

 Very Important Publication

Threat to the Throne: Can Two Cooperating Boron Atoms Rival Transition Metals in Chemical Bond Activation and Catalysis?

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Dedicated to Professor Todd B. Marder on the occasion of his 65th birthday

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Abstract: Certain electron-rich 1,4-diborabenzene derivatives efficiently activate single, double, and triple bonds and thereby increasingly compete with transition metals in homogeneous catalysis. This review compares the activation of three model substrates (H_2 , $H_2C=CH_2$, CO_2) by (i) 9,10-dihydro-9,10-diboraanthracene dianions, (ii) their neutral carbene-stabilized congeners, (iii) 1,3,2,5-diazadiborinines, and (iv) 1,4,2,5-diazadiborinines. Distinct structure-properties relationships become apparent, the most influential factors being (i) the steric demands of the B-bonded substituents, (ii) the charges on the B-doped (hetero)arenes, (iii) charge polarization as a result of additional N-doping, and (iv) the energies and nodal structures of the frontier orbitals. The observed reactions are explained by a transition metal-like activation mechanism. If the two boron atoms are chemically inequivalent, contributions of a B(+I)/B(+III) mixed-valence state determine the observed regioselectivities when polar substrates are added. The lessons learned from the conversions of the model substrates are subsequently used to rationalize the behavior of the B_2 heterocycles also toward more sophisticated substrate molecules. Finally, catalytic cycles based on H_2 - and H^- -transfers, hydroboration reactions, and CO_2 reductions will be covered.

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Keywords: boron heterocycles; homogeneous catalysis; main group elements; nucleophilic boron; sub-valent compounds



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1. Introduction

The selective, time- and cost-efficient making and breaking of chemical bonds is at the core of advanced synthesis and catalysis. Element–element-bond activation generally proceeds via the outflow of charge density from bonding orbitals (σ or π in the cases of single or multiple bonds, respectively) and a concomitant inflow into antibonding orbitals (σ^* or π^*). In turn, the activating entity should ideally provide both vacant and filled orbitals of appropriate energy and symmetry for electron acceptance and donation. These prerequisites are fulfilled by many transition metal (TM) complexes that are stable in various oxidation states and possess an only partially occupied set of d orbitals at their respective metal centers. The terms "d-block metals" and "homogeneous catalysis" were therefore long regarded as two sides of one coin. Yet, this view changed fundamentally with the discovery of so-called "Frustrated Lewis Pairs (FLPs)", which are combinations of Lewis acidic and basic p-block species, sterically incapable of neutralizing each other's reactivity through adduct formation. When an FLP concertedly acts on the same substrate molecule, it also provides the combination of electron acceptor and donor sites required to cleave the attacked bond. During the past 15 years, the FLP concept has proven to be extremely fruitful to the extent that main group compounds can nowadays compete with transition metal complexes as mediators of chemical transformations.^[1] Even more recently, electron-rich, doubly B-doped (hetero)arenes have emerged as a new class of activating p-block molecules; prominent examples $[A]^{2-}-F$ are compiled in Figure 1. They all have in common a central six-membered ring with an aromatic π -electron system (except $[C]^-$) and two

boron atoms at the 1,4-positions. As will be discussed in detail below, this structural motif enables a high degree of cooperativity between the two boron atoms. It also leads to local frontier orbital symmetries at the boron atoms, which are ideal for the activation of molecules as different as element hydrides, carbonyls, imines, alkenes, alkynes, and (iso)nitriles. Both TM-like and FLP-like reaction mechanisms have been postulated. In Figure 1, suitable substrate classes for each member of the series $[A]^{2-}-F$ are shown in red, the reaction types observed so far are marked in blue, and those that have already been conducted catalytically are highlighted in bold letters.

After the introductory chapter 1), the main text comprises five sections: *Section 2)* reviews the most efficient synthesis routes to $[A]^{2-}-F$ -type molecules. *Section 3)* compares the behavior of these B_2 platforms toward the model substrates H_2 , $H_2C=CH_2$, and CO_2 , as well as toward related saturated and unsaturated compounds. *Section 4)* is devoted to promising optimization strategies and mechanistic considerations. *Section 5)* summarizes the currently known catalytic cycles that use $[A]^{2-}-F$ -type catalysts. *Section 6)* offers an outlook on B_2 platforms with non-aromatic central rings. The numbering scheme for the compounds covered by this review is as follows: General substance classes are given in capital letters ($[A]^{2-}-F$, **G**) while Arabic numerals are used to address specific derivatives. In the cases of ionic species $[M(solvent)]_n[X]$, the counterions M^+ and/or their solvent spheres are only mentioned if they are likely to influence the reactivity or molecular structure of $[X]^{n-}$ in the given context. Whenever a solvent molecule (e.g., THF) serves as a ligand, its acronym is written in lower case letters (e.g., thf).

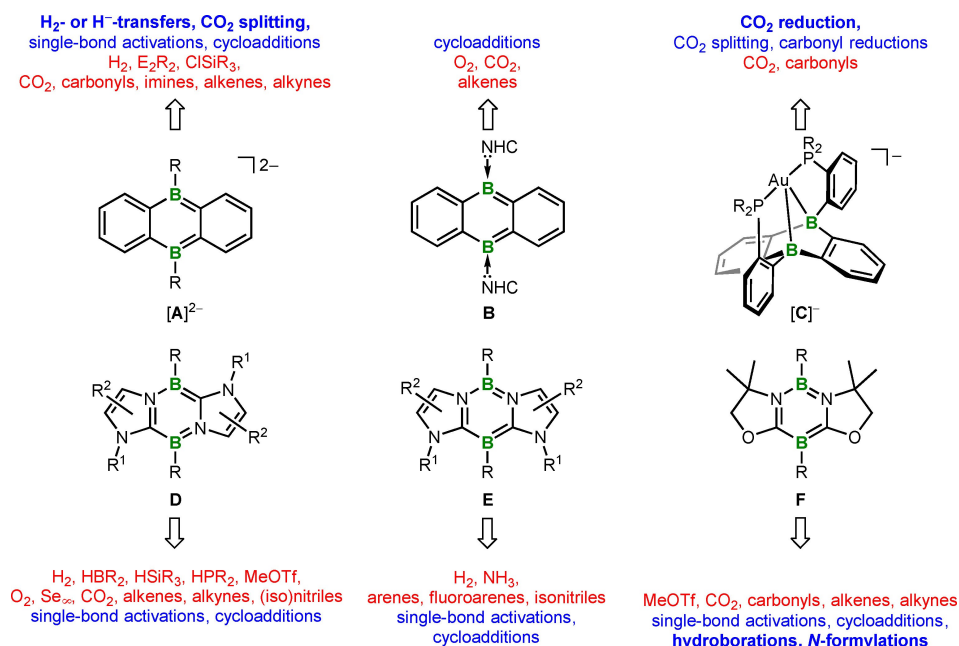
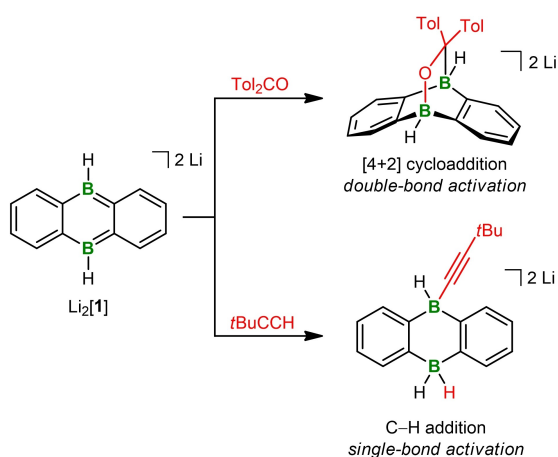


Figure 1. Prominent examples of electron-rich, doubly boron-doped (hetero)arenes [A]²⁻-F that are capable of activating a large number of substrates (red) via a variety of reaction types (blue); transformations that have been performed catalytically are highlighted in bold letters (MeOTf = MeOSO₂CF₃).

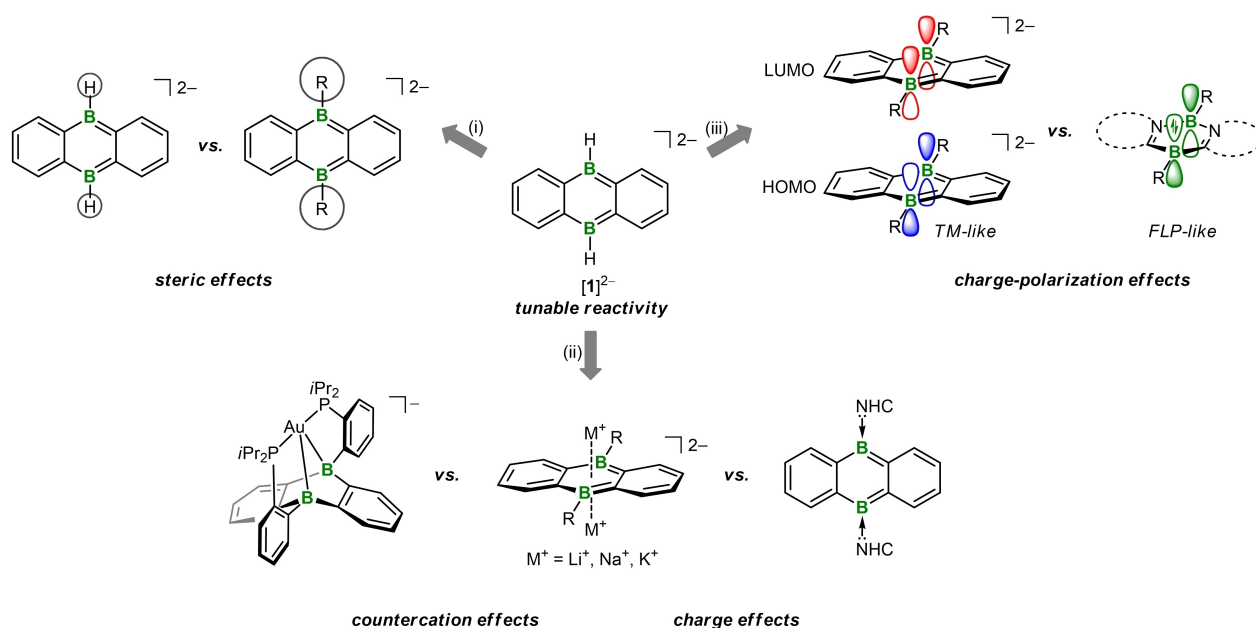
In 2010, our group investigated the behavior of the pristine 9,10-dihydro-9,10-diboraanthracene dianion salt Li₂[1] toward Tol₂CO and *t*BuCCH (Scheme 1; Tol = *para*-tolyl).^[2] The question was whether [1]²⁻ will still perform hydroboration reactions although the boron p_z orbitals are occupied by the two excess electrons, or whether [4+2] cycloadditions will occur. With the ketone, [1]²⁻ indeed reacts as a B=C-C=B diene and cleanly furnishes a diborabicyclo[2.2.2]-octadiene derivative (Scheme 1, top). The alkyne, however, undergoes neither hydroboration nor cyclo-

addition, but its terminal C-H bond is added across the two boron atoms of [1]²⁻, resulting in an alkynyl borate (Scheme 1, bottom).

With its ability to activate single and double bonds under ambient conditions, [1]²⁻ performs the same key reactions as TM complexes or FLPs. In view of this promising performance and the distinct simplicity of its molecular scaffold, we herein suggest [1]²⁻ as a formal lead structure of the species [A]²⁻-F in the discussion to follow. Numerous set screws for adjusting the properties of the parent system to a specific purpose become apparent (Scheme 2): (i) Given that the reactions take place at the boron centers, the steric demand of the B-bonded substituents R has a decisive influence on the reaction outcome. (ii) By choosing counteranions with different tendencies to form contact-ion pairs one can modulate not only the accessibility to the boron centers for an incoming substrate molecule but also the energy levels of the dianion's frontier orbitals. When the hydride substituents of [1]²⁻ are replaced by neutral carbene ligands, the 9,10-dihydro-9,10-diboraanthracene (DBA) scaffold loses all negative charges, thus eliminating any counteranion effects. (iii) The introduction of additional heteroatoms into the central six-membered ring provides an effective means of rendering the two boron atoms chemically inequivalent. As a consequence, polarized resonance forms in which one boron atom carries a lone pair of electrons [formally B(+I)] while the other has a vacant p_z orbital [formally B(+III)] gain relative weight, giving the molecule some



Scheme 1. Reactions of Li₂[1] with Tol₂CO and *t*BuCCH as early examples of double- and single-bond activations (Tol = *para*-tolyl; ambient conditions).



Scheme 2. Set screws for tuning the reactivity of $[1]^{2-}$, which serves here as a formal lead structure: (i) steric demand of the boron-bonded substituents; (ii) counteranions and charges of the B_2 platforms; (iii) charge polarization by additional heteroatoms (NHC = *N*-heterocyclic carbene; HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital).

character of a “two-boron FLP”^[3] and potentially shifting the mode of activation from “TM-like” to “FLP-like”.

The main objective of this review is to identify particularly effective set screws and essential structure-properties relationships for compounds of the form $[A]^{2-}-F$ concerning potential catalytic behavior. For this purpose, we have selected archetypal substrate molecules, including H_2 , $H_2C=CH_2$, and CO_2 , and will critically evaluate all available information about their reactions with members of the $[A]^{2-}-F$ series.^[4,5]

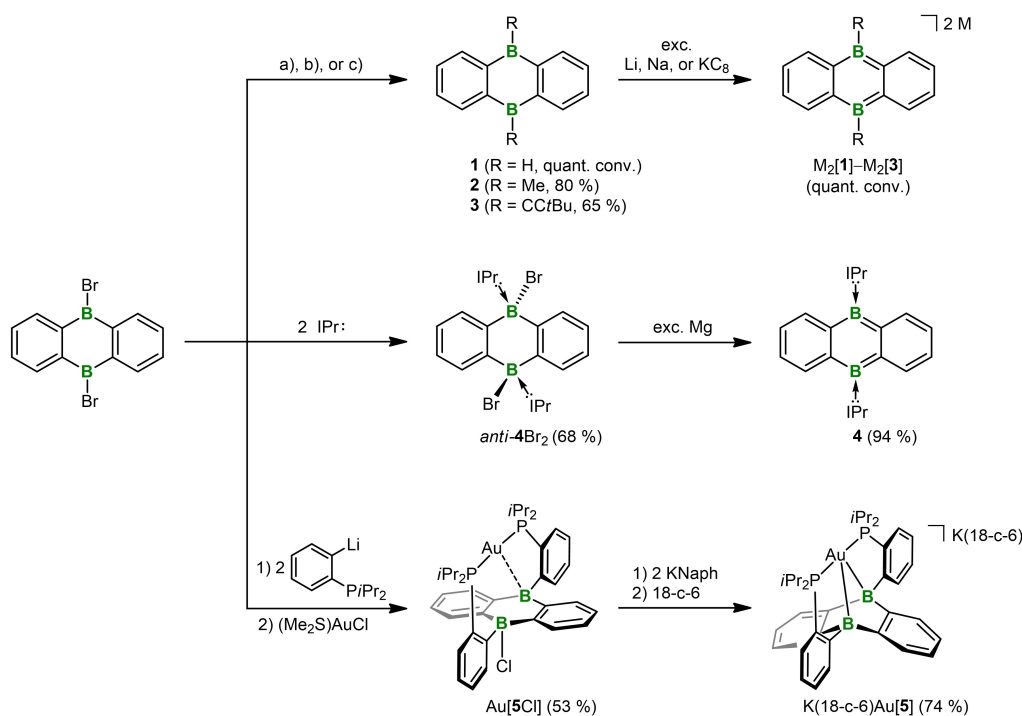
2. Syntheses of $[A]^{2-}-F$ -Type Molecules

Numerous protocols have been developed for the synthesis of DBAs.^[6–10] Simple DBAs such as **A-C** without substituents on their *ortho*-phenylene rings are most conveniently prepared by a cyclocondensation reaction between $1,2-(Me_3Si)_2C_6H_4$ ^[11,12] and BBr_3 .^[6,10]

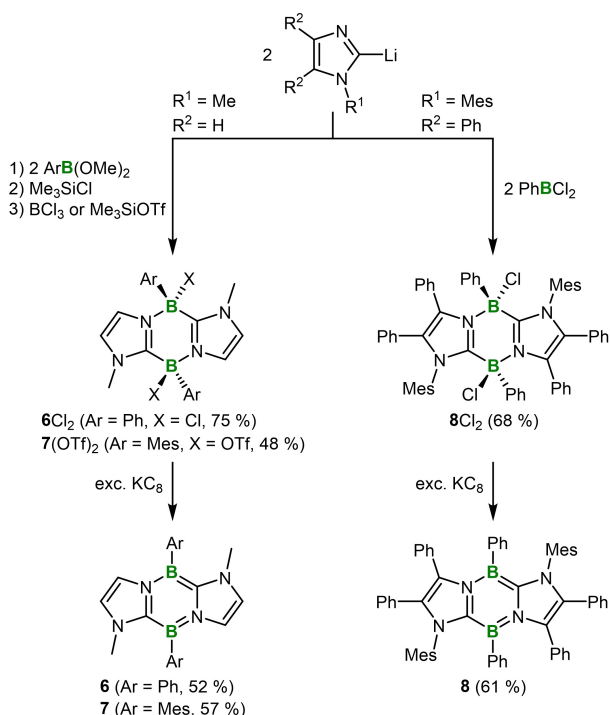
Treatment of the resulting 9,10- Br_2 -DBA with Et_3SiH , $MeMgI$, or $tBuCCLi$ furnishes the corresponding hydro- or organylboranes **1-3** (Scheme 3).^[13–16] The hydroborane **1** tends to oligomerize via B–H–B two-electron-three-center (2e3c) bonds and is thus poorly soluble in non-coordinating solvents.^[13] A nicely soluble low molecular weight derivative of $(1)_n$ that can easily be purified by crystallization and used for further transformations in a homogeneous liquid phase, is the dimethyl sulfide diadduct *syn-1*-(SMe_2).^[17] The two-electron reduction of $(1)_n$, *syn-1*-(SMe_2), **2**, or **3** with an excess of Li, Na, or KC_8 in THF at room

temperature leads to the salts $M_2[1]-M_2[3]$ ($M=Li$, Na, or K), which all have monomeric DBA dianions.^[2,16,18] Similar to the case of *syn-1*(SMe_2), 9,10- Br_2 -DBA can bind two equiv. of the bulky *N*-heterocyclic carbene (NHC) ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr). Magnesium reduction of the resulting diadduct *anti-4* Br_2 in Et_2O furnishes the dark green, neutral, IPr-supported 9,10-diboroanthracene **4** through $MgBr_2$ elimination.^[19] The macrocyclic Au(+I) complex Au[**5**Cl] can be prepared by treatment of 9,10- Br_2 -DBA with 2-(*iPr*₂P)₂C₆H₄Li in toluene and by subsequent complexation of the obtained ditopic Z-type ligand^[20] with $(Me_2S)AuCl$ in CH_2Cl_2 . Further two-electron reduction of Au[**5**Cl] with potassium naphthalenide (KNaph) in THF/ C_6H_6 produces the boraoauride $K(18-c-6)Au[5]$.^[21,22]

D-F-type B,N(O) heterocycles are also accessible via a fairly universal and modular synthesis approach reminiscent of the well-established chemistry of pyrazoles and scorpionate ligands (Scheme 4).^[23] Equimolar mixtures of $ArBY_2$ ($Y=Cl$ or OMe) and suitably substituted 2-lithioimidazolides generate the 1,4,2,5-diazadiborinine derivatives **6**Cl₂, **7**(OTf)₂, and **8**Cl₂ after workup (Scheme 4).^[24–26] In a similar vein, 1 equiv. of $PhBCl_2$ reacts with 2 equiv. of a 2-lithioimidazole or 2-lithiooxazolide to give the corresponding monoborates, which react further with a second equiv. of $PhBCl_2$ to produce the 2,5-dichloro-1,3,2,5-diazadiborinines **9**Cl₂ and **10**Cl₂ (Scheme 5).^[3,27] The unsymmetrically substituted **11**Cl₂ featuring $Ph(Cl)B$ and Cl_2B moieties has been prepared in close analogy to the syntheses of **9**Cl₂



Scheme 3. Synthesis of the $[A]^{2-}-[C]^{-}$ -type molecules $M_2[1]-M_2[3]$, **4**, and $K(18-c-6)Au[5]$, starting from 9,10- Br_2 -DBA. Note that **1** tends to form oligomers (**1**)_n via B–H–B 2e3c bonds in solution and the solid state. Reagents: a) exc. Et_3SiH , b) 2 $MeMgI$, c) 2 $tBuCClLi$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene; KNaph = potassium naphthalenide; 18-c-6 = 18-crown-6).



Scheme 4. Synthesis of the compounds **6-8** (Mes = mesityl; OTf = OSO_2CF_3).

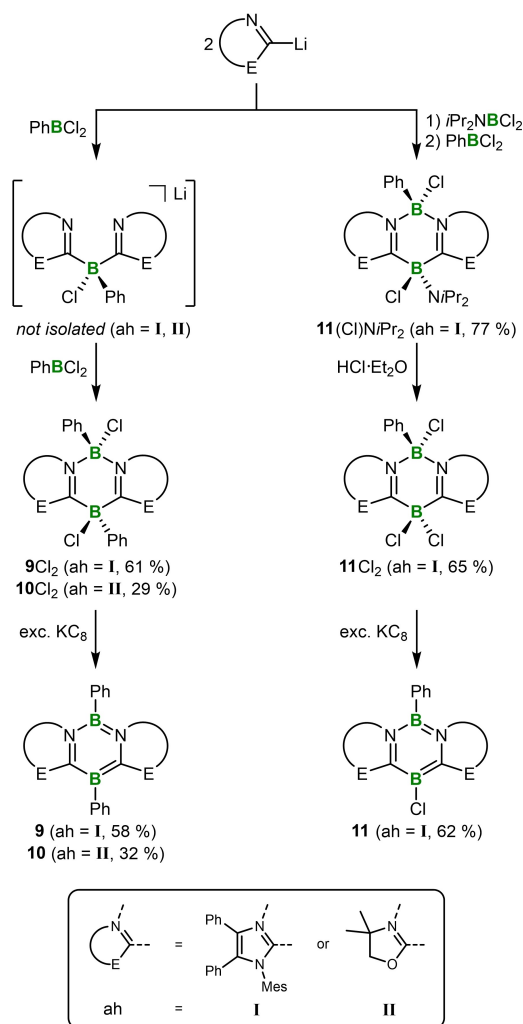
and $10Cl_2$ by using iPr_2NBCl_2 instead of the first equiv. of $PhBCl_2$ and applying ethereal HCl for the subsequent iPr_2N/Cl exchange.^[28] Finally, the room-temperature reduction of the intermediate borates $6Cl_2-11Cl_2$ with an excess of KC_8 in toluene or C_6H_6 provides the target products **6-11**.^[3,24-28]

As is evident from Schemes 3, 4, and 5 the overall yields of $M_2[1]-11$ differ significantly, but all these compounds are sufficiently accessible for further use in substrate-activation reactions.

3. Comparative Assessment of the Behavior of $[A]^{2-}$ -F-Type Molecules Toward H_2 , $H_2C=CH_2$, and CO_2

3.1. Dihydrogen and Further Examples of Single-Bond Activations

H_2 is a non-polar, volatile compound with a high dissociation enthalpy of $104 \text{ kcal mol}^{-1}$,^[29] which renders H–H-bond activation kinetically and thermodynamically challenging. Remarkably, a dearomative *syn*-addition of H_2 across the two boron centers has nevertheless been achieved for $M_2[1]-M_2[3]$ ($M = Li, Na, \text{ or } K$)^[14,16] as well as 1,4,2,5-diazadiborinine **7** with chemically equivalent boron atoms^[30] and 1,3,2,5-diazadiborinine **9** with chemically inequivalent boron sites.^[27] In the cases of DBA dianions $M_2[1]-M_2[3]$, it



Scheme 5. Synthesis of the compounds **9–11** (ah = annulated heterocycle; Mes = mesityl).

was found that the H₂-addition reaction is governed by the following factors:^[16] (i) *Counteraction effects*: The velocity of the H₂-activation reaction increases drastically in the order Li₂[**1**]/Li₂[**2**] < Na₂[**1**]/Na₂[**2**] < K₂[**1**]/K₂[**2**] ([D₈]THF; determined at reaction temperatures of T = 50 °C as well as 100 °C). This trend is probably due to different degrees of cation-anion association in solution. All crystallographically characterized derivatives of M₂[**1**]-M₂[**3**] exist as inverse sandwich complexes in the solid state with the two M⁺ cations residing above and below the respective B₂C₄ core.^[31] Li⁺ coordination is retained even in THF solution,^[14,32] whereas the Na⁺ and K⁺ salts seem to have an increasing tendency to form solvent-separated ion pairs under these conditions.^[16] As a result, the presence of Na⁺ and K⁺ should impede the access of H₂ to the boron sites to a lesser extent than the presence of Li⁺. (ii) *Electronic effects of the B-bonded substituents R*: The M₂[**3**] (R = CCtBu) has not been included in

the kinetic study, because H₂ activation by Li₂[**3**] is reversible and a dynamic addition-elimination equilibrium exists at T = 100 °C. This effect has been traced to the much less cathodic redox potential of **3** compared to, e.g., **2**, which leads to the conclusion that the electronegativities (EN) of the B-bonded substituents [**2**: EN(C(sp³)) < **3**: EN(C(sp))] constitute another influential and potentially useful set screw. (iii) *Steric effects of the B-bonded substituents R*: H₂ addition is fastest for the sterically less demanding substituents R = H, Me, C≡tBu, significantly slower for R = Et, Tol, and prohibitively slow for the bulky R = Mes (Mes = mesityl).^[16] Given this background, we selected K₂[**2**] for direct comparison with the diazaborinines **7** and **9** (Table 1).

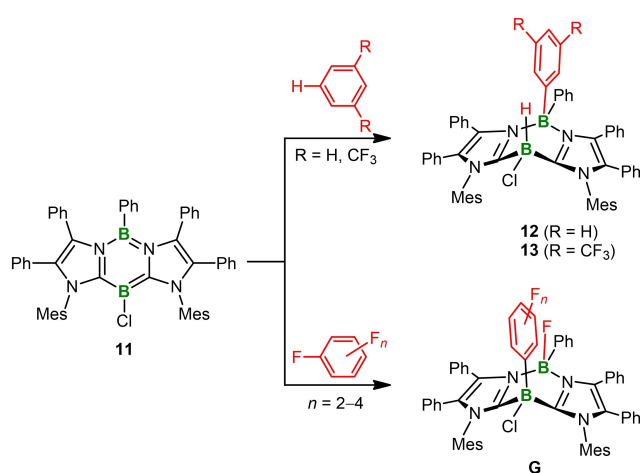
All three compounds activate H₂ (1 atm) at moderately elevated temperatures of T = 50–90 °C and in an irreversible manner. The reaction is the slowest for the Mes-substituted derivative **7**,^[30] but not completely inhibited – in contrast to the case of the Mes-substituted DBA dianion. A switch from **7** to **9** accelerates the reaction to a level more comparable to that of K₂[**2**].^[27] Since **7** and **9** differ in several aspects, it is difficult to decide at this point if the reason for the improved performance of **9** rests mainly in the reduced steric hindrance at its B₂C₄ ring (Ph < Mes) or whether the different polarities of the BC₂ and BN₂ fragments are also relevant. The extension of the conjugated π systems of **7** and **9** goes beyond the central B₂N₂C₂ ring and includes the nitrogen lone pairs and also the two C=C double bonds of the annulated rings. As a result, [**2**]²⁻, **7**, and **9** have the same count of 14 π electrons. There are no reports yet of the addition of H₂ to the NHC-stabilized DBA **4**, the borauride K(18-c-6)Au[**5**], or the oxazoline derivative **10**.^[33]

Table 1. Comparison of the reaction conditions applied for the addition of H₂ across the boron centers of K₂[**2**], **7**, and **9**; addition products K₂[2H₂], **7H₂**, and **9H₂** (Mes = mesityl).

K ₂ [2]	7	9
[D ₈]THF	toluene	C ₆ H ₆
1 atm H ₂	1 atm H ₂	1 atm H ₂
50 °C	90 °C	70 °C
3 h	36 h	5 h
K ₂ [2H ₂]	7H₂	9H₂

Only for those members of the $[A]^{2-}-F$ series, which demonstrably mediate the cleavage of the H–H bond, has the activation of other homo- and moderately heteropolar single bonds been reported. $Li_2[2]$ reductively cleaves the dichalcogens O_2tBu_2 , S_2Me_2 , S_2Tol_2 , Se_2Ph_2 , and Te_2Ph_2 under ambient conditions and with perfect selectivity. In THF solution, the resulting neutral DBA **2** and the respective lithium chalcogenides engage in dynamic association-dissociation equilibria. In the solid state, **2** and $Li[OtBu]$ give a diadduct $syn-Li_2[2(OtBu)_2]$, $Li[SMe]$ forms a [2.2.1]-bicyclic B-(μ -SMe)-B monoadduct $Li[2(SMe)]$, and in the three remaining cases the crystal lattices contain chalcogenide monoadducts $Li[2(EAr)]$ in which only one boron atom is tetracoordinated.^[34] The activation of grey selenium, Se_∞ , was achieved with **8** and afforded a bicyclo[2.2.2]octadiene derivative with one Se–Se bridge between the two boron atoms.^[26] Also, the heteropolar element–element bonds of H–Bpin, H–Si(H)₂Ph, and H–Si(H)Ph₂ are *syn*-added to the imidazole-containing species **6**, whereupon the respective hydrogen atoms end up at one boron center while a B–B/Si bond is established at the other (HBpin = pinacolborane).^[24]

Concerning the successful heterolytic splitting of H–B and H–Si bonds, the obvious question is whether $[A]^{2-}-F$ -type compounds can also be used to activate H–C bonds. Recently, Kinjo's group reported that **9**, when stirred in C_6H_6 at 90 °C for 30 h, does not remain inert, but is converted into a product containing two tetracoordinate boron centers, one of which carries a newly introduced hydrogen substituent.^[28,35] A switch from **9** to **11** (Scheme 6), which features not only BC_2/BN_2 sites, but also different B-bonded substituents Cl/Ph, considerably improves the chemoselectivity of the

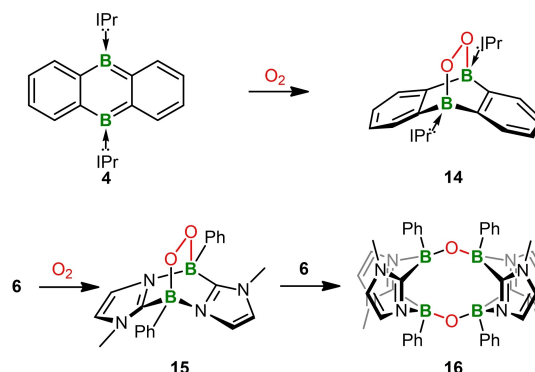


Scheme 6. Reactions of the 1,3,2,5-diazadiborinine **11** with H–C bonds of arenes (**12**, **13**) and F–C bonds of partially fluorinated arenes (**G**).

reaction; the H–C₆H₅-activation product **12** was isolated in 76% yield.

An analogous compound **13** was obtained from **11** in 1,3-(F₃C)₂C₆H₄. In partially fluorinated benzenes C₆F_nH_{6-n} (*n* = 3–5), however, **11** performs F–C-bond rather than H–C-bond activation (**G**).^[28] These observations suggest that **11** prefers H–C(*sp*²) over F–C(*sp*³) bonds but F–C(*sp*²) over H–C(*sp*²) bonds.^[36] It has been emphasized that the Ph/Cl-exchange upon going from **9** to **11** reduces the steric congestion in the transition states of C₆H₆ or C₆F_nH_{6-n} addition, which should facilitate these processes. In the cases of the fluorobenzenes, the fluorophenyl rings are indeed attached to the less bulky CIBC₂ sites of **11**, whereas the small F atom always binds to the bulkier PhBN₂ sites (*syn*-addition; Scheme 6). For C₆H₆, however, the regioselectivity is inverted,^[37] indicating that matching polarities of the single bonds to be activated and the B(+I)C₂/B(+III)N₂ sites may exceed steric concerns (see section 4).

Due to its triplet ground state, the O₂ diradical is a special case of a non-polar small-molecule substrate. Exposure of **4** in C₆H₆ to dry air generates the [2.2.2]-bicyclic endoperoxide **14** (1 atm, room temperature, 5 min; Scheme 7).^[19] Concerning the reaction mechanism, the involvement of single-electron transfer (SET) processes has been given consideration. The resulting B–O–O–B moiety resembles the B–Se–Se–B unit mentioned above and also Piers' B–O–O–C endoperoxides, which were obtained from NHC-stabilized 9-boraanthracenes and O₂.^[38–40] Likewise, a C₆H₆ solution of Kinjo's 1,4,2,5-diazadiborinine **6** reacts with neat O₂ to form the endoperoxide **15** (Scheme 7).^[41] At elevated temperatures of 80 °C (10 h), the O–O bond of **15** can be added across the two boron atoms of a second equiv. of **6** to afford the macrocyclic species **16**, albeit with moderate selectivity and in yields of only 15% (compare the above-mentioned reaction of $Li_2[2]$ with the O–O bond of O_2tBu_2 , which proceeds cleanly and quantitatively).



Scheme 7. Reactions of **4** and **6** with O₂ afford the endoperoxides **14** and **15**; splitting of the O–O bond in **15** with 1 equiv. of **6** furnishes the macrocycle **16**.

3.2. Ethylene and Further Examples of C=C- and C≡C-Bond Activations

The [4+2] cycloaddition reaction between $\text{H}_2\text{C}=\text{CH}_2$ and $\text{Li}_2[2]$ quantitatively furnishes the diborabicyclo[2.2.2]octadiene $\text{Li}_2[17]$ (Table 2).^[16] In a similar vein, Harman's neutral NHC-DBA adduct **4** and Kinjo's oxazoline system **10** form cycloadducts **18**^[19] and **19**,^[42] respectively. Cycloreversion reactions of $\text{Li}_2[17]$ ($T=100^\circ\text{C}$) and **18** ($T=70^\circ\text{C}$)^[43] have not been observed; **19** is subject to a quantitative *retro*-[4+2]-cycloaddition at $T=150^\circ\text{C}$.

$\text{Li}_2[2]$ also captures $\text{Ph}_2\text{C}=\text{CH}_2$ quickly and efficiently, but this time in a reversible manner ($T=100^\circ\text{C}$), which is of crucial importance, e.g., with regard to catalytic hydrogenation reactions (see section 5).^[16] Cycloadditions of Kinjo's 1,3,2,5-diazadiborinine **10** with different *para*-substituted styrene derivatives^[44] $p\text{-RC}_6\text{H}_4(\text{H})\text{C}=\text{CH}_2$ were generally slower at ambient conditions than in the case of $\text{H}_2\text{C}=\text{CH}_2$. Compared to $\text{R}=\text{H}$ in pristine styrene (12 h), electron-withdrawing substituents $\text{R}=\text{Br}$, CF_3 resulted in short-

er reaction times (6 h, 3 h) than electron-donating substituents $\text{R}=\text{Me}$, OMe ($>12\text{ h}$).^[42] All these cycloadditions were reversible at $T>100^\circ\text{C}$. Internal olefins are less susceptible to C=C-bond activation than the terminal ones. While both $\text{Li}_2[2]$ and **10** are inert toward cyclohexene even at $T>100^\circ\text{C}$,^[16,42] **10** forms a cycloadduct with the strained norbornene.^[42]

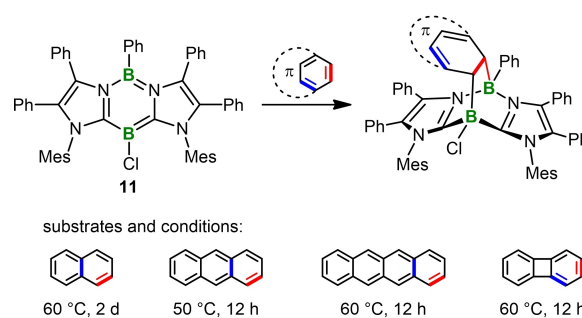
Remarkably, the unsymmetrically BCl/BPh-substituted 1,3,2,5-diazadiborinine **11** forms bicyclic diboration products with naphthalene, anthracene, and tetracene regioselectively at their C(1)–C(2) edges (reversible at $80\text{--}140^\circ\text{C}$); biphenylene also reacts in this fashion, albeit at its C(2)–C(3) edge (Scheme 8).^[28,45] Note that C_6H_6 , which has a more delocalized π -electron system, rather undergoes H–C-activation under comparable conditions (see Scheme 6). $\text{Li}_2[2]$ does not react with naphthalene or phenanthrene, despite the rather localized C(9)=C(10) double bond of phenanthrene.^[16]

Reactions of $[\text{A}]^{2-}\text{F}$ -type compounds with 1-alkynes can, in principle, follow two different pathways: (i) H–C activation of the acidic terminal hydrogen atom or (ii) [4+2] cycloaddition of the C≡C bond. As mentioned above (Scheme 1), $\text{Li}_2[1]$ attacks the H–C bond of $t\text{BuC}\equiv\text{CH}$ (cf. $\text{Li}_2[20]$; Figure 2).^[2] Compounds **6** and **10**, however, cleanly produce diborabicyclo[2.2.2]octatrienes with ($p\text{-BrC}_6\text{H}_4$)C≡CH (**21**)^[24] and $\text{PhC}\equiv\text{CH}$ (**22**),^[3] respectively.

Even though it is tempting to attribute this striking difference to the different B_2 platforms, a definite interpretation has to await reactions of $\text{Li}_2[1]$, **6**, and

Table 2. Comparison of the reaction conditions applied for the addition of $\text{H}_2\text{C}=\text{CH}_2$ across the boron centers of $\text{Li}_2[2]$, **4**, and **10**; addition products $\text{Li}_2[17]$, **18**, and **19**.

$\text{Li}_2[2]$	4	10
$[\text{D}_8]\text{THF}$	C_6H_6	C_6D_6
1 atm $\text{H}_2\text{C}=\text{CH}_2$	1 atm $\text{H}_2\text{C}=\text{CH}_2$	1 atm $\text{H}_2\text{C}=\text{CH}_2$
r.t.	70°C	r.t.
3 h	20 h	3 h
irreversible (up to 100°C)	irreversible (up to 70°C)	reversible (at 150°C)
$\text{Li}_2[17]$	18	19



Scheme 8. Hetero-Diels-Alder reactions of the 1,3,2,5-diazadiborinine **11** with polycyclic aromatic hydrocarbons.

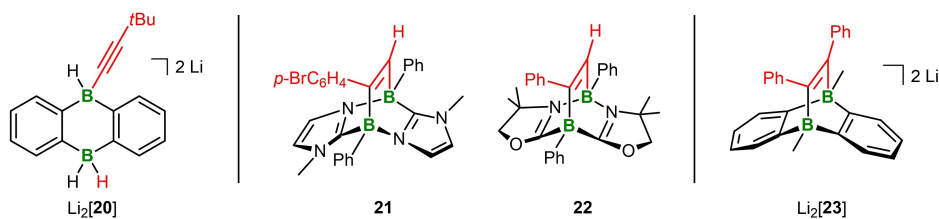


Figure 2. Products $\text{Li}_2[20]$ –**22** of the reactions of $\text{Li}_2[1]$ (H–C activation), **6** (C≡C activation), and **10** (C≡C activation) with terminal alkynes; product $\text{Li}_2[23]$ results from the reaction of $\text{Li}_2[2]$ with the internal alkyne $\text{PhC}\equiv\text{CPh}$.

10 with exactly the same 1-alkyne such that steric and/or electronic substituent effects can safely be excluded. In the case of the alkyne $\text{PhC}\equiv\text{CPh}$, which is devoid of a terminal hydrogen atom, the DBA dianion $\text{Li}_2[\mathbf{2}]$ no longer ignores the triple bond and undergoes a fast and irreversible [4+2] cycloaddition at room temperature ($\text{Li}_2[\mathbf{23}]$; Figure 2).^[16,46]

3.3. Carbon Dioxide and Further Examples of C=O-, C=NR-, and C≡N-Bond Activations

Similar to the C=C bond of $\text{H}_2\text{C}=\text{CH}_2$, the C=O bond of CO_2 instantaneously adds across the boron atoms of $\text{M}_2[\mathbf{2}]$ ($\text{M}=\text{Li}, \text{Na}$; Table 3).^[16] The resulting cycloadducts $\text{M}_2[\mathbf{24}]$ are stable and can be isolated if strictly 1 equiv. of CO_2 is administered. In the presence of an excess of CO_2 , a follow-up reaction leads to a net disproportionation, which provides CO and CO_3^{2-} and paves the way for a potential catalytic cycle (cf. section 5). The reaction between CO_2 and the neutral DBA **4** is far more sluggish and requires excess CO_2 , an elevated temperature of 60°C , and a reaction time of 8 h.^[19] Similar to $\text{M}_2[\mathbf{2}]$ the cycloadduct **25** is obtained and CO_2 is not released again up to $T=70^\circ\text{C}$.^[43] Contrary to the case of the DBA dianion, no follow-up reaction takes place even though much more than 1 equiv. of CO_2 is present. Harman's boroauride $\text{K}(\text{18-c-6})\text{Au}[\mathbf{5}]$, when stirred under a blanket of CO_2 (1 atm) at room

temperature in C_6H_6 , is transformed to a corresponding CO_3^{2-} complex $\text{K}(\text{18-c-6})\text{Au}[\mathbf{29}]$ (see Scheme 10), which is unstable in solution in the absence of CO_2 .^[47,48] The primary [4+2] cycloadduct $\text{K}(\text{18-c-6})\text{Au}[\mathbf{26}]$ has not been detected so far, but is a proposed intermediate (Table 3). Rather, a 1:1 mixture of $\text{K}(\text{18-c-6})\text{Au}[\mathbf{5}]$ and CO_2 , prepared at low temperatures in $[\text{D}_8]\text{toluene}$ and monitored by variable-temperature NMR spectroscopy, ultimately contained equimolar amounts of unconsumed $\text{K}(\text{18-c-6})\text{Au}[\mathbf{5}]$, the CO_3^{2-} complex $\text{K}(\text{18-c-6})\text{Au}[\mathbf{29}]$, and CO. In summary, the stability of the primary CO_2 -DBA adducts toward additional CO_2 follows the trend $\mathbf{25} \gg \text{M}_2[\mathbf{24}] > \text{K}(\text{18-c-6})\text{Au}[\mathbf{26}]$. Both Kinjo's 1,4,2,5-diazadiborinine **6** (room temperature, 5 min, irreversible) and 1,3,2,5-diazadiborinine **10** (70°C , 2 h, reversible) give bicyclic products **27** and **28** with excess CO_2 (1 atm).^[3,24] The stability of the primary CO_2 adducts toward excess CO_2 correlates with the B–O bond lengths in the solid state. While the CO_2 -inert compounds **25** (av. 1.5088 Å), **27** (1.475(15) Å), and **28** (1.509(6) Å) possess rather short B–O bonds, the CO_2 -capturing $[\text{Na}][\text{Na}_3(\text{thf})_6][\mathbf{24}]_2$ (av. 1.589 Å) has a significantly longer bond.

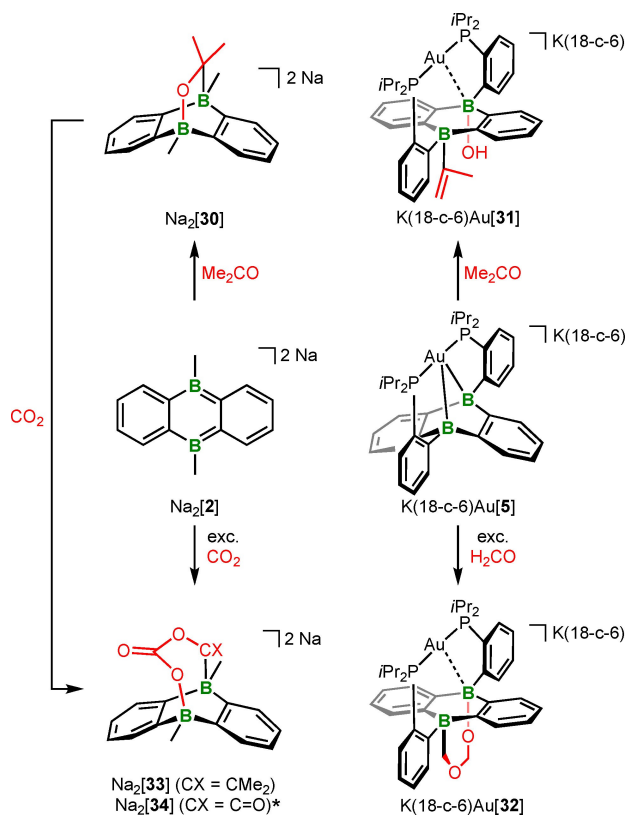
Similar to the case of CO_2 , a number of carbonyl substrates undergo analogous C=O-addition reactions with $\text{Li}_2[\mathbf{1}]$ (ToI_2CO),^[2] $\text{Na}_2[\mathbf{2}]$ (Ph_2CO , Me_2CO),^[15] $\text{K}(\text{18-c-6})\text{Au}[\mathbf{5}]$ ($\text{Ph}(\text{H})\text{CO}$),^[49] and **10**

Table 3. Comparison of the reaction conditions applied for the addition of CO_2 across the boron centers of $[\text{A}]^{2-}$ -F-type compounds; addition products $\text{M}_2[\mathbf{24}]$ -**28**. *) proposed intermediate.

$\text{M}_2[\mathbf{2}]$ ($\text{M}=\text{Li}, \text{Na}$)	4	$\text{K}(\text{18-c-6})\text{Au}[\mathbf{5}]$	6	10
$[\text{D}_8]\text{THF}$	toluene	C_6H_6	C_6H_6	C_6H_6
1 equiv. CO_2	1 atm CO_2	1 atm CO_2	1 atm CO_2	1 atm CO_2
r.t.	60°C	r.t.	r.t.	70°C
< 5 min	8 h	15 min	5 min	2 h
reversibility not tested	irreversible (up to 70°C)	irreversible (not isolable)	irreversible (up to 150°C)	reversible (at 90°C)
follow-up reaction	no follow-up reaction	follow-up reaction	no follow-up reaction	no follow-up reaction

$\text{M}_2[\mathbf{24}]$ ($\text{M}=\text{Li}, \text{Na}$)	25	$\text{K}(\text{18-c-6})\text{Au}[\mathbf{26}]^*$	27	28

(Ph(Me)CO).^[50] The clean [4+2] cycloaddition between the strong Brønsted base Na₂[**2**] and the enolizable Me₂CO (which affords Na₂[**30**]; Scheme 9) is particularly remarkable, as simple deprotonation reactions would have been plausible alternative/additional options. This view is further underscored by Harman's results on the reaction between K(18-c-6)Au[**5**] and Me₂CO, which furnishes the Au-DBA complex K(18-c-6)Au[**31**],



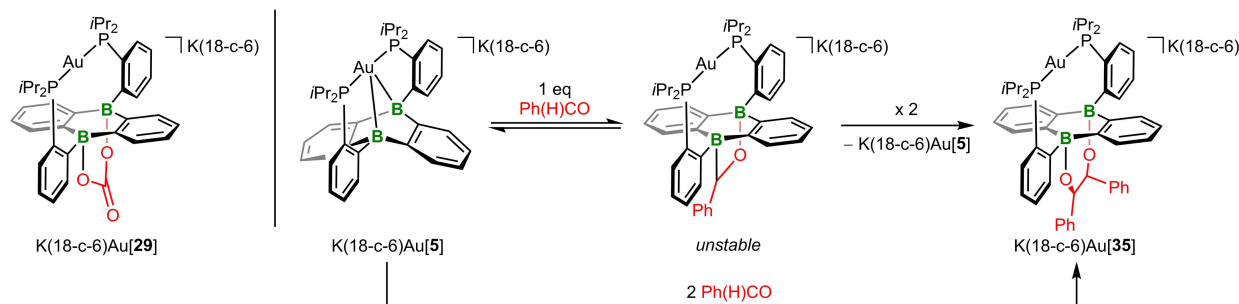
Scheme 9. Comparison of the reactions of Na₂[**2**] and K(18-c-6)Au[**5**] with Me₂CO and CO₂/H₂CO. Only in the case of K(18-c-6)Au[**5**] the C=O bond of Me₂CO is completely cleaved (Na₂[**30**] vs. K(18-c-6)Au[**31**]); the structural motifs of the products Na₂[**33**] or Na₂[**34**] and K(18-c-6)Au[**32**] obtained via corresponding reactions with CO₂/H₂CO are closely similar. *) proposed intermediate.

carrying a hydroxide ligand at one boron center and a prop-1-ene-2-yl substituent at the other (60 °C, 48 h; Scheme 9); evidently, one of the methyl groups of acetone was deprotonated in the course of the reaction.^[49] Harman also found that K(18-c-6)Au[**5**] and excess H₂CO undergo a C–O-coupling reaction with formation of K(18-c-6)Au[**32**] (Scheme 9).

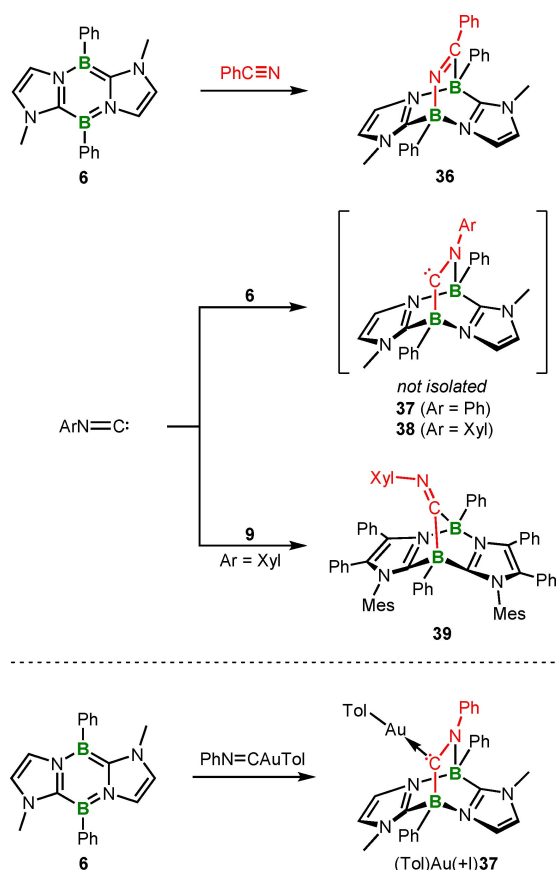
This outcome bears strong resemblance to the insertion of CO₂ into the B–O bond of Na₂[**24**] and Na₂[**30**], as both transformations generate products featuring B–OCOC–B fragments, which are analogous to that of K(18-c-6)Au[**32**] (Scheme 9; see also section 5). Finally, the reaction between K(18-c-6)Au[**5**] and Ph(H)CO ultimately results in C–C coupling to afford compound K(18-c-6)Au[**35**] with a B...B-bridging pinacolate ligand (Scheme 10). Pinacol-type C–C-coupling reactions have not been observed for Li₂[**1**] or Na₂[**2**] and Tol₂CO or Ph₂CO. The behavior of Li₂[**2**] toward carbonyl imines has been investigated in detail for the sterically demanding Ph(H)C=N*t*Bu: The hetero-Diels-Alder reaction is rather slow and can largely be reversed at *T* = 100 °C, which, as already mentioned in the discussion of the Li₂[**2**]/Ph₂C=CH₂ combination, is essential for the catalytic hydrogenation of both substrates (see section 5).^[16]

Akin to the reaction of the 1,4,2,5-diazadiborinine **6** with (*p*-BrC₆H₄)C≡CH, [4+2] cycloadducts are generated also with PhC≡N (**36**; Scheme 11).^[24] The conversion of **6** with the isonitriles PhN=C: or XylN=C: take similar courses and afford the bicyclic carbenes **37** and **38** (Xyl = 2,6-Me₂C₆H₃; Scheme 11), which could not be isolated in free form. Yet, **37** has been trapped and structurally characterized as its (Tol)-Au(+I)**37** complex.^[51] In contrast to the [4+2] cycloadduct **38** obtained with **6**, XylN=C: produces a [4+1] cycloadduct **39** with the 1,3,2,5-diazadiborinine **9** (Scheme 11).^[27] A conclusive explanation has not yet been disclosed; however, an obvious difference between **6** and **9** is that the former platform provides chemically equivalent boron centers, whereas the latter features inequivalent boron sites.

In summary, we have so far shown that [A]²⁻-F-type compounds are capable of interacting with a



Scheme 10. Left: CO₃²⁻ diadduct K(18-c-6)Au[**29**]. Right: Pinacol-coupling reaction of Ph(H)CO at the platform K(18-c-6)Au[**5**].



Scheme 11. Reactions of the diazadiborinines **6** and **9** with nitriles (**36**) and isonitriles (**37**, **38**). Similar to the case of $\text{PhC}\equiv\text{N}$, $\text{PhN}=\text{C}$: undergoes a [4 + 2] cycloaddition reaction, whereupon a carbene is formed, which can serve as a ligand toward Au(+I). The reactivity of $\text{XylN}=\text{C}$: depends on the choice of the diazadiborinine (**6**: [4 + 2] cycloaddition, **9**: [4 + 1] cycloaddition; Xyl = 2,6-Me₂C₆H₃; Tol = *para*-tolyl).

variety of saturated as well as unsaturated substrates, albeit often under different reaction conditions and with different outcomes. In the following section we will use the available information from quantum-chemical calculations to explain these findings.

4. Evaluation of Potential Set Screws and Mechanistic Considerations

The set screws outlined in Scheme 2 act via the steric demand of the B-bonded substituents, the influence of excess charges on the frontier orbitals, and charge polarization through symmetry breaking by N-doping. In the following, we put these factors in the context of the observed reactivity patterns.

4.1. Steric Factors and Resulting Kinetic Effects

The above-mentioned investigations in the activation of H₂ by different DBA-dianion salts M₂[A] revealed a strong dependence on the steric demands of the B-bonded substituents R, with larger substituents leading to slower reaction rates. The readily available dianions [1]²⁻ and [2]²⁻ carry the smallest possible substituents (R = H and Me), which therefore restrict access to the boron sites the least. As a caveat, however, one should keep in mind that such negatively charged B₂ platforms are necessarily associated with potentially coordinating and thus sterically non-innocent counteranions. In the cases of uncharged NHC-DBA complexes like **4**, the inevitable steric bulk of the carbene ligand reaches its lower limit already with the 1,3-dimethylimidazol-2-ylidene, which would still put a comparable steric strain on the DBA skeleton as the Mes substituents in the H₂-inert [9,10-Mes₂-DBA]²⁻ dianion. Most of Kinjo's diazadiborinines have been equipped with medium-sized Ph groups (**6**, **9**, **10**), one exception being the Mes-substituted **7** (Schemes 4, 5). At first glance, already the consideration of steric effects is helpful to rationalize the reactivity trends along the series [1]²⁻, [2]²⁻ > **9** > **7** (H₂ activation), [2]²⁻ ≈ **10** > **4** (H₂C=CH₂ activation), and [2]²⁻ ≈ **6** > **10** ≈ **4** (CO₂ activation; cf. Tables 1-3), but deeper insight is gained only by inspecting the corresponding frontier orbitals and their relative energies.

4.2. Frontier-Orbital Symmetries, Energies, and Charge Effects

The HOMO and LUMO symmetries and energies, as well as the HOMO-LUMO gaps of the B₂ platforms are decisive factors for the efficient interaction with substrate molecules. A comparison of the HOMOs of selected derivatives [Li(thf)₂]₂[9,10-Mes₂-DBA], **6**, **9**, and **10** reveals informative qualitative similarities (Figure 3):^[52] All the HOMOs correspond to delocalized π systems with nodal planes between the BC₂/BC₂, BCN/BCN, and BC₂/BN₂ halves of the central rings. Orbital contributions from the boron atoms are substantial. In contrast, the respective LUMOs are less uniform. Those of [Li(thf)₂]₂[9,10-Mes₂-DBA], **6**, and **9** show in-phase combinations of the boron p_z orbitals. Major contributions from aryl substituents to the LUMOs of **6** and **9** (but *not* [Li(thf)₂]₂[9,10-Mes₂-DBA]) are also apparent. The LUMO of compound **10** is almost exclusively located at the orthogonally positioned Ph ring with a nodal plane running through both boron centers. Because of their different spatial distributions, the LUMOs of [Li(thf)₂]₂[9,10-Mes₂-DBA], **6**, **9**, and **10** are far less straightforward to compare than the largely uniform HOMOs. In terms of substrate activation, the nature of the HOMO → substrate donations should thus largely be alike, whereas any substrate → LUMO back-

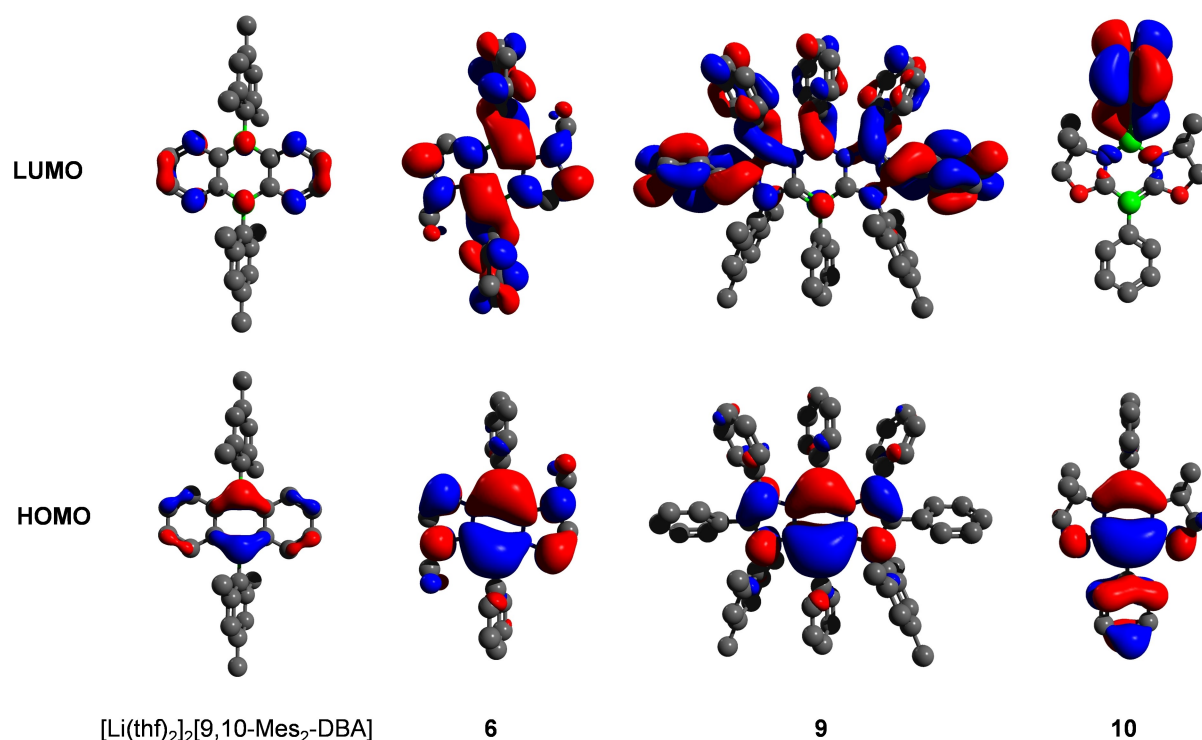


Figure 3. Plots of the HOMOs and LUMOs of $[\text{Li}(\text{thf})_2]_2[9,10\text{-Mes}_2\text{-DBA}]$, **6**, **9**, and **10**. Orbital surfaces are drawn at an isovalue of $0.05 a_0^{-3/2}$ for $[\text{Li}(\text{thf})_2]_2[9,10\text{-Mes}_2\text{-DBA}]$ and at $0.02 a_0^{-3/2}$ for **6**, **9**, and **10**; hydrogen atoms and counterions have been omitted for clarity.

donations will be different for all the B_2 platforms. For this reason, one must be careful when using the HOMO-LUMO gaps of certain B_2 platforms to predict or explain their reactivities.^[27] We note in this context that a recent theoretical treatment of small molecule activation by **10** has mainly considered the strong interactions between the HOMO of **10** and the LUMOs of the substrate molecules in the transition states. However, it was also emphasized that charge donation into the higher-lying LUMO+3 of **10** may well be important.^[53]

Having discussed the nodal structures of the frontier orbitals of the B_2 platforms, we now turn to the relative HOMO energies, which should decisively influence the reactivity patterns, too. Due to their double negative charges, dianions $[\mathbf{1}]^{2-}$ - $[\mathbf{3}]^{2-}$ possess particularly high-lying HOMOs. In fact, a *positive* orbital energy was computed for the HOMO of the bare dianion $[9,10\text{-Mes}_2\text{-DBA}]^{2-}$ (as well as for the HOMO of pristine $[\mathbf{1}]^{2-}$). However, in the presence of two coordinating Li^+ cations, the electrons occupying the HOMO of the resulting inverse-sandwich complex $[\text{Li}(\text{thf})_2]_2[9,10\text{-Mes}_2\text{-DBA}]$ are no longer formally unbound.^[14,32] As a consequence, both the use of donor solvents and the selection of less coordinating counterions (e.g., K^+ vs. Li^+) should increase the HOMO-energy levels and reactivities of $M_2[\mathbf{1}]$ - $M_2[\mathbf{3}]$ by promoting

cation-anion dissociation.^[16] Harman's complex $\text{K}(18\text{-c-6})\text{Au}[\mathbf{5}]$, which has been categorized as an auride anion interacting with two *cis*-disposed neutral borane ligands via a $\text{B-Au}(-1)\text{-B}$ $2e3c$ bond,^[21] constitutes an example of extreme counterion interaction that leaves only little excess charge density on the DBA scaffold (cf. Scheme 2). The neutral NHC-supported DBA **4** should suffer even less from intramolecular Coulomb repulsion than the aforementioned metal complexes and consequently possess energetically even more favorable HOMOs, which is in agreement with cyclic-voltammetric measurements.^[19,32] The diazadiborinines **6**, **9**, and **10** are uncharged and contain two electronegative nitrogen atoms in their central rings, which should further stabilize the corresponding HOMOs. On the other hand, the two strongly π -donating N/O atoms in the annulated rings will push electron density into the molecules' cores, thereby destabilizing the HOMOs. Taken together, these two opposing factors confer reactivities to **6**, **9**, and **10** that are comparable to those of $M_2[\mathbf{1}]$ - $M_2[\mathbf{3}]$ but higher than that of **4**. Overall, our conclusions are supported by quantum-chemical calculations, which predict the following trend for $E(\text{HOMO})$: $[9,10\text{-Mes}_2\text{-DBA}]^{2-} > [\text{Li}(\text{thf})_2]_2[9,10\text{-Mes}_2\text{-DBA}] > \mathbf{6} \approx \mathbf{9} > \mathbf{10}$.^[52]

4.3. Charge-Polarization Effects and Resulting Modes of Substrate Activation

The donor and acceptor orbitals of a TM atom are located at the same reactive center, whereas the electron lone pair and the vacant orbital of an FLP usually reside at different sites. By analogy, the extent of π delocalization in a B_2 platform determines the degree of equivalence of the two B atoms and thus influences whether substrate activation takes place via a concerted “TM-like” or an “FLP-like” mechanism. Our respective assessment of concrete examples will exclude the special case of the Au(-I)/DBA(0) anion Au[5]⁻, as its B_2C_4 core adopts a pronounced boat conformation due to strong Au(-I)→B back donation.^[21] For the central rings of [1]²⁻,^[32] **4**,^[19] and **6-10**,^[3,24,27] a cyclic delocalization of the 6 π electrons and a concomitant aromatic character has been explicitly evoked. The members of the subset [1]²⁻, **4**, and **6-8** with symmetry-related boron atoms are thus best described by canonical forms with little charge separation (see “form I” in Figure 4), whereas **9-11** featuring chemically non-equivalent boron atoms may adopt some mixed-valence character with formal B(+I)/B(+III) centers (see “form II” in Figure 4).^[3,32,53]

This view, though not visibly confirmed by an inspection of the HOMO plots of **9** and **10** (Figure 3), gains support from the following experimental findings, which consistently point toward the assignment B(+I)C₂/B(+III)N₂ (“form II”):^[3,27,28,50] (i) The polar substrates NH₃ and MeOTf react with **9** and **10**, respectively, such that “H^{δ+}” and “Me^{δ+}” are bonded to the BC₂ sites, whereas “δ⁻NH₂” and “δ⁻OTf” are attached to the BN₂ sites (MeOTf = MeOSO₂CF₃). (ii) The [4 + 2] cycloadditions between CO₂ or Ph(Me)CO and **10** form regioselectively δ⁺C–BC₂ and δ⁻O–BN₂ bonds (see Table 3). (iii) As the polarities of the δ⁺H–C^{δ-} and δ⁻F–C^{δ+} bonds in C₆H₆ and C₆F_nH_{6-n} are inverted, the Ph ring resides on the BN₂ and the fluorophenyl rings on the BC₂ fragment after H–C/F–C-bond activation by **11** (see Scheme 6). The assumed mixed valency of the BC₂/BN₂ species **9** and **10** is, however, not a prerequisite for the observed B-centered nucleophilicity. For example, the symmetric BCN/BCN com-

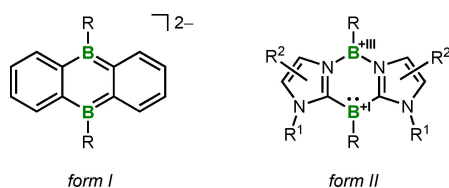


Figure 4. Relevant resonance structures of B_2 platforms featuring equivalent (form I) and inequivalent boron atoms (form II).

pound **6** also adds Me–OTf and H–P(*p*-FC₆H₄)₂ across its boron atoms^[24] and the DBA-dianion salt Na₂[**2**] nucleophilically attacks Et₃Si–Cl with formation of an Et₃Si–B bond.^[16,54,55]

Plausible mechanistic scenarios for small molecule activation, based on the juxtaposition of a dominant “form I” and a dominant “form II”, can be nicely illustrated by taking H₂ as the model substrate.^[14] Figure 5 shows potential transition-state orbital interactions during the cleavage of H₂ by a TM center (left), an FLP (right), or [A]²⁻- vs. E-type species (middle). *TM-like activation*: As the HOMO and the LUMO of [A]²⁻ have the same local symmetries at the boron atoms as the corresponding frontier orbitals involved in TM-mediated H₂ splitting, a similar kind of concerted oxidative addition reaction could take place.^[56] *FLP-like activation*: In an extreme view, the two excess electrons can be placed in the BC₂-boron p_z orbital of **E** while the BN₂-boron p_z orbital remains empty such that the two boron atoms could take the roles of, e.g., phosphorus and boron in a P/B-FLP (Figure 5).^[57]

A unifying concept that explains the reactivities not only of E-type (non-equivalent B(+I)/B(+III) centers) but also of D-type platforms (equivalent boron centers) was put forward by Kinjo, who suggested that the two indistinguishable boron atoms of the 1,4,2,5-diazadiborinines can function both as nucleophilic and electrophilic centers, rendering D-type species “main-group ambiphiles”.^[24] Taking into account our comparative assessment of all

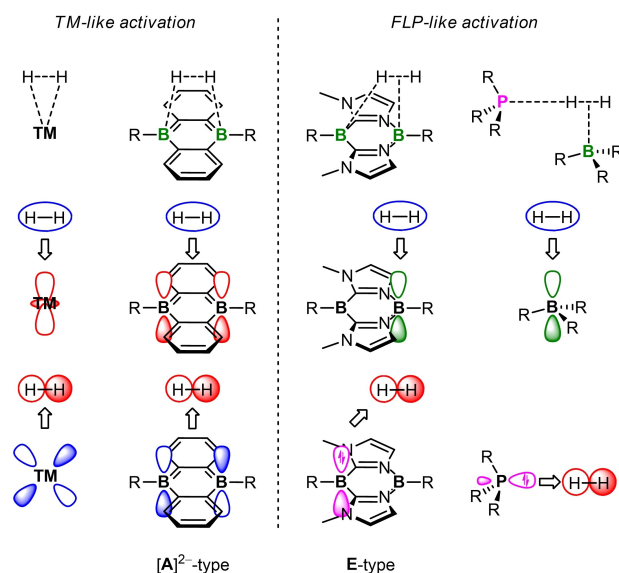


Figure 5. Transition-state orbital interactions relevant for the cleavage of H₂ at a TM center (left), a P/B-FLP (right), and at [A]²⁻- or E-type platforms (middle). HOMOs/LUMOs are shown in blue/red and electron lone pairs/vacant p_z orbitals in magenta/green.

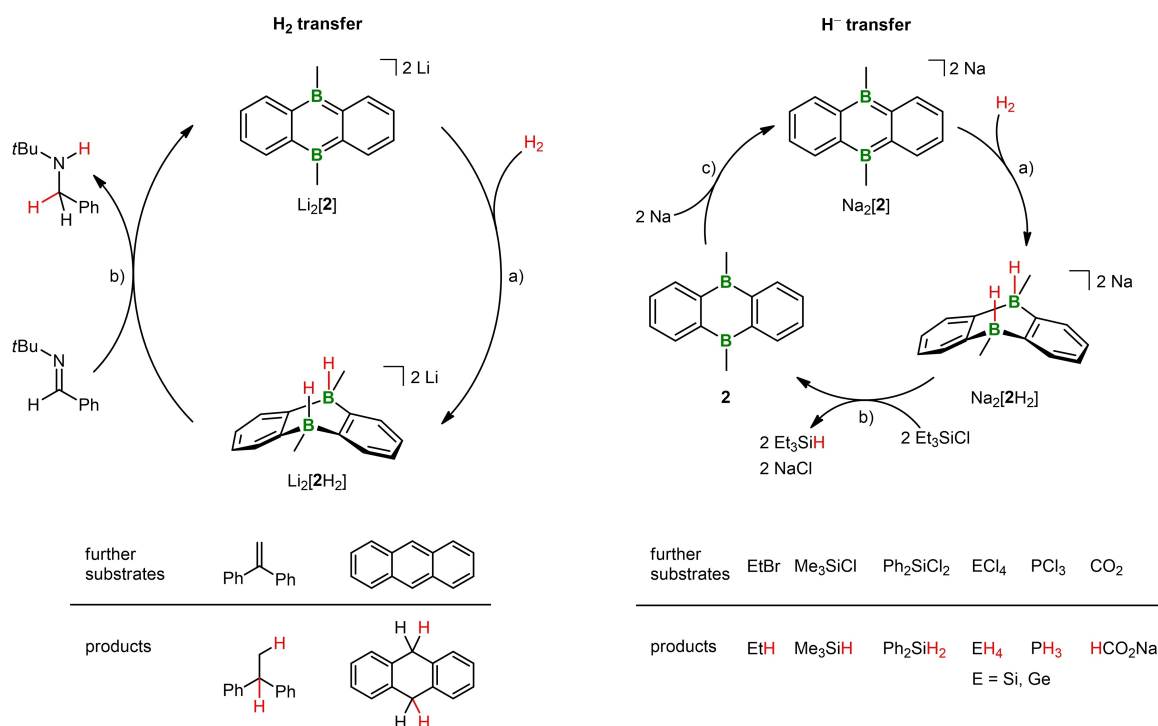
available experimental and theoretical evidence, in particular the frontier-orbital symmetries and energies of the B₂ platforms, this view can now be extended as follows: We propose that the actual *activation* of chemical bonds by the whole set of compounds [A]²⁻, B, D-F proceeds essentially via a “TM-like” mechanism involving a concerted (and in certain cases polarized) transition state. The partial B(+I)C₂/B(+III)N₂ mixed-valence character of E and F, in turn, determines the *regioselectivities* of addition reactions involving heteropolar substrates.

5. Catalytic Transformations

The substrate-activation reactions discussed so far set the stage for subsequent transformations and even full catalytic cycles, further closing the gap between B-containing and TM-based compounds as useful synthetic tools. Starting with the addition of H₂ to M₂[2] (M=Li-K), our group succeeded in establishing catalytic H₂-transfer and H⁻-transfer reactions.^[16] The H₂ transfer to olefins and carbonyl imines produced alkanes and amines in excellent yields (Scheme 12, left). Substrates that fail to undergo the desired hydrogenation reactions fall into two categories: (i) irreversible binders that undergo [4+2] cycloaddition reactions with [2]²⁻, thereby outcom-

peting H₂ as a substrate and poisoning the catalyst [e.g., H₂C=CH₂ and Ph₂C=O (unsuitable substrates) vs. Ph₂C=CH₂ and Ph(H)C=N*t*Bu (suitable substrates)]. (ii) Substrates that behave inertly toward the H₂-addition product Li₂[2H₂] (e.g., phenanthrene). Contrary to classical P/B-FLPs, which tend to transfer first H⁺ and then H⁻ and therefore prefer to hydrogenerate electron-rich element=element bonds,^[58] Li₂[2H₂] supplies H⁻ first and is thus better designed for the conversion of electron-poor unsaturated compounds.^[16] It is also important to mention the counteraction effects in this case. Although the velocity of the H₂ addition follows the sequence Li₂[2] < Na₂[2] < K₂[2], the highest overall H₂ transfer rates are nevertheless observed for Li₂[2] under the conditions applied (1 atm H₂, 100 °C, 10% catalyst loading). Obviously, the formation of strong contaction pairs promotes the actual H₂ transfer by thermodynamic stabilization of the released [2]²⁻ dianion to such an extent that the beneficial influence of Li⁺ coordination on this second step outweighs its negative impact on the first step of the catalytic cycle.

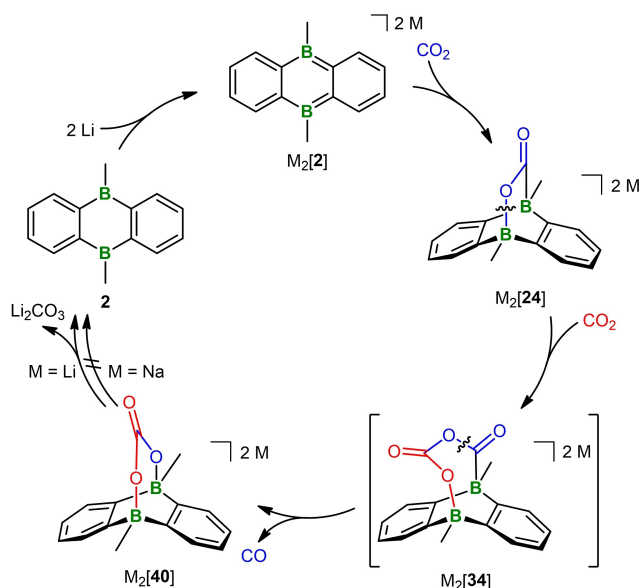
Due to their nature as ditopic hydridoborates, M₂[2H₂] can not only deliver a formal H⁻/H⁺ ion pair, but also two H⁻ ions and thereby convert various element halides to the corresponding element hydrides (Scheme 12, right).^[16] Here, the DBA is liberated in its



Scheme 12. Left: Catalytic cycle for Li₂[2] as the hydrogenation catalyst. Right: Cyclic process for the transformation of Et₃SiCl into Et₃SiH by using Na₂[2H₂] as the hydride donor. Reaction steps: a) H₂ activation; b) H₂/H⁻ transfer; c) DBA reduction. Adapted with permission from E. von Grothuss, S. E. Prey, M. Bolte, H. W. Lerner, M. Wagner, *J. Am. Chem. Soc.* **2019**, *141*, 6082–6091. Copyright 2020 American Chemical Society.

neutral form **2** such that the choice of the counterions is largely irrelevant for the second step of the catalytic cycle. H₂ addition therefore becomes rate-determining and the best performing catalysts contain Na⁺ or K⁺ rather than Li⁺ cations. Other than the H₂ transfer, the H⁻ transfer requires the re-reduction of **2** by an added alkali metal to complete the catalytic cycle. Given that many element halides would also react with this reducing agent, a temporal separation of the reduction/H₂-activation steps from the H/Cl-exchange step demands a repeated sequential addition of the three components to the reaction vessel (“alternating process management” analogous to the industrial anthraquinone process for the synthesis of H₂O₂ from H₂ and O₂^[59]).

Our group also accomplished the DBA-mediated disproportionation of CO₂ to give CO and Li₂CO₃ (Scheme 13).^[15] When put under a blanket of CO₂ at room temperature in THF, the salts M₂[**2**] (M = Li, Na) first form the [4 + 2] cycloadducts M₂[**24**] (cf. Table 3), which immediately react further by inserting a second equiv. of CO₂ into their B–O bonds. The resultant intermediates M₂[**34**] do not remain stable but expel CO and provide CO₃²⁻-bridged DBA salts M₂[**40**]. In the case of M = Na the product remains stable and the reaction stops. In the case of M = Li, however, the diadduct dissociates and quantitatively releases **2** while Li₂CO₃ precipitates. By addition of Li metal, **2** can be reduced again and the resulting Li₂[**2**] is afterwards ready for a new cycle.^[15] The behavior of Na₂[**2**] resembles the above-mentioned reaction of Harman’s K(18-c-6)Au[**5**] with excess CO₂, which produces

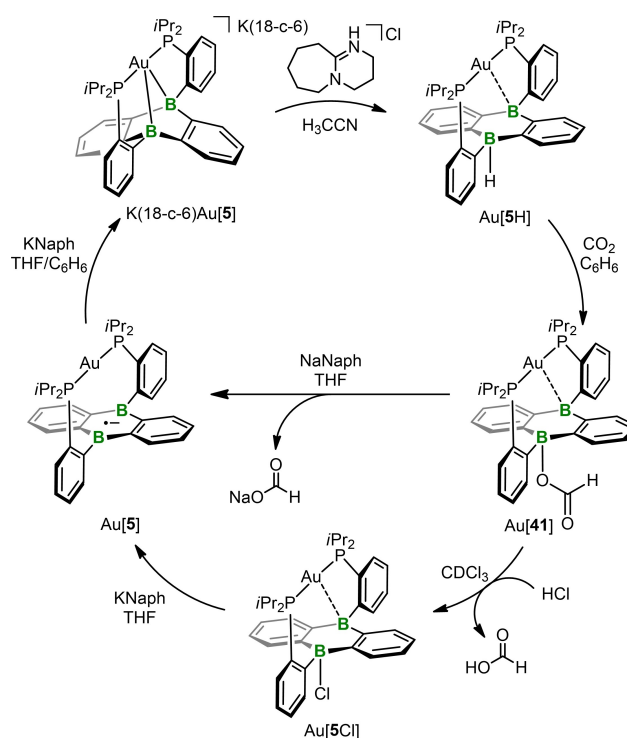


Scheme 13. Proposed mechanism for the Li₂[**2**]-catalyzed conversion of M = Li metal and CO₂ to Li₂CO₃ and CO. In the case of M = Na metal, the reaction stops at the stage of Na₂[**40**] without closing the catalytic cycle.

stoichiometric quantities of CO and the CO₃²⁻ diadduct K(18-c-6)Au[**29**] (Scheme 10).

Alternatively, we have treated the double borohydride Na₂[**2H**₂] (Scheme 12, right) with CO₂ and achieved a clean conversion to the H⁻-transfer product sodium formate, Na[HCO₂].^[16] The [HCO₂]⁻ ion initially remains coordinated to the DBA **2** (cf. the related carbonate adduct Na₂[**40**]; Scheme 13). During crystallization, this complex dissociates so that the free Lewis acid is released and only a subsequent two-electron reduction with Na metal is required to restart the process.

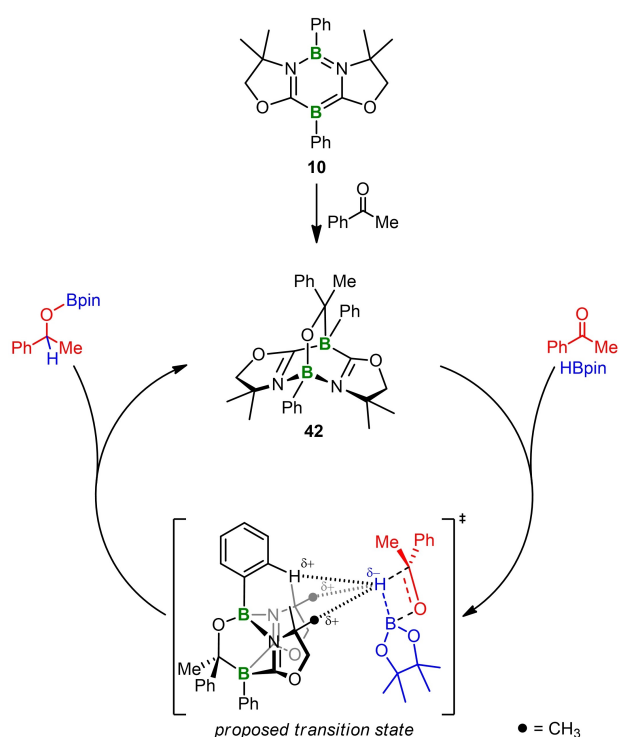
With a similar goal in mind, Harman protonated his borauride K(18-c-6)Au[**5**] at one boron atom to produce the borohydride Au[**5H**]; the use of [DBU-H]Cl in H₃CCN was found to be crucial for the success of this reaction step (Scheme 14; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).^[47] Upon exposure of Au[**5H**] to CO₂ in C₆H₆, the formate complex Au[**41**] is formed. So far, two options have been proposed for splitting the O–B bond of Au[**41**], regenerating the borauride catalyst and harvesting either Na[HCO₂] or HCOOH: (i) two sequential one-electron reductions of Au[**41**] in THF, first with 1 equiv. of NaNaph and then with 1 equiv. of KNaph; or (ii) the protonation of Au[**41**] with ethereal HCl in CDCl₃ and a subsequent two-electron reduction of the resulting Au[**5Cl**] with



Scheme 14. Six individually performed reactions, which, in principle, add up to a synthetic cycle for CO₂ reduction at an Au-DBA platform (MNaph = alkali metal naphthalenide).

2 equiv. of KNaph in THF/C₆H₆. To quote the authors' summary: "Collectively, these results outline a synthetic cycle for CO₂ reduction".^[47]

Kinjo disclosed the catalytic hydroboration of various aliphatic and aromatic carbonyl derivatives using HBpin and **10**. Interestingly, **10** turned out to only be the precatalyst in these transformations. The actual active catalyst forms in situ through a [4+2] cycloaddition reaction of **10** with equimolar quantities of the respective carbonyl substrate. Scheme 15 shows the catalytic cycle for Ph(Me)CO, which Kinjo selected as a representative model system.^[50] The cycloadduct **42** neither dissociates in the course of this catalytic cycle nor are the boron atoms directly involved in catalyst-substrate interactions, which fundamentally distinguishes this system from the previously described catalysts. DFT calculations suggest that **42** functions as an "electrostatic catalyst", which activates the H–Bpin bond for carbonyl insertion through attractive forces between the hydridic borane-H atom and positively polarized H₃C and H substituents that frame the pocket made of the two oxazoline units. The computed activation barrier is 27 kcal mol⁻¹, which seems to be quite high in light of the experimentally observed fast room-temperature reaction.

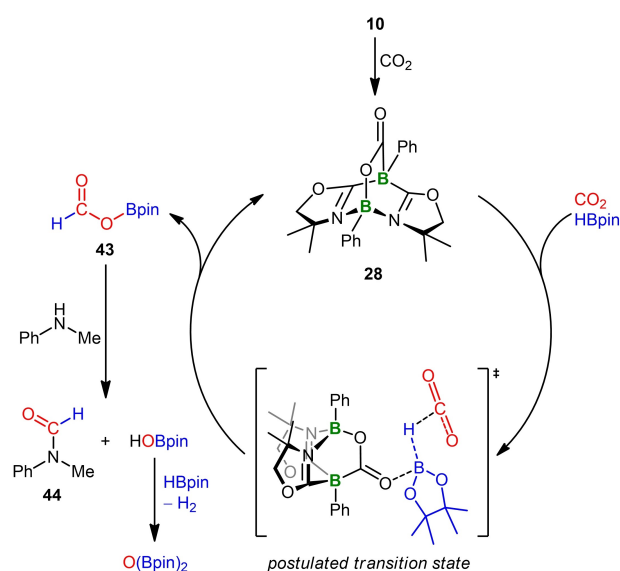


Scheme 15. Hydroboration of Ph(Me)CO with pinacolborane (HBpin), mediated by the electrostatic catalyst **42**, which is formed in situ through [4+2] cycloaddition between the ketone and the 1,3,2,5-diazadiborinine **10**.

CO₂ is a special carbonyl substrate in this context. As before, a C=O bond is first added across the two boron atoms of **10** to furnish the bicyclic compound **28** (Scheme 16, Table 3). Quantum-chemical calculations suggest that **28**, unlike the other carbonyl adducts, interacts with H–Bpin via the double-bonded oxygen atom and not via the oxazoline pocket. The resulting C=O...B complex is ready to hydroborate an incoming CO₂ molecule and thereby generate the mixed anhydride **43**. The targeted aminolysis of the latter leads to *N*-formylation products such as **44** together with (ultimately) the byproduct O(Bpin)₂.^[50]

6. Non-Identical Twins: B₂ Platforms with Varying π -Electron Counts

Apart from the set screws outlined above, variation of the π -electron count of the B₂ platforms should have a particularly strong influence on the compounds' reactivities. As an example, the B-centered nucleophilicity of the DBA dianion [**2**]²⁻ is only one side of the coin. The two-electron oxidized neutral form **2**, a structurally well-defined bidentate Lewis acid,^[17,60] has already been applied by Wegner et al. for catalyzing inverse electron-demand Diels-Alder (IEDDA) reactions between 1,2-diazines and electron-rich dienophiles.^[61,62] The same group has shown that the chlorinated congener 9,10-Cl₂-DBA catalyzes the dehydrogenation of ammonia-borane (H₃N–BH₃), which is relevant for



Scheme 16. The in situ formed cycloadduct **28** catalyzes the hydroboration of CO₂ with pinacolborane (HBpin). Upon treatment with amines (e.g., Ph(Me)NH), the primary product **43** undergoes aminolysis and produces the corresponding *N*-formylation products (e.g., **44**) and stoichiometric quantities of O(Bpin)₂.

the development of new materials and hydrogen storage media.^[63]

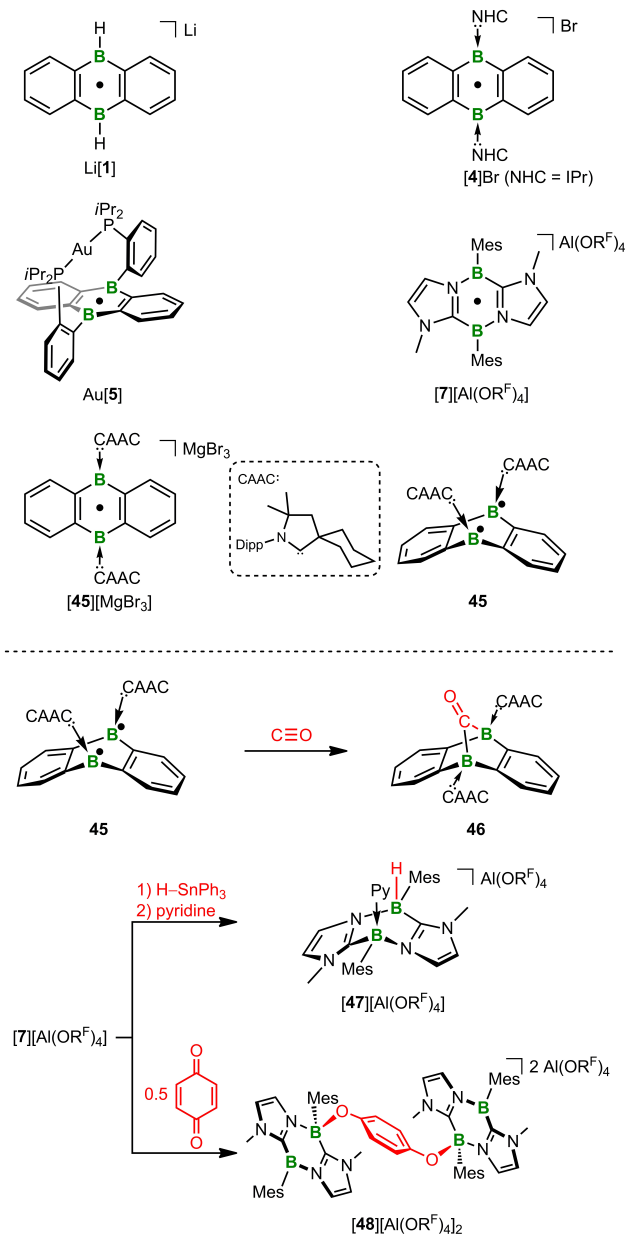
However, there is also a third redox state that can be adopted by DBAs and, in analogous form, by certain diazadiborinines, namely radicals with formally 5 π electrons in their central rings. Such open-shell B_2 platforms could develop into main-group counterparts of paramagnetic TM complexes, which are already well-established in homogeneous TM catalysis. As a proof-of-principle, we refer to the recently published species $Li[1]$ -[45][MgBr₃] (Scheme 17). In 2010, our

group prepared $Li[1]$ through comproportionation of $Li_2[1]$ and the diadduct *syn*-1(SMe₂)₂ in THF; treatment of the $Li[1]$ solution with Li metal quantitatively regenerates the dianion salt $Li_2[1]$.^[2,18] Following a similar approach, Harman obtained [4]Br from equimolar mixtures of **4** and *anti*-4Br₂ in toluene.^[19]

The radical species $Au[5]$ is accessible from $Au[5Cl]$ by one-electron reduction with KNaph in THF. The compound was formulated as a $[Au(+I)]^+[5]^-$ zwitterion, the spin density of which is mainly located on the central B_2C_4 ring.^[21] Kinjo's radical [7][Al(OC(CF₃)₃)₄] forms upon one-electron oxidation of **7** with $Ag[Al(OC(CF_3)_3)_4]$ in C₆H₅F.^[25] Here, the use of bulky Mes substituents on boron was necessary, as the corresponding Ph derivative **6** did not provide a stable radical cation. Finally, Braunschweig generated the CAAC-stabilized radical-cation salt [45][MgBr₃] and the corresponding neutral **45** through the reduction of the CAAC analog of *anti*-4Br₂ (see Scheme 3) with 0.5 and 1.1 equiv. of Bogdanović magnesium, MgAnth (CAAC = cyclic (alkyl)(amino) carbene, Anth = anthracene; see Scheme 17).^[64] While the NHC-/CAAC-supported radicals [4]Br/[45][MgBr₃] show similar structural and EPR-spectroscopic parameters, the neutral species **4/45** (6 π electrons in the central B_2C_4 rings) are strikingly different from each other: The NHC adduct **4** possesses a closed-shell ground state (EPR silent, NMR active), whereas the CAAC adduct **45** (EPR active, NMR silent) has an open-shell singlet biradical ground state of disjointed character. The DBA skeleton of **4** is essentially planar, whereas the B_2C_4 core of **45** assumes a distinct boat conformation with mutually *syn*-oriented CAAC ligands in the solid state.

The observed electron configuration of **45** results from a very small HOMO-LUMO gap, which is a desirable feature for organic electronic materials and often correlates with high charge-carrier mobilities.^[65] In the class of the carbonaceous (oligo)acenes, comparably small HOMO-LUMO gaps can only be achieved by the synthetically challenging linear fusion of a significantly larger number of benzene rings.

In terms of reactivity, **45** readily captures CO in a formal [4 + 1] cycloaddition reaction to yield the [2.2.1]-bicyclic structure **46** (Scheme 17).^[64] Given that Kinjo obtained an analogous cycloadduct **39** from the closed-shell 1,3,2,5-diazadiborinine **9** and the isonitrile $XylN=C$: (see Scheme 11), the formation of **46** does not necessarily have to be rooted in the biradical character of **45**. Clear-cut radical behavior was found for [7][Al(OC(CF₃)₃)₄], which abstracts a hydrogen atom from H-SnPh₃; the product was isolated in the form of its pyridine adduct [47][Al(OC(CF₃)₃)₄] (Scheme 17). A 2:1 mixture of [7][Al(OC(CF₃)₃)₄] and *p*-benzoquinone undergoes double-SET to generate the *p*-hydroquinonate-bridged [48][Al(OC(CF₃)₃)₄]₂.^[25] We note in passing that the closed-shell 1,3,2,5-diazadibor-



Scheme 17. Radicals derived from doubly boron-doped (hetero)arenes (top) and their boron-centered reactivity (bottom; R^F = C(CF₃)₃; Dipp = 2,6-diisopropylphenyl).

ine **10** reacts stoichiometrically with *p*-benzoquinone to produce the expected [4+2] cycloadduct.^[50] The field of open-shell B₂ platforms is still in its infancy. Nevertheless, the results achieved so far give every reason to believe in a fruitful future development.

7. Conclusion

In this review, we have shown that electron-rich six-membered heterocycles containing two cooperating B atoms can activate single, double, and triple bonds – in certain cases even in a catalytic fashion. Similar to transition metal (TM) complexes, whose properties can be optimized by the right ligand design, these boron compounds also offer numerous set screws to adjust their reactivities for a specific purpose. Under an inert atmosphere, the stability of the B₂ platforms is sufficient to enable high turnover numbers and the required reaction conditions are no more drastic than for many d-block species. This field of “main-group compounds as transition-metal mimics” is only just emerging and further fundamentally interesting and synthetically useful reactions are yet to be discovered. Nevertheless, boron heterocycles are already beginning to establish themselves as a third class of catalysts alongside TMs and FLPs.

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