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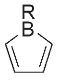
Boron Ligands

Synthesis and Electronic Structure of a Ferroborirene

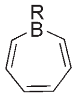
Holger Braunschweig, Israel Fernández, Gernot Frenking,* Krzysztof Radacki, and Fabian Seeler*

Dedicated to Professor Walter Siebert on the occasion of his 70th birthday.

Unsaturated boron-containing heterocycles such as boroles (**I**)[1] or borepines (**II**)[2] have been intensively studied, in particular with regard to the question of how the sp^2-hybridized boron center affects the π-electron delocalization in these conjugated systems.



I



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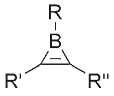

III

Experimental studies on derivatives of **I** and **II** revealed electronic interaction between the π electrons of the carbon backbone with the empty p$_z$ orbital of the boron atom.[1,3] As a consequence of extended π conjugation across the boron center, substituted, electron-rich boroles have already attracted interest owing to their potentially useful photophysical and electrochemical properties.[4]

Although delocalization of π electrons in boroles and borepines was demonstrated, the degree of aromatic stabilization, or antiaromatic destabilization in the case of of **I**, appears to be less pronounced than in the respective carbon analogues, that is, cyclopentadienyl- and tropylium cations.[5,6] The chemistry of **I** and **II** is well-established, in particular with respect to transition-metal complexes derived from boroles.[7] Corresponding borirenes (**III**) represent boron analogues of cyclopropenyl cations, the smallest cyclic aromatic system, and were, on the basis of earlier ab initio studies, predicted to exhibit π delocalization.[8] Presumably because of problems associated with their isolation and crystallization, however, borirenes have been scarcely investigated experimentally. Moreover, some earlier proposed syntheses were found to be difficult to reproduce.[9,10]

Recently, it was demonstrated that borylene complexes,[11] such as [(OC)$_5$Cr=B=N(SiMe$_3$)$_2$],[12] act as a facile source for elusive borylenes under ambient conditions and effectively transfer BN(SiMe$_3$)$_2$ not only to different transition metals[13] but also to alkynes, thus providing a high-yield synthesis for various *B*-amino borirenes.[14] To study the influence of the exocyclic substitutents on the properties of borirenes, it was necessary to search for borylene sources that provide an alternative substitution pattern at the boron center. Since [(OC)$_5$Cr=B−Si(SiMe$_3$)$_3$] is known to be thermally rather labile,[15] which attenuates its potential for borylene transfer reactions, we turned our attention to the metalloborylene complex [(OC)$_5$Cr=B−Fe(CO)$_2$(η^5-C$_5$Me$_5$)] (**1**).[16] Herein, we report the synthesis of a novel *B*-ferroborirene obtained by unprecedented metalloborylene transfer and the elucidation of its electronic structure by DFT methods.

Photolysis of a mixture of **1** with 1,2-bis(trimethylsilyl)-ethyne in hexane, THF, or benzene leads, as judged by ^{11}B NMR spectroscopy, to the quantitative formation of the new boron-containing compound **2** ($\delta = 63.5$ ppm) within 0.5 h. In the ^{1}H NMR spectrum, a new set of signals is present in the expected ratio for one C$_5$Me$_5$ ligand and two Me$_3$Si groups. After extraction with hexane and removal of [Cr(CO)$_6$] by crystallization, a red solution was obtained. Storage at −30 °C yielded yellow crystals of **2** suitable for X-ray structure determination.[17] The molecular structure of **2** is shown in Figure 1, and relevant bond lengths and angles are given in the caption. Analogous to the aminoborirene (Me$_3$Si)$_2$NBC$_2$(SiMe$_3$)$_2$ (**3**), compound **2** is characterized by a C-B-C three-membered ring, which results from the [B−Fe(CO)$_2$(η^5-C$_5$Me$_5$)] borylene transfer to the C−C triple bond. The B1−C3/C4 (149.0(4) and 149.3(4) pm) and C3−C4 (137.1(3) pm) bond lengths are equivalent within experimental error to those in **3**. The Fe1−B1 (197.9(3) pm) bond length is in the lower range for neutral iron half-sandwich boryl complexes (194–204 pm),[11b] which indicates a substantial degree of Fe−B d$_\pi$–p$_\pi$ back-bonding. However, the IR data of **2** (1983, 1927 cm^{-1}) are almost identical to those of the corresponding iron methyl complex (1988, 1936 cm^{-1}).[18] This similarity suggests a different bonding situation with no Fe−B d$_\pi$–p$_\pi$ interactions, probably owing to significant π delocalization in the borirene ring. An explanation for these contradictory data may be found in the high strain of the borirene ring, which is reflected by the C3-B1-C4 (54.75(16)°) and Fe1-B1-C3/C4 (152.8(2)° and 152.5(2)°) angles and results in a shorter Fe−B bond owing to low steric bulk.

To analyze the bonding situation in **2** in more detail, we carried out DFT calculations (BP86/TZ2P) of the model compound [(η^5-Cp)(OC)$_2$FeBC$_2$(SiH$_3$)$_2$] (**2M**; Cp = C$_5$H$_5$).[19]

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[*] Prof. Dr. H. Braunschweig, Dr. K. Radacki, Dipl.-Chem. F. Seeler
Institut für Anorganische Chemie
Julius-Maximilians Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de
Dr. I. Fernández, Prof. Dr. G. Frenking
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35043 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de

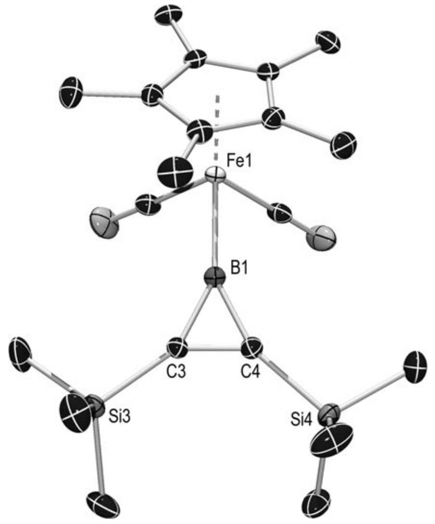


Figure 1. Molecular structure of **2**, thermal ellipsoids set at 50%, hydrogen atoms omitted for clarity. Selected bond lengths [pm] and angles [°]: Fe1-B1 197.9(3), B1-C3 149.0(4), C3-C4 137.1(3); C3-B1-C4 54.75(16), Fe1-B1-C3 152.8(2), Fe1-B1-C4 152.5(2).

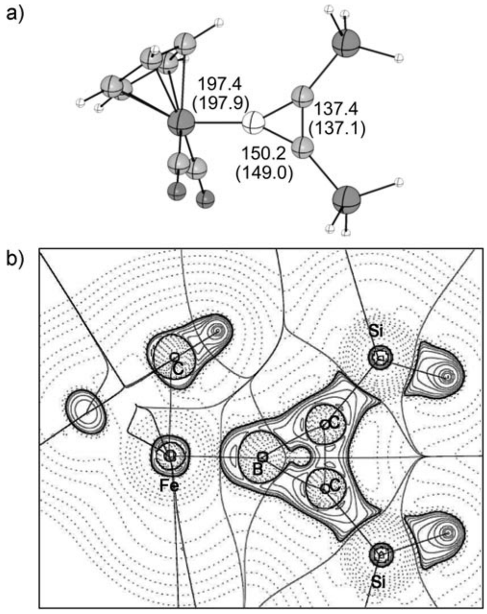


Figure 2. a) Calculated structure of **2M** and comparison of theoretical and experimental (in parentheses) bond lengths [pm]. b) Contour-line diagram $\nabla^2\rho(r)$ for **2M** in the BC_2 ring plane. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The solid lines connecting atomic nulei are bond paths. The solid lines separating atomic basins indicate zero-flux surfaces crossing the molecular planes.

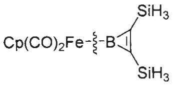
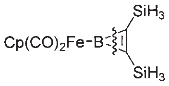
The nature of the bonding interactions of the boron atom was investigated with the AIM (atoms in molecules)[20] method and with the EDA (energy decomposition analysis) partitioning procedure,[19e,f,21] which we have used previously to investigate chemical bonds in boron compounds.[22,23]

Figure 2 shows the optimized geometry of **2M** and the contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the plane of the three-membered ring. The calculated bond lengths for **2M** are in very good agreement with the experimental values for **2**. Note that the conformation of **2M** with regard to rotation about the B–Fe bond is different from the conformation found in the experimental structure of **2**. In the latter compound, both CO ligands are on the same side of the BC_2 ring (Figure 1), while in **2M** they are on opposite sides of the ring plane. We calculated **2M** using the conformation of **2** as the starting geometry. The geometry optimization yielded a shallow minimum, which is 0.9 kcal mol^{-1} higher in energy than the structure shown in Figure 2. The calculated bond lengths of the two conformations were nearly identical, and the C–O stretching frequencies differed by less than 1 cm^{-1}. Therefore, we used the optimized structure shown in Figure 2 for the analysis of the bonding situation.

The Laplacian distribution of **2M** in the B–Fe bonding region exhibits an area of charge concentration at the boron atom ($\nabla^2\rho(r) < 0$, solid lines), which has the shape of a droplet-like appendix directed towards the iron atom, while the iron end carries an area of charge depletion ($\nabla^2\rho(r) > 0$, dashed lines). This situation is typical for a closed-shell donor–acceptor bond, which was previously found for transition-metal complexes with Group 13 diyl ligands ER (E = B–Tl).[24] Compound **2M** is clearly characterized by the AIM method as a three-membered cyclic species possessing two B–C and one C–C bond path and one BC_2 ring critical point.

More detailed information about the bonding situation at the boron atom in **2M** is given by the EDA results, which are summarized in Table 1. We analyzed the B–Fe bond using two different fragments that are in accord with an electron-sharing bond and a donor–acceptor bond, respectively. The interacting fragments for the electron-sharing bond are {(η^5-C_5H_5)(OC)$_2$Fe} and $BC_2(SiH_3)_2$ in the electronic doublet

Table 1: Results of the EDA for **2M** at BP86/TZ2P. Energy values in kcal mol^{-1}.

	 Cp(CO)$_2$Fe-B(C$_2$(SiH$_3$)$_2$)		 Cp(CO)$_2$Fe-B(C$_2$(SiH$_3$)$_2$)
ΔE_{int}	−75.4	−225.8	−229.8
ΔE_{Pauli}	152.0	276.8	445.8
ΔE_{elstat}[a]	−127.3 (56.0%)	−341.4 (67.9%)	−252.1 (37.3%)
ΔE_{orb}[a]	−100.2 (44.0%)	−161.2 (32.1%)	−423.4 (62.6%)
ΔE_{σ}[b]	−89.4 (89.2%)	−148.4 (92.1%)	−393.4 (92.9%)
ΔE_{π}[b]	−10.8 (10.8%)	−12.8 (7.9%)	−30.0 (7.1%)
ΔE_{prep}	4.6	9.3	161.3
ΔE (= $-D_e$)	−70.8	−216.5	−68.5
fragments[c]	{Fe(CO)$_2$Cp}(d) $BC_2Si_2H_6$(d)	[Fe(CO)$_2$Cp]$^+$(s) [$BC_2Si_2H_6$]$^-$(s)	{B–Fe(CO)$_2$Cp}(os) $C_2Si_2H_6$(os)

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb}. [c] d = doublet; s = singlet; os = open-shell singlet.

states, while the fragments for the donor–acceptor bond are $[(\eta^5\text{-}C_5H_5)(OC)_2Fe]^+$ and $[BC_2(SiH_3)_2]^-$ in the electronic singlet states.

The calculations suggest that the B–Fe bond in **2M** is rather strong. The theoretically predicted bond-dissociation energy (BDE) is $D_e = 70.8\ \text{kcal mol}^{-1}$. The EDA results indicate that the attractive B–Fe interactions mainly result from electrostatic attraction. The covalent character of the B–Fe bond in **2M** is less pronounced, as shown by the percentage contribution of the orbital interactions in the electron-sharing bond (44.0%) and the donor–acceptor bond (32.1%). The most interesting EDA data come from the breakdown of the orbital term ΔE_{orb} into σ and π contributions. Table 1 shows that the strength of $\Delta E_{orb}(\pi)$ in **2M** is only $-10.8\ \text{kcal mol}^{-1}$ when the electron-sharing model is employed. The $\Delta E_{orb}(\pi)$ value for a B–Fe donor–acceptor bond is very similar ($-12.8\ \text{kcal mol}^{-1}$). The weakness of the Fe→B π bonding in **2M** becomes obvious when its $\Delta E_{orb}(\pi)$ value is compared with the previous EDA results for the borylene complexes $[(CO)_4Fe{-}BR]$.[23] The $\Delta E_{orb}(\pi)$ values for the axial Fe–BR bonds are between $-22.1\ \text{kcal mol}^{-1}$ (R = Cp) and $-52.2\ \text{kcal mol}^{-1}$ (R = phenyl).[22a]

Table 1 also gives the EDA results for the $B{-}C_2(SiH_3)_2$ bonds in **2M** using the appropriate fragments in open-shell singlet states. The calculated BDE ($D_e = 68.5\ \text{kcal mol}^{-1}$) has a similar value as the BDE for the B–Fe bond ($D_e = 70.8\ \text{kcal mol}^{-1}$), which could be interpreted as an indication of a similar bond strength. However, the intrinsic strength of the $B{-}C_2(SiH_3)_2$ interactions is much higher. This effect is revealed by the interaction energies ΔE_{int} between the fragments in the equilibrium geometry. The latter term shows a much larger value for the $B{-}C_2(SiH_3)_2$ bonding interactions in **2M** ($\Delta E_{int} = -229.8\ \text{kcal mol}^{-1}$) than for the B–Fe bond ($\Delta E_{int} = -75.4\ \text{kcal mol}^{-1}$). The preparation energies of the fragments $\{BFe(CO)_2Cp\}$ and $C_2(SiH_3)_2$ are very large ($\Delta E_{prep} = 161.3\ \text{kcal mol}^{-1}$), particularly for the latter species, because the closed-shell molecule is excited into an open-shell singlet diradical. Unlike the B–Fe bond, the $B{-}C_2(SiH_3)_2$ bonds in **2M** have a larger covalent character (62.6%) than electrostatic character (37.3%). Note that the calculated values for the $B{-}C_2(SiH_3)_2$ π interactions in the three-membered ring ($-30.0\ \text{kcal mol}^{-1}$) are clearly stronger than the B–Fe π interactions, which indicates substantial cyclic delocalization.

In conclusion, **1** can be used as a source for the metalloborylene $\{B{-}Fe(CO)_2(\eta^5\text{-}C_5Me_5)\}$. Reaction with 1,2-bis(trimethylsilyl)ethyne under photolytic conditions leads to the formation of the metalloborirene **2**. Both spectroscopic data and theoretical calculations suggest a bonding situation in **2** with significant π delocalization in the borirene ring and no relevant Fe–B d_π–p_π back-bonding.

Experimental Section

All manipulations were performed in an atmosphere of dry argon using standard Schlenk line and glovebox techniques. Photolysis experiments were performed with quartz NMR tubes using a Hg/Xe arc lamp (400–550 W) equipped with IR filters as the light source.

2: A yellow solution of **1** (0.050 g, 0.11 mmol) and 1,2-bis(trimethylsilyl)ethyne (0.034 g, 0.20 mmol) in benzene (0.5 mL) was irradiated for 0.5 h at room temperature. All volatiles were removed in vacuo, and the dark brown residue was extracted with hexane (0.5 mL). The red solution was filtered and stored overnight at −30 °C. The solution was then decanted from crystallized $[Cr(CO)_6]$ and filtered through silica gel, and all volatiles were removed in vacuo, yielding **2** as a red solid (0.017 g, 35%). IR (hexane): $\tilde{\nu} = 1983$ (s; CO), 1927 (s; CO) cm^{-1}; ^1H NMR (500 MHz, C_6D_6, 17 °C, TMS): $\delta = 1.63$ (s, 15H; C_5Me_5), 0.42 ppm (s, 18H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 17 °C, TMS): $\delta = 217.3$ (s; CO), 94.95 (s; C_5Me$_5$), 10.30 (s; C_5*Me*$_5$), 0.01 ppm (s; $SiMe_3$), BC resonances were not observed; ^{11}B NMR (64.22 MHz, C_6D_6, 17 °C, $Et_2O{\cdot}BF_3$): $\delta = 63.5$ ppm ($\omega_{1/2} = 170$ Hz). Elemental analysis (%) calcd for $C_{20}H_{33}BFeO_2Si_2$: C 56.09, H 7.77; found: C 55.40, H 7.47.

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Keywords: borirenes · boron · boryl complexes · borylene complexes · density functional calculations

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[17] The crystal data for **2** were collected on a Bruker X8 APEX diffractometer with a CCD area detector and multilayer mirror monochromated $\mathrm{Mo}_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, Universität Göttingen, **1997**), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure-factor calculations. Crystal data for **2**: $C_{20}H_{33}BFeO_2Si_2$, $M_r = 428.30$, yellow block, $0.18 \times 0.12 \times 0.05\ \mathrm{mm}^3$, triclinic, space group $P\bar{1}$, $a = 7.0700(3)$, $b = 9.8671(4)$, $c = 17.4633(7)$ Å, $\alpha = 86.591(2)$, $\beta = 81.624(2)$, $\gamma = 84.886(2)°$, $V = 1199.12(9)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.186\ \mathrm{g\,cm^{-3}}$, $\mu = 0.739\ \mathrm{mm}^{-1}$, $F(000) = 456$, $T = 100(2)$ K, $R_1 = 0.0749$, $wR^2 = 0.1678$, 11075 independent reflections ($2\theta = 74.34°$) and 246 parameters. CCDC-633058 (**2**) contains 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.

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