DOI: 10.1002/anie.201304972

Phosphine-Triggered Co-catenation of :BR and CO on an Iron Atom[**]

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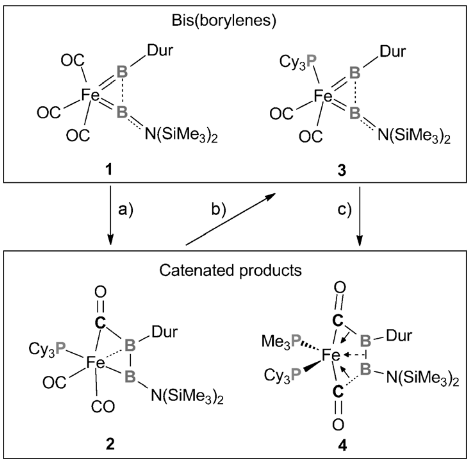
Since the early 19th century, carbon monoxide CO has been known to undergo reductive coupling reactions when exposed to molten potassium, affording potassium salts of croconate $[C_5O_5]^{2-}$ and rhodizonate $[C_6O_6]^{2-}$.[1] At the end of the 20th century, the scope of CO coupling reactions was extended to intramolecular C–C bond formation between two metal-coordinated CO ligands.[2] To stabilize the final product, Lewis acids were introduced to form strong bonds with oxygen. Thus, the otherwise unstable acetylenes with the general formula of ROC≡COR (R = H, trialkylsilyl, BF_3) were generated in the coordination sphere of transition metals. More recently, a handful of U^{III} complexes turned out to be able to couple CO, leading to [U]OC≡CO[U][3] as well as cyclic (C_nO_n) ($n = 3, 4$) moieties that are stabilized by two uranium(IV) fragments.[4]

In stark contrast to carbon monoxide, the isoelectronic borylene ":BR" is highly reactive. To date, conclusive evidence for the existence of free borylenes is still missing. The generation of :BR moieties, mostly under drastic conditions, has been supported by trapping,[5] which (with the exception of a few carbene-stabilized examples[5j,k,6]) are mostly poorly selective. Hence, the controlled coupling of two or more free borylenes to afford diborenes RB=BR or corresponding cyclic species B_nR_n is a great challenge. Nevertheless, borylene ligands on transition metals have shown the potential to couple and form B–B bonds. In 2002, our laboratory disclosed the first intermolecular borylene coupling reaction between two terminal BCl ligands on Mn, affording a dimetallic *nido*-Mn_2B_2 cluster in which the B_2Cl_2 fragment was demonstrated to be a non-classical dichlorodiborene ligand.[7] However, it took a decade to discover the next example of this kind of reaction: the binding of four borylene ligands to a $\{Fe(CO)_2\}$ fragment, leading to borylene coupling and formation of a 1D B_4R_4 chain ($R_4 = Dur_2\{N(SiMe_3)_2\}_2$) consisting of three electron-precise B–B σ-bonds.[8] More recently, reactivity studies on terminal borylene complexes $[Cp(OC)_2Mn{=}B\textit{t}Bu]$ ($Cp = \eta^5\text{-}C_5H_5$)[9] and $[(OC)_5Cr{=}BAr']$ $\{Ar' = 2,6\text{-}(2,4,6\text{-}\textit{i}Pr_3C_6H_2)_2C_6H_3\}$[10] revealed that the borylene ligand underwent intramolecular coupling reactions with CO upon treatment with isonitrile or KC_8, respectively.

The previously published studies on bis(borylene) iron complex **1** have revealed that the borylene ligands in **1** are not fully coupled owing to the strong electron donation from the filled B–B σ-bond to an empty orbital on the Fe center.[8a] Herein, we attempted to employ phosphines as strong σ-donor ligands to populate this empty orbital, to decrease the amount of B–B σ-bond→Fe interaction and effect complete B–B coupling.

To this end, a red hexane solution of iron bis(borylene) **1** was treated with an equimolar amount of PCy_3 at ambient temperature (Scheme 1). The color slowly turned from red to purple within 4 days. A nearly quantitative conversion of starting materials into new boron- and phosphorus-containing species was indicated by the presence of ^{11}B and ^{31}P NMR resonances at $\delta_B = 74$ (*B*N) and 51 (*B*Dur) and $\delta_P = 68.2$, respectively. The NMR spectroscopic data, in particular the remarkable high-field shift of the ^{11}B NMR signals indicate the presence of a strengthened B–B σ-bond. The same reaction was observed when the smaller phosphine PMe_3 was applied. Moreover, the reaction with PMe_3 was significantly faster, reaching completion within several minutes (see the Supporting Information).



Scheme 1. Stepwise catenation of CO and :BR on iron. Key reagents and conditions: a) PCy_3 (1.2 equiv), benzene, RT, 4 d; b) *hν*, hexane, 2 d; c) PMe_3 (1 equiv), benzene, RT, 4 h.

The results of X-ray diffraction analysis of **2** partially confirmed our proposed structure.[14] As shown in Figure 1, the B1–B2 bond distance (1.646(4) Å) is significantly shortened in comparison to that (1.982(3) Å) in the precursor **1**, and is comparable with that (1.686(6) Å) of the central B–B bond in the iron B_4 complex $[(OC)_2Fe\{BN(SiMe_3)_2\}_2(BDur)_2]$

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[**] Financial support from the European Research Council (ERC Advanced Grant to H.B.) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304972.

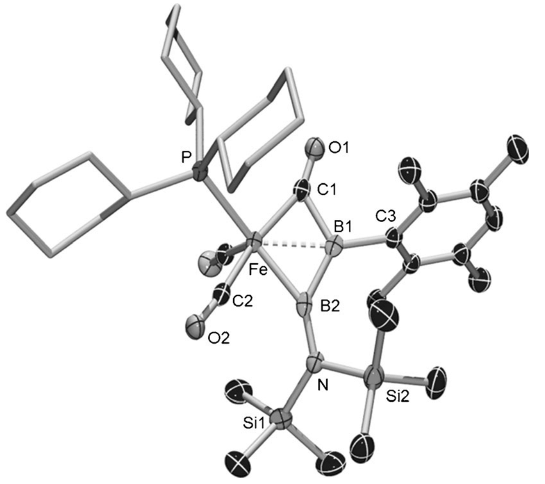

Figure 1. Molecular structure of **2** in the solid state. Ellipsoids are set at 50% probability. All hydrogen atoms, solvent molecules, and the ellipsoids of cyclohexyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–C1 1.819(2), Fe–B1 2.015(3), Fe–B2 1.993(3), Fe–C2 1.779(2), C1–B1 1.658(3), B1–B2 1.646(4); Fe-C1-O1 155.14(19), Fe-C2-O2 174.1(2), Fe-C1-B1 70.65(12), Fe-B2-B1 66.45(13).

(**5**).[8a] Furthermore, the borylene [:BDur]–carbonyl [CO] coupling was achieved simultaneously, as indicated by the B1–C1 separation of 1.658(3) Å as well as the significant bending of the Fe-C1-O1 axis (155.14(19)°), thus suggesting a bridging coordination mode of the C1O1 group. This is further supported by the presence of a significantly red-shifted absorption band at 1763 cm^{-1} (bridging CO) plus bands at 1974 and 1901 cm^{-1} (terminal CO) in the IR spectrum. The Fe–B2 bond length of 1.993(3) Å is about 8% longer than the corresponding bond in the precursor **1**, which is due to the increased coordination number at boron. Remarkably, the B1–C1 bond of **2** is about 6% longer than the B–C single bond (1.578(2) Å) found between sp^2-hybridized boron and carbon atoms,[11] and is comparable to the B–C distances in transition state structures of Pt-mediated B–C bond activation of $H_3C–B(OH)_2$ (1.687–1.756 Å).[12] These structural data suggest the presence of side-on σ-coordination of the B1–C1 bond to the electronically unsaturated (formally 16e$^-$) iron center. This is further supported by the acute Fe-C1-B1 (70.65(12)°), Fe-B2-B1 (66.45(13)°) angles and the short Fe–B1 separation (2.015(3) Å). The central Fe-B2-B1-C1 ring is planar, as indicated by the sum (359.7°) of internal angles. In contrast to the iron B_4 complex $[(OC)_2Fe\{BN(SiMe_3)_2\}_2(BDur)_2]$ (**5**) featuring a catenated B_4 chain,[8a] here a 1D B-B-C chain has formed. Notably, the N-bound boron only weakly interacts with the adjacent CO ligand, as indicated by the large B2–C2 separation of 2.133(3) Å, which is, however, significantly shorter than the calculated B–C distances (2.336–2.611 Å) in *cis*-$[(R_3P)_2Pt\{B(OH)_2\}(CH_3)]$ ($R_3 = H_3$, H_2Me, H_2Et).[12] Wiberg bond indices (WBI) confirmed the presence of a chain of fully formed B1–B2 (1.05) and B1–C1 (0.91) single bonds, while the B2–C2 interaction has a WBI of only 0.45. The highest-occupied molecular orbital (HOMO) consists of conventional B1–B2 and B1–C1 σ-bonds and a semi-formed B2–C2 σ-bond (Figure 4a).

Previous computational studies on the iron B_4 complex **5** demonstrated that the elongation of the outer B–B bonds in comparison to the inner B–B bond was mainly due to the significant outer σ-bond donations to the metal center. Thus, to strengthen the semi-formed B2–C2 bond in complex **2** we sought to increase electron density at the iron atom by replacing a carbonyl in **2** with a strong donor ligand, such as a trialkylphosphine. Room-temperature photolysis of a hexane solution of **2** with UV light led to loss of one equivalent of CO and formation of a new bis(borylene) complex **3**, as indicated by new ^{11}B and ^{31}P NMR resonances at $\delta_B = 124$ (*B*Dur) and 81 (*B*N), and $\delta_P = 84.2$, respectively. The constitution of **3** was further confirmed by X-ray structural analysis (Figure 2).[14] Complex **3** crystallized in the triclinic space group $P\bar{1}$, adopting a similar overall geometry to the phosphine-free bis(borylene) complex **1**, in particular the acute B1-Fe-B2 angle of 65.84(10)° and the short B1–B2 separation of 1.972(3) Å.

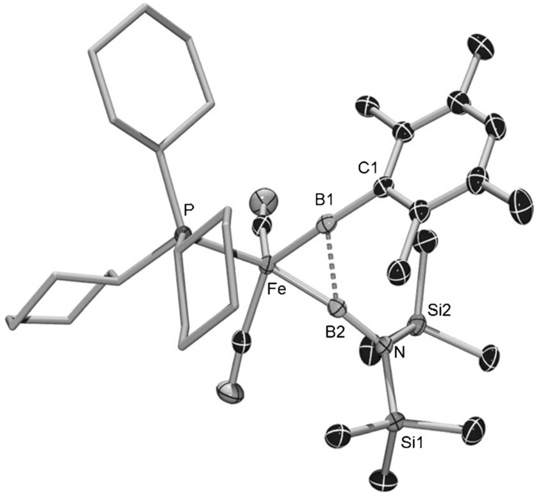

Figure 2. Molecular structure of **3** in the solid state. Ellipsoids are set at 50% probability. All hydrogen atoms and the ellipsoids of cyclohexyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–B1 1.805(2), Fe–B2 1.823(2), B1–B2 1.972(3); B1-Fe-B2 65.84(10).

An equimolar amount of PMe_3 was then added to a C_6D_6 solution of **3** at ambient temperature. The reaction was monitored by multinuclear NMR spectroscopy, which revealed gradual consumption of the starting materials and formation of the expected bis(phosphine) complex **4**, as indicated by new NMR resonances at $\delta_B = 67$ (*B*N) and 49 (*B*Dur), $\delta_P = 63.5$ (PCy_3) and 13.8 (PMe_3). In contrast to **2** and **3**, the ^1H NMR spectrum displays two signals for $N(SiMe_3)_2$ ($\delta_H = 0.48$ and 0.22) as well as for the *o*-Me substituents of the duryl group ($\delta_H = 2.37$ and 1.99) at ambient temperature, suggesting a higher rotational barrier about the B–N and B–Dur bonds. This could be explained by the increased steric congestion in the catenated CBBC chain. Most remarkably, while the ^{11}B NMR resonance of the BDur moiety is negligibly shifted with respect to that of **2**, the 7 ppm upfield shift of the N-bound boron reflects the strengthening of the [N]B−CO bond. This is further supported by 1) a ^{13}C NMR resonance for [N]B-*CO* ($\delta_C = 228$), which lies between that of DurB-*CO* ($\delta_C = 238$) and [N]B-*CO* ($\delta_C = 217$) in **2**; and 2) the solid-state IR spectrum, which displays exclusively red-shifted CO absorption bands at 1853 and 1738 cm^{-1}, thus excluding the presence of any terminal CO groups.

X-Ray diffraction analysis revealed an analogous structure of **4** compared to the recently reported iron B_4 complex **5**: Two borylene units are replaced by isoelectronic carbonyl groups, thus forming a 1D OC-B-B-CO network on iron (Figure 3).[14] The central Fe-C1-B1-B2-C2 ring is planar, as indicated by the sum of angles (540.0°) within the five-membered ring. However, the geometry of this ferroheterocycle significantly deviates from the regular pentagon, as indicated by the acute Fe-C1-B1 (69.19(17)°), Fe-C2-B2 (62.70(14)°) angles and the obtuse C1-Fe-C2 (167.35(14)°) angle. The B−B bond is thereby held close to the iron center, suggesting the presence of side-on σ-bond coordination. Most remarkably, when compared with **2**, the B1−C1 (1.692(5) Å) and B1−B2 (1.655(5) Å) bond lengths are slightly affected by replacing a CO by PMe_3 on the metal center, but the B2−C2 separation of 2.030(5) Å is shortened by about 10 pm. Nevertheless, the latter is still longer than the experimentally observed B−C bond distance (1.89(1) Å) in the platinum–borirene adduct $[(Et_3P)_2Pt\{(\sigma\text{-B,C})\text{-}cyclo\text{-PhB(PhCCMes)}]$ (Mes = 2,4,6-$Me_3C_6H_2$), the only example of a non-agostic B−C σ-complex.[13]

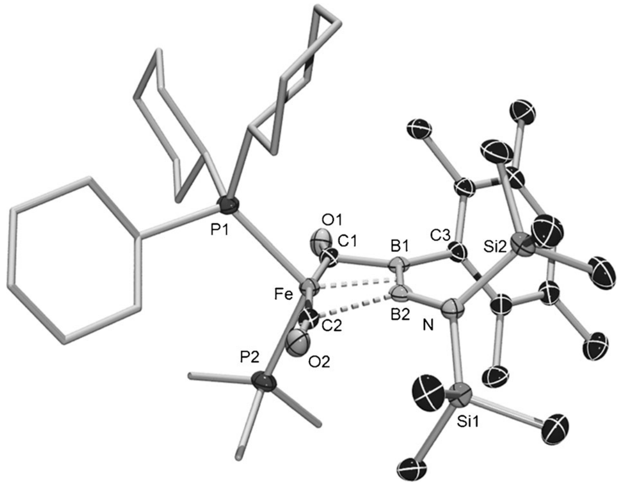

Figure 3. Molecular structure of **4** in the solid state. Ellipsoids are set at 50% probability. All hydrogen atoms and the ellipsoids of cyclohexyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe–C1 1.803(3), Fe–C2 1.759(3), C1–B1 1.692(5), B1–B2 1.655(5), B2–C2 2.030(5), Fe–B1 1.987(3), Fe–B2 1.985(4); Fe-C1-B1 69.19(17), Fe-C2-B2 62.70(14), C1-Fe-C2 167.35(14), Fe-C1-O1 158.1(3), Fe-C2-O2 170.4(3).

To provide further insight into the bonding situation in complex **4**, Kohn–Sham density functional theory (DFT) calculations at the OLYP/TZVP level of theory were performed. The calculated structure of **4** is in good agreement with the experimental structure, and is reminiscent of the iron B_4 complex **5**.[8a] Indeed, the bonding in the OC-B-B-CO chain follows the same pattern, which is unsurprising considering that CO is isoelectronic and isolobal to borylenes. The HOMO of **4** indicates a σ-network consisting of three conventional B−C and B−B σ-bonds (Figure 4c,e). Moreover, the WBIs confirm the presence of fully-formed B1−B2 (1.08) and B1−C1 (0.85) single bonds as well as a strengthened B2−C2 interaction (0.53; Figure 4d). Though the Fe−B separations (B1 1.987(3) Å exp., 1.995 Å calcd.; B2 1.985(4) Å exp., 2.011 Å calcd.) lie in the expected range of Fe−B single bonds, no classical σ-bonds between the boron atoms and the iron

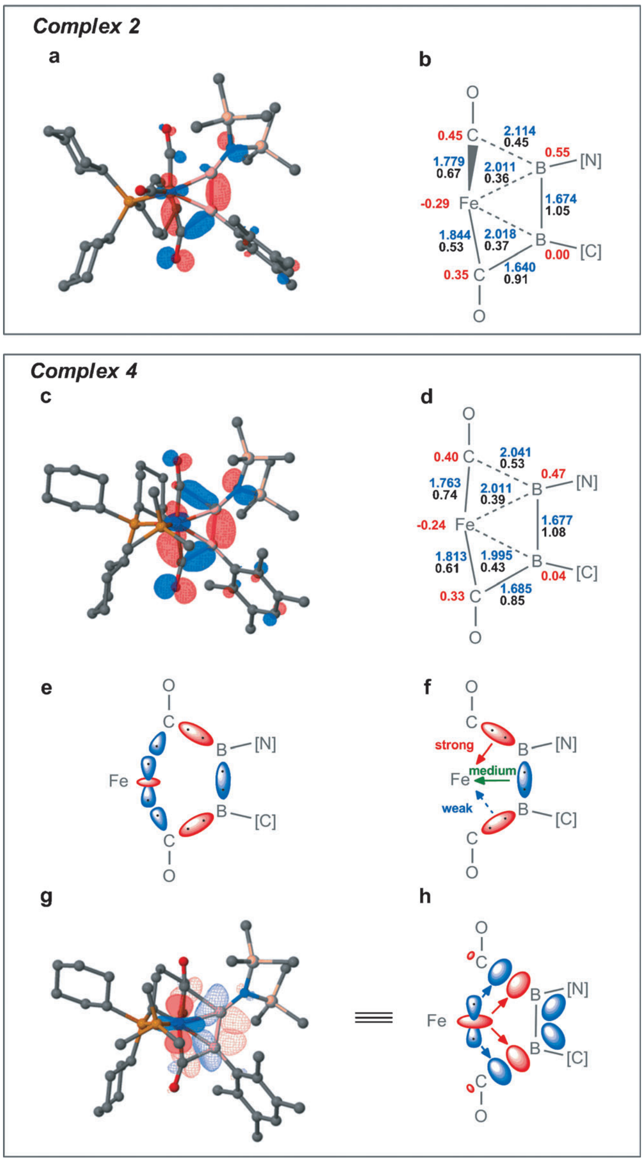

Figure 4. Results of DFT calculations on **2** and **4**. a) HOMO of complex **2**. b) Metrics calculated for **2**. c,e) the σ-network in the FeB_2C_2 plane. d) Metrics calculated for **4**. f) σ-Bond donation from B−C and B−B bonds to Fe. g,h) Back donation from Fe into B−C antibonding orbitals. For the metrics, bond lengths are shown in blue [Å], Wiberg bond indices in black, and natural charges in red.

are observed. Second-order perturbative analysis of donor–acceptor interactions in the NBO framework confirmed the side-on σ-coordination of all three B–B and B–C bonds to the metal (Figure 4 f). The interaction energy for the OC–B[N] σ-bond donation (3.0 kcal mol^{-1}) is noticeably stronger than those from the OC–B[C] (2.0 kcal mol^{-1}) and the B–B (2.4 kcal mol^{-1}) bonds. Moreover, there exists considerable backbonding from a metal d_{z^2} orbital to antibonding B–C orbitals. This interaction energy is significantly higher for OC–B[N] (16.5 kcal mol^{-1}) than that for OC–B[C] (3.9 kcal mol^{-1}). Therefore, the stronger σ-donating and σ*-accepting properties of the OC–B[N] bond with respect to the OC–B[C] bond make the former significantly longer than the latter (1.692(5) Å vs. 2.030(5) Å).

In conclusion, treatment of iron bis(borylene) complex **1** with one equivalent of the phosphine PCy_3 led to one-step formation of an iron-coordinated 1D OC-B[C]-B[N] chain. Upon subsequent stepwise substitution of a CO ligand by PMe_3, a catenated 1D OC-B-B-CO chain was obtained, which is a CO analogue of the 1D B_4 chain in the iron complex **5**. DFT calculations revealed a similar bonding situation in **4**: σ-donation from the formed σ-bond network to Fe, and backbonding from Fe to the σ* B–CO orbitals. Moreover, the interactions between the B–CO bonds and the iron are stronger than those of the inner B–B bond. The previously disclosed protocol for borylene homocatenation to 1D chains can thus be extended to heterocatenation of multiple (and different) borylene ligands with CO ligands, resulting in unprecedented, isoelectronic 1D OC-B-B-CO chains.

Received: June 10, 2013
Revised: July 10, 2013

Keywords: borylene · carbonyl · catenation · iron · phosphine

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[14] CCDC 943112 (**2**), CCDC 943113 (**3**), and CCDC 943114 (**4**) 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.