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1,1′-Diborylferrocenes from [2]Boraferrocenophanes by Boron–Boron Exchange

Holger Braunschweig,*[a] Bernd Grünewald,[a] Katrin Schwab,[a] and Rainer Sigritz[a]

Dedicated to Prof. Dr. Wolfdieter Schenk on the occasion of his 65th birthday

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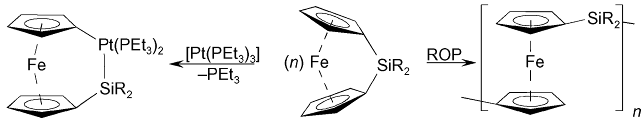
The reactivity of [2]boraferrocenophane [(η^5-C_5H_4)–$BNMe_2$–$BNMe_2$–(η^5-C_5H_4)Fe] (**3**) with borane and diborane compounds was examined, resulting in the complete loss of the –$BNMe_2$–$BNMe_2$– bridge and the concomitant formation of 1,1′-borylated ferrocenes. With this unprecedented reactivity pattern, an alternative access to this class of compounds is established.

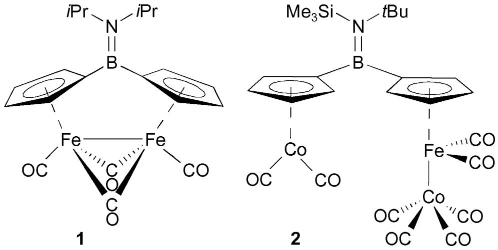
Introduction

The reactivity of *ansa*-ferrocenes, in particular that of [1]-silaferrocenophanes, is dominated by their propensity to undergo ring-opening polymerisation (ROP).[1] This process may be initiated in various ways, e.g. thermally, or by employing anionic starters or suitable transition metal catalysts. In case of the latter, the insertion of a Pt-fragment into the silicon–carbon bond was observed with formation of a [2]platinasilaferrocenophane, which is believed to serve as intermediate for transition-metal-catalysed ROP (Scheme 1).[2] In contrast, [1]stanna- and [1]silaferrocenophanes do not form polymeric compounds in the presence of various boron halides but a ring-opening addition reaction is observed. Polymerisation has been established for boron-bridged [1]ferrocenophanes as well, but only under thermal conditions.[3] The obtained polymer was completely insoluble in all common solvents and therefore not as applicable as related poly(ferrocenyl)silanes.[4]



Scheme 1. Reactivity of [1]silaferrocenophanes.

It should be noted, though, that Wagner et al. have developed a different protocol for the synthesis of well-defined poly(ferrocenyl)boranes.[5] Moreover, the reactivity of highly strained [1]boraferrocenophanes towards transition-metal carbonyls such as [$Co_2(CO)_8$] or [$Fe(CO)_5$] has been investigated, which results in the insertion of the latter into the Fe–Cp bond to yield the boron-bridged diiron compound **1** and the heterotrinuclear half-sandwich species **2**, respectively (Scheme 2).[4]



Scheme 2. Products upon reacting [1]boraferrocenophanes with [$Fe(CO)_5$] or [$Co_2(CO)_8$].

The synthesis of a [2]boraferrocenophane (**3**) was reported in 1997 by Herberhold and Wrackmeyer[6] and we contributed an alternative synthesis for this compound as well as its structural characterisation.[7] Subsequently, we extended the number of [2]bora- and [2]silametallocenophanes and -arenophanes and consequently started to investigate their reactivity. As a result, we proved the potential, particularly of the former, to readily insert low valent platinum and palladium complex fragments into the boron–boron bond by oxidative addition. This led to various metal-mediated functionalisations of azobenzene[8] and alkynes (Scheme 3),[9–11] and most notably, to the first diboration of alkynes under conditions of heterogeneous catalysis.[12]

It should be noted that [2]stannaferrocenophanes were also found to insert alkynes via homogeneous catalysis.[13]

Thus, the reactivity of [2]borametallocenophanes and related disila- and distanna-bridged metallocenes is restricted to cleavage reactions of the element–element bridge. In the

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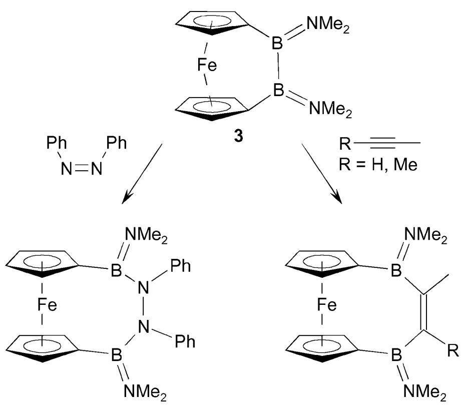
[a] Universität Würzburg, Institut für Anorganische Chemie,
Am Hubland, 97074 Würzburg, Germany
Fax: +49-931-888-4623
E-mail: h.braunschweig@uni-wuerzburg.de



Scheme 3. Metal-mediated diboration of azobenzene and alkynes in the presence of [$Pt(PEt_3)_3$] (5 mol-%).

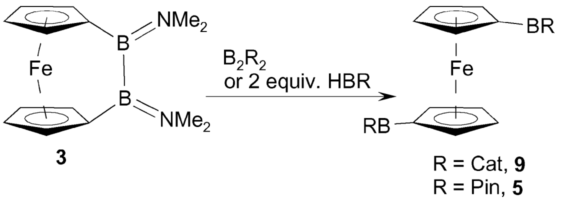
present contribution we report on the facile exchange of a dibora bridge with concomitant cleavage of the B–C_{ipso} linkage.

Results and Discussion

The starting compound **3** was dissolved in heptanes and an equimolar amount of B_2Pin_2 (**4**) in heptanes was added. The mixture was refluxed for 6 h during which the colour changed from red to orange. Monitoring the reaction by multinuclear NMR spectroscopy revealed gradual decrease of the ^{11}B NMR shifts associated with the starting materials at $\delta = 44.4$ (**3**)[6] and 30.1 ppm (**4**),[14] respectively, with concomitant build-up of a single new resonance at $\delta = 32.1$ ppm. These findings indicate the formation of one new compound with a single chemical environment for the boron atom(s). Further support is gained from the ^1H NMR spectra, which revealed two virtual triplets at $\delta = 4.31$, 4.27 ppm for the cyclopentadienyl-bound protons and a sharp singlet at $\delta = 1.25$ ppm for the methylgroups of the pinacolato substituent in a ratio of 4:4:24. Thus, the new compound was assigned as 1,1′-$Fc(BPin)_2$ (**5**) and subsequently isolated in 79% yield as a moderately air and moisture sensitive orange solid. The formation of **5** was accompanied by the gradual formation of an off-white solid in significant amounts (vide infra).

As to provide further information on this unexpected and unprecedented cleavage reaction of an *exo*-boryl substituent, **3** was treated with two equiv. of HBPin (**6**) in heptanes under refluxing conditions for 2 h. Interestingly, this also results in the formation of **5** albeit in significantly lower yield of only 35%, as indicated by the aforementioned characteristic ^1H NMR and ^{11}B NMR spectroscopic data. Thus, an alternative access to **5** is provided in addition to common condensation routes[15–17] and the recently developed protocol employing **4** and various ferrocenes in the presence of a suitable Ir catalyst.[18]

Additionally, it was investigated whether this reaction is restricted to pinacolatoboranes or displays a somewhat wider applicability. To this end **3** was reacted under similar conditions with B_2Cat_2 (**7**) and HBCat (**8**) (Scheme 4). Indeed, both experiments resulted in the clean formation of 1,1′-$Fc(BCat)_2$ (**9**) as the only soluble boron-containing product as indicated by a ^{11}B NMR signal at $\delta = 33.9$ ppm that is significantly shielded with respect to the resonance at $\delta = 44.4$ ppm of the starting material **3**. Accordingly, the ^1H NMR spectra exhibit two multiplets at $\delta = 7.02$–6.94, 6.83–6.75 ppm for the catecholato groups, and two virtual triplets at $\delta = 4.67$, 4.15 ppm for the substituted cyclopentadienyl ligands in equal intensities. Interestingly, the reactions proceed with yields comparable to those observed for **4** and **6**, respectively. Thus, the diborane(4) B_2Cat_2 (**7**) provided the diborylated species **9** in much higher yield (76%) than the corresponding borane **8** (35%). Likewise, the synthesis of **9** from **7** was accompanied by the formation of an off-white solid as observed before for the corresponding reaction with **4**. It should be noted that all volatiles obtained from the reactions of **3** with **4** and **7** were collected and examined by ^1H and ^{11}B NMR spectroscopy. In both cases, the corresponding samples were devoid of any resonances indicating the presence of $(Me_2N)B$ groups. Thus, it appears well justified to assume that the aforementioned off-white solid obtained from these reactions consists of the remainder of the former –$(Me_2N)B$–$B(NMe_2)$– bridge. While the presence of a hypovalent oligomeric species of the type $[(Me_2N)B]_n$ seems plausible, the solid residue proved intractable in all common solvents, thus precluding its characterization by NMR methods. Besides, elemental analyses of the washed and dried residues proved the presence of C, H and N, but not in a ratio that agrees with the simple formula BNC_2H_6.



Scheme 4. The reaction of **3** with boranes **6**, **8** and diboranes **4**, **7**.

While spectroscopic data for boronic acids of the type 1,1′-$Fc\{B(OR)_2\}_2$, and particularly **5** (vide supra), have been reported before, the structure of the title compounds in the crystal has not been solved as yet. As to confirm the constitution of **5** and **9** in the solid state, single crystals, suitable for X-ray diffraction were grown from hexanes or benzene for both complexes at room temperature. **5** crystallises as orange plates in the monoclinic space group $P2_1/n$, **9** as red blocks in the triclinic space group $P\bar{1}$ (Figure 1). Selected distances and angles are shown in Table 1. The starting compound **3** is moderately strained as indicated by a tilt angle α of 12.82° and the reaction results for both compounds in a noticeable release of ring strain which is displayed by an almost parallel orientation of the two borylated cyclopentadienyl rings with corresponding interplanar angles of 2.14° (**5**) and 3.80° (**9**). Additionally the angle between the centroids of the cyclopentadienyl rings is enlarged from 170.1° (**3**) to 176.3° (**9**) and 179.3° (**5**).

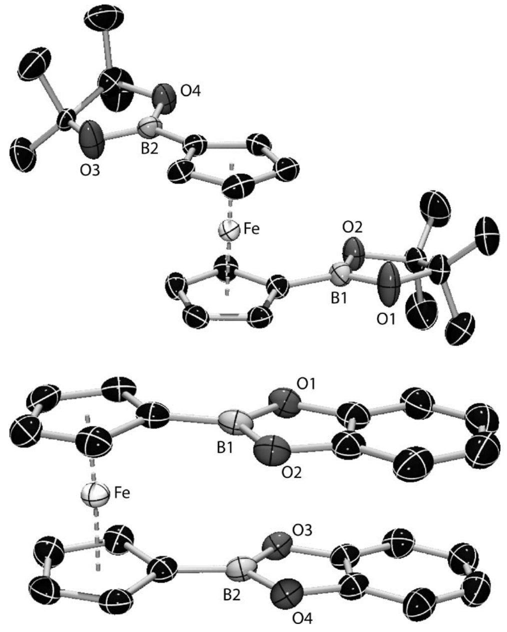


Figure 1. Structure of **5** (top) and **9** (bottom) in the crystal (ellipsoids at 50% probability). Hydrogen atoms were omitted for clarity.

Table 1. Selected bond lengths, distances [Å] and angles of **5** and **9**.

	5	**9**		**5**	**9**
B–O	1.358(2) 1.368(2) 1.368(2) 1.358(2)	1.393(2) 1.393(2) 1.392(2) 1.395(2)	α	2.14°	3.80°
B–C	1.546(2) 1.549(2)	1.521(3) 1.521(3)	δ	179.32°	176.29°
B–Fe	3.176 3.169	3.222 3.130	tors	113.02°	9.59°

α = tilt angle, δ = $Cp_{centroid}$–Fe–$Cp'_{centroid}$, tors = B–$Cp_{centroid}$–$Cp'_{centroid}$–B′

The boryl groups in **9** adopt an eclipsed disposition in contrast to those of **5**, which are staggered – most likely a result of different steric hindrance. The Fe–B distances amount to 3.176 and 3.169 Å and the value of the dip angles α^* is 3.14 and 3.17° for **5**. Likewise, the Fe–B distances for **9** are 3.130 and 3.222 Å with values of 0.94 and 5.15° for α^*.

Borylferrocenes have been in the focus of attention because of their particular geometric and electronic properties.[19] It is well documented that in the absence of electronic stabilization provided by π-donating substitutents, the boryl group is bent towards the iron atom. This is interpreted as an effect of attracting interactions between the empty *p*-orbital on boron and filled d-orbitals at iron, and has been thoroughly studied in a series of different borylated ferrocenes. For instance, *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$[20] as one extreme displays an angle α^* of –6.5°, thus indicating an electronically saturated boryl group devoid of any iron-to-boron interaction. The compounds $Fc(BBr_2)_n$ (*n* = 1, 2, 4)[19] or $[(\eta^5\text{-}C_5R_4)(OC)_2Fe\{B(Fc)Br\}]$ (R = H, Me)[20] as well as the title compounds **5** and **9** display corresponding values for α^* between 0.9° and 18.9° that are indicative of weak interactions. The strongest iron boron interactions as yet were reported for 9-ferrocenyl-9-borafluorene (25.5°)[21] and for the ferrocenylborole $[FcBC_4Ph_4]$ (29.4°).[22]

Conclusions

Treatment of $[(\eta^5\text{-}C_5H_4)\text{–}BNMe_2\text{–}BNMe_2\text{–}(\eta^5\text{-}C_5H_4)Fe]$ (**3**) with borane and diborane compounds resulted in the clean formation of 1,1′-$Fc(BPin)_2$ (**5**) and 1,1′-$Fc(BCat)_2$ (**9**), respectively with unexpected degradation of the –$BNMe_2$–$BNMe_2$– bridge. This reaction establishes an alternative access to 1,1′-bisborylated ferrocenes and represents the first example for a B–C_{ipso} bond cleavage reaction observed for borametallocenophanes.

Experimental Section

General: All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glove box. Solvents were dried according to standard procedures, freshly distilled prior to use, degassed and stored under argon over activated molecular sieves. Deuterated solvents were distilled from potassium. The starting material $[(\eta^5\text{-}C_5H_4)\text{–}B(NMe_2)\text{–}B(NMe_2)\text{–}(\eta^5\text{-}C_5H_4)Fe]$ (**3**), was prepared according to published methods.[6,7] Bis(catecholato)diborane(4) = B_2Cat_2 (**7**), bis(pinacolato)dibor-

Table 2. Selected crystallograpic data for **5** and **9**.

Compound	**5**	**9**
Empirical formula	$C_{22}H_{32}B_2FeO_4$	$C_{22}H_{16}B_2FeO_4 \cdot C_6H_6$
Formula weight [g mol^{-1}]	437.96	421.83
Temperature [K]	167(2)	167(2)
Mo-K_α radiation, λ [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a /Å	12.257(9)	7.7352(9)
b /Å	9.891(7)	11.3102(13)
c /Å	18.899(14)	13.9267(16)
α /°	90.00	75.703(2)
β /°	90.119(10)	88.312(2)
γ /°	90.00	75.419(2)
Volume [Å^3]	2291(3)	1141.9(2)
Z	4	2
Calculated density [Mg m^{-3}]	1.270	1.454
Absorption coefficient [mm^{-1}]	0.682	0.695
F(000)	928	516
Theta range for collection	1.98–28.38°	2.13–28.31°
Reflections collected	58823	30323
Independent reflections	5697	5671
Min. / max. transmission	0.6006759 / 0.953	0.63388 / 0.920
Refinement method	full-matrix least-squares on F^2	
Data / parameters / restraints	5697 / 378 / 0	5671 / 316 / 0
Goodness-of-fit on F^2	1.059	1.145
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0356 wR_2 = 0.0905	R_1 = 0.0415 wR_2 = 0.1071
R indices (all data)	R_1 = 0.0424 wR_2 = 0.0956	R_1 = 0.0431 wR_2 = 0.1084
Max. / min. residual electron density [e Å^{-3}]	0.345 / –0.193	1.304 / –0.302

ane(4) = B_2Pin_2 (**4**), catecholborane = HBCat (**8**) and pinacolborane = HBPin (**6**) were purchased and purified by sublimation or distillation, respectively. The NMR spectra were recorded on a Bruker AV 500 (^{1}H, 500.13 MHz; ^{11}B, 160.46 MHz; ^{13}C, 125.75 MHz) FT-NMR spectrometer. Elemental analyses were performed on a vario micro cube elemental analyzer. The crystal structure data were collected at a Bruker D8 diffractometer with an APEX CCD area detector and graphite monochromated Mo-K_α radiation. The structures were solved by direct methods, refined with the Shelx software package[23] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations (Table 2).

1,1′-Fc(BPin)$_2$ (5): A red solution of 63 mg (0.21 mmol) of **3** in heptane (5 mL) was added to a colourless solution of 55 mg (0.21 mmol) of **6** in heptane (5 mL) and the mixture was refluxed for ca. 2 h. All volatile compounds were removed in vacuo, the orange precipitate was extracted into hexane and insoluble material removed by filtration through Celite. After removal of the solvent in vacuo, 25 mg (35%) of an orange solid was obtained. Crystals suitable for X-ray diffraction were grown in a concentrated hexane solution at 20 °C. ^{1}H NMR ($CDCl_3$): δ = 4.31 (pseudo-t, 4 H, C_5H_4), 4.27 (pseudo-t, 4 H, C_5H_4), 1.25 (s, 24 H, CH_3) ppm. ^{11}B NMR ($CDCl_3$): δ = 32.1 ppm. ^{13}C NMR ($CDCl_3$): δ = 83.4, 74.2, 72.7, 25.1 ppm.

Alternatively, 31 mg (0.11 mmol) of **3** in heptane (5 mL) and 27 mg (0.11 mmol) of **4** in heptane (5 mL) were mixed and allowed to reflux for 6 h. All volatile compounds were removed in vacuo, and the product was extracted with hexane out of the suspension; yield 36 mg (79%).

1,1′-Fc(BCat)$_2$ (9): A red solution of 50 mg (0.17 mmol) of **3** in heptane (5 mL) was added to a colourless suspension of 40 mg (0.34 mmol) **8** in heptane (5 mL) and the mixture was refluxed for ca. 2 h. All volatile compounds were removed in vacuo, the orange precipitate was extracted into hexane and the insoluble material removed by filtration through Celite. After removal of the solvent in vacuo, 25 mg (35%) of an orange solid was obtained.

Alternatively, 20 mg (0.07 mmol) of **3** in heptane (5 mL) and 16 mg (0.07 mmol) **7** in heptane (5 mL) were mixed and allowed to reflux for 6 h. All volatile compounds were removed in vacuo, and the product was extracted with hexane out of the suspension; yield 22 mg (76%). Crystals suitable for X-ray diffraction were grown in a concentrated benzene solution at 20 °C. ^{1}H NMR (C_6D_6): δ = 7.02–6.94 (m, 4 H, C_6H_4), 6.83–6.75 (m, 4 H, C_6H_4), 4.67 (pseudo-t, 4 H, C_5H_4), 4.15 (pseudo-t, 4 H, C_5H_4) ppm. ^{11}B NMR (C_6D_6): δ = 33.9 ppm. ^{13}C NMR (C_6D_6): δ = 149.1, 122.7, 112.5, 74.9, 73.8 ppm. $C_{22}H_{16}B_2FeO_4$ (421.83): calcd. C 62.64, H 3.82; found C 62.21, H 3.90.

CCDC-737851 (for **5**) and -737852 (for **9**) 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.

Acknowledgments

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