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## Complete and Partial 1,2-Additions across Transition Metal–Boron Double Bonds

Holger Braunschweig,<sup>\*,†</sup> Qing Ye,<sup>†</sup> Alfredo Vargas,<sup>‡</sup> Rian D. Dewhurst,<sup>†</sup> and Florian Hupp<sup>†</sup><sup>†</sup>Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany<sup>‡</sup>Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, United Kingdom

## S Supporting Information

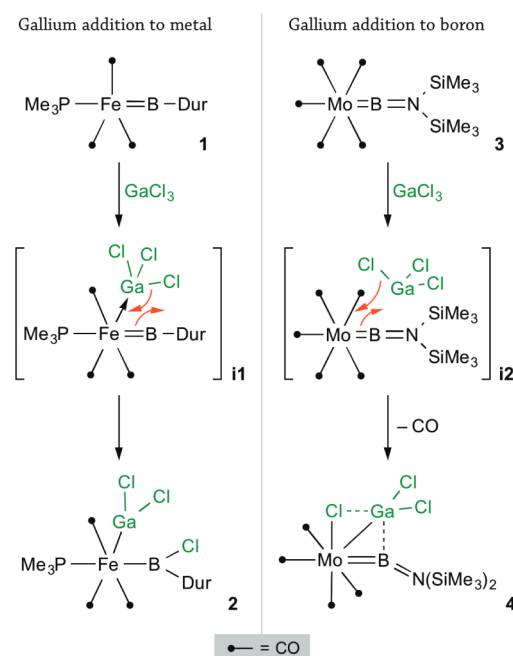
**ABSTRACT:** The first 1,2-additions across a metal–boron double bond are reported, one a definitive chlorogallation of a Fe=B bond, the other a partial chlorogallation of a Mo=B bond that leads to a highly unusual, planar Mo–B–Ga–Cl rhombus. The two reactions occur with opposite regiochemistry, with the Ga atom bound to the Fe atom in the former and to both the Mo and B atoms in the latter. The bonding in the Mo adduct and the reasons for the differing regiochemistry of the reaction are explored computationally.

The 1,2-addition of polar substrates to C–C multiple bonds is a staple of organic chemistry, and the concept extends with high fidelity to main group multiply bound species.<sup>1</sup> Likewise, 1,2-additions of polar bonds to metal–element multiple bonds are also well-known reactions in inorganic chemistry—metal–carbon triple bonds<sup>2</sup> and metal–nitrogen double bonds<sup>3</sup> are known to undergo 1,2-addition of anhydrous HCl and other reagents with polar bonds. In 2013 we reported the  $\sigma$ -coordination of a metal–boryl bond to gold(I) in a complex which appeared to have undergone an incomplete 1,2-addition of Au and Cl across a Mn=B bond.<sup>4</sup> However, given the scope of the concept in organic, inorganic, and main-group chemistry, it is surprising that no 1,2-addition chemistry of borylene complexes has thus far been demonstrated. Here we present the first definitive 1,2-addition of a gallium–chloride bond of GaCl<sub>3</sub> across a metal–boron double bond of a transition metal borylene complex of iron. Moreover, using an alternative borylene complex of molybdenum, treatment with GaCl<sub>3</sub> led to a partial 1,2-addition of the opposite regiochemistry, generating an unusual complex in which the Ga center is loosely bound to the B, the metal, and the metal-bound chloride ligand.

In 2005, Fischer and et al. discovered<sup>5</sup> that gallium trichloride can form metal-only Lewis pairs (MOLPs)<sup>6</sup> in which a monovalent rhodium fragment acts as the Lewis base. Three years later our group demonstrated<sup>7</sup> that, depending on the halide used, gallium trihalides can either form MOLPs (X = Cl) or undergo Ga–X oxidative addition (X = Br, I) when treated with the zerovalent Pt complex [Pt(PCy<sub>3</sub>)<sub>2</sub>]. Given the known reactivity of transition metal complexes with gallium halides, we were interested in their reaction with transition metal borylene complexes. Our group has recently uncovered a number of reactions wherein borylene ligands couple in novel ways with Lewis basic and acidic molecules and ligands,

including borylene–borylene,<sup>8</sup> borylene–alkyne,<sup>9</sup> and borylene–CO coupling reactions.<sup>10</sup> Thus, the question arose as to whether the gallium center of gallium trihalide would preferentially react with the metal center or the borylene B-atom. Further motivation for the work came from the realization that B–Ga bonds are rare and before this year had been found to exist only as part of polyborane clusters,<sup>11</sup> Ga<sup>I</sup> → B<sup>III</sup> Lewis adducts with monovalent gallium,<sup>12</sup> and a handful of compounds with electron-precise B–Ga single bonds in two very recent reports.<sup>13</sup>

Treatment of iron borylene complex [(Me<sub>3</sub>P)(OC)<sub>3</sub>Fe=B–Dur] (**1**, Figure 1)<sup>14</sup> with GaCl<sub>3</sub> led to new, significantly upfield, signals in both the <sup>11</sup>B ( $\delta_B$  113; cf. **1**:  $\delta_B$  146) and <sup>31</sup>P NMR spectra ( $\delta_P$  0.58; cf. **1**:  $\delta_P$  17.63) of the reaction mixture within several minutes. A white solid (**2**, Figure 1) was obtained after precipitation, filtration, washing and recrystallization in good yield (65%). The <sup>11</sup>B NMR signal of **2** ( $\delta_B$  113) fits

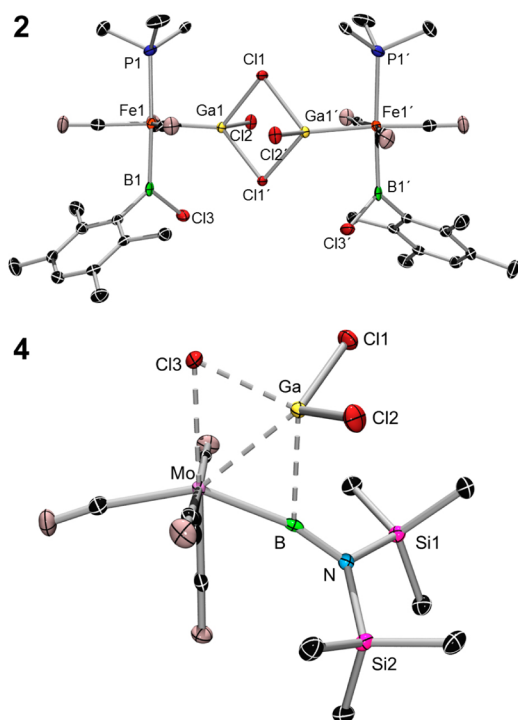


**Figure 1.** Divergent outcomes of GaCl<sub>3</sub> addition to different transition metal borylene complexes, and possible Lewis adduct intermediates in the process.

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perfectly with those of a series of aryl(halo)boryl complexes of  $\text{Fe}^{\text{II}}$  featuring cyclopentadienyl ligands, which fall within a remarkably narrow range despite significant structural variation ( $\delta_{\text{B}}$  111–113).<sup>15</sup> The molecular structure of **2** obtained by single crystal X-ray diffraction was found to be in accordance with this  $^{11}\text{B}$  NMR signal, revealing an octahedral complex of  $\text{Fe}^{\text{II}}$  in which a dichlorogallyl ligand is found to be mutually *cis* to both aryl(halo)boryl and trimethylphosphine ligands. The complex **2** additionally forms a dimer with a neighboring complex through one bridging chloride atom per iron (Figure 2). As expected, the Fe–B distance in boryl complex **2**



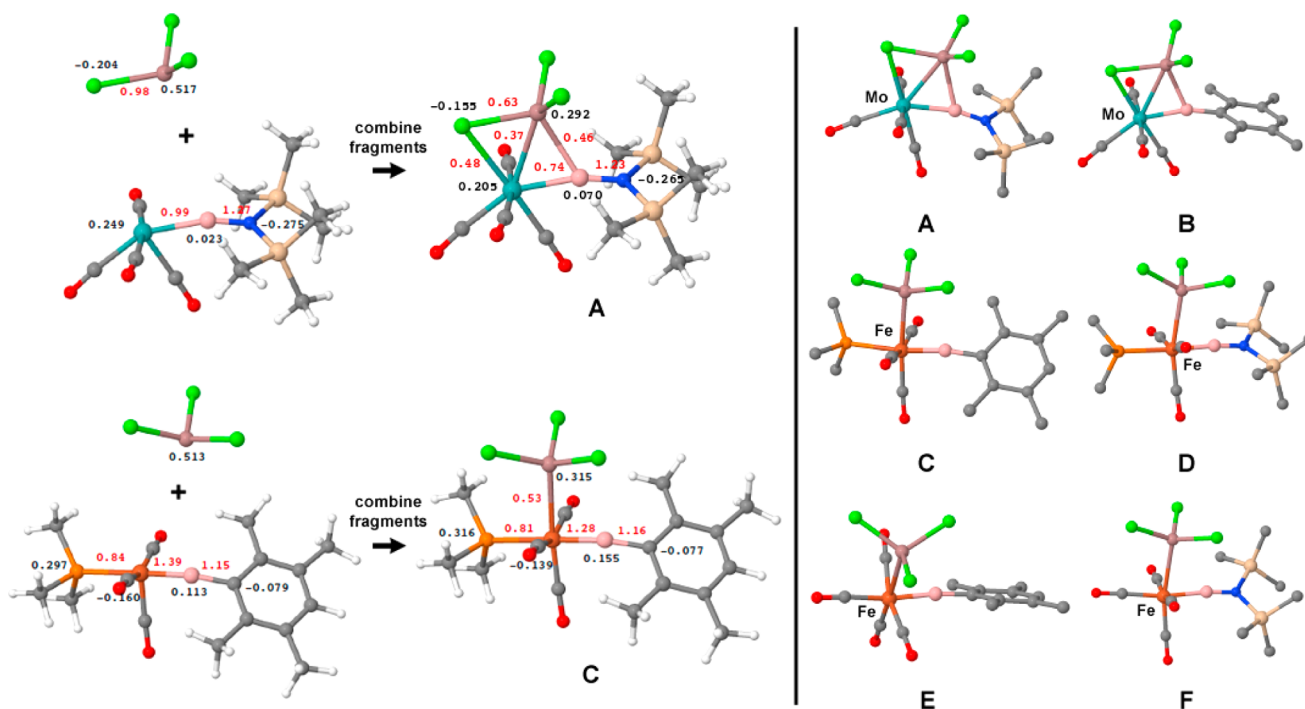
**Figure 2.** Molecular structures of **2** and **4**. Thermal ellipsoids are shown at the 50% probability level. H-atoms have been omitted. Selected distances (Å) and angles (deg) for **2**: Fe1–Ga1 2.3586(7), Fe1–B1 2.058(4), Fe1–P1 2.276(1), Ga1–Cl2 2.1995(9), Ga1–Cl1 2.3725(9), Ga1–Cl1' 2.4288(9); B1–Fe1–Ga1 88.4(1). For **4**: Mo–B 2.103(3), Mo–Cl3 2.6065(7), Mo–Ga 2.6146(5), B–N 1.349(4), B–Ga 2.379(3), Ga1–Cl3 2.3052(7), Ga–Cl1 2.1721(7), Ga–Cl2 2.1757(8); Cl3–Mo–Ga 52.401(17), B–Mo–Ga 59.41(8), Mo–B–N 166.2(2).

(2.058(4) Å) is much longer than that in borylene complex **1** (1.793(1) Å). The Fe–Ga distance in **2** (2.3586(7) Å) also fits very well with that of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{Fe}\{\text{GaCl}_2(\text{NMe}_3)\}]$  (2.361(1) Å), a representative  $\text{Fe}^{\text{II}}$  complex containing a dichlorogallyl ligand bearing one Lewis basic “unit”.<sup>16</sup> However, it should be emphasized that the Fe–Ga distances of iron gallyl complexes vary greatly and there are few truly comparable structures known in the literature due to extensive bridging of the chlorides on the gallyl ligand.<sup>17</sup> The monomer **2**, *mer*-[Fe(BClDur)(CO)<sub>3</sub>{GaCl( $\mu$ -Cl)}(PMe<sub>3</sub>)], is a result of regioselective chlorogallylation of the Fe=B bond and the first definitive example of a 1,2-addition across a metal–boron double bond. Given the known propensity of  $\text{Fe}^0$  complexes to form MOLPs with strongly Lewis-acidic compounds,<sup>6,18</sup> we consider it likely that a MOLP containing a Fe  $\rightarrow$  Ga dative bond, **i1** (Figure 1), may act as an intermediate in this reaction.

Addition of an excess of  $\text{GaCl}_3$  to molybdenum borylene complex  $[(\text{OC})_5\text{Mo}=\text{BN}(\text{SiMe}_3)_2]$  (**3**) led to the precipitation of yellow crystals (**4**) after storage at low temperature. As in the above reaction, the  $^{11}\text{B}$  NMR signal of the yellow compound was found higher-field of that of the precursor (**4**:  $\delta_{\text{B}}$  81; **3**:  $\delta_{\text{B}}$  89.7),<sup>19</sup> suggesting an increase in the coordination number of the boron center. A single signal was observed for the trimethylsilyl protons in the  $^1\text{H}$  NMR spectrum; however, due to a lack of diagnostic NMR handles in the molecule, structural confirmation was required in order to determine its connectivity. The molecular structure of **4** derived from single-crystal X-ray diffraction (Figure 2) shows a highly unusual structure containing a completely flat Mo–B–Ga–Cl unit (sum of internal angles: 359.99°) that is nearly a parallelogram; in fact the Mo, B, Cl, Ga, and two CO ligands are all roughly coplanar. The chloride and four CO ligands form a conventional square pyramid around the molybdenum center; however, the remaining binding site is filled with a slightly bent {BN(SiMe<sub>3</sub>)<sub>2</sub>} (Mo–B–N 166.2(2)°), and GaCl<sub>2</sub> ligands. The Mo–Ga distance of **4** (2.6146(5) Å) appears to be well within the range of other molybdenum gallyl complexes;<sup>20</sup> however, its Mo–Cl distance is unusually long (2.6065(7) Å). The B–Ga interaction (2.6146(5) Å) appears to be much weaker than those in previously reported  $\text{CpGa} \rightarrow \text{BAR}_3$  Lewis adducts.<sup>12</sup> Likewise the Ga–Cl<sub>3</sub> distance (2.3052(7) Å) is ca. 0.13 Å longer than the remaining two Ga–Cl bonds and is thus indicative of a weak interaction. Surprisingly, despite the interaction of the boron with the gallium center, the Mo–B distance of **4** (2.103(3) Å) is slightly shorter than that of the precursor **3** (2.152(2) Å), reminiscent of a similar phenomenon observed recently in hydridoborylene complexes of molybdenum, in which bridging elements actually shorten the M–B bond.<sup>21</sup> Given the short Mo–B and Mo–Ga distances, the slight bending of the Mo–B–N angle, and the modest change in the  $^{11}\text{B}$  NMR signal, complex **4** is best described as a (borylene)(chloro)(gallyl) complex of  $\text{Mo}^{\text{II}}$  based on the experimental data. It should also be noted that complex **4** was obtained in low yield (18%) but was the only boron-containing product in the reaction mixture as judged by  $^{11}\text{B}$  NMR spectroscopy.

Density functional theory calculations at the B3LYP/Def2-SVP and OLYP/TZP (ZORA) levels were undertaken to obtain a better picture of the bonding in complex **4**. Hirshfeld charges and Mayer bond indices of the corresponding computational model, **A**, and its separated fragments, are shown in Figure 3, left. Upon adduct formation, the charge at the Mo center becomes slightly more negative, and that at the boron and bridging chloride centers become slightly more positive, all by around the same amount (0.05 e). The only dramatic change in charge is that at the gallium center (+0.517  $\rightarrow$  +0.292), which unsurprisingly gains electron density upon adduct formation. The calculated Mayer bond indices in the Mo–B–Ga–Cl rhombus (Mo–B: 0.74; B–Ga: 0.46; Ga–Cl: 0.63; Cl–Mo: 0.48; Mo–Ga: 0.37) suggest both that the Mo–B bond order has been significantly reduced and that there is significant covalent bonding, but not full single bonds, between all of the atoms in this unit (except between the B and Cl).

One of the key questions that arose in this work is that regarding the seemingly opposite regiochemistry of the  $\text{GaCl}_3$  addition to the Mo and Fe borylene complexes. Theoretical calculations on the adducts  $[(\text{OC})_4\text{Mo}\{\text{BN}(\text{SiMe}_3)_2\}(\text{GaCl}_3)]$  (**A**, theoretical model of complex **4**) and *mer*-[Fe(BClDur)(CO)<sub>3</sub>(GaCl<sub>3</sub>)(PMe<sub>3</sub>)] (**C**, model of the hypothetical inter-



**Figure 3.** Left: Key Hirshfeld charges (black) and Mayer bond indices (red) for the adduct models A, C, and their constituent separated fragments. Right: Theoretical models of experimentally observed and hypothetical adducts of  $\text{GaCl}_3$  with borylene complexes. Gray: carbon. Red: oxygen. Pink: boron. Beige: silicon. Brown: gallium. Green: chloride. Light blue: molybdenum. Light orange: phosphorus. Dark orange: iron.

mediate **11**), as well as their constituent fragments, were performed, and key Hirshfeld charges and Mayer bond indices are shown in Figure 3, left. The charges in the borylene fragments give an explanation of why differing regiochemistry is observed. In the separated molybdenum borylene fragment, the Mo atom has a much more positive charge than the boron atom (+0.249 vs +0.023), leading to the electron-deficient gallium atom attacking the boron atom, perhaps partially via the strongly negatively charged nitrogen atom (−0.275). Such a process would be reminiscent of the well-known coordination of aluminum trihalides with metal–carbonyls, which can lead to  $\text{M}–\text{C}–\text{O}–\text{Al}–\text{Br}$  rings.<sup>22</sup> Alternatively, the formation of **4** could involve initial donation of electron density from one Cl atom to the electrophilic molybdenum center, although this proposal would require spontaneous CO loss to allow the Cl to coordinate, or an increase in coordination number, and is presumably less likely. Conversely, in the iron borylene fragment, the Fe atom has a high negative charge (−0.160) compared to that of boron (+0.113), suggesting iron-based nucleophilicity. This fragment analysis provides some suggestion based on electronic properties as to why the orientation of the  $\text{GaCl}_3$  substrate differs in the observed products. However, the precursor borylene complexes **1** and **3** display significant differences in their steric properties. Thus, the combination of a pentacoordinate  $[(\text{OC})_4\text{Mo}=\text{BN}(\text{SiMe}_3)_2]$  borylene fragment with  $\text{GaCl}_3$  is presumably not the operative mechanism in this reaction (it should be emphasized here that the models shown in Figure 3 are merely fragments obtained from breakage of the bonds of the products **A** and **C** and are not intended to imply a mechanistic proposal). Much more likely is that the gallium attacks the boron and/or nitrogen atoms (as there is no free coordination site at the metal center of hexacoordinate precursor  $[(\text{OC})_5\text{Mo}=\text{BN}(\text{SiMe}_3)_2]$  (**3**)), leading subsequently to CO loss. In contrast, monovalent  $\text{FeL}_5$  complexes

like the precursor  $[(\text{Me}_3\text{P})(\text{OC})_3\text{Fe}=\text{BDur}]$  (**1**) have both an empty coordination site and precedence as Lewis bases, providing persuasive rationalization of the ultimate coordination of gallium to the iron center.

Calculation of a series of structurally similar adducts with both Mo and Fe (**A–F**, Figure 3, right) showed that changing the borylene substituent from duryl to  $\{\text{N}(\text{SiMe}_3)_2\}$ , or vice versa, had only a small effect on the geometry of the complexes (Table 1). However, exchanging the phosphine ligand of **C** and

**Table 1.** Calculated Ga–B and Ga–Fe Bond Distances (Å) and Qualitative Description of Charge Flux upon Adduct Formation (as Derived from EDA Analysis) in Different Model Systems

model	$d(\text{Ga}–\text{B})$	$d(\text{Ga}–\text{Fe})$	charge flux
A	2.417	–	$\text{OC}–\text{Mo} \leftarrow \text{B} \leftarrow \text{N}$
B	2.356	–	$\text{OC}–\text{Mo} \leftarrow \text{B} \leftarrow \text{C}$
C	–	2.598	$\text{P} \rightarrow \text{Fe} \leftarrow \text{B} \leftarrow \text{C}$
D	–	2.571	$\text{P} \rightarrow \text{Fe} \leftarrow \text{B} \leftarrow \text{N}$
E	–	2.688	$\text{OC}–\text{Fe} \leftarrow \text{B} \leftarrow \text{C}$
F	–	2.632	$\text{OC}–\text{Fe} \leftarrow \text{B} \leftarrow \text{N}$

**D** with a CO ligand caused more appreciable lengthening of the Ga–Fe bond. The relatively minor structural effect of changing the borylene substituent leads us to infer that the major contributor to the observed regiochemistry is the nature of the metal–ligand fragment, be it relatively electron-rich (Fe-phosphine) or electron-poor ( $\text{Mo}(\text{CO})_5$ ). Furthermore, the Energy Decomposition Analysis (EDA) rationalizes the observed Ga–B/Fe distances very well, showing that the greater the charge flux received by an atom, the shorter (and thus presumably stronger) the bond is to gallium in these complexes.



We present herein the first 1,2-additions across metal–boron double bonds of borylene complexes, using the Lewis base gallium trichloride. The results show that the two electronically and structurally different borylene complexes can both act as Lewis bases toward the Lewis acid, but that the nucleophilic center is different in each case: boron- or nitrogen-based in the case of the group 6 aminoborylene complex and metal-based in the case of the group 8 arylborylene complex. Our theoretical investigations indicate that, in this case, the nature of the metal fragment has a much stronger influence on the reactivity of the borylene complex than the nature of the borylene substituent.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

[h.braunschweig@uni-wuerzburg.de](mailto:h.braunschweig@uni-wuerzburg.de)

### Notes

The authors declare no competing financial interest.

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