9-Ferrocenyl-9-borafluorene—A Redox-Switchable Main Group Lewis Acid

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9-Ferrocenyl-9-borafluorene ($FcBC_{12}H_8$; **3**) is readily accessible from FcHgCl and $BrBC_{12}H_8$. The 9-borafluorenyl substituent is bent out of the plane of the cyclopentadienyl ring toward the iron center with corresponding dip angles of $\alpha^* = 25.5°$ and 17.1° for the two crystallographically independent molecules in the asymmetric unit of **3**. The degree of ligand bending is one of the highest ever measured for a ferrocenylborane derivative, thereby indicating a pronounced Fe−B interaction. In line with that, oxidation of the Fe center to its Fe^{III} state using $AgBF_4$ results in a substantial decrease of the dip angle in the ferricinium species [**3**]BF_4 ($\alpha^* = 6.3°$). Compound **3** can therefore be considered a rare example of a redox-switchable main group Lewis acid. The stability of the molecular framework of **3** is sufficiently high to allow for the isolation and structural characterization of its pyridine-*N*-oxide adduct (**4**). Moreover, reaction of **3** with 0.5 equiv of 1,1′-dilithioferrocene (1,1′-$fcLi_2 \times 2/3$ tmeda) and subsequent limited access of O_2 leads to the formation of the trinuclear mixed-valence complex Li[Fc-($BC_{12}H_8$)-fc-($BC_{12}H_8$)-Fc], which has been structurally characterized as 12-crown-4 adduct (Li(12-c-4)$_2$[**6**]).

Introduction

Boryl and borate functionalized metallocenes are valuable starting materials for the preparation of molecules that cover a wide range of structural types and chemical applications.[1,2] Especially borylated ferrocenes have found widespread use, for example, as constituents of redox-active ligands,[3−8] electron sponges,[9−11] and redox-active macrocycles.[12−15] More recently, the promising potential of 1,1′-diborylated ferrocene derivatives for the preparation of oligonuclear complexes[16−26] and poly(ferrocenylene) macromolecules[15,27−33] has been unveiled. The fact that boryl groups easily engage in Lewis acid−base pairing has been exploited for the facile synthesis of unusual *ansa*-

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(1) Ma, K.; Scheibitz, M.; Scholz, S.; Wagner, M. *J. Organomet. Chem.* **2002**, *652*, 11–19.

(2) Aldridge, S.; Bresner, C. *Coord. Chem. Rev.* **2003**, *244*, 71–92.

(3) Jäkle, F.; Polborn, K.; Wagner, M. *Chem. Ber.* **1996**, *129*, 603–606.

(4) Fabrizi de Biani, F.; Jäkle, F.; Spiegler, M.; Wagner, M.; Zanello, P. *Inorg. Chem.* **1997**, *36*, 2103–2111.

(5) Voloshin, Y. Z.; Kron, T. E.; Belsky, V. K.; Zavodnik, V. E.; Maletin, Y. A.; Kozachkov, S. G. *J. Organomet. Chem.* **1997**, *536–537*, 207–216.

(6) Herdtweck, E.; Peters, F.; Scherer, W.; Wagner, M. *Polyhedron* **1998**, *17*, 1149–1157.

(7) Schebler, P. J.; Riordan, C. G.; Liable-Sands, L.; Rheingold, A. L. *Inorg. Chim. Acta* **1998**, *270*, 543–549.

(8) Guo, S. L.; Peters, F.; Fabrizi de Biani, F.; Bats, J. W.; Herdtweck, E.; Zanello, P.; Wagner, M. *Inorg. Chem.* **2001**, *40*, 4928–4936.

(9) Fabrizi de Biani, F.; Gmeinwieser, T.; Herdtweck, E.; Jäkle, F.; Laschi, F.; Wagner, M.; Zanello, P. *Organometallics* **1997**, *16*, 4776–4787.

(10) Ding, L.; Ma, K.; Fabrizi de Biani, F.; Bolte, M.; Zanello, P.; Wagner, M. *Organometallics* **2001**, *20*, 1041–1043.

(11) Ma, K.; Fabrizi de Biani, F.; Bolte, M.; Zanello, P.; Wagner, M. *Organometallics* **2002**, *21*, 3979–3989.

(12) Dinnebier, R. E.; Ding, L.; Ma, K.; Neumann, M. A.; Tanpipat, N.; Leusen, F. J. J.; Stephens, P. W.; Wagner, M. *Organometallics* **2001**, *20*, 5642–5647.

(13) Ding, L.; Ma, K.; Dürner, G.; Bolte, M.; Fabrizi de Biani, F.; Zanello, P.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **2002**, 1566–1573.

(14) Scheibitz, M.; Winter, R. F.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 924–927.

(15) Day, J. K.; Bresner, C.; Fallis, I. A.; Ooi, L.-L.; Watkin, D. J.; Coles, S. J.; Male, L.; Hursthouse, M. B.; Aldridge, S. *Dalton. Trans.* **2007**, 3486–3488.

(16) Cowan, D. O.; Shu, P.; Hedberg, F. L.; Rossi, M.; Kistenmacher, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1304–1306.

(17) Jäkle, F.; Priermeier, T.; Wagner, M. *Chem. Ber.* **1995**, *128*, 1163–1169.

(18) Hagenau, U.; Heck, J.; Hendrickx, E.; Persoons, A.; Schuld, T.; Wong, H. *Inorg. Chem.* **1996**, *35*, 7863–7866.

(19) Jäkle, F.; Berenbaum, A.; Lough, A. J.; Manners, I. *Chem.−Eur. J.* **2000**, *6*, 2762–2771.

(20) Scheibitz, M.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2004**, *23*, 3556–3559.

(21) Scheibitz, M.; Heilmann, J. B.; Winter, R. F.; Bolte, M.; Bats, J. W.; Wagner, M. *Dalton Trans.* **2005**, 159–170.

(22) Venkatasubbaiah, K.; Zakharov, L. N.; Kassel, W. S.; Rheingold, A. L.; Jäkle, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5428–5433.

(23) Ferguson, G.; Lawrence, S. E.; Neville, L. A.; O'Leary, B. J.; Spalding, T. R. *Polyhedron* **2007**, *26*, 2482–2492.

(24) Kaufmann, L.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2007**, *26*, 1771–1776.

(25) Venkatasubbaiah, K.; Nowik, I.; Herber, R. H.; Jäkle, F. *Chem. Commun.* **2007**, 2154–2156.

(26) Venkatasubbaiah, K.; Doshi, A.; Nowik, I.; Herber, R. H.; Rheingold, A. L.; Jäkle, F. *Chem.−Eur. J.* **2008**, *14*, 444–458.

(27) Braunschweig, H.; Dirk, R.; Müller, M.; Nguyen, P.; Resendes, R.; Gates, D. P.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2338–2340.

(28) Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1453–1465.

(29) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669–4672.

(30) Berenbaum, A.; Braunschweig, H.; Dirk, R.; Englert, U.; Green, J. C.; Jäkle, F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765–5774.

(31) Braga, D.; Polito, M.; Bracaccini, M.; D'Addario, D.; Tagliavini, E.; Sturba, L.; Grepioni, F. *Organometallics* **2003**, *22*, 2142–2150.

(32) Heilmann, J. B.; Scheibitz, M.; Qin, Y.; Sundararaman, A.; Jäkle, F.; Kretz, T.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 920–925.

(33) Heilmann, J. B.; Qin, Y.; Jäkle, F.; Lerner, H.-W.; Wagner, M. *Inorg. Chim. Acta* **2006**, *359*, 4802–4806.

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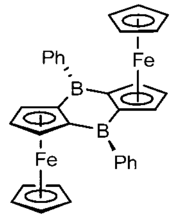
ferrocenes with interannular B−N-[34−36] and B−P-adduct bridges.[37,38] Adduct formation with ferrocenylboranes is also the working principle of various electrochemically addressable anion sensors.[39−42] If, in addition to the boryl substituent, a second Lewis acid group is present at the edge of ferrocene, even cooperative binding of Lewis bases may be observed.[43−47]

One reason why ferrocenylboranes are so popular for numerous applications lies in their ease of preparation. Mono-, bis- and tetrakis(dibromoboryl) ferrocenes are readily accessible via electrophilic substitution reactions,[48−51] and the parent compound $FcBH_2$ has also been isolated and structurally characterized as amine adduct (Fc: $(C_5H_5)Fe(C_5H_4)$).[52] The other important reason is that the iron center and the boron atom(s) of ferrocenylboranes are electronically coupled.[53,54] As a result, tetra-coordination of the boron atom in $FcBR_2$ generally results in a pronounced cathodic shift of the Fe^{II}/Fe^{III} redox potential of the adduct $FcBR_2{-}LB$,[21,28] with the magnitude of this shift being influenced by the nature of the attached Lewis base (LB).

A closer inspection of the electronic structure of selected ferrocenylborane derivatives by both experimental and quantum chemical means indicates a direct through-space interaction between filled *d*-type orbitals at Fe and the vacant *p*-orbital at B.[53,54] As a consequence, the boryl group tends to be bent out of the plane of the cyclopentadienyl ring toward the iron atom. For BR_2-groups of identical constitution, the dip angle α^* is largest in the monoborylated species. Introduction of π-donating substituents R or tetra-coordination of the boron atom(s) reduces the degree of bending. The observed substituent effects are reproduced by density functional theory (DFT) calculations.[54] We therefore considered it a reliable result when theory predicted that Fe^{II}/Fe^{III} oxidation of the iron center in $FcBR_2$ causes a significant decrease in the dip angle (e.g., $FcBH_2$: $\alpha^*(\text{calcd.}) = 25.1°$; $[FcBH_2]^+$: $\alpha^*(\text{calcd.}) = 5.0°$).[54] Unfortunately, the definitive experimental proof of this prediction by X-ray crystallography was long hampered by the lack of $FcBR_2$ derivatives that are long-term stable in their Fe^{III} state. Potentially suitable candidates would be ferrocenylboronic acids and esters like those used for sensor applications (see above). However, the boron atom in these compounds is only weakly Lewis acidic which results in small dip angles α^* already when the molecules are in the reduced Fe^{II} state (e.g., $FcB(OMe)_2$: $\alpha^* = 6.1°$[54] versus $FcBBr_2$: $\alpha^* = 18.3°$[53]).



A

Figure 1. Representation of the doubly boron-bridged 1,2-diferrocene **A** reported by Jäkle et al.[22]

Fundamentally new insight into the problem of Fe−B bonding in ferrocenylboranes came from the work of Jäkle et al. who studied the chemical properties and structural features of the doubly boron-bridged 1,2-diferrocene **A** (Figure 1) in its Fe^{II}/Fe^{II} (**A**), Fe^{II}/Fe^{III} ($\mathbf{A}^+$), and Fe^{III}/Fe^{III} ($\mathbf{A}^{2+}$) state.[22,25,26] Their most important findings in the context of this paper are: (i) the dihedral angle $C_5H_3//C_4B_2$ changes from 15.9° in neutral **A** to 8.8° (ferricenyl-C_5H_3) and 22.7° (ferrocenyl-C_5H_3) in monooxidized $\mathbf{A}^+$,[55] (ii) the Lewis acidity of the B atoms is strongly enhanced through oxidation of the ferrocene moieties.[25] The structural features of $\mathbf{A}^+$ are in excellent agreement with our theoretical studies[54] in that the boron atoms are far less bent toward the Fe^{III} ion as they had been toward the Fe^{II} center in **A**. The observation that the remaining Fe^{II} ion in $\mathbf{A}^+$ appears to be more strongly bound to the boron bridges than the Fe^{II} centers in **A** is in line with an oxidation-induced Lewis acidity enhancement of the B atoms.

Our group has a long-standing interest in redox-switchable Lewis acids derived from ferrocenylboranes. Moreover, we are continuing to exploit the adduct formation between 1,1′-diborylated ferrocenes and ditopic Lewis bases for the preparation of poly(ferrocenylene) macromolecules. In both cases it is of utmost importance to make certain that the compounds remain intact upon ferrocene oxidation. The purpose of this paper is therefore to report on the novel compound 9-ferrocenyl-9-borafluorene which we anticipated to be a strong, redox-responsive Lewis acid with a stable molecular framework (**3**; Scheme 1). To test this assumption and to evaluate the potential of **3** in the context just mentioned, we have investigated (i) whether the corresponding Fe^{III} derivative $\mathbf{3}^+$ is an isolable species, (ii) how **3** behaves toward pyridine-*N*-oxide as representative of reactive Lewis bases, (iii) whether the oligomeric model compound $[\text{Fc-BR}'_2\text{-fc-BR}'_2\text{-Fc}]^{2-}$ can be oxidized to a stable mixed-valence species $[\text{Fc-BR}'_2\text{-fc-BR}'_2\text{-Fc}]^-$ (fc: $Fe(C_5H_4)_2$, HBR'_2: 9-borafluorene), which has not been possible

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(34) Jäkle, F.; Priermeier, T.; Wagner, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1765–1766.

(35) Jäkle, F.; Priermeier, T.; Wagner, M. *Organometallics* **1996**, *15*, 2033–2040.

(36) Herdtweck, E.; Jäkle, F.; Opromolla, G.; Spiegler, M.; Wagner, M.; Zanello, P. *Organometallics* **1996**, *15*, 5524–5535.

(37) Jäkle, F.; Mattner, M.; Priermeier, T.; Wagner, M. *J. Organomet. Chem.* **1995**, *502*, 123–130.

(38) Herdtweck, E.; Jäkle, F.; Wagner, M. *Organometallics* **1997**, *16*, 4737–4745.

(39) Dusemund, C.; Sandanayake, K. R. A. S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1995**, 333–334.

(40) Aldridge, S.; Bresner, C.; Fallis, I. A.; Coles, S. J.; Hursthouse, M. B. *Chem. Commun.* **2002**, 740–741.

(41) Bresner, C.; Aldridge, S.; Fallis, I. A.; Jones, C.; Ooi, L.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3606–3609.

(42) Bresner, C.; Day, J. K.; Coombs, N. D.; Fallis, I. A.; Aldridge, S.; Coles, S. J.; Hursthouse, M. B. *Dalton Trans.* **2006**, 3660–3667.

(43) Jäkle, F.; Lough, A. J.; Manners, I. *Chem. Commun.* **1999**, 453–454.

(44) Gamboa, J. A.; Sundararaman, A.; Kakalis, L.; Lough, A. J.; Jäkle, F. *Organometallics* **2002**, *21*, 4169–4181.

(45) Boshra, R.; Sundararaman, A.; Zakharov, L. N.; Incarvito, C. D.; Rheingold, A. L.; Jäkle, F. *Chem.−Eur. J.* **2005**, *11*, 2810–2824.

(46) Boshra, R.; Venkatasubbaiah, K.; Doshi, A.; Lalancette, R. A.; Kakalis, L.; Jäkle, F. *Inorg. Chem.* **2007**, *46*, 10174–10186.

(47) Pakkirisamy, T.; Venkatasubbaiah, K.; Kassel, W. S.; Rheingold, A. L.; Jäkle, F. *Organometallics* **2008**, *27*, 3056–3064.

(48) Renk, T.; Ruf, W.; Siebert, W. *J. Organomet. Chem.* **1976**, *120*, 1–25.

(49) Ruf, W.; Renk, T.; Siebert, W. *Z. Naturforsch.* **1976**, *31b*, 1028–1034.

(50) Appel, A.; Nöth, H.; Schmidt, M. *Chem. Ber.* **1995**, *128*, 621–626.

(51) Eckensberger, U. D.; Kunz, K.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2008**, *27*, 764–768.

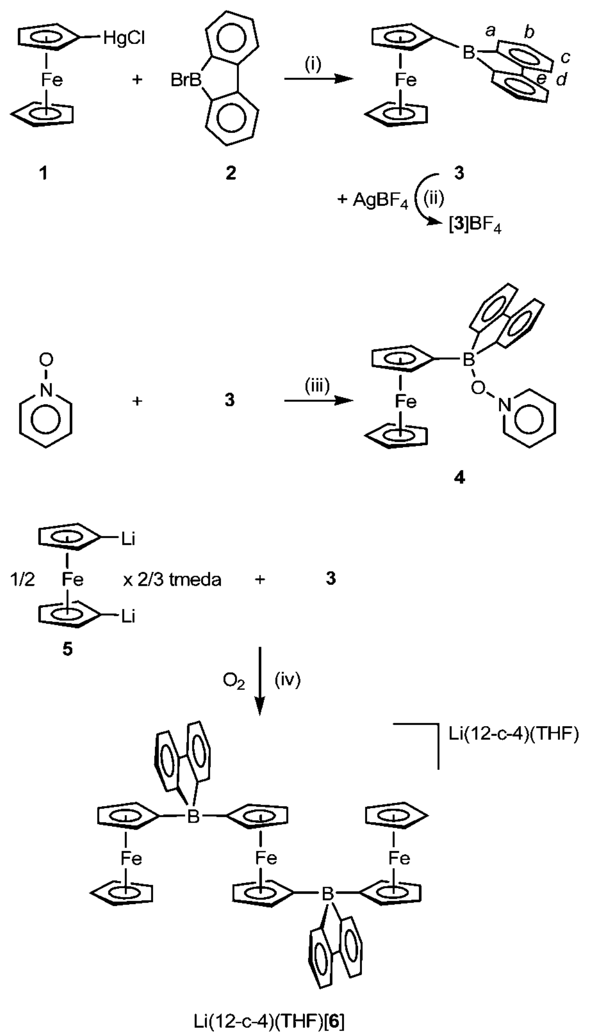
(52) Scheibitz, M.; Bats, J. W.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2004**, *23*, 940–942.

(53) Appel, A.; Jäkle, F.; Priermeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188–1194.

(54) Scheibitz, M.; Bolte, M.; Bats, J. W.; Lerner, H.-W.; Nowik, I.; Herber, R. H.; Krapp, A.; Lein, M.; Holthausen, M. C.; Wagner, M. *Chem.− Eur. J.* **2005**, *11*, 584–603.

(55) Compound $\mathbf{A}^+$ crystallizes with two independent molecules in the asymmetric unit. The values for the dihedral angles $C_5H_3//C_4B_2$ in the second molecule are 12.5° (ferricenyl-C_5H_3) and 19.0° (ferrocenyl-C5H3).

Scheme 1. Synthesis of 9-Ferrocenyl-9-borafluorene 3 and its Ferricinium Form [3]BF$_4$, Adduct 4 between 3 and Pyridine-*N*-oxide, and the Trinuclear Fe^{II}/Fe^{III}/Fe^{II} Mixed-Valence Complex Li(12-c-4)(THF)[6][a]



[a] (i) hexane, −78 °C to r.t.; (ii) CH$_2$Cl$_2$, −35 °C to r.t.; (iii) CH$_2$Cl$_2$, r.t.; (iv) THF, −78 °C to r.t.

in the case of the corresponding methyl derivative [Fc-BMe$_2$-fc-BMe$_2$-Fc]$^{2-}$.[21]

Results and Discussion

The design of **3** is based on the following considerations: (i) Arylboranes tend to be less sensitive than alkylboranes. (ii) The introduction of a bond between two phenyl substituents will further enhance the stability of the system. (iii) Such a bond will also force the phenyl groups into coplanarity which in turn will lower the steric bulk around the boron atom. As a consequence, the size of the dip angle α* is limited as little as possible by steric constraints so that the electronic Fe−B interaction can approach its maximum. Moreover, adduct formation with external Lewis bases becomes kinetically more feasible which is beneficial for both application projects outlined above.

Synthesis and NMR Spectroscopical Characterization. Our first attempts to synthesize 9-ferrocenyl-9-borafluorene **3** relied on the reaction of dibromoborylferrocene[48] with 9,9-dimethyl-9-silafluorene (Me$_2$SiC$_{12}$H$_8$)[56] or 9,9-dimethyl-9-stannafluorene (Me$_2$SnC$_{12}$H$_8$).[57] However, in both cases satisfactory yields of **3** could not be obtained. We also tried the reaction between monolithioferrocene[58] and 9-methoxy-9-borafluorene (MeOBC$_{12}$H$_8$),[59] but again with limited success. Treatment of chloromercuriferrocene **1**[60] with 9-bromo-9-borafluorene (BrBC$_{12}$H$_8$; **2**)[61] in hexane, however, gave the target compound **3** in yields of 75% (Scheme 1). **3** can be oxidized to its ferricinium state using AgBF$_4$ in CH$_2$Cl$_2$. Recrystallization of crude [**3**]BF$_4$ from CHCl$_3$/hexane provided crystals suitable for X-ray analysis (Table 1). Single crystals of adduct **4** formed from an equimolar mixture of **3** and pyridine-*N*-oxide in CH$_2$Cl$_2$ at −35 °C (Scheme 1). The compound is not long-term stable in solution at r.t. NMR spectra recorded in C$_6$D$_6$ revealed severe broadening of all proton signals and the appearance of numerous new ^{13}C NMR resonances after a period of 12 h. For the synthesis of the mixed-valence species Li[**6**], 2 equiv of **3** were added to 1,1′-dilithioferrocene × 2/3 tmeda[62,63] (**5**) in THF. The resulting orange solution was briefly exposed to air whereupon its color changed to brown. Crystallization of Li(12-c-4)(THF)[**6**] was induced by addition of 12-crown-4 and hexane to a THF solution of the crude product (Scheme 1). After the first crop had been harvested, few more single crystals of slightly different composition but higher crystal quality (Li(12-c-4)$_2$[**6**]) grew upon storage of the mother liquid at r.t. over a prolonged period of time (Table 2).

Table 1. Selected Crystallographic Data for 3 and [3]BF$_4$

compound	**3**	[**3**]BF$_4$
formula	C$_{22}$H$_{17}$BFe	C$_{22}$H$_{17}$B$_2$F$_4$Fe
fw	348.02	434.83
color, shape	red, plate	dark violet, rod
temperature (K)	173(2)	173(2)
radiation	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å
crystal system	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*c*
a (Å)	28.7036(16)	9.7741(12)
b (Å)	11.0886(5)	7.6859(12)
c (Å)	23.9109(15)	25.183(3)
α (°)	90	90
β (°)	120.345(3)	92.787(10)
γ (°)	90	90
V (Å^3)	6567.8(6)	1889.5(4)
Z	16	4
$D_{calcd.}$ (g cm^{-3})	1.408	1.529
F(000)	2880	884
μ (mm^{-1})	0.916	0.841
crystal size (mm^3)	0.27 × 0.26 × 0.12	0.21 × 0.13 × 0.12
no. of rflns collected	40259	15954
no. of indep rflns (R_{int})	6160 (0.0801)	3543 (0.1276)
data/restraints/parameters	6160/0/433	3543/0/263
GOOF on F^2	0.988	0.853
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.0367, 0.0763	0.0866, 0.2076
*R*1, *wR*2 (all data)	0.0562, 0.0818	0.1679, 0.2516
largest diff peak and hole (eÅ^{-3})	0.222, −0.423	0.695, −0.388

The ^{11}B NMR spectrum of compound **3** is characterized by one broad signal at 53.0 ppm. Compared to 9-phenyl-9-

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(56) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257–1264.

(57) Romero, P. E.; Piers, W. E.; Decker, S. A.; Chau, D.; Woo, T. K.; Parvez, M. *Organometallics* **2003**, *22*, 1266–1274.

(58) Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121–3124.

(59) Narula, C. K.; Nöth, H. *J. Organomet. Chem.* **1985**, *281*, 131–134.

(60) Fish, R. W.; Rosenblum, M. *J. Org. Chem.* **1965**, *30*, 1253–1254.

(61) Gross, U.; Kaufmann, D. *Chem. Ber.* **1987**, *120*, 991–994.

(62) Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127–136.

(63) Butler, I. R.; Cullen, W. R.; Ni, J.; Rettig, S. J. *Organometallics* **1985**, *4*, 2196–2201.

Table 2. Selected Crystallographic Data for 4 and Li(12-c-4)$_2$[6]

compound	**4**	Li(12-c-4)$_2$[**6**]
formula	$C_{27}H_{22}BFeNO$	$C_{70}H_{74}B_2Fe_3LiO_8$
fw	443.12	1239.40
color, shape	orange, plate	orange, plate
temperature (K)	173(2)	173(2)
radiation	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	12.4839(7)	8.8567(9)
b (Å)	11.3114(4)	12.9851(18)
c (Å)	15.0039(7)	13.5310(14)
α (°)	90	78.523(10)
β (°)	97.820(4)	80.930(8)
γ (°)	90	82.496(10)
V (Å^3)	2099.00(17)	1498.0(3)
Z	4	1
$D_{\text{calcd.}}$ (g cm^{-3})	1.402	1.374
F(000)	920	649
μ (mm^{-1})	0.738	0.774
crystal size (mm^3)	0.26 × 0.23 × 0.12	0.22 × 0.17 × 0.03
no. of rflns collected	43212	14570
no. of indep rflns (R_{int})	4831 (0.0564)	5583 (0.0974)
data/restraints/parameters	4831/0/281	5583/6/490
GOOF on F^2	1.031	0.945
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0306, 0.0753	0.0575, 0.1008
$R1$, $wR2$ (all data)	0.0387, 0.0782	0.1192, 0.1199
largest diff peak and hole (eÅ^{-3})	0.337, −0.343	0.307, −0.363

borafluorene ($\delta(^{11}B) = 64.5$),[57] the resonance of **3** is shifted to higher field by 11.5 ppm which can be taken as an indication for an Fe−B interaction in the latter molecule. The ^{11}B NMR signal of the pyridine-*N*-oxide adduct **4** possesses a chemical shift value of 12.7 ppm, testifying to the presence of tetracoordinated boron nuclei.[64]

In the ^{1}H NMR spectrum, the free Lewis acid **3** gives rise to three ferrocenyl signals (3.77 ppm, 4.57 ppm, 4.73 ppm) and four resonances for the 9-borafluorenyl substituent (two virtual triplets of doublets at 7.10 ppm and 7.21 ppm; two doublets of virtual triplets at 7.45 ppm and 7.69 ppm). The corresponding integral ratios are in accord with the proposed molecular structure of **3** (Scheme 1). Coordination of pyridine-*N*-oxide in **4** does not have a major effect on the signal pattern in the ferrocenyl part of the proton spectrum ($\delta(^1H) = 3.88$, 4.41, 4.69). The resonances of the 9-borafluorenyl group, however, exhibit less well-defined line shapes than in **3** and appear as complex multiplets. Signals for the ortho, meta, and para protons of the pyridine-*N*-oxide moiety are observed at 7.51 ppm, 5.69 ppm, and 5.96 ppm, respectively. A ratio ferrocenyl/9-borafluorenyl/pyridine-*N*-oxide of 1:1:1 is confirmed by the corresponding integral values.

The ^{13}C NMR spectrum of **3** reveals the expected number of signals in shift ranges typical of ferrocenyl derivatives on one hand and 9-borafluorenyl moieties on the other. A meaningful ^{13}C NMR spectrum of **4** was not obtained because the signals are broadened and the compound decomposes to a significant extent during the long time span required to obtain a decent signal-to-noise ratio.

X-ray Crystal Structure Determinations. 9-Ferrocenyl-9-borafluorene **3** crystallizes from hexane with two crystallographically independent molecules in the asymmetric unit (**3$_A$**, **3$_B$**). Since most of the key structural parameters of the two molecules are the same within the experimental error margins, only **3$_A$** will be described here (Figure 2).

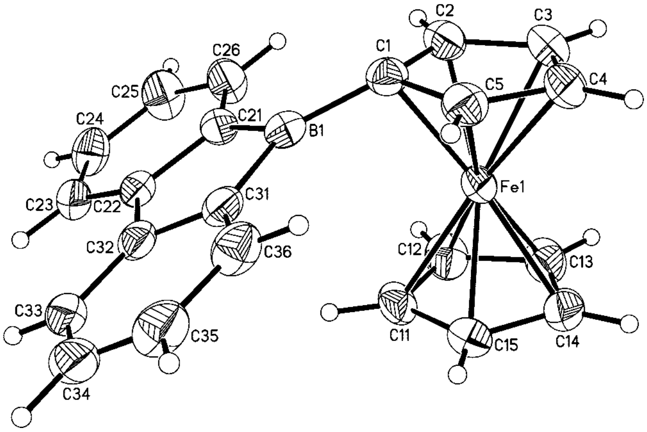

Figure 2. Structure of **3$_A$** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): B(1)−C(1) = 1.528(4), B(1)−C(21) = 1.592(4), B(1)−C(31) = 1.593(4), C(1)−C(2) = 1.459(4), C(1)−C(5) = 1.457(3), C(2)−C(3) = 1.422(4), C(3)−C(4) = 1.425(4), C(4)−C(5) = 1.419(4); C(1)−B(1)−C(21) = 128.9(2), C(1)−B(1)−C(31) = 128.1(2), C(21)−B(1)−C(31) = 103.0(2), α^* = 25.5 (**3$_B$**: 17.1).

As is to be expected, **3$_A$** contains a boron atom in a trigonal-planar environment (sum of angles about B(1) = 360°). The bond angle C(21)−B(1)−C(31), which is part of the planar five-membered ring, is contracted to a value of 103.0(2)° whereas the other two angles are expanded to 128.1(2)° and 128.9(2)°. An interesting pattern becomes apparent upon inspection of the bond lengths within the $C_5H_4-BC_2$ fragment of **3$_A$**: (i) Compared to the endocyclic B−C bonds (B(1)−C(21) = 1.592(4) Å, B(1)−C(31) = 1.593(4) Å), the exocyclic B-Cp bond (B(1)−C(1) = 1.528(4) Å) is shorter by about 0.065 Å. Importantly, no such effect is visible in the molecular structure of the related iron-free compound 9-phenyl-9-borafluorene (B−Ph = 1.577(10) Å; endocyclic B−C = 1.573(13) Å, 1.606(12) Å; see Supporting Information). (ii) Pronouncedly different bond lengths are also obvious in the cyclopentadienyl ring of **3$_A$**, the longer bonds being C(1)−C(2) = 1.459(4) Å and C(1)−C(5) = 1.457(3) Å, the shorter ones being C(2)−C(3) = 1.422(4) Å, C(3)−C(4) = 1.425(4) Å, and C(4)−C(5) = 1.419(4) Å (the bond length alternation in the unsubstituted Cp-ring is considerably smaller: 1.433(4)−1.415(4) Å). These structural features point toward some borafulvene character of the $C_5H_4-BC_2$ fragment in **3$_A$**, as it has already been reported for dibromoborylated ferrocene[53] and cymantrene.[51,65,66]

Another striking feature of the solid-state structure of **3$_A$** is the large dip angle α^* of 25.5° (**3$_B$**: 17.1°). A comparably large value has been described by Braunschweig et al. for the related ferrocenylborole $FcBC_4Ph_4$ ($\alpha^* = 29.4°$) and was attributed to a strong Fe−B interaction.[67]

We therefore come to the conclusion that the electron-deficient boron center of **3$_A$** simultaneously uses two pathways to gain additional charge density: p-π-conjugation with the cyclopentadienyl ring and a σ-type interaction with the iron atom.

The crystal structure analysis of the ferricinium species [**3**]BF$_4$ reveals a small dip angle α^* of only 6.3° (Figures 3 and 4).

The huge decrease in α^* (19.2° vs **3$_A$**, 10.8° vs **3$_B$**) upon iron oxidation provides important evidence for a direct Fe−B

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(64) Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR Basic Principles and Progress. Springer: Berlin, 1978.

(65) Braunschweig, H.; Kraft, M.; Schwarz, S.; Seeler, F.; Stellwag, S. *Inorg. Chem.* **2006**, *45*, 5275–5277.

(66) Kunz, K.; Vitze, H.; Bolte, M.; Lerner, H.-W.; Wagner, M. *Organometallics* **2007**, *26*, 4663–4672.

(67) Braunschweig, H.; Fernández, I.; Frenking, G.; Kupfer, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 1951–1954.

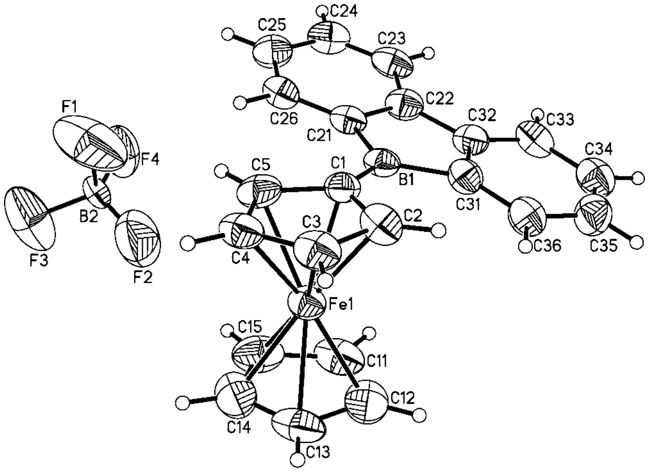

Figure 3. Structure of [**3**]BF$_4$ in the crystal. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and bond angles (°): B(1)−C(1) = 1.557(14), B(1)−C(21) = 1.544(16), B(1)−C(31) = 1.570(15); C(1)−B(1)−C(21) = 128.3(9), C(1)−B(1)−C(31) = 125.9(10), C(21)−B(1)−C(31) = 105.7(8), α* = 6.3.

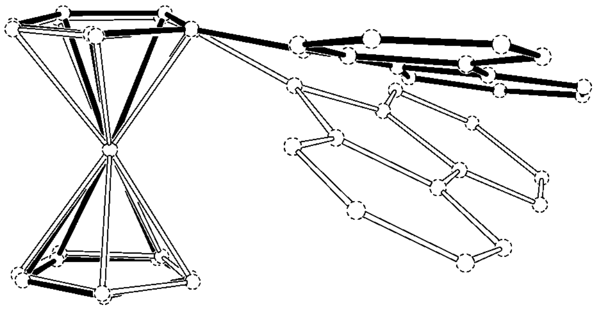

Figure 4. Decrease in the dip angle upon oxidation of the ferrocenyl derivative $\mathbf{3_A}$ (white color; α* = 25.5°) to its ferricinium state [**3**]BF$_4$ (black color, counterion omitted for clarity; α* = 6.3°).

interaction in ferrocenylboranes and is in pleasingly good agreement with our theoretical predictions.[54] As to be expected, the distance between the centroids of the two cyclopentadienyl rings in [**3**]BF$_4$ (3.395 Å) is elongated as compared to the Fe^{II} spezies $\mathbf{3_A}$ and $\mathbf{3_B}$ (3.316 Å, 3.315 Å). It is worth emphasizing that the tetrafluoroborate counterion remained intact and that no fluoride ion has been abstracted (shortest distance between [BF$_4$]$^-$ and the borafluorene boron atom: 4.299 Å). This is in contrast to observations of Piers et al. who oxidized the ferrocenylborane FcB(C$_6$F$_5$)$_2$ with [NO][BF$_4$] and isolated the zwitterionic fluoride adduct FcB(F)(C$_6$F$_5$)$_2$.[68]

Compound **4** represents the first structurally characterized adduct between pyridine-*N*-oxide and a triorganylborane (Figure 5). The fact that **4** is sufficiently long-lived to allow its isolation indicates a high inherent stability of the Lewis acid **3**, because amine oxides are commonly employed for the oxidative transformation of organoboranes into alkoxyboranes.[69]

Similar to other adducts of ferrocenylboranes,[54] C$_5$H$_4$−BC$_2$ bending is no longer observed in **4**. Compared to the free 9-ferrocenyl-9-borafluorene **3**, all B−C bonds become longer as the boron atom changes from the *sp*^{2}- to the *sp*^{3}-hybridized state. More importantly, the differences between the length of the B-Cp bond on one hand and the endocyclic B−C distances on the other almost vanish upon adduct formation (**4**: B(1)−C(1) = 1.611(2) Å, B(1)−C(21) = 1.635(2) Å, B(1)−C(31) = 1.635(2) Å). The same is true for the bond length alternation in the C$_5$H$_4$-ring of **3** which has largely leveled out in **4** (range of C−C bond lengths: 1.440(2)−1.424(2) Å). The bond lengths along the B−O−N pathway amount to B(1)−O(1) = 1.561(2) Å and O(1)−N(41) = 1.373(2) Å. For the closest structurally characterized relative of **4**, 4-cyclohexyl-6-methyl-2,2-diphenyl-1,3-dioxa-3*a*-azonia-2-borataindane, a compound consisting of a BPh$_2$-moiety and a chelating 2-oxypyridine-*N*-oxide derivative, corresponding bond lengths of B−O = 1.559(4) Å and O−N= 1.385(3) Å have been reported.[70]

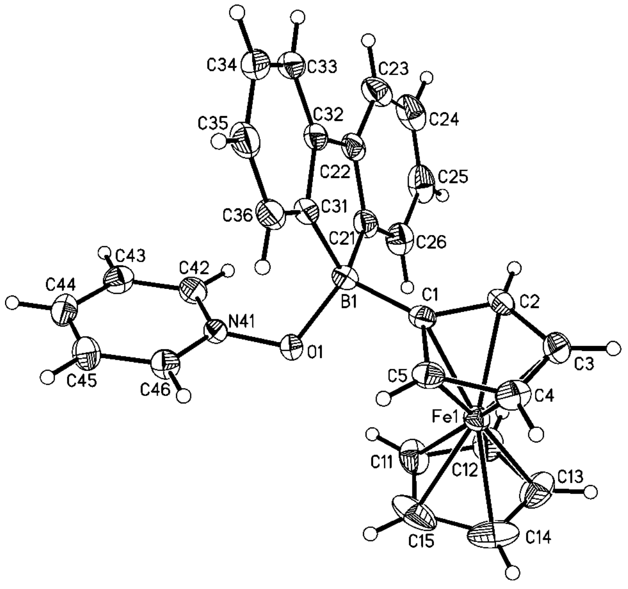

Figure 5. Structure of **4** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (°), and dihedral angles (°): B(1)−C(1) = 1.611(2), B(1)−C(21) = 1.635(2), B(1)−C(31) = 1.635(2), B(1)−O(1) = 1.561(2), O(1)−N(41) = 1.373(2); O(1)−B(1)−C(1) = 103.6(1), O(1)−B(1)−C(21) = 117.0(1), O(1)−B(1)−C(31) = 113.5(1), C(1)−B(1)−C(21) = 111.5(1), C(1)−B(1)−C(31) = 112.4(1), C(21)−B(1)−C(31) = 99.3(1); Cp(1)//pyridine = 7.9; Cp(1): cyclopentadienyl ring containing the carbon atom C(1).

The crystal lattice of compound Li(12-c-4)$_2$[**6**] includes centrosymmetric, trinuclear boron-bridged ferrocene aggregates (Figure 6). Charge neutrality is maintained by Li$^+$ ions, each of them coordinated to two crown ether molecules.

The ratio between these Li$^+$ ions and the oligoferrocene moieties is 1:1. This leads to the conclusion that each [Fc-BR′$_2$-fc-BR′$_2$-Fc] unit is carrying an overall uninegative charge, which in turn points toward a mixed-valent Fe$^{II}_2$Fe^{III} oxidation state (HBR′$_2$: 9-borafluorene). It is important to note in this context that the central ferrocenylene fragment shows a rather long distance between its cyclopentadienyl rings (COG(1)···COG(1A) = 3.427 Å), whereas in the terminal ferrocenyl groups the ligands are closer together (COG(11)···COG(21) = 3.318 Å; COG(X): centroid of the cyclopentadienyl ring containing the carbon atom C(X)). The first value is typical of ferricinium derivatives (Fe^{III}), the latter of ferrocenes containing an Fe^{II} ion.[25] On the basis of these structural data, we can not only confirm the overall charge of [**6**]$^-$ but also localize the site of oxidation (i.e., Fe(1)). Given that the central ferrocenylene

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(68) Carpenter, B. E; Piers, W. E.; Parvez, M.; Yap, G. P. A.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 857–867.

(69) (a) Köster, R.; Morita, Y. *Angew. Chem., Int. Ed.* **1966**, *5*, 580. (b) Köster, R.; Morita, Y. *Liebigs Ann. Chem.* **1967**, *704*, 70–90.

(70) Kliegel, W.; Nanninga, D.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1983**, *61*, 2493–2499.

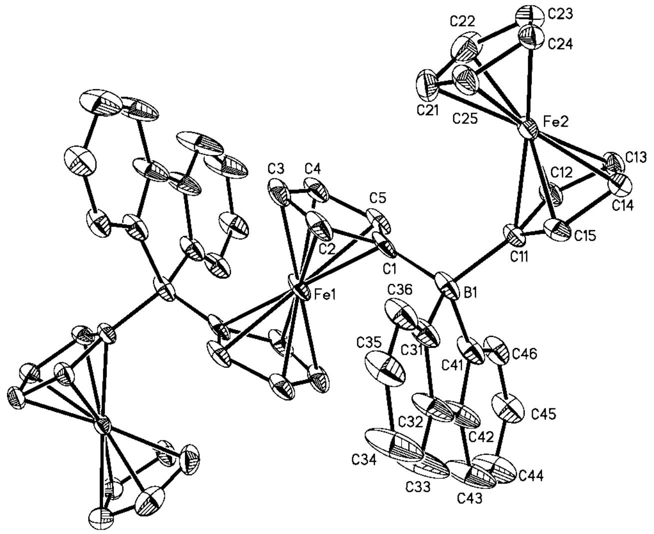

Figure 6. Structure of Li(12-c-4)$_2$[**6**] in the crystal. Displacement ellipsoids are drawn at the 30% probability level. H atoms and Li(12-crown-4)$_2^+$ ion omitted for clarity. Selected bond lengths (Å) and bond angles (°): B(1)−C(1) = 1.605(8), B(1)−C(11) = 1.623(5), B(1)−C(31) = 1.639(7), B(1)−C(41) = 1.651(7), COG(1)···COG(1A) = 3.427, COG(11)···COG(21) = 3.318; C(1)−B(1)−C(11) = 112.0(4), C(31)−B(1)−C(41) = 97.8(4); COG(X): centroid of the cyclopentadienyl ring containing the carbon atom C(X). Symmetry transformations used to generate equivalent atoms: *A*: −*x*, −*y*, −*z*.

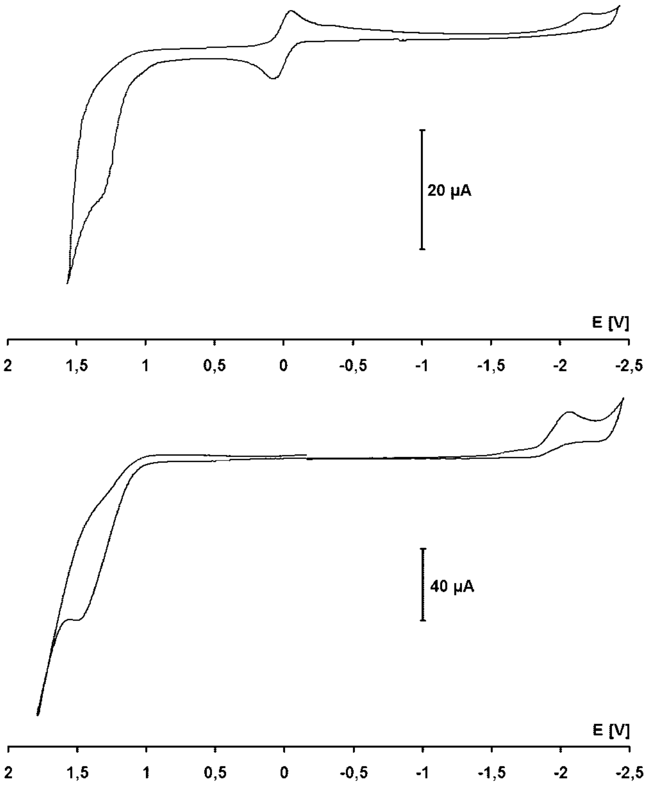

Figure 7. Cyclic voltammograms of **3** (top) and 9-phenyl-9-borafluorene (PhBC$_{12}$H$_8$; bottom). Both measurements were carried out in CH$_2$Cl$_2$ solutions at a scan rate of 0.1 V/s with [NBu$_4$][PF$_6$] (0.1 M) as supporting electrolyte. Decamethylferrocene (**3**) and ferrocene (PhBC$_{12}$H$_8$) were used as internal standards; the voltammograms are referenced against the FcH/FcH$^+$ couple.

moiety bears two borate substituents as opposed to a terminal ferrocenyl unit, which possesses only one such substituent, the preferred oxidation of Fe(1) and the apparently valence-trapped state of [**6**]$^-$ are plausible already on electrostatic grounds.

Electrochemical Investigations. Cyclic voltammetric experiments were run on the compounds **3**, PhBC$_{12}$H$_8$, and Li(12-c-4)(THF)[**6**]; the corresponding redox potentials are referenced against the FcH/FcH$^+$ couple.

The ferrocene derivative **3** shows an Fe^{II}/Fe^{III} transition at $E_{1/2}$ = 0.01 V (ΔE = 127 mV; Figure 7, top) that complies with the following criteria for electrochemical reversibility: the current ratio (i_{pc}/i_{pa}) is constantly equal to one, the current function $i_{pa}/\nu^{1/2}$ remains constant and the peak-to-peak separation (ΔE) does not deviate appreciably from the value found for the internal ferrocene or decamethylferrocene standard (theoretically expected value for a chemically and electrochemically reversible one-electron step: ΔE = 59 mV).

The redox potential of **3** is almost identical to that of parent ferrocene which may be due to the fact that boryl substituents are not only π-acceptors (which should evoke an anodic shift of the Fe^{II}/Fe^{III} transition) but also σ-donors (which is supposed to cause a cathodic shift). In addition to the reversible ferrocene-centered redox event we also observe two irreversible electron transitions with peak potentials of E_{pa} = 1.35 V and E_{pc} = −2.19 V. Since the ferrocene-free congener PhBC$_{12}$H$_8$ also undergoes an oxidation process at E_{pa} = 1.51 V and a reduction process at E_{pc} = −2.06 V (both of them irreversible) we confidently attribute the irreversible transitions in the cyclic voltammogram of **3** to electrochemically noninnocent behavior of the 9-borafluorenyl substituent.

The cyclic voltammogram of the trinuclear anion of Li(12-c-4)(THF)[**6**] is characterized by two reversible redox waves at $E_{1/2}$ = −0.45 V (two-electron transition) and $E_{1/2}$ = −1.15 V (one-electron transition). Considering the symmetry of the molecule as well as the number of negatively charged borate substituents at each of the individual ferrocene units of [**6**]$^-$, the two transitions are assigned to redox events at the ferrocenyl end-groups and the central ferrocenylene bridge, respectively. The fact that the Fe^{II}/Fe^{III} redox potential of the central iron ion is much more cathodically shifted than that of the two terminal iron centers agrees nicely with the X-ray crystal structure analysis of Li(12-c-4)$_2$[**6**] which already pointed toward an oxidation state of +III for Fe(1) (Figure 6). We note in passing that the Fe$^{II}_2$Fe^{III}- state of Li(12-c-4)(THF)[**6**] has also been confirmed by linear sweep voltammetry (LSV).

Conclusion

The aim of the work outlined in this paper was to develop a stable redox-switchable Lewis acid showing pronounced intramolecular Fe−B bonding. We found that the compound 9-ferrocenyl-9-borafluorene (**3**) meets these conditions to a large extent. The 9-borafluorenyl substituent is not only chemically robust but for the following reasons confers a high degree of Lewis acidity to the molecule: (i) 9-Borafluorenes contain a formally antiaromatic borole subunit that is destabilized as a result of π electron delocalization via the empty boron p-orbital. This provides an additional driving force for boron-donor adduct formation because cyclic π conjugation is disrupted upon boron tetra-coordination. (ii) The endocyclic C−B−C angle in 9-borafluorene derivatives is fixed to a value of about 103° which fits much better to the geometry of a tetrahedral adduct (ideal angle = 109°) than to the angle of 120° required for an unstrained free borane. Moreover, the flat structure of the 9-borafluorene disk makes adduct formation also kinetically favorable.

Applications of **3**-type compounds can be envisaged in the areas of anion sensors and ferrocene-containing polymers. We are therefore currently developing an efficient protocol for the synthesis of the disubstituted congener 1,1′-fc$(BC_{12}H_8)_2$ and we will employ it for the preparation of 9-borafluorenyl-bridged poly(ferrocenylene) macromolecules via B−C adduct formation.

Experimental Section

General Remarks. All reactions were carried out under a nitrogen atmosphere using Schlenk tube techniques. Solvents were freshly distilled under argon from Na/benzophenone (THF, C_6D_6), Na/Pb alloy (hexane) or CaH_2 (CH_2Cl_2, $CHCl_3$) prior to use. NMR: Bruker AM 250, AMX 300, and AMX 400. Chemical shifts are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external $BF_3 \cdot Et_2O$ (^{11}B{^{1}H}). Abbreviations: s = singlet, d = doublet, tr = triplet, vtr = virtual triplet, mult = multiplet, br = broad, *o* = ortho, *m* = meta, *p* = para, Ar = 9-borafluorenyl, Py = pyridine-*N*-oxide; the numbering scheme for the 9-borafluorenyl substituents is given in Scheme 1. All NMR spectra were run at r.t. Electrochemical measurements: Potentiostat EG&G Princeton Applied Research 263 A. Compounds $BrBC_{12}H_8$ (**2**),[61] $PhBC_{12}H_8$,[57] FcHgCl (**1**),[60] and 1,1′-fcLi_2 × 2/3 tmeda (**5**)[62] were synthesized according to literature procedures.

Synthesis of 3. A solution of **2** (0.10 g, 0.42 mmol) in hexane (10 mL) was added dropwise with stirring at −78 °C to a suspension of **1** (0.18 g, 0.42 mmol) in hexane (15 mL). The reaction mixture was slowly warmed to r.t. and stirred overnight, whereupon a gray solid precipitated. After filtration, the filtrate was evaporated to a volume of 8 mL and stored at −35 °C. Single crystals of **3** formed within 12 h. Yield: 0.11 g (75%). ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 53.0 (br). ^{1}H NMR (400.1 MHz, C_6D_6): δ 3.77 (s, 5H, C_5H_5), 4.57, 4.73 (2 × vtr, 2 × 2H, $^3J_{HH} = {}^4J_{HH} = 1.8$ Hz, C_5H_4), 7.10, 7.21 (2 × vtr d, 2 × 2H, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.2$ Hz, ArH-*b*,*c*), 7.45, 7.69 (2 × d vtr, 2 × 2H, $^3J_{HH} = 7.2$, 6.8 Hz, ArH-*a*,*d*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ 70.4 (C_5H_5), 76.9, 77.2 (C_5H_4), 120.1 (ArC-*a* or *d*), 128.3, 132.1 (ArC-*b*,*c*), 133.5 (ArC-*a* or *d*), 153.5 (ArC-*e*). Anal. calcd for $C_{22}H_{17}BFe$ [348.02]: C, 75.93; H, 4.92. Found: C, 75.65; H, 5.08.

Synthesis of [3]BF$_4$. CH_2Cl_2 (10 mL) was added to a solid mixture of **3** (0.06 g, 0.17 mmol) and $AgBF_4$ (0.03 g, 0.17 mmol). The resulting solution was stirred for 90 min at −35 °C, allowed to warm to r.t. and stirred for another 90 min. The resulting brown-green suspension was filtered and the filtrate evaporated to dryness in vacuo. The solid residue was dissolved in $CHCl_3$ (4 mL), carefully layered with hexane and stored at −35 °C. X-ray quality crystals of [**3**]BF_4 grew over a period of several days. Yield: 0.01 g (13%).

Synthesis of 4. CH_2Cl_2 (4 mL) was added to a solid mixture of **3** (0.10 g, 0.29 mmol) and pyridine-*N*-oxide (0.03 g, 0.30 mmol). The resulting solution was stirred for 1 h at r.t. and then stored at −35 °C. Orange single crystals of **4** were obtained after 5 d. Yield: 0.05 g (39%). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 12.7 (br). ^{1}H NMR (300.0 MHz, C_6D_6): δ 3.88 (s, 5H, C_5H_5), 4.41, 4.69 (2 × vtr, 2 × 2H, $^3J_{HH} = {}^4J_{HH} = 1.6$ Hz, C_5H_4), 5.69 (vtr, 2H, $^3J_{HH} = 7.1$ Hz, Py-*m*), 5.96 (tr, 1H, $^3J_{HH} = 7.7$ Hz, Py-*p*), 7.29 − 7.33 (mult, 4H, ArH-*b*,*c*), 7.51 (d, 2H, $^3J_{HH} = 6.5$ Hz, Py-*o*), 7.72 − 7.75, 7.80 − 7.83 (2 × mult, 2 × 2H, ArH-*a*,*d*). Anal. calcd for $C_{27}H_{22}BFeNO$ [443.12]: C, 73.18; H, 5.00; N, 3.16. Found: C, 73.25; H, 4.96; N, 3.19.

Synthesis of 6. A solution of **3** (0.10 g, 0.29 mmol) in THF (8 mL) was added dropwise with stirring to a solution of 1,1′-fcLi_2 × 2/3 tmeda (0.04 g, 0.15 mmol) in THF (12 mL) at −78 °C. The reaction mixture was slowly warmed to r.t. and stirred overnight. The volume of the mixture was reduced to 4 mL in vacuo, the concentrated solution was briefly exposed to air, and 12-crown-4 (0.19 mL) and hexane (10 mL) were added. The resulting brown precipitate was extracted with hexane (3 × 10 mL). Crystals of Li(12-c-4)(THF)[**6**] × THF were grown by gas-phase diffusion of hexane into a THF solution of Li[**6**]. Yield: 0.02 g (11%). Anal. calcd for $C_{66}H_{66}B_2Fe_3LiO_5$ [1135.29] × C_4H_8O [72.11]: C, 69.63; H, 6.18. Found: C, 69.66; H, 6.33. *Note*: The chemical composition of the sample was proven by X-ray crystallography (1 THF molecule/1 crown ether ligand per Li^+ ion; 1 equiv. of noncoordinating THF in the crystal lattice).

X-ray Crystal Structure Analysis of 3, [3]BF$_4$, 4, and Li(12-c-4)$_2$[6]. Single crystals of **3**, [**3**]BF_4, **4**, and Li(12-c-4)$_2$[**6**] were analyzed with a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo K_α radiation. Empirical absorption corrections were performed using the MULABS[71] option in PLATON.[72] The structures were solved by direct methods using the program SHELXS[73] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.[74] One of the crown ether molecules in Li(12-c-4)$_2$[**6**] is disordered over two positions about a center of inversion (occupancy factors: 0.5, 0.5). All non-hydrogen atoms were refined with anisotropic displacement parameters (only the displacement ellipsoid of C(64) was restrained to an isotropic behavior). Hydrogen atoms were refined using a riding model.

Electrochemical Measurements. All electrochemical measurements were performed employing an EG&G Princeton Applied Research 263A potentiostat with glassy carbon working electrode. Carefully dried (CaH_2) and degassed CH_2Cl_2 was used as solvent and $[NBu_4][PF_6]$ as supporting electrolyte (0.1 M). Ferrocene or decamethylferrocene were used as internal standard. All potential values are referenced against the ferrocene/ferricinium (FcH/FcH$^+$) couple.

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Supporting Information Available: New optimized synthesis of 9-methoxy-9-borafluorene. Crystallographic data of **3**, [**3**]BF_4, **4**, Li(12-c-4)$_2$[**6**], 9-methoxy-9-borafluorene, and 9-phenyl-9-borafluorene in the Crystallographic Information File format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC reference numbers: 697703 (**3**), 697705 ([**3**]BF_4), 697704 (**4**), 697707 (Li(12-c-4)$_2$[**6**]), 697996 (9-methoxy-9-borafluorene), 697706 (9-phenyl-9-borafluorene). Structure plots and key structural parameters of 9-methoxy-9-borafluorene and 9-phenyl-9-borafluorene.

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(71) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38.
(72) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
(73) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.
(74) Sheldrick, G. M. *SHELXL-97, A Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, 1997.