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Exploring the Reducing Role of Boron: Added Insights from Theory

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Abstract

Carbon-carbon coupling in CO molecules is a challenging proposition, and very few main group complexes have been shown to effect this process. A recently reported triply bonded diboryne system (**1**) is notable for coupling four CO molecules to produce a (bis)boralactone species. The current full quantum chemical computational investigation with density functional theory (DFT) provides important insights into the nature of the CO coupling process by triply bonded diboryne systems. The complete reaction pathway leading to the formation of the (bis)boralactone has been determined. Factors that make this system so successful in coupling CO groups have been elucidated, and pertinent issues, such as why the coupling process stops after four CO additions, have been explored. Also, importantly, insights have been gained through the natural bond order (NBO) analysis into how the back-donation from diboryne activates CO.

Introduction

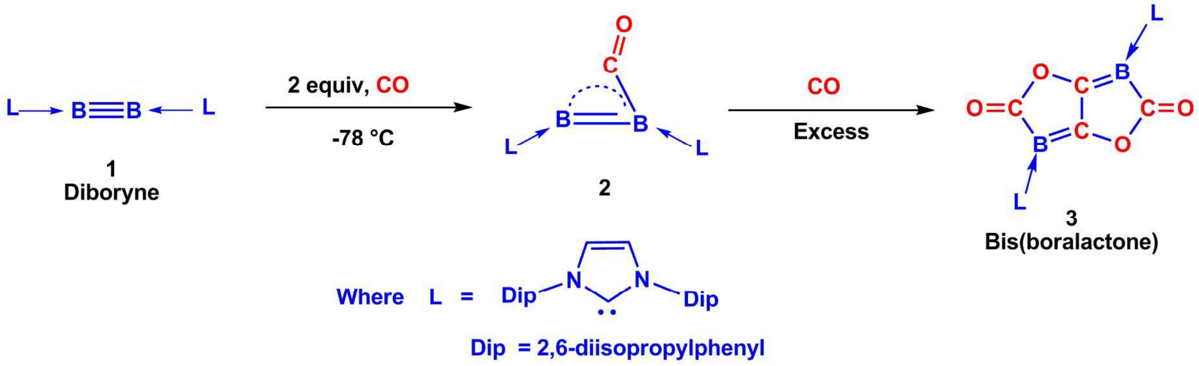
Carbon monoxide, CO, is available on an industrial scale and is used as a one-carbon-atom (or C_1) feedstock. The use of CO to generate new carbon-carbon bonds is an active area of research. The coupling of CO with unsaturated organic substrates (for example, in the hydroformylation and the carbonylation reactions) is the basis of industrially important processes.[1, 2] The Fischer-Tropsch process is another process of significant industrial relevance where CO is coupled with dihydrogen to generate alkanes of varying lengths, which could be employed as fuel.[3, 4]

All of the processes mentioned above require the use of transition metal catalysts. Considering the importance of the field of CO coupling by transition metal based systems, this area has been well explored experimentally. The reductive homologation of CO to a ketene carboxylate has been reported by Evans *et al.*[5] using an organosamarium complex. A similar CO reduction has also been done using the organolanthanium complex.[6] In addition to this, the reductive coupling of CO using uranium has gained some success. The organouranium complexes reported by Cloke[7] and Arnold[8] have coupled two CO molecules in a head-to-head (C-to-C) manner. Reductive cyclotrimerization[9] and cyclotetramerization[10]of CO has also been shown to be possible when uranium complexes were employed. The Lippard group[11] has managed the reductive coupling of CO molecules using niobium and tantalum complexes. The ditantalum hydride complex reported by Kawaguchi*et al.*[12] was shown to be able to couple six CO molecules. A rhenium carbonyl complex has been successfully employed by Labinger and Bercaw[13] for the CO coupling reaction.

Though transition metal based systems have been successful in coupling CO molecules, employing main group systems for the same has been found to be challenging. The only success in this regard has been obtained with the aid of a germylene compound reported by Philip Power's group.[14, 15] Different attempts by the groups of Siebert,[16] Chapman[17, 18], Bertrand[19] and Stephan[20] has led to some success in CO activation but head-to-head C-C coupling could not be achieved. A system having two boron atoms was found to bind a CO molecule to each of the two borons, and the formation of a thermally stable subsequent neutral OCBBCO molecule, showing boron-boron triple bond character, was observed in the matrix.[21]

However, success in this regard has been recently obtained experimentally. Exciting new work reported by Braunschweig and coworkers[22] indicates the synthesis of a new B-B complex: a diboryne(**1**), which contains a thermally stable boron-boron triple bond unit, and has N-heterocyclic carbenes as groups binding to the boron atoms. The structure of **1** is shown in Scheme 1 below. Braunschweig *et al.*[22] have shown that when excess of CO is added to a benzene solution of **1**, four CO molecules are reduced by the diboryne, and couple together to form a planar (bis)boralactone species, **3** (see Scheme 1). They have also shown that the process is initiated by the interaction of CO with the B-B triple bond, leading to a CO bridged complex **2**.[22] More recently, Braunschweig and co-workers[23] have also shown multiple complexation of CO molecules to boron. This multicarbonyl boron complex has been found to be capable of photolytic liberation of CO and subsequent intramolecular carbon–carbon bond activation, similar to transition-metal complexes.

Some aspects of the process pertaining to the work of Braunschweig and coworkers on the coupling of four CO molecules at the diboryne[22] are, however, not fully clear: (i) why does the reaction of CO with the diboryne stop after the addition of four CO groups, leading to the formation of the (bis)boralactone?, and (ii) what accounts for the facility of the CO addition to the diboryne? Furthermore, it is also interesting to ask whether the (bis)boralactone formed can interact with dihydrogen to yield new products and whether C-C bond formation is effective in syn-gas (CO + H_2). This is especially significant because of the importance of industrial processes like the Fischer-Tropsch reaction,[3,4] which involve the conversion of syn-gas to value added products such as alkanes.



Scheme 1. The metal free coupling of four CO molecules by a boron-boron triple bonded system reported by Braunschweig and coworkers[22]; L is a N-heterocyclic carbene.

The purpose of the current computational investigation is to address these issues and thereby gain a better understanding of this interesting new chemistry. This has been done with a full quantum chemical approach with density functional theory (DFT). A mechanism has been proposed for the conversion of the diboryne to the (bis)boralactone through its reaction with four CO molecules, and the driving factors behind the facile reactions have been explored. In addition to this, the reactivity of (bis)boralactone (**3**) towards dihydrogen has been discussed.

Result and Discussion

a. CO reduction using a boron-boron triple bond complex

As discussed in the Introduction, the probable path for the conversion of **1** to **3** has been explored. The results are summarized in Fig 1. As shown in the figure, the conversion of **1** to **3** goes through multiple steps. The first step is the addition of one CO to the boron-boron triple bond of **1**, leading to a bridged complex (**2**), a species that has been experimentally isolated.[22] This reaction is exergonic by 31.0 kcal/mol (see Fig 1) and proceeds *via* **TS1**, with a barrier of 19.5 kcal/mol. As mentioned above, **2** was the only intermediate that could be experimentally isolated, which indicates that this is a stable species. This is also borne out by our calculations, which show that the next step: the addition of a CO molecule to **2,** is somewhat hindered, with the obtained 33.0 kcal/mol barrier being the highest along the entire pathway (see Fig 1), leading to the formation of **2CO_a**. The rearrangement of **2CO_a** leads to the formation of the doubly bridged species **2CO_b** *via* **TS3** with a barrier of 23.4 kcal/mol. This, again, is a process that is exergonic by 4.1 kcal/mol.

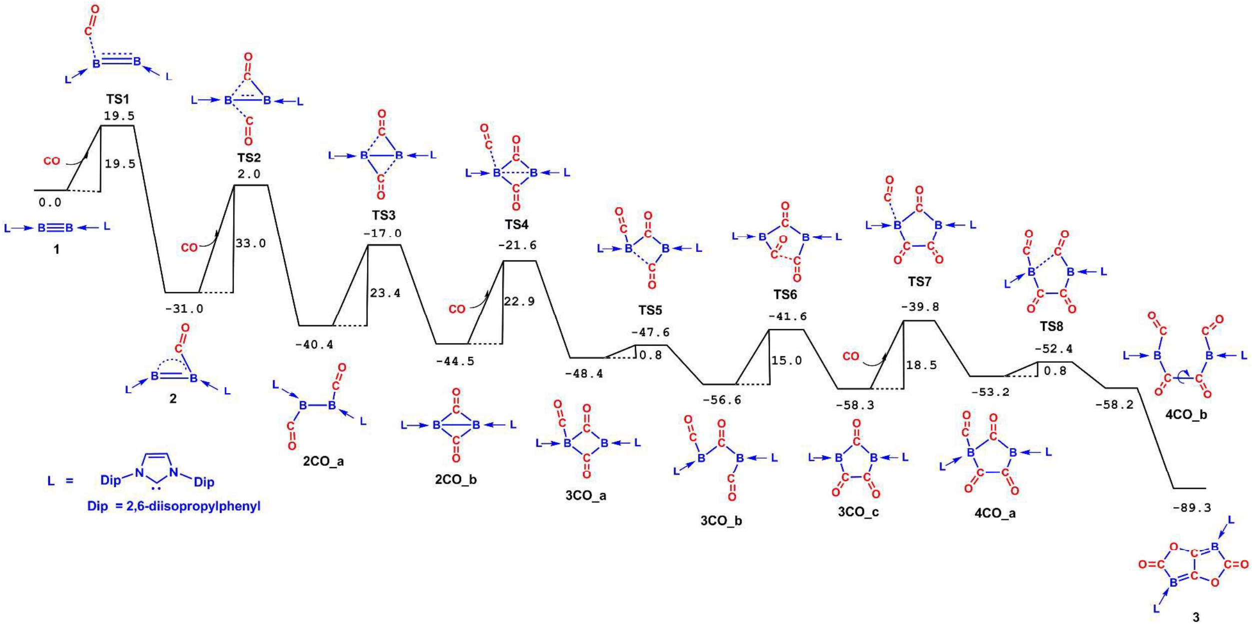


Fig 1. The free energy profile for the conversion of diboryne (**1**) to bis(boralactone) (**3**); energy values are in kcal/mol.

The addition of a third CO molecule to species **2CO_b** necessitates the crossing of a barrier, calculated to be 22.9 kcal/mol, leading to the formation of **3CO_a**, exergonic by 3.9 kcal/mol, with three CO groups attached. Interestingly, **3CO_a** can rearrange in a facile manner to yield another intermediate **3CO_b**, *via* a transition state *that is only 0.8 kcal/mol higher in energy than **3CO_a***. Intermediate **3CO_b** can rearrange through a low barrier of only 15.0 kcal/mol to conformation **3CO_c** *via* a carbon-carbon bond forming transition state **TS6** (see Fig 1). Given the reasonable value for the barrier heights and the exergonicity of all the steps discussed so far, such reactions would be expected to occur under ambient conditions when diboryne **1** reacts with excess CO, as experimentally observed. The addition of the fourth CO to **3CO_c** would lead to the formation of **4CO_a** *via* **TS7** (barrier of 18.5 kcal/mol). **4CO_a** can rearrange through the very facile cleavage of the boron-carbon bond (again, having a barrier of only 0.8 kcal/mol) to yield **4CO_b**, an open structure that can undergo rotation along the C-C to yield the final, observed (bis)boralactone species **3**.

The presented mechanism involves ten intermediates and seventeen steps. Out of the ten intermediates, only three have been experimentally observed. Thus, the conversion of **2** to **3** involves seven intermediates that have not been observed experimentally. Therefore, there is always the possibility that there could be an alternative pathway that can connect the original reactant to the products. However, the fact that every step along the reaction pathway is exergonic, with accessible barrier heights for the temperature (25 °C) at which the reactions were carried out, suggests that the mechanism proposed is quite probable. It is also to be noted that Braunschweig's group[24] has recently reported a similar mechanism with three NHC ligand sets (including the NHC ligand employed in the current work) with a combined semi-empirical/DFT approach. The major part of the reaction mechanism in their study overlaps with our proposed mechanism. The differences include the intermediates **3CO_a** and **TS5** that are part of our mechanism, which were not obtained in their work. However, the conversion of **4CO_b** to **3** was observed, in their work, to occur through four steps: a carbon-carbon bond rotation transition state **TS9** forming the intermediate **4CO_c** followed by a transition state **TS10,** leading to the formation of the (bis)boralactone (**3**) (see Fig S1. in the Supporting Information file). In our mechanism, we found the conversion of **4CO_b** to **3** to be a downhill process, without a carbon-carbon rotation transition state, or the subsequent intermediate **4CO_c** obtained by Braunschweig *et al*.[24] All of our attempts towards obtaining **4CO_c** led to the formation of the final product: the (bis)boralactone (**3**). This is likely due to the fact that the the process of converting **4CO_b** to **3** is a favourable process, and the intermediate **4CO_c** is a shallow minimum on the potential energy surface. Nevertheless, since the principal steps proposed in our mechanism and that by Braunschweig and coworkers are similar, this again suggests the feasibility and likelihood of the proposed mechanism.

We have also, in addition to investigating the complete mechanistic path, looked at the interactions present in the intermediate species along the reaction pathway, through a careful NBO analysis. This is discussed in the next section.

b. NBO analysis

In order to gain insights into the interaction of CO with the diboryne system, the intermolecular charge transfer in the different complexes has been analysed with the natural bond order (NBO) analysis. The energetic estimate of donor (i) - acceptor (j) orbital interactions can be obtained by the second order perturbation theory analysis of the fock matrix in the NBO basis. The donor-acceptor interaction energy E(2) is given by

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_i - \varepsilon_j},$$

where q_i is the donor orbital occupancy, ε_I and ε_j are the diagonal elements (orbital energies), and $F(i, j)$ is the off-diagonal NBO Fock matrix element. In the present investigation, the important interactions are between CO and the B_2 unit of the diboryne, and these have been carefully analysed. The results are summarized in Table 1.

Table 1. Second order perturbation theory analysis of the Fock matrix in NBO basis for all the complexes shown in Fig 1.

Complex	Donor (i)	Occupancy	Acceptor (j)	Occupancy	E(2)[a] (kcal/mol)	E(j)-E(i)[b] (a.u.)	F(i,j)[c] (a.u.)
1	LP (1) C3	1.02368	LP*(1) B1	0.70409	51.9	0.16	0.088
	LP*(1) C10	1.02010	LP*(1) B2	0.69974	50.2	0.16	0.087
	LP (1) N4	1.57980	LP (1) C3	1.02368	79.9	0.11	0.102
	LP (1) N9	1.57875	LP (1) C3	1.02368	80.6	0.11	0.102
	LP (1) N11	1.57752	LP*(1) C10	1.02010	81.1	0.11	0.103
	LP (1) N16	1.57801	LP*(1) C10	1.02010	80.7	0.11	0.102
2	LP*(1) B14	0.58308	BD*(2) C1-O2	0.48062	237.2	0.01	0.068
	LP (1) B 15	0.74839	BD*(2) C1-O2	0.48062	439.0	0.01	0.090
	BD (2) C1-O2	1.98559	LP*(1) B14	0.58308	2.5	0.29	0.028
	BD (2) C1-O2	1.98559	LP (1) B15	0.74839	3.4	0.29	0.035

2CO_ a	BD(2) B12 - C13	1.56864	LP*(1) C8	0.98009	101.2	0.03	0.059
	BD(2) B25 - C26	1.56971	LP*(1) C28	0.97976	100.6	0.03	0.059
	BD (1) B12 - B25	1.70030	LP*(1) C13	0.69185	31.1	0.22	0.082
	BD (1) B12 - B25	1.70030	LP*(1) C26	0.69184	31.1	0.22	0.082
2CO_ b	LP (1) B12	0.60598	BD*(2) C13 - O14	0.39080	139.7	0.03	0.082
	LP (1) B12	0.60598	BD*(2) C 26 - O 27	0.38983	121.0	0.03	0.077
	LP*(1) B25	0.60458	BD*(2) C 13 - O14	0.39080	122.6	0.03	0.077
	LP*(1) B25	0.60458	BD*(2) C26 - O27	0.38983	139.3	0.03	0.082
	BD (2) C13 - O14	1.98601	LP (1) B12	0.60598	2.8	0.29	0.030
	BD (2) C13 - O14	1.98601	LP*(1) B 25	0.60458	2.7	0.29	0.030
	BD (2) C26 -O27	1.98599	LP (1) B 12	0.60598	2.7	0.29	0.030
	BD (2) C 26 -O27	1.98599	LP*(1) B 25	0.60458	2.8	0.29	0.030
3CO_ a	LP (1) B 27	0.84302	BD*(2) C25 -O26	0.37769	408.3	0.01	0.088
	LP (1) B 27	0.84302	BD*(2) C28 - O29	0.37836	405.5	0.01	0.088
	BD (1) B12 - C25	1.70684	BD*(2) C13 - O 14	0.36943	10.2	0.33	0.053
	BD (1) B12 - C28	1.70689	BD*(2) C13 - O14	0.36943	10.0	0.33	0.053
3CO_ b	BD (2) B12 - C25	1.56261	LP*(1) C8	0.96447	105.4	0.03	0.062
	BD (2) B 27 -C28	1.56243	LP*(1) C30	0.96580	106.0	0.03	0.062
3CO_ c	LP*(1) B12	0.50491	BD*(2) C13 - O14	0.30579	142.8	0.02	0.083
	LP*(1) B12	0.50491	BD*(2) C29 - O30	0.42104	186.2	0.02	0.083
	LP (1) B31	0.50935	BD*(2) C29 - O 30	0.42104	191.2	0.02	0.084
	LP (1) B31	0.50935	BD*(2) C32 - O33	0.30677	147.9	0.02	0.083
	LP (1) B 29	0.73126	BD*(2) C30 - O31	0.42662	327.2	0.02	0.087

4CO_ a	BD (1) B12 - C13	1.75191	BD*(2) C 67 - O68	0.31667	10.4	0.36	0.056
	BD (1) B12 - C57	1.82200	BD*(2) C67 - O 68	0.31667	5.7	0.41	0.045
4CO_ b	BD (2) B12 - C25	1.58596	LP*(1) C8	0.95162	89.8	0.04	0.059
	BD (2) B29 - C30	1.56624	LP*(1) C32	0.95241	100.7	0.04	0.062
3	BD (2) B12 - C13	1.55344	LP*(1) C8	0.93625	150.5	0.02	0.049
	BD (2) B27-C28	1.55349	LP*(1) C32	0.93617	150.2	0.02	0.049
	LP (1) N7	1.53033	LP*(1) C8	0.93625	95.9	0.12	0.108

[a] E(2) means energy of donar-acceptor interactions

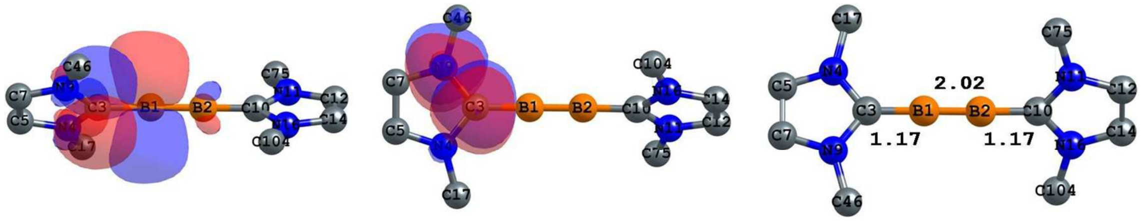
[b] energy difference between donor and acceptor i and j NBO orbitals

[c] F(i,j) is the Fock matrix element between i and j NBO orbitals.

Here BD(1), BD(2), LP, BD*(1), BD*(2) means σ bonding, π bonding, lone pair, σ* anti-bonding, π* anti-bonding atomic orbitals respectively.

The perusal of Table 1 shows that the LP* orbitals have been used as donor orbitals in different interactions. Conventionally, these orbitals should be empty, and hence not have any electron density. However, as reported in Table 1, these orbitals do have electron occupancy of more than 0.5 and can therefore transfer electron density to other, acceptor, orbitals. The reason for the occupancy in the LP* orbitals is because of the transfer of electron density from the canonical orbitals into the LP* orbitals. This is the reason why what is nominally labeled LP* has a non-zero occupation. Similar results have been obtained when a full geometry optimization was done in Gaussian 9.0[25] at the pbepbe/tzvp level of theory, for a model compound, by putting a methyl group in place of the Dip group for the intermediate **2**, which indicates that the current approach of doing single point calculations for the NBO analysis on fully optimized real structures gives reliable results. The NBO output files for intermediate **2** and the model intermediate **2** have been provided in the Supporting Information files.

As shown in Table 1, complex **1** is stabilized by electron donation from the N-heterocyclic carbene ligand to the B2 unit of diboryne. The charge transfer energies for the interaction of the lone pair (LP) containing orbital, LP(C3) to orbital LP*(B1) and the LP*(C10) to LP*(B2) are more than 50.0 kcal/mol, indicating strong electron donation from the ligand to both the borons of the diboryne. Furthermore, the lone pair of nitrogen donates electron density to the carbene carbon attached to boron, with charge transfer stabilization energy of around 80.0 kcal/mol. There are four such donor-acceptor interactions (see Table 1). This further explains the role of N-heterocyclic carbenes in stabilizing the diboryne **1**. The effect of this charge transfer can also be seen through the Wiberg bond indices (WBI). The WBI values for the boron-carbon bonds is more than 1.00 (1.17); furthermore, the WBI value for the boron-boron triple bond is 2.02, which is lower than the expected value of 3.00. This shows the charge delocalization over the C-B-B-C unit in complex **1**, though it should also be noted that WBI values for multiple bonds in main-group elements are usually underestimated.[26] The NBO plots for the selected interactions, as well as the WBI values for complex **1** are shown below in Fig 2. It is to be noted that the reason for the lone pair on the NHC carbon having electron occupancy is that electron density moves from the LP orbitals of the adjoining nitrogens in the NHC to the LP orbital on the carbon (see second structure of Figure 2 below), leading to a non-zero occupation in the orbital on carbon having π symmetry.



LP(1) C3 ⟶ LP*(1) B1

E(2) = 51.9 kcal/mol

LP(1) N9 ⟶ LP(1) C3

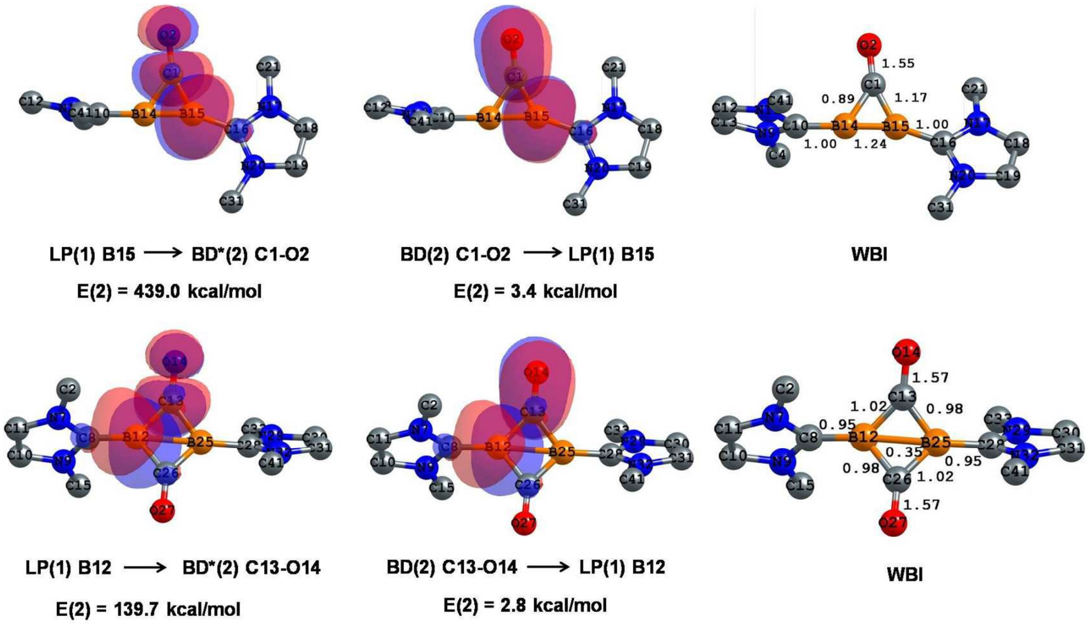
E(2) = 80.6 kcal/mol

WBI

Fig 2. The NBO plots for the intra-molecular donor-acceptor interactions and WBI index values for **1**. The color scheme is as follows: boron: yellow, carbon: gray, oxygen: red and nitrogen: blue; only one carbon of the Dip group attached to nitrogen has been shown; the rest of the carbons of the Dip group and all the hydrogens have been removed for the purpose of clarity. Thus the methyl group attached to the nitrogen represents the Dip group.

As reported by Braunschweig *et al.*[22], **2** is an experimentally obtained complex, in which the CO molecule has been semi-bridged with the borons of diboryne, as shown in Scheme 1. In the current work, the optimization of **2** shows an exact semi-bridged binding of CO with the diboryne. NBO analysis sheds further light on the semi-bridged binding of CO with the diboryne. The charge transfer interaction energy for LP(B15) to π*(C1-O2) is 439.0 kcal/mol whereas the charge transfer energy from LP*(B14) to π*(C1-O2) is 237.2 kcal/mol, as shown in Table 1. This significant difference in donor-acceptor interaction energies leads to the bond length of B15-C1 being 1.488 Å, and the B14-C1 bond length being longer: 1.607 Å. This effect of the stronger interaction of CO with B15 is also clearly seen through the WBI values. The WBI value for the B15-C1 bond is 1.17, while it is 0.89 for B14-C1, as shown in Fig 3. Thus, due to the strong interation with one of the boron atoms in the diboryne, the CO coordinates in a semi-bridged manner with the diboryne in complex **2**.

Though it has been stated by Braunschweig *et al.*[22] that there is significant back-donation from the B_2 unit to the π* orbital of the CO, the precise description regarding the back-donation is worth understanding, as the diboryne complex does not have molecular orbitals with significant d-orbital contribution, unlike the case of CO coordinating transition metal complexes. NBO analysis sheds light on this aspect as well. The donor-acceptor interactions listed in Table 1 for complex **2** clearly show that the back-donation from the boron atoms of the B2 unit is much more prominent than the donation by CO to the B2 unit. The charge stabilization energy from the interaction of π (C1-O2) to LP*(B14) and LP(B15) is 2.4 kcal/mol and 3.5 kcal/mol respectively. On the other hand, the back-donation from LP*(B14) to π*(C1-O2) and LP(B15) to π*(C1-O2) is 237.2 kcal/mol and 439.0 kcal/mol respectively. This clearly indicates that back-donation is the prominent interaction in CO activation. The NBO plots for the important donation and back-donation interactions has been shown in Fig 3.



LP(1) B15 → BD*(2) C1-O2
E(2) = 439.0 kcal/mol

BD(2) C1-O2 → LP(1) B15
E(2) = 3.4 kcal/mol

WBI

LP(1) B12 → BD*(2) C13-O14
E(2) = 139.7 kcal/mol

BD(2) C13-O14 → LP(1) B12
E(2) = 2.8 kcal/mol

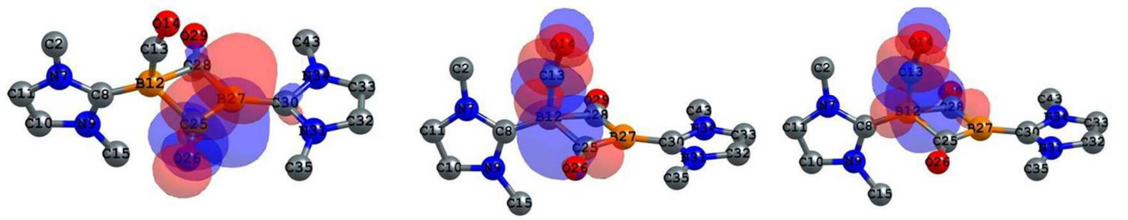
WBI

Fig 3. The NBO plots for the intra-molecular donor-acceptor interactions and WBI values for **2** and **2CO_b**. Here BD(2), LP, BD*(2) are the π bonding, lone pair, and π* anti-bonding atomic orbitals respectively. The color scheme is as follows: boron: yellow, carbon: gray, oxygen: red and nitrogen: blue; only one carbon of the Dip group attached to nitrogen has been shown; the rest of the carbons of the Dip group and all the hydrogens have been removed for the purpose of clarity. Thus the methyl group attached to the nitrogen represents the Dip group.

As the diboryne system is experimentally reported[22] to activate four CO molecules, it is important to investigate the energetics at every CO insertion step. After the activation of the second CO molecule, the complex **2CO_a** forms *via* **TS1,** which subsequently converts to **2CO_b**, a stable intermediate, before the addition of a third CO, as shown in Fig 1. In order to understand the second CO molecule activation, the **2CO_b** intermediate has been analyzed with NBO. A perusal of the values in Table 1 makes it clear that the back-donation from the borons of the B2 unit is prominent in this intermediate. The charge transfer stabilization energy for the donation interaction, i.e., donation of electron density from the CO to the B_2 unit is lower than 3.0 kcal/mol for all the donation interactions as shown in Table 1. The charge transfer stabilization energy for back-donation i.e. transfer of electron density from the borons of the B_2 unit to the π* orbitals of the CO in complex **2CO_b** is more than 120.0 kcal/mol for all the back-donation interactions. Hence, the NBO analysis makes it clear that the second CO activation is similar to the first (see Fig 3).

However, the activation of the third and fourth CO molecules is somewhat different in comparison to the first and second CO activation steps. In case of the **2** and **2CO_b** complexes, the orbitals involved in the back-donation are the LP or the LP* of boron, with a greater amount of charge stabilization energy. On the other hand, in the **3CO_a** and **4CO_a** cases, the orbitals involved in back-donation are the σ(B-C) to π*(CO), i.e., the sigma bonding orbital between the boron and the CO carbon donates electron density into the π* orbital of CO. As shown in Table

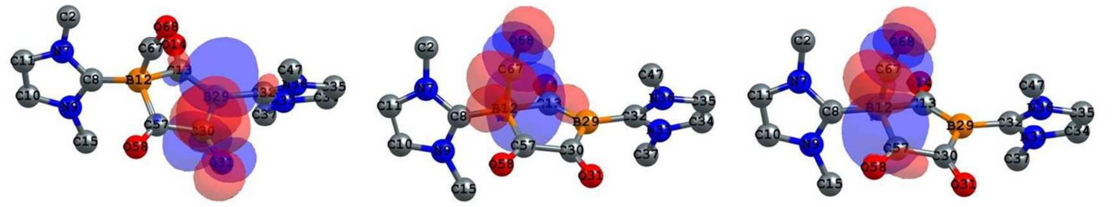
1, for the third CO activation in complex **3CO_a**, the charge stabilization energy for the donor acceptor interactions is σ(B12-C25) to π*(C13-O14) and σ(B12-C28) to π*(C13-O14) are 10.2 kcal/mol and 10.0 kcal/mol respectively, where the carbonyl in question is the terminal one. Similarly, for the fourth CO activation in complex **4CO_b**, the charge stabilization energy for the donor-acceptor interactions σ(B12-C13) to π*(C67-O68) and σ(B12-C57) to π*(C67-O68) are 10.4 kcal/mol and 5.7 kcal/mol respectively. These values are smaller than the values obtained for the back-donation interactions for the intermediates formed with the first and second CO activations, which makes it clear that the charge transfer from the B_2 unit to the π* of the latest CO added is reduced after the second CO activation. The reason for this is the back-donation from boron to the initially activated, bridging CO molecules. As shown in Table 1 for the case of **3CO_a**, the donor-acceptor energies for LP(B27) to π*(C25-O26) and LP(B27) to π*(C28-O29) are 408.3 kcal/mol and 405.5 kcal/mol respectively. Similarly, in case of **4CO_a**, the charge transfer stabilization energy for LP(B29) to π*(C30-O31) is 327.2 kcal/mol. This higher interaction with the initially activated CO molecules reduces the electon density on the boron and hence leads to reduced back-donation to the π* of the third and the fourth COs added. The NBO plots for the selected interactions for the complex **3CO_a** and **4CO_a** have been shown in Table 1 and Fig 4.



LP(1) B27 ⟶ BD*(2) C25-O26
E(2) = 408.0 kcal/mol

BD(1) B12-C25 ⟶ BD*(2) C13-O14
E(2) = 10.2 kcal/mol

LP(1) B12-C28 ⟶ BD*(2) C13-O14
E(2) = 10.0 kcal/mol



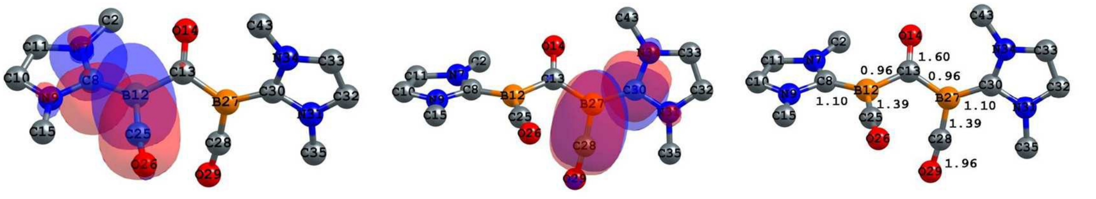
LP(1) B29 ⟶ BD*(2) C30-O31
E(2) = 327.2 kcal/mol

BD(1) B12-C13 ⟶ BD*(2) C67-O68
E(2) = 10.4 kcal/mol

BD(1) B12-C57 ⟶ BD*(2) C67-O68
E(2) = 5.7 kcal/mol

Fig 4. The NBO plots for the intra-molecular donor-acceptor interactions for complexes **3CO_a** and **4CO_a**. Here BD(1), BD(2), LP, BD*(1), BD*(2) means σ bonding, π bonding, lone pair, σ* anti-bonding, and π∗ anti-bonding atomic orbitals respectively. The color scheme is as follows: boron: yellow, carbon: gray, oxygen: red and nitrogen: blue; only one carbon of the Dip group attached to nitrogen has been shown; the rest of the carbons of the Dip group and all the hydrogens have been removed for the purpose of clarity. Thus the methyl group attached to the nitrogen represents the Dip group.

It is also interesting to note, as mentioned earlier, that the breaking of the boron-carbon bond is seen to be a highly feasible process (barriers of only 0.8 kcal/mol for the conversion of **3CO_a** to **3CO_b** and **4CO_a** to **4CO_b**, see Fig1), converting the sp^3-sp^2 system to an sp^2-sp^2 system. This ability of diboryne systems to convert from sp^3-sp^2 to sp^2-sp^2 in a facile manner has also been reported for a different, diborane, system.[27] The NBO analyses for the complexes **3CO_b** and **4CO_b** suggests the presence of multiple bonding between the terminal carbonyl carbon and boron and sheds light on the stability of sp^2-sp^2 complexes. As shown in Table 1, the donor-acceptor interactions π(B12-C25) to LP*(C8) and π(B27-C28) to LP*(C30) in complex **3CO_b** has a charge transfer stabilization energy of 105.4 kcal/mol and 106.0 kcal/mol respectively. Similarly, in complex **4CO_b**, the donor-acceptor interactions π (B12-C25) to LP*(C8) and π(B29-C30) to LP*(C32) has charge transfer stabilization energies of 89.8 kcal/mol and 100.7 kcal/mol respectively. This suggests substantial overlap between the π orbital of the boron-carbon bond with the lone pair of carbon attached to the boron, thereby providing stability to the three sp^2-sp^2 complexes. The WBI values obtained for these complexes further indicates the double-bond character in the boron-terminal carbonyl carbon bond: the value of the carbon-boron bond in complexes **3CO_b** and **4CO_a** is seen to be around 1.4. These multiple bonding interactions lead to stable sp^2-sp^2 complexes, thereby providing an explanation as to why the conversion of sp^3-sp^2 boron based complexes to sp^2-sp^2 is so facile. A similar bonding pattern has been found in the **2CO_a** complex: a perusal of the donor-acceptor stabilization energies and WBI values suggests multiple bonding between the terminal carbonyl carbons and the boron atoms in complex **2CO_a**. The NBO plots and the important interactions for **2CO_a**, **3CO_c** and **3** complexes are shown in the Supporting Information file.



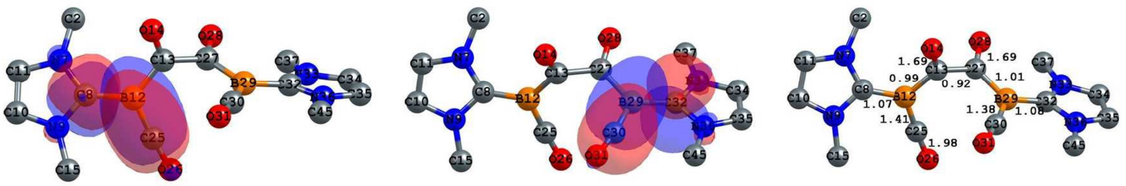
BD(2) B12-C25 ⟶ LP*(1) C8

E(2) = 105.4 kcal/mol

BD(2) B27-C28 ⟶ LP*(1) C30

E(2) = 106.0 kcal/mol

WBI



BD(2) B12-C25 ⟶ LP*(1) C8

E(2) = 89.8 kcal/mol

BD(2) B29-C30 ⟶ LP*(1) C32

E(2) = 100.7 kcal/mol

WBI

Fig 5. The NBO plots for the intra-molecular donor-acceptor interactions for complexes **3CO_b** and **4CO_b**. Here BD(1), BD(2), LP, BD*(1), BD*(2) means σ bonding, π bonding, lone pair, σ* anti-bonding, π* anti-bonding atomic orbitals respectively. The color scheme is as follows: boron: yellow, carbon: gray, oxygen: red and nitrogen: blue; only one carbon of the Dip group attached to nitrogen has been shown; the rest of the carbons of the Dip group and all the hydrogens have been removed for the purpose of clarity. Thus the methyl group attached to the nitrogen represents the Dip group.

Thus, the NBO analysis sheds light on different aspects of this interesting conversion of diboryne (**1**) to (bis)boralactone (**3**). It explains the role of the N-heterocyclic carbene in stabilizing all the B_2 complexes. It also provides insight into the back-donation from the B_2 unit to the π* of the carbonyl groups. Furthermore, it explains the multiple bonding in sp^2-sp^2complexes and provides explanation for the facile conversion of sp^3-sp^2 diboryne complexes to the sp^2-sp^2 complexes. The NBO analysis also provides an explanation for the experimentally observed semi-bridged binding of CO with the diboryne. In addition to the understanding gained from the NBO analysis, the frontier molecular orbital analysis, discussed in the next section, provides further details about the CO activation process.

c. Frontier Molecular Orbital analysis

In chemical systems, the interactions between two reacting species occurs between their respective frontier orbitals: the HOMOs and the LUMOs. The strength of the interaction usually depends on the symmetry and the energy difference between the interacting orbitals. In order to understand the stepwise activation of the CO moleules by the diboryne (**1**), the frontier molecular orbitals analysis for all the complexes - the reactants, intermediates and product structures shown in Fig.1 - has been done. The HOMO and LUMO orbital energy values corresponding to each complex has been listed in Table 2 below. A graph showing the values is shown in Fig 6 and the HOMO-(LUMO of CO) plots for all the complexes has been shown in Fig 7. The information in Table 2, and Figures 6 and 7 provides insight into the reasons behind the success of diboryne at activating CO molecules and explains why **1** is able to activate only four CO molecules.

Table 2. The energy values for the frontier molecular orbitals at the PBEPBE/TZVP level of theory, obtained using Gaussian 09.[25]

Complexes/Molecules	**HOMO/ kcal/mol**	**LUMO/ kcal/mol**	**Gap (HOMO-LUMO of CO) kcal/mol**	**Gap (HOMO-LUMO of H_2) kcal/mol**
1	-66.2	-32.7	18.5	91.8
2	-61.7	-35.2	14.0	87.3
2CO_a	-68.1	-32.9	20.4	93.7
2CO_b	-70.5	-37.7	22.8	96.1
3CO_a	-77.4	-37.0	29.7	103.0
3CO_b	-80.5	-36.8	32.8	106.1
3CO_c	-78.0	-52.9	30.3	103.6
4CO_a	-79.6	-43.4	31.9	105.2
4CO_b	-83.9	-40.4	36.2	109.5
3	-85.0	-50.5	37.3	110.6
CO	-208.5	-47.7	160.8	234.1
H_2	-238.1	25.6	190.4	263.7

As shown in a previous section, the back-donation from the B_2 unit to the anti-bonding orbital of CO is a prominent interaction in the activation of CO. Therefore, the energy difference between the HOMO of the B_2 complexes and the LUMO of CO is an important factor in determining the efficacy of activation of CO. As shown in Table 2, the energy difference between the HOMO of the complexes **1**, **2**, **2CO_b**, **3CO_c** and the LUMO of CO is 18.5 kcal/mol, 14.0 kcal/mol, 22.8 kcal/mol and 30.3 kcal/mol respectively. It is to be noted that **1**, **2**, **2CO_b**, and **3CO_c** are, respectively, the complexes before the activation of the first, second, third and the fourth CO molecule. Therefore, the results show that a gap below 30.5 kcal/mol facilitates the activation of CO by the B2 complex: for the cases **4_CO_a**, **4_CO_b** and **3**, where the gaps are 31.9 kcal/mol, 36.2 kcal/mol and 37.3 kcal/mol respectively, no activation of CO takes place. Furthermore, as shown in Fig. 7, the HOMO for the complexes **1**, **2**, **2CO_b**, and **3CO_c** is concentrated on the boron atoms, while for **2CO_a** (where the HOMO-LUMO of CO is 20.4 kcal/mol), the HOMO is distrubuted between boron and the adjacent carbon. Therefore, the small energy difference between the HOMO of the B_2 complexes and the LUMO of CO, and the fact that the HOMOs in certain B_2 complexes are concentrated on boron atoms leads to easier back-donation from specific B_2 complexes to CO, resulting in the room temperature activation of CO.

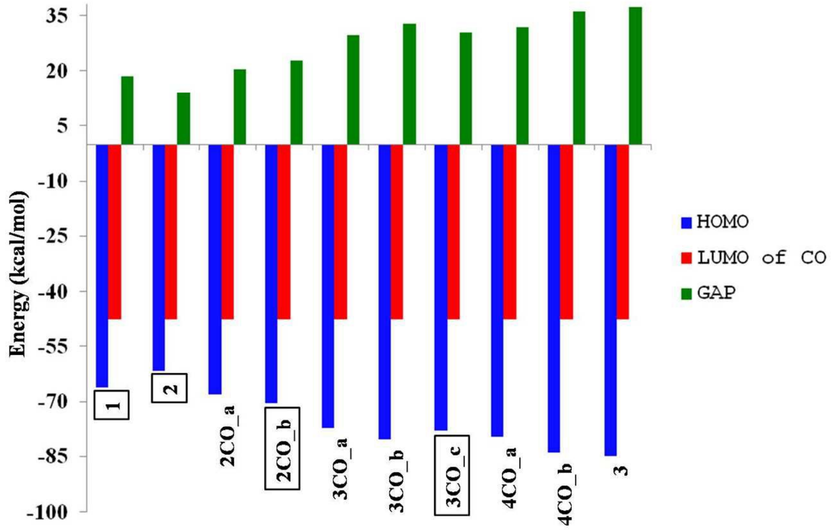


Fig 6. The HOMO energy values for the different B2 complexes, compared to the LUMO energy value of CO; the intermediate species, **1**, **2**, **2CO_b**, **3CO_c**, shown in the rectangular boxes, are the ones that accept CO (see Fig 1).

It is also important to note that the stepwise addition of CO has a considerable influence on the stability of the HOMOs of the newly formed complexes. The HOMOs for complexes **3CO_b**, **4CO_b** and **3** are concentrated on the boron and adjacent carbon atoms, as shown in Fig 7. Due to this delocalization over the B-C bond, these HOMOs are stabilized. The stabilization of the HOMO increases the energy difference between the HOMO of the diborane complexes and the LUMO of CO, consequently hindering subsequent CO activation. It is interesting to note that the HOMO of complex **3** is more stabilized in comparison to the other complexes: the energy gap between the HOMO of **3** and the LUMO of CO is 37.3 kcal/mol, which is higher than the energy difference for the **1**, **2**, **2CO_b**, and **3CO_c** complexes. Due to this, **3** is unable to activate further CO molecules and thus CO activation stops after the formation of the energetically stabilized product: the (bis)boralactone **3**. In order to emphasize this point, we have done calculations binding a fifth CO molecule to **3**, and found that the CO molecule is removed from the vicinity of **3** during the optimization. Thus, our calculations and analyses provide the explanation for why the CO activation stops after the addition of four CO molecules to **1**.

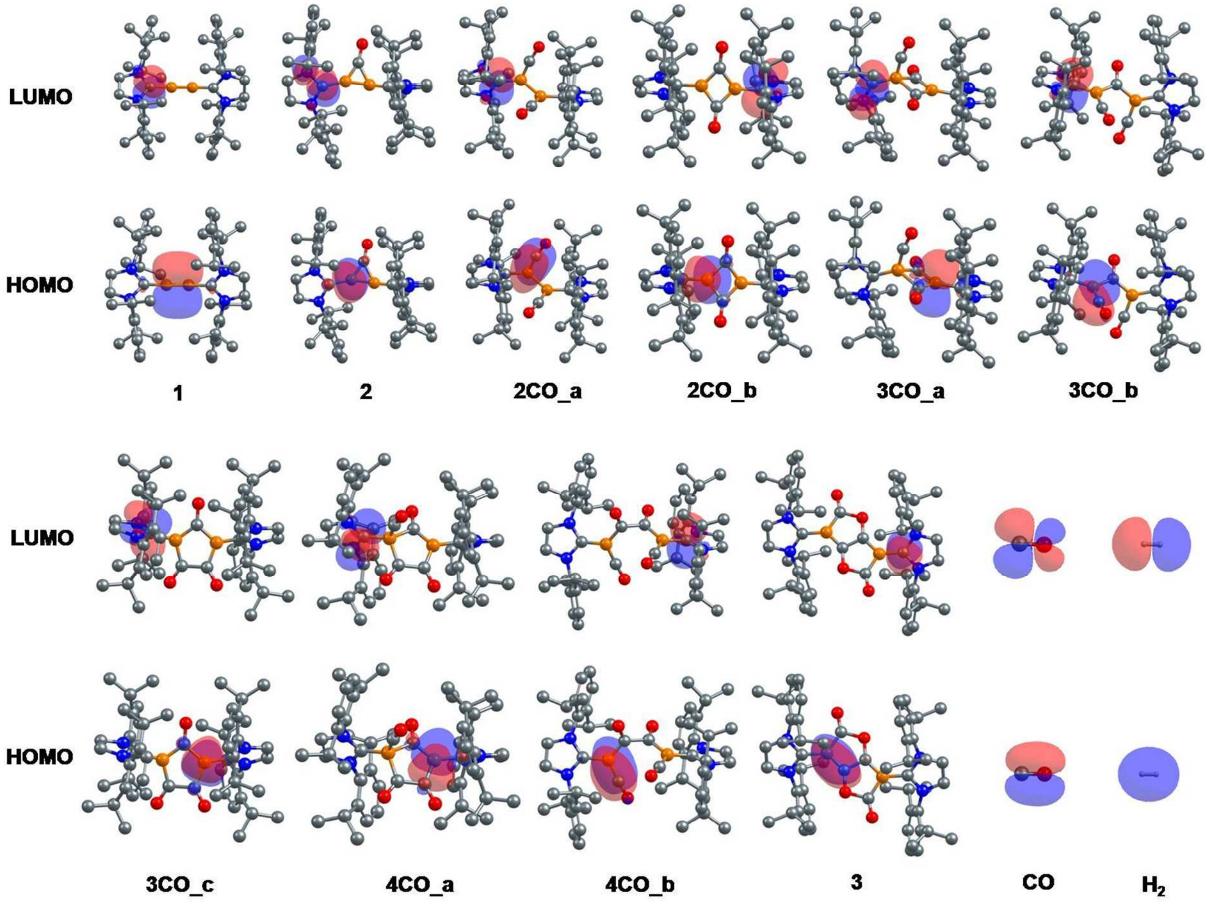


Fig 7. The HOMO and LUMO plots for the all the investigated complexes, as well as for the CO and the H_2 molecules.

In order to investigate whether **3** can take part in other reactions, we have considered the possibility of the reaction of dihydrogen, H_2, with **3**. This has significance because the coupling of CO to form C-C bonded products in syn-gas is an active area of research. The frontier orbital analysis of dihydrogen suggests that the activation of H_2 with **3** is a challenging prospect. The energy difference between the HOMO of **3** and LUMO of H_2 is 110.6 kcal/mol, which suggests that H_2 activation by **3** is unlikely. To further illustrate this point, we have considered the structures **4** and **5**, shown in Fig 9, where a dihydrogen molecule has been added to **3**, between the boron-carbon and the carbon-oxygen bonds respectively. This reaction of adding H_2 to **3** was found to be endothermic by 20.6 kcal/mol and 16.8 kcal/mol respectively for **4** and **5**, suggesting that both would be unlikely reactions. Furthermore, as shown in Table 2 and Fig S4 in the Supporting Information file, the energy difference between the HOMOs of all the investigated B_2 complexes and the LUMO of H_2 is higher by at least 87.0 kcal/mol, indicating that the activation of H_2 with diboryne-type complexes would be difficult.

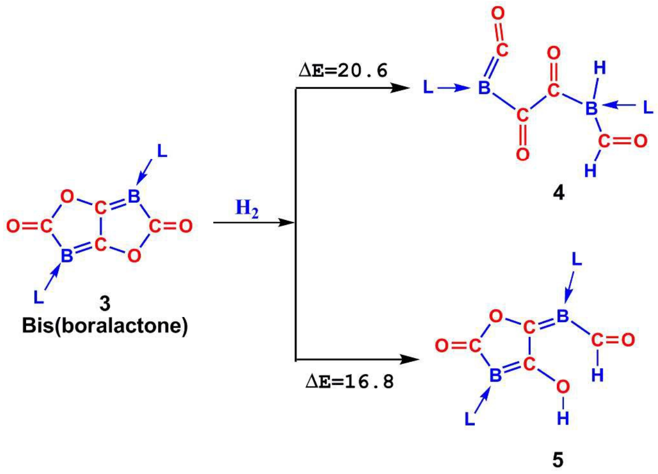


Fig 8. The possibility of the reaction of the (bis)boralactone **3** with dihydrogen.

Computational Details

All the DFT calculations were carried out using the Turbomole 6.0 suite of programs.[28] Geometry optimizations were performed using the Perdew, Burke, and Erzenhof density functional (PBE).[29] The electronic configuration of the atoms was described by a triple-ζ basis set augmented by a polarization function (Turbomole basis set TZVP).[30] The resolution of identity (ri),[31] along with the multipole accelerated resolution of identity (marij)[32] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. The real system has been employed for all the calculations. Care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode. Single point calculations were then done with the hybrid PBE0[32] functional on all the obtained minima and transition state structures, in order to obtain more reliable energy values for the investigated potential energy surface. Solvent effects were incorporated through single point calculations using the COSMO model,[33] with $\varepsilon = 2.3$ for benzene. The contributions of internal energy and entropy were obtained from frequency calculations done on the DFT structures at 298.15 K: thus, the energies reported in the figures are the ΔG values. Single point calculations have been done with the Gaussian 09 software[25] on all the fully optimized intermediate structures obtained by the TZVP/PBE/PBE0 calculations mentioned above. Specifically, the determination of the frontier molecular orbitals, Wiberg bond indices and intermolecular charge transfer analyses from natural bond order (NBO)[34-36] calculations was done at PBEPBE/TZVP level of theory.

Conclusions

C-C coupling of CO molecules employing main group systems is a significant challenge. Recent experimental work by Braunschweig and coworkers[22] reveals that such a process is possible when a diboryne system having N-heterocyclic carbene groups is employed. The current computational investigation employing density functional theory (DFT) reveals the complete mechanistic pathway for the metal-free coupling of four CO molecules by the diboryne system, thereby providing valuable insights into this newly discovered important process. Significant outcomes of the current investigation are as follows:

i. The NBO analysis suggests that back-donation from the B_2 unit to the π^* orbital of CO is of greater significance than the corresponding donation interaction.

ii. The diboryne is successful in coupling four CO molecules because the conversion of sp^3-sp^2 B_2 complexes to the corresponding sp^2-sp^2 B_2 complexes is a facile process; indeed the barrier for this conversion is seen to be only 0.8 kcal/mol. Without this facile conversion, the addition of the next CO molecule would be more difficult.

iii. The frontier molecular orbital analysis suggests that the stepwise addition of CO stabilizes the HOMO of the newly formed complexes, and also explains why the activation stops after the addition of four CO molecules.

iv. The frontier molecular orbital analysis also reveals why the possibility of other molecules, such as dihydrogen, being activated by the diborynes is a challenging prospect.

Supporting Information

Electronic Supplementary Information (ESI) available.

Acknowledgment

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Graphical Abstract

Why are boron containing systems so effective at CO coupling? Full quantum chemical calculations with density functional theory (DFT) provide interesting insights into why recently reported CO coupling by diboryne systems is such a facile process.