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Borylene Transfer

Borylene Transfer from an Iron Bis(borylene) Complex: Synthesis of 1,4-Diboracyclohexadiene and 1,4-Dibora-1,3-Butadiene Complexes**

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Dedicated to Professor Thomas P. Fehlner on the occasion of his 75th birthday

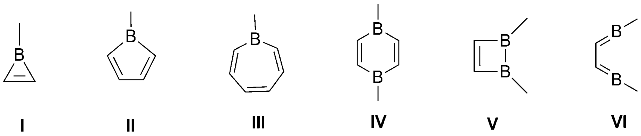

Figure 1. Unsaturated heteroboracycles containing one or two boron atoms. **VI** is the constitutional isomer of **V**.

Heteroboracycles that contain one boron atom, such as borirenes (**I**),[1] boroles (**II**),[1c,2]< and borepines (**III**)[3] (Figure 1) have attracted interest with regard to Hückel aromaticity/anti-aromaticity and their potential application as building blocks for π-conjugated oligomeric or polymeric systems with potentially remarkable linear, nonlinear, and electro-optical properties.[4] Recently, we turned our attention to diboraheterocycles that contain more than one electron-deficient center, that is, 1,4-diboracyclohexadienes (**IV**), the heretofore unknown 1,2-diborabutenes (**V**) and their constitutional isomers 1,4-dibora-1,3-butadienes (**VI**; Figure 1). Similar to other boraheterocycles, only a limited number of synthetic routes to **IV** have been published, and most are laborious. The procedures reported by Timms in 1968[5] and by van der Kerk[6] et al. in 1980 involved generation of transient borylene species :BF upon treatment of BF_3 with elemental boron at 1800–2000 °C,[7] and generation of :BMe upon reduction of Br_2BMe with KC_8, respectively. The subsequent borylene trapping reaction with alkynes led unselectively to 1,4-diboracyclohexadienes (**IV**). In 1978, Herberich and Hessner reported the tin–boron exchange reaction between 1,1,4,4-tetramethyl-l,4-distanna-2,5-cyclohexadiene and organoboron dihalides, which afforded the expected product in satisfactory yield.[8] Nevertheless, the scope of this synthetic approach is severely limited by the boron-bound substituent, that is, the bulky ferrocenyl fragment. Moreover, 1,4-diboracyclohexadienes with small boron-bound substituents, such as methyl or hydrogen, are susceptible to rearrangement, forming thermodynamically favored carboranes.[9] The labile diboraheterocycles of this type can nevertheless be stabilized by complexation with transition metals in an η^4-fashion.[10] In contrast, annulated derivatives of **IV**, such as *B,B*-dimethyl-derivatives of 1,4-diboranaphthalenes[18] and 9,10-diboraanthracenes,[19] are thermally stable. Their electron deficiency is effectively reduced by the electronically confused aromatic rings. In 2009, Wagner, Jäckle, Holthausen and co-workers highlighted the significance of 9,10-dihydro-9,10-diboraanthracene by disclosing its application as a building block for luminescent conjugated polymers.[20]

Very recently we reported the high yield synthesis of the neutral arylborylene complex $[(OC)_3(Me_3P)Fe{=}BDur]$ (Dur = 2,3,4,6-Me_4C_6H),[11] which can undergo a phosphine–borylene exchange reaction in the presence of $[(OC)_5Mo{=}BN(SiMe_3)_2]$, yielding the iron bis(borylene) complex $[(OC)_3Fe(BDur)\{BN(SiMe_3)_2\}]$ (**1**).[12] Remarkably, the borylene ligands in **1** showed an inclination for borylene coupling as indicated by the short B–B separation.[12]

We had noted in previous work that borylene complexes which undergo borylene transfer exclusively have CO ligands in *trans* position, while half-sandwich borylene complexes without a labilizable *trans* ligand do not transfer the borylene ligand (instead favoring metathesis reactions).[13] Likewise, the half-sandwich bis(borylene) complex $[(\eta^5\text{-}C_5Me_5)Ir\{BN(SiMe_3)_2\}_2]$[13d] does not appear prone to borylene transfer. We reasoned that the new bis(borylene) complex **1**, containing three CO ligands, should be a superior candidate for borylene transfer and may even facilitate double borylene transfer. We thus used bis(borylene) **1** to address the question of whether the dibora-π-systems **IV**–**VI** can be synthesized by addition of alkyne units.

To this end, a deep red hexane solution of **1** was irradiated in the presence of 2 equivalents of 2-butyne (**2**) at ambient temperature. The reaction was monitored by ^{11}B NMR spectroscopy, which revealed gradual consumption of **1** and formation of a new boron-containing species displaying significantly upfield shifted resonances at $\delta_B = 28$ and 26 ppm. The reaction was complete within 24 h. A certain amount of the dinuclear byproduct $[(OC)_2Fe(\mu\text{-}BDur)\{BN(SiMe_3)_2\}]_2$[12] was concomitantly generated as a black solid.

After workup, the boron-containing product was obtained as yellow crystals in a yield of 12 %. Notably, the ^1H NMR spectrum displayed four singlets ($\delta_H = 2.70$, 2.28, 2.23, and 2.10 ppm) for the methyl groups of the duryl substituent and two singlet signals ($\delta_H = 0.55$ and 0.19 ppm) for the amino

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group, suggesting a considerable rotational barrier around the exocyclic B−N and B−C bonds. This hindrance is most likely due to the steric congestion imposed by exocyclic substituents (Figure 2, top). The ^{13}C NMR resonance at $\delta_C = 212.04$ ppm indicated the presence of carbonyl ligands, that is, the complexation of the generated 1,4-diboracyclohexadiene with an iron tricarbonyl fragment. The equivalence of the three CO signals suggests also the rotation of the heterocycle on the metal center.

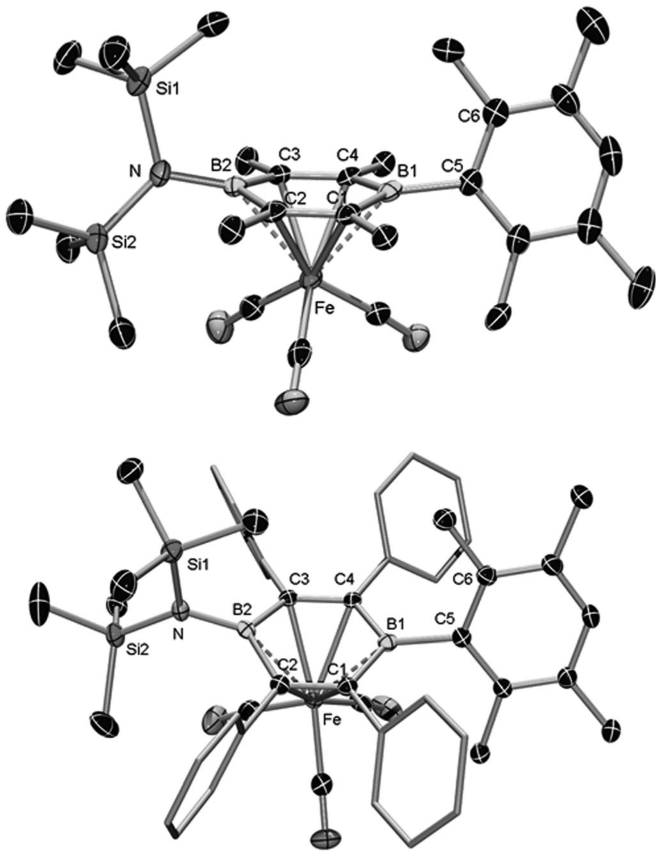


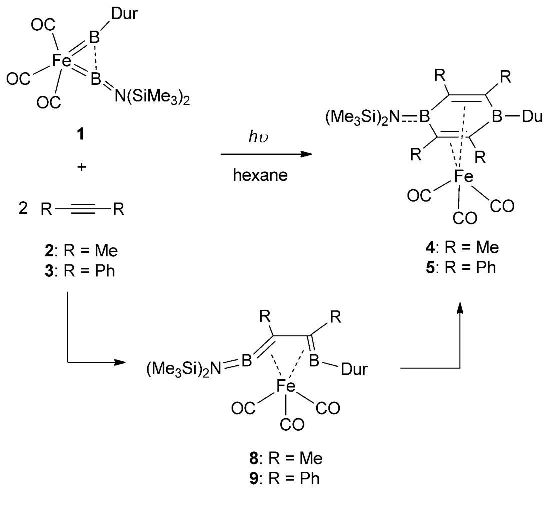
Figure 2. Crystal structures of **4** and **5**. Thermal ellipsoids set at 50% probability. Hydrogen atoms, the second independent molecule of **4** in the asymmetric unit, and the ellipsoids of phenyl groups in **5** are omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: C1–C2 1.424(5), C2–B2 1.537(6), B2–C3 1.550(6), C3–C4 1.420(5), C4–B1 1.550(6), B1–C1 1.537(6), B2–N 1.491(5), B1–C5 1.600(6), Fe–B1 2.311(5), Fe–B2 2.334(4), Fe–C1 2.246(4), Fe–C2 2.262(4), Fe–C3 2.207(4), Fe–C4 2.208(4); Si1-N-B2-C2 97.1(4), C6-C5-B1-C4 62.1(5). For complex **5**: C1–C2 1.429(2), C2–B2 1.561(2), B2–C3 1.569(3), C3–C4 1.425(2), C4–B1 1.552(2), B1–C1 1.537(3), B2–N 1.481(2), B1–C5 1.598(2), Fe–B1 2.3629(19), Fe–B2 2.4113(19), Fe–C1 2.2760(17), Fe–C2 2.2001(17), Fe–C3 2.2169(16), Fe–C4 2.2752(16); Si2-N-B2-C2 98.23(18), C1-B1-C5-C6 65.7(2).

Complex **4** crystallizes in triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, both featuring very similar structural parameters. The results of X-ray structural analysis are depicted in Figure 2, top. The overall geometry of the diboracyclohexadiene ring resembles the previously determined structure of this type:[10]

1) similar endocyclic B−C and C−C bond lengths;
2) the ring bends slightly away from iron center with respect to C1–C2 and C3–C4, as indicated by the longer Fe–B (mean: 2.32 Å) separations compared with those of Fe-C_n ($n = 1$–4; mean: 2.23 Å);
3) remarkable elongation of the exocyclic B2–N (1.491(5) Å) and B1–C5 (1.600(6) Å) bonds in comparison to that between tricoordinate boron and nitrogen in $[(OC)_4Cr(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}Pd(PCy_3)]$ (1.38 Å)[14] and that between the tricoordinate boron and sp^2-hybridized carbon in $[(OC)_2(Me_3P)Fe(\mu\text{-}CO)(\mu\text{-}BDur)Pt(PCy_3)]$ (1.55 Å).[11]

The almost orthogonal orientation of the duryl and bis(trimethylsilyl)amino substituents with respect to the central six-membered ring confirmed the steric congestion around the B2–N and B1–C5 bonds. In view of overall structural parameters, the diboracyclohexadiene ring can be regarded as a four-electron donor with pronounced olefinic η^2-coordination and a comparatively weak interaction between the vacant p-orbital of boron and a filled d-orbital of iron. Additionally, this weak interaction might account for the remarkable elongation of exocyclic B2–N and B1–C5 bonds.

Subsequently we investigated the influence of stoichiometry on this reaction. Iron bis(borylene) complex **1** was irradiated in the presence of an equimolar amount of borylene acceptor **2** and monitored by ^{11}B NMR spectroscopy, in the hope that complex **8** (Scheme 1) could be generated. However, the only new signals to be observed were at $\delta_B = 28$ and 26 ppm and are indicative of complex **4**.



Scheme 1. Reaction of **1** with 2-butyne (**2**) and diphenylacetylene (**3**).

To probe the versatility of the synthetic method, the reaction of **1** with 2 equivalents of diphenylacetylene (**3**) was carried out under identical conditions (Scheme 1). Complete conversion of the starting material **1** into the expected product **5**, as indicated by two new resonances at $\delta_B = 35$ and 26 ppm in the ^{11}B NMR spectrum, required 3 days. Interestingly, two signals at $\delta_B = 80$ and 61 ppm were observed for intermediates, which are comparable to those

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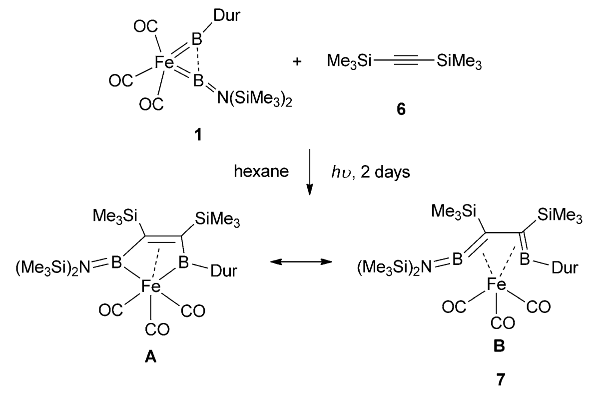
of complex **7** ($\delta_B = 93$ and 60 ppm; see below), suggesting the formation of complex **9** and the reaction process as shown in Scheme 1. The contrast between the reactions with **2** and **3** could be explained by steric reasons. In the case of **2**, the addition of the first equivalent of alkyne should be rate-limiting, which may explain why the intermediate was not observed. However, in the case of **3**, the phenyl group might significantly slow the addition of the second C≡C bond relative to the first equivalent, thus enabling the detection of complex **9**.

After workup, **5** was isolated as orange crystals in yield of 34%. Multinuclear NMR spectra of **5** displayed all relevant signals in the expected range. Analogous to **4**, the presence of boron-bound substituents, that is, duryl and bis(trimethylsilyl)amino, was again indicated by four singlets ($\delta_H = 2.42$, 2.29, 1.98, and 1.97 ppm) and two singlets ($\delta_H = 0.30$ and 0.03 ppm) respectively, suggesting a significant rotational barrier about B2–N and B1–C5 as a result of steric congestion imposed by the bulky exocyclic substituents, which consequently adopt a propeller-like arrangement (Figure 2, bottom). Complex **5** crystallizes in the monoclinic space group $P2_1/n$. The overall geometry of **5** in the solid state, in particular the central six-membered ring, strongly resembles that of **4**, thus suggesting an identical coordination mode of the 1,4-diboracyclohexadiene ligand.

After demonstrating a synthetic approach to 1,4-diboracyclohexadiene complexes by photochemical borylene transfer from **1**, and following the information with regard to the reaction process (Scheme 1), we decided to further study the steric influence of acetylenic substituents. In view of the steric congestion imposed by exocyclic substituents as shown in Figure 2, substitution of the phenyl ring by sterically more demanding groups, such as trimethylsilyl, might completely impede the reaction with a second equivalent of alkyne, and thus allow the isolation of the aforementioned intermediate, the novel diborabutenes **V** or 1,4-dibora-1,3-butadienes **VI**.

Hence, the reaction of **1** with an equimolar amount of bis(trimethylsilyl)acetylene (**6**) was carried out under identical reaction conditions, in the hope that the borylene moieties in **1** would be selectively transferred to only one C≡C bond. The reaction was monitored by ^{11}B NMR spectra, which revealed gradual formation of new ^{11}B resonances at $\delta_B = 93$ and 60 ppm. These values, which differ significantly from those of 1,4-diboracyclohexadiene complexes **4** and **5**, are in good agreement with the proposed structure (Scheme 2). The photochemical reaction was accomplished within 2 days. Notably, multinuclear NMR spectroscopy revealed no formation of 1,4-diboracyclohexadiene complexes. Upon filtration and storing the reaction solution at −30 °C, **7** was isolated as yellow crystals in a yield of 20%. The constitution of **7** in solution and in solid state was confirmed by multinuclear NMR spectroscopy and X-ray diffraction analysis, respectively. Again, impeded rotation around B2–N and B1–C3 was indicated by the presence of six singlets in the expected range for the methyl groups of duryl and bis(trimethylsilyl)amino substituents. In addition, the isolated complex **7** was further irradiated in the presence of **6**. As expected, no reaction was observed.



Scheme 2. Reaction of **1** with bis(trimethylsilyl)acetylene (**6**).

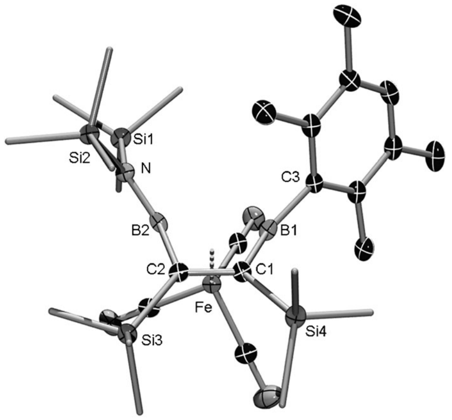


Figure 3. Crystal structure of **7**. Thermal ellipsoids set at 50% probability . For clarity, hydrogen atoms and ellipsoids of trimethylsilyl groups have been removed. Selected bond lengths [Å] and angles [°]: B1–C1 1.512(5), C1–C2 1.452(4), C2–B2 1.528(5), B2–N 1.385(4), B1–C3 1.557(5), Fe–B1 2.043(4), Fe–B2 2.135(4), Fe–C1 2.118(3), Fe–C2 2.140(3); N-B2-C2 145.7(3), C1-B1-C3 143.6(3), Fe1-B2-N-Si1 −2.9(5).

Complex **7** crystallizes in the monoclinic space group $P2_1/c$ (Figure 3). The Fe1-B2-N-Si1 torsion angle of −2.9(5)° as well as the significantly shortened B2–N separation (1.385(4) Å) in comparison to that in **5** (1.481(2) Å) indicated a pronounced B–N π-interaction in **7**. Furthermore, the bond lengths of Fe–B1 (2.043(4) Å) and Fe–B2 (2.135(4) Å) are comparable to the Fe–B distances commonly observed for neutral iron half-sandwich boryl complexes of iron (1.96–2.09 Å).[15] The inner C1–C2 unit (1.452(4) Å) can be regarded as a double bond that is side-on coordinated to the iron center in a η^2 fashion, thus explaining the bond lengthening with respect to non-coordinated C=C bonds. On the other hand, the C1–C2 bond (1.452(4) Å) is slightly longer compared with η^2-coordinated C=C bonds in **4** and **5** (mean, 1.42 Å), but is still somewhat shorter than the bond lengths between two sp^2-hybridized carbon atoms (e.g. 1.466(7) Å in [ClPt(PMe$_3$)$_2$(*cyclo*-{BN-(SiMe$_3$)$_2$}C=C)Ph][1g]). In fact, analogous structural parameters for the central C−C bond (i.e. bond length between those of single bonds and η^2-coordinated double bonds) were observed for complexation of 1,3-dienes with the ruthenium tricarbonyl fragment.[16] In addition, for the central B−C bond

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in **7**, in particular, the decrease of B1–C1 (1.512(5) Å) in comparison to the adjacent B1–C3 single bond (1.557(5) Å) as well as the endocyclic B–C bonds (mean value of 1.56 Å) in **5** indicate the presence of B–C double bond character. Hence, the central BCCB skeleton can be regarded as a four-electron donor ligand with B=C η^2-coordination. In view of these findings, the overall bonding situation in **7** can be described with both mesomeric forms **A**, an iron-*cis*-diboryl complex with side-on coordinated alkenyl function, and **B**, an iron 1,4-dibora-1,3-butadiene complex (Scheme 2).

In conclusion, upon tuning the size of acetylenic substituents, 1,4-diboracyclohexadiene and unprecedented 1,4-dibora-1,3-butadiene complexes were generated in a controlled manner by borylene transfer from an iron bis(borylene) complex. Furthermore, the 1,4-dibora-1,3-butadiene complexes have expanded the scope of B-C η^2-coordination mode to transition metals.[17,13c] Studies targeting the synthesis of poly-1,4-dibora-1,3-butadiene systems by borylene transfer from **1** to diynes are currently underway.

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