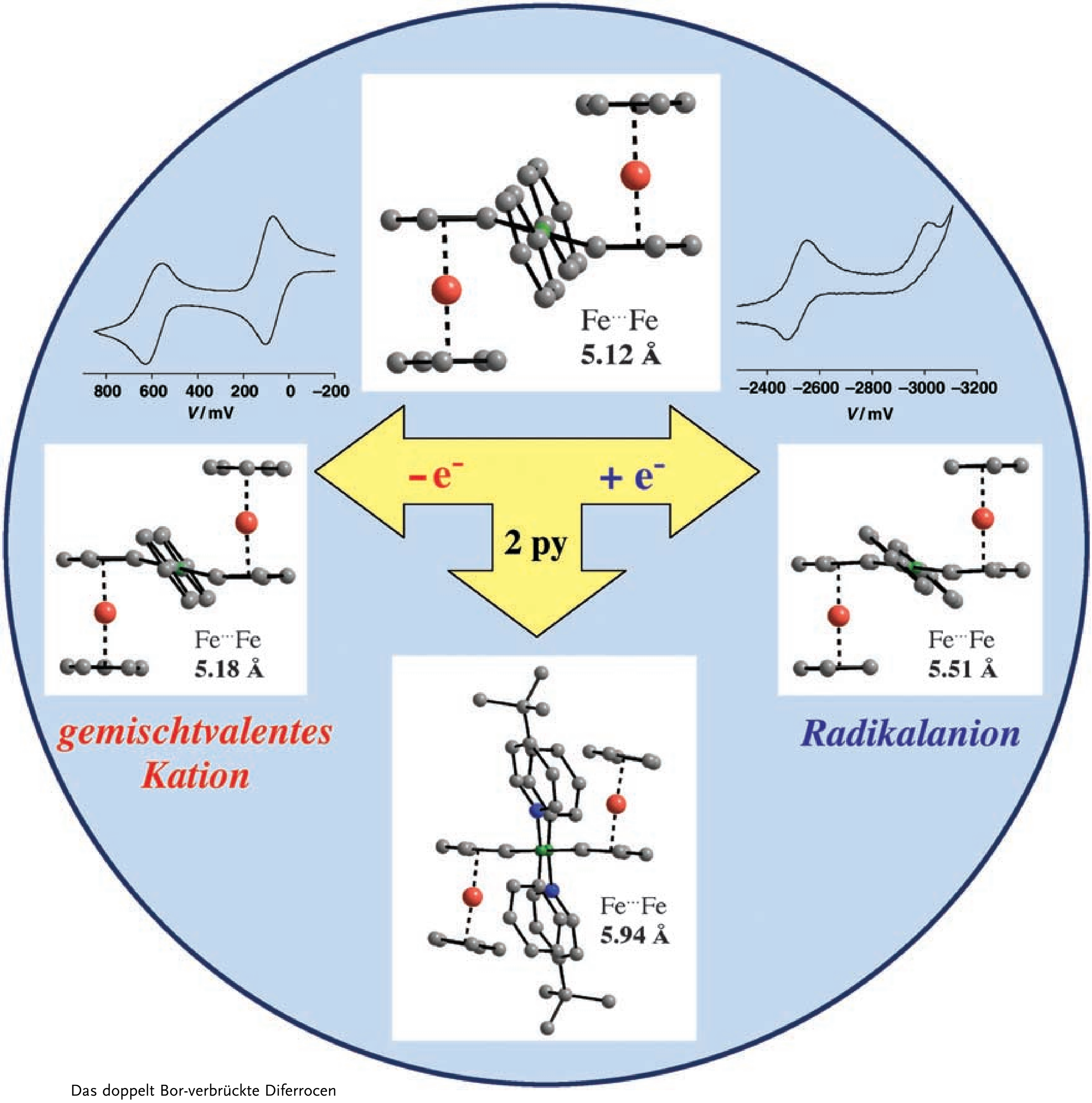
Zuschriften

DOI: 10.1002/ange.200502148



Das doppelt Bor-verbrückte Diferrocen $[CpFe\{C_5H_3(BPh)_2C_5H_3\}FeCp]$ ist das erste 1,2-diborylierte Ferrocen. Konformationsänderungen lassen sich in dieser starren, redoxaktiven, difunktionellen Lewis-sauren Verbindung kontrolliert durch Redoxchemie oder das Binden von Nucleophilen auslösen. Mehr über das System finden Sie in der Zuschrift von F. Jäkle et al. auf den folgenden Seiten.

Ferrocenes

DOI: 10.1002/ange.200502148

Reversible Expansion and Contraction of a 1,2-Diborylated Ferrocene Dimer Promoted by Redox Chemistry and Nucleophile Binding**

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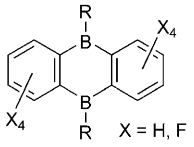
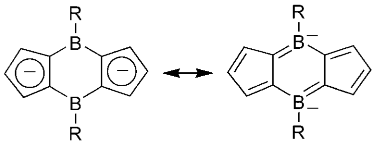
*Frieder Jäkle**

Diboraanthracenes **A** have been extensively used as precursors to various di- and multimetallic (and multidecker) sandwich complexes,[1–3] and more recently a perfluorinated derivative ($X = H$, $R = C_6F_5$) was employed as an activator in the polymerization of olefins.[4,5] Boracycles in general also serve as fluorescent materials, as probes for anions, and as building blocks for the assembly of new materials.[6] Finally, the "doping" of boron into larger organic π systems such as fullerenes and conjugated organic polymers continues to attract much interest owing to potentially interesting electronic effects.[7,8]



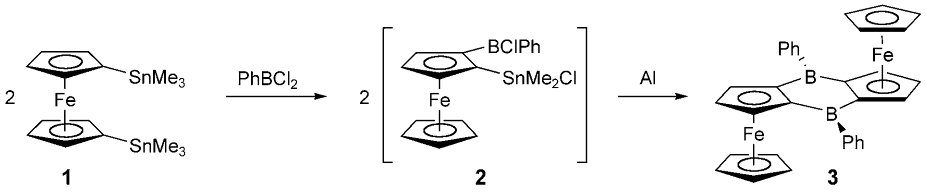
A



B

We previously showed that heteronuclear bidendate Lewis acids comprised of Lewis acidic boron and tin groups adjacent to one another are readily available through a rearrangement reaction from 1,1′-bis(trimethylstannyl)ferrocene (**1**) and boron halides.[9] For instance, the 1-stannyl-2-borylferrocene **2** is formed as the major product upon reaction of **1** with an excess of $PhBCl_2$ (Scheme 1). However, examples of ferrocenes that contain metals or semi-metals in neighboring positions at the same cyclopentadienyl (Cp) ring are generally still rare.[10] Among diborylated ferrocenes, for example, only 1,1′-diborylated species have been isolated and 1,3-diborylated isomers have been confirmed as minor byproducts by NMR spectroscopy.[11] Herein, we report the synthesis and properties of the first example of a 1,2-diborylated bisferrocene, in which two CpFe fragments are bridged by the novel dibora-*s*-indacenediyl ligand **B**.

When the reaction mixture of **1** and $PhBCl_2$ was kept for an extended period of time in an aluminum-capped vial, dark red crystals of the novel 1,2-diborylated ferrocene dimer **3** formed reproducibly in approximately 36% yield. The presence of aluminum was found to be critical, as confirmed by the lack of formation of product in the absence of a source of Al. While addition of Al powder to the reaction mixture accelerated the reaction, the selectivity for **3** was diminished. The ^1H NMR spectrum of **3** showed a doublet ($\delta = 4.89$ ppm, 4H) and a triplet ($\delta = 5.05$ ppm, 2H) with a coupling constant of $^3J = 2.5$ Hz, which is characteristic of a 1,2-disubstituted ferrocene.[10] A broad signal in the $^{11}B\{^1H\}$ NMR spectrum at $\delta = 57.7$ ppm is indicative of the formation of a triarylborane. The mass spectrum of **3** clearly shows a peak for the molecular ion at $m/z = 544$, which is consistent with the proposed dimeric structure.



Scheme 1. Formation of diboracycle **3**.

Single-crystal X-ray diffraction analysis of **3** confirmed that two ferrocene units are doubly bridged with two tricoordinate boron atoms (Figure 1).[12] The CpFe moieties adopt a *trans* configuration relative to the central B_2C_4 ring.[13] A pronounced tilting of the boron atoms towards the iron center (Cp_{cent}-C6-B1 = 167.9°; Cp_{cent}-C10-B1* = 164.4°) is evident, as is also observed in other ferrocenyl boranes; recent studies based on a combination of X-ray crystallography, cyclic voltammetry, Mössbauer spectroscopy, and theoretical calculations show that this feature results from a delocalized through-space interaction between iron and boron.[14] This interaction leads to a strong deviation from planarity for the diboraindacene ligand in **3** with an interplanar angle between the substituted Cp rings and the central B_2C_4 cycle of around 15.9° (see Figure 3a). In comparison, the related diboraanthracenes, **A**, are planar in the absence of steric strain.[2,4,15] The B–C bond lengths in **3** are similar to

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[**] Acknowledgement is made to the National Science Foundation (CAREER award CHE-0346828 to F.J.), to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Rutgers University Research Council for support of this research. We are grateful to Prof. Nicholas J. Turro and Alberto Moscatelli for recording of the EPR spectrum and to Dr. Kakalis for acquisition of 2D NMR spectra. We would also like to thank Prof. Jack Norton for insightful discussions.

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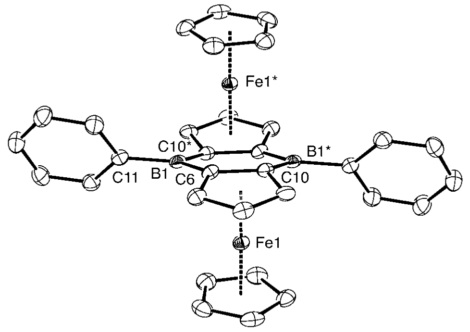


Figure 1. Molecular structure of **3** with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: B1–C6 1.546(2), B1–C10* 1.546(2), B1–C11 1.564(2), B1···B1* 3.103, Fe1···B1 3.032, Fe1···B1* 2.957, Fe1···Fe1* 5.123, C6-B1-C10* 115.8(1), C6-B1-C11 123.7(1), C10*-B1-C11 120.4(1), C10-C6-B1 121.6(1), C6-C10-B1* 122.5(1).

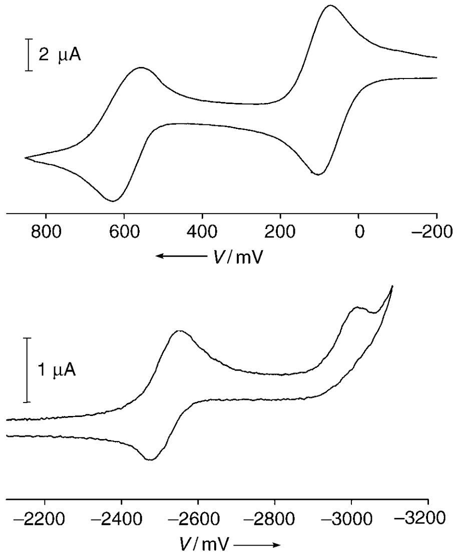


Figure 2. Cyclic voltammogram of **3** (vs. FcH/FcH$^+$). a) Oxidation waves of **3** (10^{-3} M) at 100 mV s^{-1} with $Bu_4N^+B(C_6F_5)_4^-$ (0.1 M) in CH_2Cl_2 as the supporting electrolyte; b) reduction waves of **3** (10^{-3} M) at 100 mV s^{-1} with $Bu_4N^+PF_6^-$ (0.1 M) in DME as the supporting electrolyte.

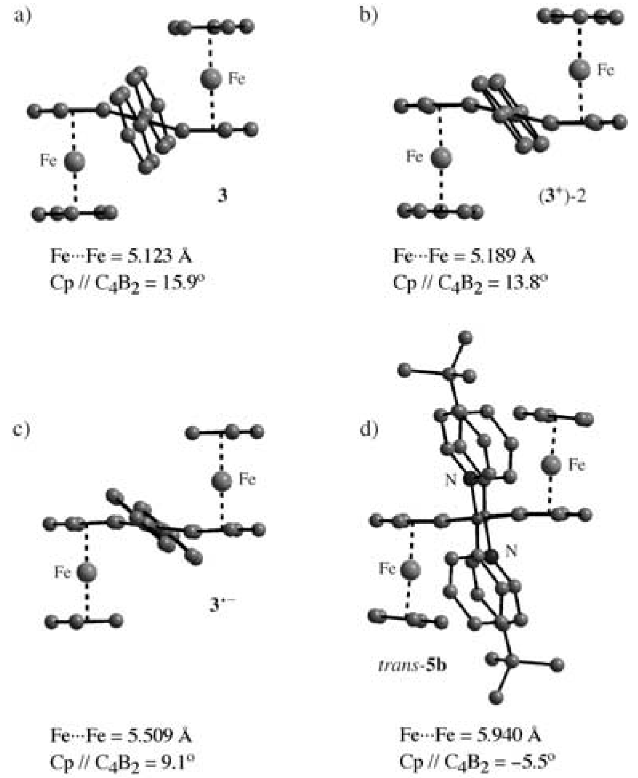
those in 9,10-diboraanthracenes **A** with organic substituents at the boron center (1.554–1.580 Å).[2,4,15] However, the B–C bonds to the Cp rings (1.546(2) Å) are significantly shorter than the exocyclic B–C bonds to the phenyl groups (1.564(2) Å), which suggests a significant contribution of the chinoid resonance structure of **B**.[9,16]

An intriguing feature of **3** is the presence of both redox-active ferrocene and triorganoborane moieties, which may allow one to electrochemically trigger conformational changes based on changes in the nature of the Fe···B interaction as suggested by DFT calculations by Wagner and co-workers[14] Such processes have attracted much interest recently with regard to the design of molecular machines that can be addressed through external stimuli.[17]

Cyclic voltammograms of **3** were recorded in $CH_2Cl_2/Bu_4N^+PF_6^-$ as well as $CH_2Cl_2/Bu_4N^+B(C_6F_5)_4^-$ (Figure 2a). In both cases two separate one-electron oxidation events were observed. However, improved chemical reversibility was achieved with $Bu_4N^+B(C_6F_5)_4^-$ as reported by Geiger and co-workers for related systems.[18] The first oxidation of **3** occurs at $E_{1/2} = +60$ mV (versus the ferrocene/ferrocenium (FcH/FcH$^+$) couple; $E_{1/2} = +88$ mV with PF_6^-), which is slightly higher than that reported for $FcBMe_2$ ($E = +9$ mV).[14] The second oxidation takes place at a much higher potential of $E_{1/2} = +570$ mV ($E_{1/2} = +432$ mV with PF_6^-). The pronounced difference between the results for the two electrolytes is due to differences in the degree of ion-pairing interactions.[18] In either case the separation between the two oxidation waves ($\Delta E = 510$ mV in $CH_2Cl_2/Bu_4N^+B(C_6F_5)_4^-$; $\Delta E = 344$ mV in $CH_2Cl_2/Bu_4N^+PF_6^-$) is considerably larger than those for the related doubly silyl-bridged ferrocenes [CpFe{Cp(SiR$_2$)$_2$Cp}FeCp] ($\Delta E = 195$–210 mV for R = Me, Et, and *n*Bu in propionitrile/$Bu_4N^+PF_6^-$),[19] which indicates unusually strong electronic coupling through the dibora-*s*-indacene bridge. However, the interaction is smaller than that for the all-carbon analogue, the *s*-indacene-bridged dimer [Cp*Fe{Cp(CH)$_2$Cp}FeCp*] (Cp* = pentamethylcyclopentadienyl), which shows a splitting of $\Delta E = 820$ mV and forms a fully valence-delocalized cation upon monooxidation.[20]

The mono-oxidized mixed-valence species $(3^+)I_3{\cdot}I_2$ was prepared in 85% yield upon treatment of **3** with an excess of I_2 in CH_2Cl_2/toluene and crystallization at −37 °C. The X-ray crystal structure shows two independent molecules, (**3**$^+$)-1 and (**3**$^+$)-2, along with I_3^- counterions and co-crystallized molecules of I_2.[12,21] There are two independent half cations on inversion centers, which render the Fe atoms in each of the dimers (**3**$^+$)-1 and (**3**$^+$)-2 equivalent. The latter has been shown to be indicative of valence delocalization owing to very rapid electron transfer.[22] In line with this interpretation, the Cp_{cent}–Cp_{cent} distances of 3.355 Å and 3.357 Å for (**3**$^+$)-1 and (**3**$^+$)-2, respectively, are intermediate between those of **3** (3.308 Å) and those of typical oxidized ferrocenes (ca. 3.4 Å). In contrast, the mixed-valent zwitterion ferricenyl(III)-trisferrocenyl(II)borate (Fc_4B), which contains a coordinatively saturated boron bridge, shows distinct ferrocene and ferrocenium moieties with Cp_{cent}–Cp_{cent} distances of 3.291–3.320 Å for the former and 3.428 Å for the latter.[23] The geometric parameters for (**3**$^+$)-1 and (**3**$^+$)-2 (Figure 3b) are similar apart from the tilting of the C_4B_2 ring relative to the Cp ring.[21] The interplanar angle of 16.5° for (**3**$^+$)-1 is larger than that of 13.8° for (**3**$^+$)-2 and even larger than in the free acid **3** itself. This unexpected feature is likely a result of packing effects involving the counterions, which form infinite helical chains $\{I_3^-{\cdot}I_2\}_n$ through short intermolecular I···I contacts.[21]

Hendrickson and co-workers have shown that IR spectroscopy may also serve as a convenient tool to evaluate the valence detrapping in diferrocene-type species. Particularly sensitive to oxidation of Fe is the perpendicular C–H bending vibration, which occurs at 815 cm^{-1} in ferrocene and is shifted to approximately 850 cm^{-1} in ferrocenium salts.[22a,b] A KBr pellet of the mixed-valence species $(3^+)I_3{\cdot}I_2$ shows a single broad band at 841 cm^{-1}, which is shifted relative to the neutral



Fe···Fe = 5.123 Å
Cp // C_4B_2 = 15.9°

Fe···Fe = 5.189 Å
Cp // C_4B_2 = 13.8°

Fe···Fe = 5.509 Å
Cp // C_4B_2 = 9.1°

Fe···Fe = 5.940 Å
Cp // C_4B_2 = −5.5°

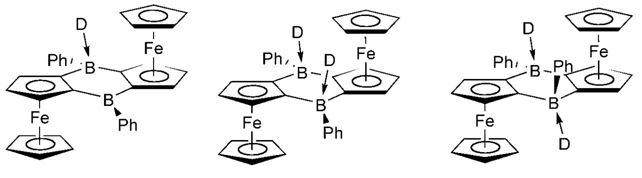
Figure 3. Comparison of structures of **3**, (**3**$^+$)-2, **3**$^{\bullet-}$, and *trans*-**5 b**; hydrogen atoms are omitted for clarity; Cp//C_4B_2 denotes the interplanar angle between the Cp and C_4B_2 rings.

molecule **3** (820 cm^{-1}) and thus further indicates rapid electron transfer on the IR timescale (ca. 10^{12} s^{-1}).[21,22a,b]

The electrochemical reduction of **3** was studied by cyclic voltammetry in 1,2-dimethoxyethane (DME, Figure 2 b) and revealed a quasi-reversible reduction wave at $E_{1/2} = -2.52$ V (vs. FcH/FcH$^+$) followed by an irreversible reduction at $E_{p2} = -3.02$ V. These data suggest the boracycle in **3** to be considerably more electron-rich than the respective diboraanthracene (**A**, R = Me), which was reported to show reversible reduction waves at −1.41 and −2.07 V in DME versus the saturated calomel electrode (SCE; or ca. −1.80/−2.46 V vs. FcH/FcH$^+$).[2] The latter is to be expected if extensive delocalization between the electron-rich ferrocene moieties and the boron atoms is present, which is evident from the relatively short endocyclic B−C bonds and the significant tilting of the boryl groups towards the iron atoms in the X-ray crystal structure of **3**.

The diboracycle **3** was chemically reduced by treatment with potassium in THF in the presence of 18-crown-6 (18-c-6). ESR spectroscopy of the solution in THF at −50 °C showed a signal, from which the ^{11}B hyperfine coupling could not be resolved. Dark brown thermally labile single crystals of the monoreduced species [K(18-c-6)(THF)$_2$][**3**$^{\bullet-}$] were obtained by crystallization from THF at −35 °C.[12,21] The bending of the boryl groups in **3**$^{\bullet-}$ towards Fe and the interplanar angle of 9.2° between the Cp rings and the C_4B_2 ring are significantly smaller than those in the parent compound **3** (interplanar angle: 15.9°), which in turn results in partial flattening of the dibora-*s*-indacene moiety and a significant increase in the Fe···Fe separation from 5.123 to 5.509 Å (Figure 3 c). Both boryl groups are bent towards Fe at a similar angle (170.5° and 171.4°) which suggests that the electron is delocalized. A shortening of the B−C bond lengths within the six-membered diboracycle, as reported by Siebert and co-workers for the reduced diboraanthracene [K(18-c-6)(THF)$_2$][**A**$^{\bullet-}$] in comparison to the neutral diboraanthrancene **A** (R = Me),[2] is not observed. In this context, note that reduction of 1,8-bis(diphenylboryl)naphthalene, which shows a B···B separation of 3.002 Å similar to that of **3**, has been studied by Gabbaï and co-workers.[24] Upon chemical or electrochemical reduction, a monoanionic species was detected, for which a one-electron σ bond between the two boron centers has been proposed on the basis of EPR spectroscopy and DFT calculations. The calculations predict a shortening of the B···B distance upon reduction.[25] Although reduction apparently leads to a delocalized radical anion in our system, a decrease in the B···B distance (3.111 Å) in **3**$^{\bullet-}$ is not observed. The latter is due to incorporation of boron into the rigid ring system in **3**$^{\bullet-}$ which does not allow for direct overlap of the p orbitals of the two boron atoms.

Lewis acid/Lewis base binding offers yet another opportunity to trigger conformational changes in **3**.[14,26] Adducts **5 a** and **5 b** were obtained upon treatment of **3** with two equivalents of pyridine (py) and *tert*-butylpyridine (*t*Bu-py), respectively.[21] Weak binding of pyridine to **3** is evident from partial dissociation into the monoadducts **4** and the free acid **3** in solution. Single crystals of *trans*-**5 b** were obtained by slow evaporation of solvent from a 1:2 mixture of **3** and *tert*-butylpyridine in chloroform.[12,21] A strong effect of the binding of pyridine on the geometric features is observed. In contrast to the free acid **3**, the central C_4B_2 ring of the dibora-*s*-indacene moiety is slightly bent away from the CpFe fragments, with interplanar angles between the Cp and C_4B_2 rings of 5.5° (Figure 3 d). The latter is a result of electronic saturation and steric congestion around boron[26] which ultimately leads to expansion of the molecule and a much greater Fe···Fe distance of 5.940 Å relative to that of 5.123 Å in **3**.



4a: D = py
4b: D = *t*Bu-py

cis-**5a**: D = py
cis-**5b**: D = *t*Bu-py

trans-**5a**: D = py
trans-**5b**: D = *t*Bu-py

In conclusion, the first 1,2-diboradiferrocene **3** was readily prepared from 1,1′-distannylferrocene and shows unusually strong electronic coupling between the ferrocene groups upon partial oxidation, which is indicative of fast electron transfer through the dibora-*s*-indacene ligand framework. Conformational changes in this highly rigid diferrocene can be triggered either through redox chemistry or through the binding of nucleophiles to render **3** an interesting candidate for the design of new types of molecular machines.

Experimental Section

Experimental procedure for **3**: Neat $PhBCl_2$ (0.62 g, 3.90 mmol) was added to a solution of **1** (2.00 g, 3.90 mmol) in toluene (15 mL) at room temperature. The reaction mixture was kept for three months in an aluminum-capped vial. Large dark red crystals of **3** formed and were filtered off, washed with hexanes, and dried under high vacuum (0.38 g, 36 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 7.94$, 7.49–7.48 (m, 10 H, Ph), 5.05 (t, $J = 2.5$ Hz, 2 H, Cp-4), 4.89 (d, $J = 2.5$ Hz, 4 H, Cp-3,5), 3.88 ppm (s, 10 H, C_5H_5); ^{13}C NMR (125.69 MHz, CD_2Cl_2, 25 °C): $\delta = 144.5$ (br, *i*-Ph), 135.5 (*o*-Ph), 130.9 (*p*-Ph), 129.5 (*m*-Ph), 84.1 (br, Cp-1,2), 83.3 (Cp-3,5), 81.4 (Cp-4), 72.1 ppm (C_5H_5); ^{11}B NMR (160 MHz, CD_2Cl_2, 25 °C) $\delta = 57.7$ ($w_{1/2} = 1280$ Hz); GC-MS: m/z: 544 [M^+] (100 %); UV/Vis (CH_2Cl_2, 10^{-4} M): λ_{max} (ε) = 498 (6040), 411 (4360), 335 nm (5810 $cm^{-1}M^{-1}$); Elemental analysis (%) calcd for $C_{32}H_{26}Fe_2B_2$: C 70.67, H 4.82; found: C 70.72, H 4.78. See Supporting Information for further experimental details.

Received: June 20, 2005

Keywords: boron · cyclopentadienyl ligands · iron · Lewis acids · mixed-valent compounds

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[1] W. Siebert, *Adv. Organomet. Chem.* **1993**, *35*, 187.

[2] P. Müller, S. Huck, H. Köppel, H. Pritzkow, W. Siebert, *Z. Naturforsch. B* **1995**, *50*, 1476.

[3] P. Müller, H. Pritzkow, W. Siebert, *J. Organomet. Chem.* **1996**, *524*, 41.

[4] M. V. Metz, D. J. Schwartz, C. L. Stern, P. N. Nickias, T. J. Marks, *Angew. Chem.* **2000**, *112*, 1368; *Angew. Chem. Int. Ed.* **2000**, *39*, 1312.

[5] V. C. Williams, C. Dai, Z. Li, S. Collins, W. E. Piers, W. Clegg, M. R. J. Elsegood, T. B. Marder, *Angew. Chem.* **1999**, *111*, 3922; *Angew. Chem. Int. Ed.* **1999**, *38*, 3695.

[6] a) S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2002**, *124*, 8816; b) D. J. H. Emslie, W. E. Piers, M. Parvez, *Angew. Chem.* **2003**, *115*, 1290; *Angew. Chem. Int. Ed.* **2003**, *42*, 1252; c) S. Kim, K.-H. Song, S. O. Kang, J. Ko, *Chem. Commun.* **2004**, 68; d) S. Bieller, F. Zhang, M. Bolte, J. W. Bats, H.-W. Lerner, M. Wagner, *Organometallics* **2004**, *23*, 2107.

[7] a) N. Matsumi, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **1998**, *120*, 5112; b) S. Yamanaka, T. Inoue, T. Aoyagi, T. Komatsu, *Synth. Met.* **1992**, *46*, 221; c) U. Salzner, J. B. Lagowski, P. G. Pickup, R. A. Poirier, *Synth. Met.* **1998**, *96*, 177.

[8] a) Z. Chen, H. Jiao, A. Hirsch, W. Thiel, *Chem. Phys. Lett.* **2000**, *329*, 47; b) L. Türker, A. Azizoglu, *Theochem* **2001**, *535*, 151; c) X. Xu, Y. Xing, Z. Shang, G. Wang, Z. Cai, Y. Pan, X. Zhao, *Chem. Phys.* **2003**, *287*, 317.

[9] J. A. Gamboa, A. Sundararaman, L. Kakalis, A. J. Lough, F. Jäkle, *Organometallics* **2002**, *21*, 4169.

[10] "Metallocene-Based Bidentate Lewis Acids": F. Jäkle, *ACS Symp. Ser.* **2002**, *822*, and references therein.

[11] a) B. Wrackmeyer, U. Dörfler, M. Herberhold, *Z. Naturforsch. B* **1993**, *48*, 121; b) B. Wrackmeyer, U. Dörfler, J. Rinck, M. Herberhold, *Z. Naturforsch. B* **1994**, *49*, 1403; c) B. Wrackmeyer, U. Dörfler, W. Milius, M. Herberhold, *Polyhedron* **1995**, *14*, 1425; d) A. Appel, H. Nöth, M. Schmidt, *Chem. Ber.* **1995**, *128*, 621; e) P. A. Deck, T. S. Fisher, J. S. Downey, *Organometallics* **1997**, *16*, 1193.

[12] X-ray crystal structure analyses: **3**: $C_{32}H_{26}B_2Fe_2$, $M_r = 543.85$, monoclinic, space group $P2_1/c$, $a = 9.1414(6)$, $b = 8.7739(6)$, $c = 15.1355(10)$ Å, $\beta = 101.4410(10)°$, $V = 1189.83(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.518\ g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 150(2)$ K, crystal dimensions $0.40 \times 0.30 \times 0.20\ mm^3$, $\mu(Mo_{K\alpha}) = 1.240\ mm^{-1}$, θ range from 2.27 to 28.28°, 7302 measured reflections, 2789 independent reflections ($R_{int} = 0.0206$), R_1 ($I > 2\sigma(I)$) = 0.0313, wR_2 ($I > 2\sigma(I)$) = 0.0777, GOF = 1.484, 163 parameters, final difference map within 0.517 and $-0.353\ e\,Å^{-3}$. (**3**$^+$)$I_3 \cdot I_2$: $C_{32}H_{26}B_2Fe_2I_5$, $M_r = 1178.35$, monoclinic, space group $P2_1/n$, $a = 18.141(3)$, $b = 11.5344(19)$, $c = 18.752(3)$ Å, $\beta = 118.474(2)°$, $V = 3449.1(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.269\ g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 213(2)$ K, crystal dimensions $0.30 \times 0.10 \times 0.10\ mm^3$, $\mu(Mo_{K\alpha}) = 5.338\ mm^{-1}$, θ range from 2.15 to 28.19°, 25675 measured reflections, 8083 independent reflections ($R_{int} = 0.0300$), R_1 ($I > 2\sigma(I)$) = 0.0333, wR_2 ($I > 2\sigma(I)$) = 0.0946, GOF = 1.025, 370 parameters, final difference map within 1.532 and $-0.735\ e\,Å^{-3}$. There are two independent half cations on inversion centers and one co-crystallized molecule of I_2. [K(18-c-6)(THF)$_2$][**3**$^{\cdot-}$]: $C_{52}H_{66}B_2Fe_2KO_8$, $M_r = 991.47$, triclinic, space group $P\bar{1}$, $a = 10.049(5)$, $b = 10.913(5)$, $c = 12.313(6)$ Å, $\alpha = 67.864(8)°$, $\beta = 79.656(8)°$, $\gamma = 86.403(8)°$, $V = 1230.4(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.338\ g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 100(2)$ K, crystal dimensions $0.14 \times 0.04 \times 0.04\ mm^3$, $\mu(Mo_{K\alpha}) = 0.727\ mm^{-1}$, θ range from 2.01 to 24.00°, 3900 measured reflections, 3480 independent reflections ($R_{int} = 0.0211$), R_1 ($I > 2\sigma(I)$) = 0.0967, wR_2 ($I > 2\sigma(I)$) = 0.2614, GOF = 1.092, 285 parameters, final difference map within 1.371 and $-1.241\ e\,Å^{-3}$. *trans*-**5b**: $C_{50}H_{52}B_2Fe_2N_2$, $M_r = 814.26$, monoclinic, space group $C2/c$, $a = 28.2223(18)$, $b = 8.3188(5)$, $c = 21.8954(14)$ Å, $\beta = 127.6860(10)°$, $V = 4068.1(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.329\ g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 213(2)$ K, crystal dimensions $0.30 \times 0.20 \times 0.15\ mm^3$, $\mu(Mo_{K\alpha}) = 0.751\ mm^{-1}$, θ range from 1.82 to 28.22°, 14480 measured reflections, 4785 independent reflections ($R_{int} = 0.0362$), R_1 ($I > 2\sigma(I)$) = 0.0527, wR_2 ($I > 2\sigma(I)$) = 0.1257, GOF = 1.150, 253 parameters, final difference map within 0.517 and $-0.423\ e\,Å^{-3}$. For all four structures, SADABS (Sheldrick, G. M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was used. Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. CCDC 275645, 275648, 275647, and 275646 (**3**, (**3**$^+$)$I_3 \cdot I_2$, [K(18-c-6)(THF)$_2$][**3**$^{\cdot-}$], and *trans*-**5b**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] *Cis* isomers are known for related doubly silyl-bridged species; see: M. Herker, F. H. Köhler, M. Schwaiger, B. Weber, *J. Organomet. Chem.* **2002**, *658*, 266. However, the Fe···B interactions for **3** would lead to severe steric congestion in the *cis* isomer.

[14] M. Scheibitz, M. Bolte, J. W. Bats, H.-W. Lerner, I. Nowik, R. H. Herber, A. Krapp, M. Lein, M. Holthausen, M. Wagner, *Chem. Eur. J.* **2005**, *11*, 584.

[15] H. Akutsu, K. Kozawa, T. Uchida, *Synth. Met.* **1995**, *70*, 1109.

[16] B. E. Carpenter, W. E. Piers, M. Parvez, G. P. A. Yap, S. J. Rettig, *Can. J. Chem.* **2001**, *79*, 857.

[17] a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348; b) P. Jutzi, N. Lenze, B. Neumann, H.-G. Stammler, *Angew. Chem.* **2001**, *113*, 1469; *Angew. Chem. Int. Ed.* **2001**, *40*, 1423; c) Z. Dominguez, H. Dang, M. J. Strouse, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 2398; d) M. F. Hawthorne, J. I. Zink, J. M. Skelton, M. J. Bayer, C. Liu, E. Livshits, R. Baer, D. Neuhauser, *Science* **2004**, *303*, 1849; e) D. Horinek, J. Michl, *J. Am. Chem. Soc.* **2003**, *125*, 11900.

[18] a) R. J. LeSuer, W. E. Geiger, *Angew. Chem.* **2000**, *112*, 254; *Angew. Chem. Int. Ed.* **2000**, *39*, 248; b) F. Barriere, N. Camire, W. E. Geiger, U. T. Mueller-Westerhoff, R. Sanders, *J. Am. Chem. Soc.* **2002**, *124*, 7262.

[19] F. H. Köhler, A. Schell, B. Weber, *J. Organomet. Chem.* **1999**, *575*, 33.

[20] J. Kreisz, R. U. Kirss, W. M. Reiff, *Inorg. Chem.* **1994**, *33*, 1562.

[21] See Supporting Information for experimental details, ORTEP plots of ($\mathbf{3}^+$)$I_3{\cdot}I_2$, [K(18-c-6)(THF)$_2$][$\mathbf{3}^{\cdot-}$], and *trans*-**5b**, a plot of the extended structure of ($\mathbf{3}^+$)$I_3{\cdot}I_2$, and a comparative plot of the IR spectra of **3** and ($\mathbf{3}^+$)$I_3{\cdot}I_2$.

[22] a) J. A. Kramer, D. N. Hendrickson, *Inorg. Chem.* **1980**, *19*, 3330; b) J. A. Kramer, F. H. Herbstein, D. N. Hendrickson, *J. Am. Chem. Soc.* **1980**, *102*, 2293; c) T.-Y. Dong, D. N. Hendrickson, C. G. Pierpont, M. F. Moore, *J. Am. Chem. Soc.* **1986**, *108*, 963; d) R. J. Webb, S. J. Geib, D. L. Staley, A. L. Rheingold, D. N. Hendrickson, *J. Am. Chem. Soc.* **1990**, *112*, 5031.

[23] D. O. Cowan, P. Shu, F. L. Hedberg, M. Rossi, T. J. Kistenmacher, *J. Am. Chem. Soc.* **1979**, *101*, 1304.

[24] a) J. D. Hoefelmeyer, F. P. Gabbaï, *J. Am. Chem. Soc.* **2000**, *122*, 9054; b) J. D. Hoefelmeyer, S. Solé, F. P. Gabbaï, *J. Chem. Soc. Dalton Trans.* **2004**, 1254.

[25] The X-ray crystal structure of the radical anion $(BMes_3)^{\cdot-}$ (Mes = mesityl) has been reported; see: M. M. Olmstead P. P. Power, *J. Am. Chem. Soc.* **1986**, *108*, 4235.

[26] M. Scheibitz, J. B. Heilmann, R. F. Winter, M. Bolte, J. W. Bats, M. Wagner, *Dalton Trans.* **2005**, 159.