

Singular Metal Activation of Diboron Compounds

Stephen A. Westcott^a and Elena Fernández^b

^a*Department of Chemistry and Biochemistry, Mount Allison University, Sackville, NB, Canada. E-mail: swestcott@mta.ca*

^b*Departament Química Física i Inorgànica. University Rovira i Virgili. C/Marcel·li Domingo s/n Tarragona, Spain. E-mail: mariaelena.fernandez@urv.cat*

Abstract

Organoboron compounds are part of many synthetic routes and target compounds for bio- and medicinal applications. One origin for their preparation was by means of direct interaction between $\text{Cl}_2\text{B}-\text{BCl}_2$ and unsaturated organic compounds but progress towards simple and convenient diboron reagents put tetra(alkoxy)diborons in the spotlight. The less reactive B-B bond in tetra(alkoxy)diborons requires transition metal complexes to activate the diboron and transfer the boryl units to unsaturated substrates. Importantly, the mode of activation differs from the metal involved and is also influenced by the ligands modifying the metal center. Oxidative addition and σ -bond metathesis are the most representative modes of activation and metal complexes become catalytic systems by completing the substrate transformation into the desired organoboron compound. Selectivity is a fundamental issue in the activation and precise delivery of the boryl moiety to the unsaturated substrate. Particularly, asymmetric induction is accomplished by the enantioselective influence of the chiral ligands around the metal centers. Even nanoparticles are known to activate diboron reagents and provide chemoselective diboration processes. The power of diboron reagents in organoboron synthesis is pushing the search of new activation modes and nowadays the sole presence of Lewis bases can also play a definitive role to generate Lewis acid-base adducts that directly interact with unsaturated substrates in a fashionable way. Each situation requires the use of the appropriate mode of activation of diboron reagents and here we collect these singular metal activation modes and analyze their advantages and limitations.

Keywords

Diboron reagents, transition metal complexes, tetra(alkoxy)diborons, organoboron compounds, oxidative addition, sigma bond-metathesis, Lewis acidity

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1. Introduction: The activation of Cl₂B-BCl₂ and beyond

Compounds containing direct boron-boron bonds have been of considerable interest for many years owing to their unusual electron-deficient nature. A successful proof of concept was the eminent reactivity between Cl₂B-BCl₂ and ethylene representing the first addition of a borane reagent to an alkene,¹ even before any hydroboration reaction between B₂H₆ and olefins was described.² Despite the fact that the diborated compound formed at -80°C was characterized as Cl₂B(CH₂)-(CH₂)-BCl₂, the authors deferred to assign a name to the new organoboron compound until “a committee, considering nomenclature of boron compounds in 1954, had reached a final decision”. Looking at this incipient novel reactivity, the addition of Cl₂B-BCl₂ was carried out to a wider range of alkenes, including diboration of cyclopropene and double addition to butadiene.³ For ethyne, *cis*-addition of B₂Cl₄ was defined, and later extended to other terminal alkynes.⁴ A first hypothesis for the activation of the diboron tetrachloride was suggested by Feeney, Holliday and Marsden in 1961, indicating that the initial fission of B-B bond and then addition to olefins was unlikely.⁵ Based on the observed rapid reaction of Cl₂B-BCl₂ with ethylene at low temperature, these authors postulated as a first stage the π -donation from the olefin into the vacant p-type orbital of the boron atoms, since these being on adjacent bonded atoms might constitute a “vacant π -orbital”. As a consequence, this interaction would give a π -complex (**1**) which might either dissociate again or suffer fission of the B-B to give the product **2** (Scheme 1).

Insert **Scheme 1** here

In parallel, Fox and Wartik evidenced a slow interaction between Cl₂B-BCl₂ and aromatic compounds, leading to a single electrophilic substitution product C₆H₅BCl₂ from benzene, but to a double addition product from naphthalene towards complete saturation of one ring.⁶ Subsequently, Zeldin and Wartik assumed *cis* addition of Cl₂B-BCl₂ to the π bonds of the

conjugated systems in 1,3-cyclohexadiene and naphthalene.⁷ Again, the rapidity of the reaction between the diboron tetrachloride and the carbon-carbon π -bond of the conjugated system, even at very low temperatures, weighted in the author's criteria against B-B rupture prior to addition. Besides this intuitively favored activation of the diboron tetrachloride, Rudolph simultaneously proposed a four-center transition state **3** (Figure 1).⁸ The favored orientation in the suggested transition state, (Figure 1), would seem to require that $\text{Cl}_2\text{B}-\text{BCl}_2$ assume a near-planar configuration,⁹ the driving force for which should be the maximum orbital overlap between the vacant p orbitals on the boron atoms and the basic site of the π orbital on the hydrocarbon, represented in structure **4** (Figure 1).¹⁰

Insert **Figure 1** here

In contrast to the above mechanism, which must give rise to a *cis* product, a process involving prior homolytic cleavage of the boron-boron bond to generate free dichloroboryl radicals would, because of the opportunity for free rotation about the carbon-carbon single bond, not be expected to proceed in a stereospecific manner. Furthermore, calculation carried out on bond energy do not favor dissociation as an initiating step ($\Delta H_{\text{B-B}} = 79.0 \text{ kcal/mol}^{-1}$).¹¹ The activation of $\text{Cl}_2\text{B}-\text{BCl}_2$ involving the formation of a cyclic organoboronium ion **5** (Scheme 2) was also discarded because of the lack of *trans* diborated compounds observed.

Insert **Scheme 2** here

The activation of $\text{Cl}_2\text{B}-\text{BCl}_2$ with ferrocene has also been suggested to proceed through a π complex, **6** to form the ferrocenyldichloroborane **7**, discarding other intermediates of lower stability where Fe directly interacts with B (Scheme 3).¹²

Insert **Scheme 3** here

The slower reactivity observed for the addition of $\text{Cl}_2\text{B}-\text{BCl}_2$ to the haloolefins might be a consequence of the less favored formation of the π complex in this case. The diborated product suffers an elimination of trihaloborane, and subsequent addition of $\text{Cl}_2\text{B}-\text{BCl}_2$ to the resulting vinyltrihaloborane, gives as a final product the poly(dihaloboryl)ethane.¹³

The π acidity of $\text{Cl}_2\text{B}-\text{BCl}_2$ and the fact that it was the first isolated compound containing a localized two-center-two-electron (2c/2e) boron-boron bond, gave rise to tremendous interest into routes to prepare organoboron compounds from this tetra(chloro)diboron.¹⁴⁻¹⁷ This issue was further revisited by Morrison highlighting the possibility to use $\text{Cl}_2\text{B}-\text{BCl}_2$ as the precursor for the synthesis of $\text{Br}_2\text{B}-\text{BBr}_2$, $\text{F}_2\text{B}-\text{BF}_2$, $(\text{R}_2\text{N})_2\text{B}-\text{B}(\text{NR}_2)_2$ and $(\text{RO})_2\text{B}-\text{B}(\text{OR})_2$ when reacted with BBr_3 , SbF_3 , dialkylamines and alcohols, respectively.¹⁸ However, at that stage progress became limited by the instability and restricted availability of $\text{Cl}_2\text{B}-\text{BCl}_2$, which was originally produced by an electric discharge through BCl_3 at low temperatures,¹⁹⁻²¹ and a further improved method from copper vapour and BCl_3 .^{22,23} A more accessible diboron compound was then required to continue with the expected applicability on organoborane synthesis although the activation model should be conceptually changed.

2. General trends on activation of symmetrical diboron compounds

The stability of diboron compounds $\text{X}_2\text{B}-\text{BX}_2$ depends on the nature of the substituent on B, decreasing from $\text{X} = \text{R}_2\text{N}$, $\text{RO} > \text{F} > \text{ary}$, alkyl, Cl, whereupon $\text{Cl}_2\text{B}-\text{BCl}_2$ being the most prone towards disproportionation. Organodiboron compounds, $\text{R}_2\text{B}-\text{BR}_2$, are stable only when sterically demanding R groups, such as *t*-Bu, CH_2 -*t*-Bu and mesityl, are protecting the B atom.²⁴⁻²⁶ On the contrary tetra(amino)diborons^{21,27,28} and tetra(alkoxy)diborons^{21,29-32} show a remarkably stability due to the extensive π -type overlap with the neighbouring nitrogen or oxygen atoms which stabilize the boron atom. The concomitant consequences are lower reactivity against unsaturated substrates but the resulting organoboron compounds become generally air and water stable and amenable to chromatography. The new scenario for tetra(amino)diboron and tetra(alkoxy)diboron compounds shows a less π acidic B-B system that

might justify the unlikely formation of the π complex between $(R_2N)_2B-B(NR_2)_2$ or $(RO)_2B-B(OR)_2$ and the olefins, diminishing the direct reactivity towards diboration. The B-B bond in tetrakis(dimethylamino)diboron is so stable that this diboron compound is generally used to prepare other boron-boron linkages.^{30,33} However, tetra(alkoxy)diboron compounds, such as B_2cat_2 ³⁴ (cat = 1,2- $O_2C_6H_4$) (**8**) and B_2pin_2 ³⁵ (pin = 1,2- $O_2C_2Me_4$) (**9**) (Figure 2), have emerged as the synthetic reagents of choice to react with unsaturated substrates, because of the appropriate balance between stability and reactivity parameters. In particular, the pinacolato derivative **9**, despite the fact that is slightly less Lewis acidic than **8** and therefore less reactive, provides the widest range of organoboron compound synthesis because of their great stability (Scheme 4).^{36,37}

Insert **Figure 2** here

Insert **Scheme 4** here

2.1. Metal activation of tetra(alkoxy)diborons

Taking into consideration that boron-boron dissociation energy in tetra(alkoxy)diboron compounds has been estimated to be slightly higher than that of the corresponding data for other diboron compounds,^{38,39} together with the low Lewis acidity of the boron centers, a new model to activate the $(RO)_2B-B(OR)_2$ has to be considered. In fact, an external activator of the tetra(alkoxy)diboron is required to accomplish its addition to unsaturated substrates. The activators can be considered transition metals or Lewis bases (LB) and the mode of interaction can be displayed as a homolytic or heterolytic B-B cleavage, as it is illustrated for B_2pin_2 in Scheme 5. When a transition metal complex, characterized by a low-valent metal, interacts with the non-polar tetra(alkoxy)diboron species, a three-centered σ -complex is invoked followed by intramolecular B-B cleavage to form the corresponding oxidized metal complex (Scheme 5a). As a product of this oxidative addition, the resulting two boryl ligands will be mutually *cis*,

although subsequent isomerisation may occur. Alternatively, a transition metal specie that includes a M-X bond (X = preferentially OR group), can perform a σ -bond metathesis with the tetra(alkoxy)diboron compound, promoting a heterolytic cleavage of the B-B with the concomitant formation of a M-boryl species and the resulting X-B(OR)₂ (Scheme 5b). The formation of the tri(alkoxy)borane compound can be considered the driving force in a sequence where the metal does not involve any change in its oxidative state. Finally, the addition of an appropriate Lewis base, establishes a selective interaction with one of the B(OR)₂ unit from the tetra(alkoxy)diboron, delivering a new Lewis acid-base adduct, MeO⁻→Bpin-Bpin, that is characterized by a quaterinized B(sp³) moiety and an enhanced nucleophilic B(sp²) unit (Scheme 5c). Within the next sections, several examples are disclosed to illustrate the ability of transition metal complexes to transform the unreactive (RO)₂B-B(OR)₂ compounds into very reactive species towards the addition to unsaturated substrates.

Insert **Scheme 5** here

2.1.1 Activation by metal complexes of group 10

Miyaura and Suzuki published in 1993 their ground-breaking work⁴⁰ on the diboration of alkynes with B₂pin₂, using a platinum(0) complex [Pt(PPh₃)₄] as the activator of the diboron. They were the first to propose a mechanism involving oxidative addition of the pinB-Bpin bond to Pt as the initial step (Scheme 6) followed by coordination of the alkyne to the bis(boryl)-Pt complex *cis*-[Pt(Bpin)₂(PPh₃)₂] (**10a**) (Scheme 6), provoking an insertion of the unsaturated substrate into the Pt-B bond and generating eventually the *cis*-1,2-diborated alkene by reductive elimination. The authors demonstrated the activation of B₂pin₂ by NMR analysis of the reaction mixture of Pt(PPh₃)₄ with 10 equiv of B₂pin₂ in toluene at room temperature for 12 h or at 100 °C for 1 h. The ¹¹B NMR spectra exhibited a new signal at 21.5 ppm besides that for the starting B₂pin₂ (29.9 ppm).

Insert **Scheme 6** here

The same authors exhibited a comparative study on the activation of $(\text{MeO})_2\text{B}-\text{B}(\text{OMe})_2$ and $(\text{Me}_2\text{N})_2\text{B}-\text{B}(\text{NMe}_2)_2$ with the platinum(0) complex $[\text{Pt}(\text{PPh}_3)_4]$, and further application to the diboration of 1-octyne. The results clearly demonstrated that both tetra(alkoxy)diboron performed in similar way (quantitative conversion on the *cis*-1,2-diborated product, under 80°C), but the tetrakis(dimethylamino)diboron was only added in 7% to the 1-octyne, even at 120°C.⁴¹ The oxidative addition of $(\text{Me}_2\text{N})_2\text{B}-\text{B}(\text{NMe}_2)_2$ to Pt(0) resulted less efficient, as it was expected, due to the enhanced stability of the diboron by the π donation of the amino groups to the B atoms.

To complement the activation study of tetra(alkoxy)diboron with Pt(0) complexes, Smith III and Iverson disclosed their findings on the reactivity of B_2cat_2 with $[\text{Pt}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PPh}_3)_2]$, which resulted in loss of ethylene, even at -80°C, followed by oxidative addition of the B-B bond to give the bis(boryl) complex *cis*- $[\text{Pt}(\text{Bcat})_2(\text{PPh}_3)_2]$ (**10b**) (Scheme 7).^{42,43} The ¹¹B NMR data for **10b** were eventually reported at δ 47.2 ppm and reactivity studies confirmed that stoichiometric addition of alkynes led to the corresponding diborated products. Interesting, mechanistic studies favoured a mechanism where phosphine dissociation generated a three-coordinate intermediate that mediated the alkyne insertion.

Insert **Scheme 7** here

The molecular structure of similar bis(boryl) complexes *cis*- $[\text{Pt}(\text{B}(4\text{-Bu}^t\text{cat})_2)(\text{PPh}_3)_2]$ (**10c**) and **10d** along with a number of diphosphine derivatives (**10e-g**), monophosphines (**10h-j**) or even mixed phosphines (**10k**) (Scheme 7), was subsequently reported by Marder and Norman who provided conclusive evidence about the activation of tetra(alkoxy)diboron with Pt(0) complexes, through oxidative addition of the B-B bond, and further reactivity with alkynes and diynes.^{44,45} It is noteworthy that the addition of 1,2-bis(dimethylphosphino)methane (dppm) to *cis*- $[\text{Pt}(\text{Bcat})_2(\text{PPh}_3)_2]$ proceeded to give predominantly *cis*- $[\text{Pt}(\text{Bcat})_2(\text{dppm})]$ (**10g**) along with minor amounts of an unusual binuclear product $[\text{Pt}_2(\mu\text{-Bcat})(\text{Bcat})(\mu\text{-dppm})_2(\text{PPh}_3)]$ (Scheme

7). The same authors concluded that either Pt(II)bis(boryls) or Pt(0)-ethylene complexes, are more efficient catalyst precursors than $[\text{Pt}(\text{PPh}_3)_4]$ for the diboration of alkynes and that B_2cat_2 reacts faster than B_2pin_2 , which in turn is much faster than $\text{B}_2(4\text{-Bu}^t\text{cat})_2$. When the basic phosphine PMe_3 is involved in the precursor $[\text{Pt}(\text{PMe}_3)_4]$, the activation of B_2cat_2 takes place smoothly.⁴⁶

The platinum precursor species $[\text{Pt}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PPh}_3)_2]$, postulated by Smith III and Iverson, hold out an inducement since the olefin ligand did not always served as an innocent "mask" for the low-valent metal center. In fact tris(bicyclo[2.2.1]heptene)platinum(0) instantaneously reacts with B_2cat_2 at room temperature to give a bis(boryl)bicyclo-[2.2.1]heptane as the chief organic product (Scheme 8).⁴² It indicated that metal-olefin complexes can rapidly mediate diboration of olefins which are otherwise unreactive with B-B bonds. This first example was published in 1995 and opened a interesting new perspective to activate tetra(alkoxy)diboron to add them to olefins.

Insert **Scheme 8** here

In general, the diboration of alkenes with $\text{Pt}(\text{dba})_2$ required $50\text{ }^\circ\text{C}$,⁴⁷ while the use of $\text{Pt}(\text{NBE})_3$ or $\text{Pt}(\text{COD})_2$ (NBE= norbornene, COD=1,5-cyclooctadiene) as precursors could diborate alkenes at room temperature.⁴⁸ The reactions proceed smoothly to give 1,2-diborylalkanes in high yield, and the catalysts were compatible with common functional groups. Further developments in the area by Baker showed that $[\text{Pt}(\text{COD})\text{Cl}_2]$ could efficiently activate B_2cat_2 and promote the diboration of terminal alkenes, vinylarenes, alkynes and aldimines (Scheme 9). The last example was a great advance because it represented the first direct approach towards α -aminoboronate esters.⁴⁹

Insert **Scheme 9** here

A theoretical study has been carried out by Morokuma for the mechanism of Pt(0)-catalyzed alkyne and alkene diboration reactions with the B3LYP density functional method.⁵⁰ The complexation energy between $(\text{OH})_2\text{B}-\text{B}(\text{OH})_2 + \text{Pt}(\text{PH}_3)_2$ has been calculated to be 3.7 kcal/mol, where the B-B and P-Pt-P axes are perpendicular to each other. The next step is the activation of the B-B bond, and the activation barrier has been calculated to be 12.5 kcal/mol, relative to the molecular complex $(\text{OH})_2\text{B}-\text{B}(\text{OH})_2-\text{Pt}(\text{PH}_3)_2$ or 8.8 kcal/mol relative to the reactants.⁵⁰ In parallel, Sakaki theoretically investigated the insertion of $\text{Pt}(\text{PH}_3)_2$ into $\text{X}_2\text{B}-\text{BX}_2$ (X=H or OH) with the ab initio MO/MP4SDQ, SD-CI, and coupled cluster with double substitutions (CCD) methods. They found that this reaction proceeds with a moderate E_a of 15 kcal/mol and a considerable E_{exo} of 20 kcal/mol for $(\text{OH})_2\text{B}-\text{B}(\text{OH})_2$. They noted that the B-B bond, undergoes the insertion reaction of $\text{Pt}(\text{PH}_3)_2$ much more easily than does the C-C bond.⁵¹ Nowadays, the Pt-catalyzed diboration of terminal alkenes can be accomplished in an enantioselective fashion in the presence of chiral phosphinite ligands. Reaction progress kinetic analysis and kinetic isotope effects suggests that the stereodefining step in the catalytic cycle is the olefin migratory insertion into a Pt-B bond.⁵²

The addition of diboranes to 1,3-dienes was first addressed by Miyaura, through the activation of B_2pin_2 with $[\text{Pt}(\text{PPh}_3)_4]$, forming selectively 1,4-bis(allyl)boronates as single *Z* isomers.⁵³ Interestingly, however, if the phosphine-free platinum species $[\text{Pt}(\text{dba})_2]$ (dba= dibenzylideneacetone) was used, the diborated products were those resulting from diene dimerisation.⁵³ Further advances in this issue, provided the design of chiral tetra(alkoxy)diboron compounds to be activated by Pt and used as asymmetric inductors in the diboration of 1,3-dienes.⁵⁴ The oxidative addition products derived from reactions of novel chiral diboranes with $[\text{Pt}(\eta^2-\text{CH}_2=\text{CH}_2)(\text{PPh}_3)_2]$ were studied by single crystal X-ray diffraction studies (Scheme 10). Unfortunately, their application in the platinum-catalysed diborations of a range of prochiral 1,3-dienes showed that chirality transfer from the diborane to the diene was not efficient in these cases.

Insert **Scheme 10** here

The B₂pin₂ activation by *cis*-[Pt(η²-CH₂=CH₂)(PPh₃)₂] was also found to be an effective catalyst precursor for the 1,4-diboration of α,β-unsaturated ketones at 80°C for 12h (Scheme 11),⁵⁵ while [Pt(PPh₃)₄] as catalyst precursor required 20h at 110 °C to add B₂pin₂ to the same activated olefins.⁵⁶ A second generation of platinum system based on Pt(0) diimine, [Pt(BIAN)(DMFU)] (BIAN=*bis*(phenylimino)acenaphthene, DMFU = dimethylfumarate) (**12**), resulted efficient in the activation of B₂pin₂ to provide exclusively the unexpected 3,4-diborated addition products for α,β-unsaturated esters (Scheme 11), but selective 1,4-addition for α,β-unsaturated ketones and aldehydes.⁵⁷ Interestingly, this performance was even better than that promoted by [Pt(NBE)₃] (NBE = norbornene) leading to mixtures of 1,4- and 3,4-diborated products after activation of B₂pin₂.⁵⁷

Insert **Scheme 11** here

The mechanism of this reaction has been studied with the aid of density functional theory (DFT) by calculating important intermediates and transition states.⁵⁸ The catalyzed diborations are believed to proceed by oxidative addition of diborons to the Pt(0) center followed by 1,4-conjugate addition of a Pt-B bond to give an O-bound enolate intermediate containing a Pt-C-C=C-O-B linkage. Reductive elimination would then generate the corresponding 1,4-addition product. In the case of methyl acrylate, a 1,3-shift of the O-bound boryl group provides the experimentally observed and thermodynamically favored 3,4-addition product (Scheme 12).

Insert **Scheme 12** here

To complete this picture, Srebnik was able to react B₂pin₂ and diazomethane with the aid of [Pt(PPh₃)₄] (Scheme 13a),⁵⁹ which afforded a new carbenoid insertion reaction into the B-B bond. The same authors extended the scope of substrates to open the possibility of preparing C1-bridged bis-boronates with a quaternary carbon atom (Scheme 13b). The issue has recently

been revisited by Wommack and Kingsbury developing a method to construct doubly C-substituted 1,1-diborons by diazoalkyl insertion into *cis*-[Pt(Bpin)₂(PPh₃)₂] (Scheme 13c).⁶⁰

Insert **Scheme 13** here

The activation of diboron by platinum complexes and further reactivity with unsaturated substrates or nucleophiles, has been always regarded to involve three or four coordinated Pt intermediates. Recently, Braunschweig has been instrumental in furthering our understanding of the platinum mediated B-B oxidation reaction.⁶¹ The reactivity of *trans*-[Pt(B(4-Bu^tcat))(Me)(PCy₃)₂] (**13**) with B₂cat₂ lead to the formation of both MeBcat and MeB(4-Bu^tcat), and two plausible mechanisms were invoked to rationalize this mixture. The first proposed mechanism involved the associative formation of a six-coordinate intermediate *via* oxidative addition of the B₂cat₂ group with a subsequent reductive elimination. This proposal required the formation of short-lived hypercoordinate Pt species (Scheme 14). The second pathway simply suggested a σ-bond metathesis of the B-B bond with the Pt-C bond. Bis(boryl) species *cis*-[Pt(Bcat)₂(PCy₃)₂] (**14**) was also examined by X-ray diffraction studies and the short B-B bonds suggested the boryl ligands were only loosely bound to the metal center, presumably arising from the steric hindrance caused by the bulky phosphine ligands.

Insert **Scheme 14** here

The activation of the diboron bond by σ-bond metathesis between B₂cat₂ and a Pt-C bond was already observed by Iverson and Smith III in 1995.⁴² They found that metallocyclopentane *cis*-[Pt(CH₂)₄(PPh₃)₂] could react cleanly with 2 molar equiv of B₂cat₂ at 95°C to form *cis*-[Pt(Bcat)₂(PPh₃)₂] (**10b**) in 68% and catB(CH₂)₄Bcat in 47% (Scheme 15).

Insert **Scheme 15** here

Although a wealth of research has focussed on the use of platinum complexes in diboron activation chemistry, much less is known about the analogous palladium chemistry.^{51,62} Indeed, early theoretical studies have claimed that although the barrier for oxidative addition of B₂(OH)₄ to Pd(PH₃)₂ is smaller than for the analogous Pt complex (8.6 kcal/mol vs 14.0 kcal/mol), the reaction is endothermic for Pd but exothermic for Pt. It has been postulated that [Pd(B(OH)₂)₂(PH₃)₂] complex resides higher in energy than the analogous Pt complex, and this energy difference persists for all the catalytic intermediates. Morken has carried out some exceptional diboration chemistry with palladium complexes and has claimed that electron-donating ligands would stabilize diborated intermediates that are in high oxidation states and thus might facilitate Pd catalysis. Isotopic-labelling experiments, kinetic analysis, computational and stereodifferentiating experiments all suggest that the catalytic cycle for the enantioselective diboration of allenes with Pd₂(dba)₃/ligand and B₂pin₂, involves a rate-determining step involving oxidative addition of the diborane(4) species to palladium.^{63,64} Several years later, Ozerov has found that B₂cat₂ heterolytically adds to a [Pd(II)(PNP)]⁺ fragment (PNP = diarylamido/bis phosphine ligand) to give the corresponding palladium-boryl species **15** (Scheme 16).⁶⁵ The activation of B-B bond across a Pd-N bond to form the N-B and Pd-B bonds, is unique. Although mechanistic implications for this reaction were not addressed, the authors suggest the possibility that the reaction is initiated by the formation of a σ-complex of the B₂cat₂ with [Pd(II)(PNP)]⁺, followed by a 1,2-addition.

Insert **Scheme 16** here

Previous computational and experimental investigations by Bo, Peris and Fernández argued in favor of a viable B-B σ-complex when [Pd(II)(NHC)(Br)]⁺ (NHC = N-Heterocyclic carbenes) promotes the heterolytic splitting of B₂cat₂.⁶⁶ Direct oxidative addition of B₂cat₂ to [Pd(II)-NHC-Br]⁺ was first calculated as an endothermic process by 22.0 kcal mol⁻¹ (Scheme 17a) while the barrier of the reverse process is extremely low. These results are in agreement with previous studies by Morokuma.^{51,62} In fact, the product from the oxidative addition is a saturated

hexacoordinated Pd(IV) complex which would require creation of a vacant site in order to enable the coordination of an alkene. The activation of B₂cat₂ by [Pd(II)(NHC)Br]⁺ resulted more favourably through σ -bond metathesis providing [Pd(NHC)(Bcat)]⁺ and BrBcat (Scheme 17b) with 3.4 kcal.mol⁻¹ above the reactants (Scheme 17b). Alternatively, the dicationic complex [Pd(II)(NHC)]²⁺ could form a very stable σ -complex with B₂cat₂, with 32.9 kcal mol⁻¹ below the two isolated reagents, which promoted the oxidative addition of the diboron (Scheme 17c).

Insert **Scheme 17** here

It seems that palladium complexes with high oxidative states and basic ligands can be involved in oxidative addition as well as in σ -bond metathesis. Cheng has demonstrated that phosphine-free Pd complexes together with alkenyl or aryl iodides are very efficient catalysts for 1,2-diboration of allenes.^{67,68} This reaction is completely regioselective and highly stereoselective affording diborated products with mainly *Z* stereochemistry. This Pd-catalyzed reaction proceeds *via* a previously unknown mechanism involving the oxidative addition of an I-B bond to the palladium center instead of the oxidative addition of a B-B bond to metal (Scheme 18). After insertion of the allene substrate to the Pd-B bond, a Pd-allyl species is formed with the boryl attached to the central carbon of the π -allyl group. Eventually the transmetallation of B₂pin₂ with the Pd-C specie regenerates the I-B bond and gives the metal intermediate B-Pd-allyl species that forms the diborated product by reductive elimination. The activation of the diboron by the Pd-allyl species is a key step for the success of the diboration of allenes.

Insert **Scheme 18** here

Since palladium complexes have proven to be efficient in activating diboron compounds throughout transmetallation, a wide range of application have been considered in the last decade, such as palladium-catalyzed transformation of allylic alcohols to allylboronates,^{69,70} borylation of allylic halides⁷¹ or allylic acetates,^{71,72} and the β -boration of α,β -unsaturated carbonyl substrates.⁷³ Interestingly both palladium and nickel showed to be similarly efficient to activate B_2pin_2 and catalyze the addition to unsaturated substrates. Oshima postulated that Ni(0) species react with substrate α,β -unsaturated esters and amides to generate the η^2 -coordinated complex, which activates the B_2pin_2 to favour the formation of η^3 -coordinated boryl-nickel(II) complex (Scheme 19a).⁷⁴ An eventual reductive elimination provides the boryl enolate product, which is susceptible to protonolysis and affords the β -boryl ester product. Westcott and Fernández demonstrated that the use of chiral ligands to modify the nickel complex, can generate asymmetric induction in the C_β -B bond.⁷³ Morken has also studied the 1,4-diboration of conjugated dienes by activating B_2pin_2 with Ni(0), and postulated an alternative mechanism where the oxidative addition of B-B to Ni(0) is not involved.⁷⁵ Instead, they postulated an initial association of Ni(0) with the diene to form a Ni-olefin complex which is the responsible to react with B_2pin_2 providing the least hindered Ni-C bond that releases the desired diborated product by reductive elimination (Scheme 19b).

Insert **Scheme 19** here

A process that involves an unprecedented B-B bond cleavage in B_2cat_2 promoted by two Ni(I) centers in the dimer $[Ni(\mu^2-PNP)]_2$, has been described by Meyer and Mindola to proceed plausibly *via* a binuclear oxidative addition reaction (Scheme 20a). The ^{11}B NMR spectrum of $[Ni(Bcat)(PNP)]$, clearly reveals the formation of a rare example of a nickel-boryl (47 ppm).⁷⁶ Alternatively, the $[Ni(Bcat)(PNP)]$ complex can be prepared by σ -bond metathesis from $[Ni(O^tBu)(PNP)]$ and B_2cat_2 (Scheme 20b).⁷⁷ A proposed intermediate could be detected by NMR spectroscopy and confirmed by DFT calculations as the isomer that conducts the σ -bond

metathesis. The weak interaction between the nickel center and the tethered borane fragment in B_2cat_2 is rationalized as a consequence of the high energy required to access the empty $d_{(x^2-y^2)}$ orbital in a sterically encumbered square planar environment.

Insert **Scheme 20** here

Moving from the Pt to Pd and Ni complexes, it can be noted a progressive change on the activation mode of the tetra(alkoxy)diboron compounds, from oxidative addition of the B-B within Pt(0) complexes to σ -bond metathesis with Pd or Ni. Going further to the right of the periodic table the activation of diboron by σ -bond metathesis becomes more frequent.

2.1.2 Activation by metal complexes of group 11

Miyaura made another proof of concept when he demonstrated the activation of B_2pin_2 with CuCl in the presence of KOAc (Scheme 21).^{78,79} Analogously, Ito and Hosomi postulated that $[(CuOTf)_2 \cdot C_6H_6]$ itself did not consume bis(catecholato)diboron (B_2cat_2) in the absence of an α,β -enone.⁸⁰ The presence of PBu_3 enhanced the β -boration of the enone, presumably because the PBu_3 coordinates to $(CuOTf)_2 \cdot C_6H_6$ and the resulting copper system activate the B_2pin_2 . The activation of diboron reagents with Cu(I) opened a new platform of copper mediated borylation reactions as the borylation of functionalized allyl acetates by Ramachandran.⁸¹

Insert **Scheme 21** here

Sadighi provides evidences of the σ -bond metathesis interaction by reacting the known complex $[(IPr)Cu(Ot-Bu)]$ with B_2pin_2 , forming a product identified as $[(IPr)Cu(Bpin)]$ (**16**) (Scheme 22). The nature of the N-heterocyclic ligand IPr seems to favor the isolation and full characterization of the Cu(I)-boryl complex, which resulted very active in reduction of CO_2 to CO ,^{82,83} or insertion of aldehydes,⁸⁴ and alkenes.⁸⁵ Ito and Sawamura also observed that ligands

with large bite-angle, such as Xantphos, would activate Cu(I)-OR for σ -bond metathesis with B₂pin₂, to form a Cu-B species **17** useful as a “formal boryl nucleophile” (Scheme 22).⁸⁶ Then, the formal S_N2’ attack of the Cu-B species on an allylic carbonate would allow γ -selective formation of an allylboron compound along with a copper carbonate that would undergo decarboxylation to regenerate the Cu-OR.

Insert **Scheme 22** here

The expansion of this chemistry came by the work of Yun,^{87,88} since the copper borylation of α,β -unsaturated carbonyl compounds could be achieved by the activation of B₂pin₂ with CuCl in the presence of base and MeOH to favor the σ -bond metathesis. Remarkably, the use of chiral diphosphines to modify the Cu(I) salt, was the key to deliver the Bpin moiety with asymmetric induction.⁸⁹ A more detailed mechanism for the borylation of α,β -unsaturated carbonyl compounds was described by Lin with the aid of density functional theory calculations.⁹⁰ The σ -bond metathesis step has also been elucidated, experimental and theoretically, in the copper-catalyzed borylation of aryl halides with B₂pin₂, by Marder and Kleeberg.⁹¹

The activation of B₂pin₂ could also be carried out in the presence of Cu(II) salts, to promote β -boration of α,β -unsaturated carbonyl compounds in water as solvent. Santos has proposed a mechanism to activate the B₂pin₂ where amine/H₂O could contribute to the preactivation of the diboron to form the Cu(II)-Boryl species (Scheme 23a).⁹² In a similar context, Kobayashi has postulated a σ -bond metathesis step between B₂pin₂ and Cu(Ac)₂ to form a Cu(II)-boryl species by assistance of a chiral 2,2’-bipyridine ligand (Scheme 23b), which resulted in a very efficient catalysts for the asymmetric β -boration of α,β -unsaturated carbonyl compounds in water as solvent.⁹³

Insert **Scheme 23** here

The first example of copper catalysed diboration of alkenes with Cu complexes involved N-heterocyclic carbene ligands, (NHC). Fernández and Pérez studied the nature of the interaction between the unsaturated complex $[\text{Cu}(\text{NHC})(\text{NCMe})]^+$ and B_2cat_2 through a theoretical DFT study with the B3LYP functional in order to understand the activation mode.⁹⁴ The results were conclusive, in favour of the $[\text{Cu}(\text{NHC})(\sigma\text{-catB-Bcat})]^+$ (**18**) description (Figure 3), where the unbroken B–B bond coordinates Cu as a B–B sigma adduct. The presence of a base seems to favour the heterolytic cleavage of the diboron in the complex $[\text{Cu}(\text{NHC})(\sigma\text{-catB-Bcat})]^+$, to generate the catalytically active copper boryl complex.

Insert **Figure 3** here

The difference on reactivity between B_2cat_2 and B_2pin_2 in the diboration reaction of alkenes catalyzed by carbene-ligated copper(I) complexes was further studied by Lin and Marder.⁹⁵ The higher reactivity of B_2cat_2 versus B_2pin_2 in this reaction results largely from the enhanced electrophilicity/Lewis acidity of the former, which significantly lowers the barrier in the product-forming σ -bond metathesis step (Figure 4). The relative barriers in the reactions of B_2cat_2 and B_2pin_2 with $(\text{NHC})\text{Cu-OMe}$ are much closer than with analogous Cu–R systems.

Insert **Figure 4** here

The reagent B_2pin_2 is, after all, the most used diboron reagent in copper borylation reactions but also in multicomponent processes whereupon the σ -bond metathesis step to form the Cu-Bpin bond is the initial key step.⁹⁶ When moving to tetra(alkoxy)diboron activation by silver complexes, we found only two significant attempts to activate B_2cat_2 and B_2pin_2 . In both cases, the common feature is that the silver complex is modified with N-heterocyclic carbene ligands. Fernández and Peris found that the dimer $[(\text{mentimid})_2\text{Ag}]\text{AgCl}_2$, (mentimid= 1-methyl-3-(+)-methylmenthoxide imidazolium chloride) could react with B_2cat_2 and promote the diboration of

alkenes.^{97,98} Almost one decade later, Yoshida used (IMes)AgCl to activate B₂pin₂ and apply the corresponding (IMes)Ag-boryl species in a formal hydroboration of alkynes.⁹⁹ While in the diboration reaction a base was not required, in the case of hydroboration, the authors justify the use of the KO^tBu to assist the σ -bond metathesis between (IMes)AgCl and B₂pin₂ (Scheme 24).

Insert **Scheme 24** here

The use of gold(I) complexes to activate diboron reagents is even less prominent, although the scarce examples represent a non-existing gold catalyzed diboration of alkenes with a concomitant high selectivity towards the diborated product.^{98,100} Westcott, Baker and Marder found that an electron-rich phosphane gold complex could be used in the first catalyzed diboration of alkenes. The reaction of B₂cat₂ with alkenes in the presence of [AuCl(PEt₃)] and ethane-1,2-diylbis(dicyclohexylphosphane) yielded *exclusively* the 1,2-bis(boronate) ester.¹⁰⁰

2.1.3 Activation by metal complexes of group 9

Although the gold-standard for diboration chemistry described in the last example represented the first highly selective diboration of alkenes by transition metal complexes, Marder, Westcott and Baker also described in the same work that [RhCl(PPh₃)₃] was found to catalyze the diboration of vinyl arenes using B₂cat₂, however product selectivities were complicated by a competing β -hydride elimination route.¹⁰⁰ Further attempts have improved only slightly the chemoselectivity on the diborated product but have made possible to run the reaction in an enantioselective manner by the selection of the appropriate chiral phosphine modifying the Rh(I) complex.¹⁰¹⁻¹⁰³ Although oxidative addition of the B-B bond in B₂cat₂ was proposed as a key step in the catalytic cycle, evidence for this reaction came from the groups of Marder and Norman. A number of different tetra(alkoxy)diboron reagents were activated by either [RhCl(PPh₃)₃] (Scheme 25) or [Rh(μ^2 -Cl)(PPh₃)₂]₂, as evidenced by multinuclear NMR spectroscopy.¹⁰⁴ The authors realized that B₂cat₂ and its 4-Bu^t and 3,5-Bu^t diborane analogs, which have shorter B-B bonds than B₂pin₂, are nonetheless easier to oxidatively add to Rh(I). It

has to be noted that the bis(boryl) complex $[\text{RhCl}(\text{PPh}_3)_2(\text{Bcat})_2]$ (**20a**) was previously detected by the slow reactivity of $[\text{Rh}(\mu^2\text{-Cl})(\text{PPh}_3)_2]_2$ with an excess of HBcat, through the intermediate $[\text{RhCl}(\text{H})(\text{PPh}_3)_2(\text{Bcat})]$.¹⁰⁵

Insert **Scheme 25** here

Likewise, addition of B_2cat_2 to the electron-rich complex $[\text{RhMe}(\text{PMe}_3)_4]$ was thought to proceed *via* initial dissociation of a phosphine ligand followed by oxidative addition of the B-B bond. A subsequent reductive elimination step generated MeBcat along with the boryl complex $[\text{Rh}(\text{Bcat})(\text{PMe}_3)_4]$ (**21**), which has trapped the dissociated ligand (Scheme 26). Addition of a second equivalent of B_2cat_2 proceeded smoothly to give the tris(boryl)rhodium(III) complex *fac*- $[\text{Rh}(\text{Bcat})_3(\text{PMe}_3)_3]$ (**22**) (Scheme 26). The *fac*-arrangement of the boryl groups was attributed to the strong *trans*-influence of these ligands, arising from their significant σ -donating ability.¹⁰⁶ DFT calculations suggest that the boryl ligands prefer to occupy sites that have minimal metal-boryl σ^* -antibonding character.¹⁰⁷

Insert **Scheme 26** here

Oxidative addition of B-B bonds has also been observed in Rh-alkene complexes. For example, $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{C}_2\text{H}_4)]$, $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{CF}_3)(\text{PMe}_3)(\text{C}_2\text{H}_4)]$ lead to B-B oxidative addition of B_2pin_2 by photolysis in hexane at $-10\text{ }^\circ\text{C}$ to form $[\text{Rh}(\eta^5\text{-C}_5\text{H}_4\text{CF}_3)(\text{PR}_3)(\text{Bpin})_2]$ (**23**) (Scheme 27).¹⁰⁸ Interestingly, competition experiments using HBpin and B_2pin_2 were performed with these rhodium complexes and results suggested a slight preference for B-B oxidative addition over B-H bond activation.

Insert **Scheme 27** here

Braun and co-workers have investigated the reactivity of $[\text{Rh}(\text{Bpin})(\text{PEt}_3)_3]$ towards a number of ketones and imines. The resulting insertion (into the Rh-B bond) products were subsequently treated with B_2pin_2 to give unique diborated products through a possible mechanism involving B-B oxidative addition and reductive elimination (Scheme 28).¹⁰⁹ B_2pin_2 has also activated by $[\text{Rh}(\text{Bpin})(\text{PEt}_3)_3]$ in the presence of SCF_3 -functionalized arenes to accomplish their selective borylation.¹¹⁰

Insert **Scheme 28** here

Bis(pinacolato)diboron and bis(neopentyl glycolato)diboron have been added to α,β -unsaturated ketones, esters, nitriles, and aldehydes through $[\text{RhCl}(\text{PPh}_3)_3]$ activation, presumably *via* oxidative addition.¹¹¹ However, Nishiyama has suggested a σ -bond metathesis step to form Rh(III)-boryl species, from B_2pin_2 and $\text{Rh}(\text{III})(\text{OAc})_2(\text{OH})(\text{Phebox})$ complex, which resulted in useful catalytic systems in the asymmetric β -boration of α,β -unsaturated carbonyl compounds (Scheme 29) from B_2pin_2 and $[\text{Rh}(\text{III})(\text{OAc})_2(\text{H}_2\text{O})(\text{Phebox})]$ complex.¹¹² Formation of a boryl acetate byproduct was confirmed by the authors using ^{11}B NMR spectroscopy, at 60°C . The same authors used this strategy to promote asymmetric diboration of terminal alkenes with high enantioselectivities and chemoselectivities. In that case the use of a base, such as NaO^tBu , accelerated the reaction, and the authors attributed the beneficial influence to the preactivation of the $[\text{Rh}(\text{III})(\text{OAc})_2(\text{H}_2\text{O})(\text{Phebox})]$ complex towards the σ -bond metathesis step.¹¹³

Insert **Scheme 29** here

Alternatively, Fernández and Bo demonstrated that Rh(III) complexes modified with NHC ligands could catalyze the diboration of cyclic systems, postulating the oxidative addition of B_2pin_2 , B_2pin_2 or bis(neopentylglycolato)diboron (B_2neop_2) to the Rh(III) system as the initial key step (Figure 5).¹¹⁴

Insert **Figure 5** here

Moving from Rh to Ir activation of diboron compounds, it is somewhat surprising that only a few studies have focussed on the stoichiometric addition of diborane compounds to iridium complexes, considering the wealth of information on the iridium-catalyzed borylation of alkanes and arenes. Early studies have shown that B₂cat₂ adds cleanly to [IrCl(PEt₃)₃] to give bis(boryl) complex [IrCl(Bcat)₂(PEt₃)₂] (**24**) with the concomitant decoordination of PEt₃ (Scheme 30).¹¹⁵ A single crystal X-ray diffraction study confirmed that this complex was isomorphous with its rhodium analogue. The iridium complex differs in solution from the rhodium species since the saturated octahedral *cis,mer*-[IrCl(Bcat)₂(PEt₃)₃] (**25**) can be formed from **24** by coordination of PEt₃ (Scheme 30). Similar reactivity of B₂cat₂ with [IrCl(η²-coe)(PMe₃)₃] (coe = cyclooctene) was reported to give *cis,mer*-[IrCl(Bcat)₂(PMe₃)₃].¹¹⁶

Insert **Scheme 30** here

Theoretical calculations, using the DFT method, examined the iridium-catalyzed borylation of benzene with diboron source B₂eg₂ (eg = ethyleneglycolato, -OCH₂CH₂O-). This study found that oxidative addition of the B-B bond occurred at a lower energy than the corresponding C-H bond activation step.¹¹⁷ A tris(boryl)iridium(III) complex was also concluded to be catalytically-active and an unusual seven-coordinate iridium(V) species is believed to be involved as a key intermediate in the catalytic cycle.¹¹⁸ A tris(boryl)iridium(III) complex has been previously prepared and structurally characterized by Marder from the reaction between [Ir[(η⁵-indenyl)(η⁴-cod)] (cod = cyclooctadiene) and excess of catecholborane.¹¹⁹

While electron-rich second and third row metals are known to readily activate the strong B-B bond in most starting diborane(4) compounds, a few studies have suggested that this step may also be carried out using selected first row metals. For instance, Marder, Norman and co-workers have shown that B₂cat₂ reacts with a cobalt(0) complex containing strong σ-donor

phosphine ligands, $[\text{Co}(\text{PMe}_3)_4]$, via oxidative addition to give the seventeen electron bis(boryl)cobalt complex *cis*- $[\text{Co}(\text{Bcat})_2(\text{PMe}_3)_3]$ (**26**) (Scheme 31).¹²⁰ The relatively short B-B interaction in **26** (it is only 0.507 Å longer than the B-B bond in B_2cat_2) suggests that this complex can be viewed as lying part way along an oxidative addition reaction coordinate.

Insert **Scheme 31** here

The activation of $\text{B}_2(4\text{-Mecat})_2$ (4-Mecat=1,2-O₂-4-MeC₆H₃) by $[\text{Co}(\text{PMe}_3)_4]$, or B_2cat_2 with $[\text{Co}(\text{PMe}_2\text{Ph})_4]$ afforded the complexes $[\text{Co}(\text{PMe}_3)_3(\text{B}(4\text{-Mecat})_2)]$ (**27**) and $[\text{Co}(\text{PMe}_2\text{Ph})_3(\text{Bcat})_2]$ (**28**) respectively. For these complexes the acute B-Co-B angle and short B-B distance are similar to complex **26** and fundamental features for this type of Co(II) bisboryl complex (Scheme 31). A molecular orbital analysis, on the basis of DFT calculations, for the model complex $[\text{Co}(\text{PH}_3)_3(\text{B}(\text{O}_2\text{C}_2\text{H}_2))_2]$ does reveal the presence of a three-centre CoB_2 interaction consistent with some degree of weak B-B bonding involving one of the Co d orbitals and the in-phase combination of the two ‘empty’ boron p orbitals from the two $\text{B}(\text{O}_2\text{C}_2\text{H}_2)$ ligands which is consistent with these observed structural features. Interestingly, an activation of B_2cat_2 by $[\text{Co}(\text{Me})(\text{PMe}_3)_4]$ through σ -bond metathesis step, could be observed resulting in the production and isolation of the Co(I) species **29** and MeBcat (Scheme 32),¹²¹ accommodating the boryl group on the axial position.¹²²

Insert **Scheme 32** here

The activation of B_2pin_2 with $[\text{Co}(\text{PNP})(\text{O}^t\text{Bu})]$ afforded a new compound $[\text{Co}(\text{PNP})(\text{Bcat})]$, which represents the first example of a square planar Co(II)-boryl complex (Scheme 33).⁷⁷ But also important is the mechanism of activation of the diboron by σ -bond metathesis and not being prepared by an oxidative addition pathway.

Insert **Scheme 33** here

2.1.4 Activation by metal complexes of group 8

Hartwig successfully demonstrated the photolytic activation of the B-B bond in B₂cat₂, and related substituted catechol derivatives, with iron pentacarbonyl.¹²³ These oxidative addition reactions of the diborane reagents, to the presumably photochemically *in situ* generated [Fe(CO)₄], were rapid. Full conversion of [Fe(CO)₅] gave the thermally-sensitive complex *cis*-[Fe(Bcat)₂(CO)₄] (**31**) and derivatives (Scheme 34).

Insert **Scheme 34** here

Although the roles of ruthenium and osmium complexes in diboration and borylation have not yet been studied in significant detail, elegant stoichiometric studies with electron-rich osmium complexes have been carried out by Roper and co-workers.^{124,125} Indeed, addition of B₂cat₂ to [Os(CO)₂(PPh₃)₂], arising from the reductive elimination of *o*-tolylBcat in a starting boryl complex, resulted in the bis(boryl) complex *trans,cis,cis*-[Os(CO)₂(PPh₃)₂(Bcat)₂] (**32**) (Scheme 35). Likewise, the analogous ruthenium complex *trans,cis,cis*-[Ru(CO)₂(Bcat)₂(PPh₃)₂] (**33**) was readily prepared by the addition of B₂cat₂ to [Ru(CO)₂(PPh₃)₃], along with loss of phosphine. Although the analogous bis(boryl) species [OsCl(H)(Bcat)₂(P^{*i*}Pr₃)₂] (**34**) has been prepared and characterized structurally, this compound was generated from the addition of excess catecholborane to [OsCl₂(H)₂(P^{*i*}Pr₃)₂].¹²⁶ The short H-Os-B angles of 54-58° in **34** suggest a type of σ-bonding interaction involving the H-B bond is present. Indeed, complex **34** reductively eliminated HBcat under an atmosphere of CO to give the boryl complex [OsCl(Bcat)(CO)₂(P^{*i*}Pr₃)₂].

Insert **Scheme 35** here

2.2 Metal activation of halide or amine substituted diboron compounds

The diboron tetrafluoride, F_2B-BF_2 , can react with olefins in a direct way, but slightly slower in comparison with Cl_2B-BCl_2 , providing relatively stable diborated products. In 1959, Schlesinger noted that the reaction of acetylene with diboron tetrafluoride did not proceed to give addition products even at 100° .³ To obtain the diborated alkene product, a mixture of the reagents was heated at $120-140^\circ C$ for 24 h in a sealed tube of such dimensions that the estimated initial pressure was about 7 atm. In that particular case, the activation of the diboron tetrafluoride by a transition metal complex could also offer a better performance towards the diboration of alkenes and alkynes. Therefore in 1998 it was demonstrated that the reaction between $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$ and a slight excess of F_2B-BF_2 , in toluene solution afforded, after work-up, pale yellow crystals of the complex $cis-[Pt(BF_2)_2(PPh_3)_2]$ (**35**) (Scheme 36).¹²⁷ There was no decisive crystallographic evidence for platinum-to-boron π -back-bonding. The reaction between complex $cis-[Pt(BF_2)_2(PPh_3)_2]$ and two equivalents of the alkyne di-*p*-tolylethyne was investigated but little reaction in dichloromethane was observed. An analogous activation of F_2B-BF_2 with $[Pt((\eta^2-C_2H_4)(dppb))]$ [$dppb=1,4$ -bis(diphenylphosphino)butane] afforded the complex $cis-[Pt(BF_2)_2(dppb)]$ (**36**) (Scheme 36).¹²⁸ The reaction between Vaska's compound, $trans-[IrCl(CO)(PPh_3)_2]$, and F_2B-BF_2 afforded a complex characterised by X-ray crystallography as the iridium(III) (tris)boryl species $fac-[Ir(BF_2)_3(CO)(PPh_3)_2]$ (**37**) (Scheme 36). The molecular structure of **37** comprises an octahedral iridium(III) centre bonded to three BF_2 groups in a *fac* configuration, two *cis* phosphines and one carbonyl ligand. A degree of positional disorder involving the carbonyl group and the *trans* related BF_2 ligand was present.

Insert **Scheme 36** here

The group of Norman studied the reactivity of $B_2(NMe_2)_2Cl_2$ towards $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$. In this case exclusively products arising from B-B bond activation were verified, that is, $cis-[Pt\{B(NMe_2)(Cl)\}_2(PPh_3)_2]$ and $trans-[Pt(Cl)\{B(NMe_2)(Cl)\}(PPh_3)_2]$.¹²⁹ Bearing the experience of

Norman in mind, the Braunschweig group reconsidered the reactivity of halide-substituted diboranes towards low-valent platinum complexes evaluating the question whether a selective oxidative addition of B-X bonds is possible in the presence of a B-B bond.^{130,131} Indeed, the addition of 2 equivalents of B₂Mes₂Br₂ to [Pt(PEt₃)₃] lead to an unusual diboran(4)yl ligand containing a dative Pt-B bond, along with the concomitant formation of the Lewis acid-base adduct (Et₃P)B₂Mes₂Br₂. This chemistry was expanded to include a number of diborane(4) derivatives and all proceeded *via* activation of the B-X and not the B-B bond.¹³²⁻¹³⁵ Conversely, oxidative addition of the B-B bond within [2]borametalloarenophanes **38** was reported to proceed smoothly and in high yields with platinum(0) phosphine complexes to give the corresponding bis(boryl)platinum(II) complexes **39** (Scheme 37).¹³⁶⁻¹³⁸ Subsequent addition of these complexes to alkynes gave the *ansa*-bis(boryl)alkene products.

Insert **Scheme 37** here

An interesting study by Braunschweig and Koster involved the activation of 1,2-diaminodichlorodiboranes B₂(NC₄H₈)₂Cl₂ and B₂(NC₅H₁₀)₂Cl₂ with Na[C₅H₅Fe(CO)₂] at ambient temperature, with concomitant formation of the iron diborane(4)yl complexes [Cl(R₂N)B-B(NR₂)Fe(C₅H₅)(CO)₂] and NaCl.¹³⁹ It is plausible that cleavage may arise from an oxidative addition pathway as these 1,2-diaminodichlorodiboranes have been subsequently activated by platinum(0) complex [Pt(PEt₃)₄].

Himmel has launched an exceptional study on the activation of specific doubly-base stabilized diborane [HB(hpp)]₂ (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido-[1,2-a]pyrimidinate). The two guanidinate bridges prevent oxidative addition reactions with complete cleavage of the B-B bond and formation of a diboryl complex. Nevertheless, the engagement of the B-B bond in the direct metal-diborane bond should lead to significantly elongated B-B bond distances in the diborane ligand. Complexes [M{HB(hpp)}₂(CO)₄] (M=Cr, Mo or W) were prepared by photolysis of a reaction mixture of [HB(hpp)]₂ and [M(CO)₆]. Reaction between [HB(hpp)]₂ and [MCl(cod)]₂ furnished the complexes [M(cod){HB(hpp)}₂Cl] (M = Rh or Ir) (Scheme 38).¹⁴⁰

The experimental results show that the bonding in the complexes $[M(\text{cod})\{\text{HB}(\text{hpp})\}_2\text{Cl}]$ ($M = \text{Rh}$ or Ir) involves predominantly the B–B bonding electrons, as a consequence of the B₂–M three-center bond converse to the bonding in the group 6 complexes. The B–B bond is significantly weakened, but the two bridging hpp substituents prevent complete cleavage with formation of a diboryl metal complex. The authors define this situation as a frozen intermediate at an early stage of an oxidative addition. A quantum-chemical investigation of the bonding of these diborane systems with a series of transition metal complexes has also been carried by the same authors.¹⁴¹

Insert **Scheme 38** here

A key step in many transition metal catalysed diboration reactions is oxidative addition of the B–B bond of a diborane(4) compound ($\text{R}_2\text{B–BR}_2$) to a low-valent transition metal centre affording a metal bis-boryl complex of the form $L_n\text{M}(\text{BR}_2)_2$.

2.3 Nanoparticles activation

Within the last decade, another source of diboron activation has been promoted in basis to the efficient application to catalysis. This is the use of nanoparticles which can interact with the diboron reagent and develop an enhance performance towards diboration reaction. Fernández observed in 2008 that the *in situ* formation of Au-nanoparticles, from Au(I) complexes, could activate the B_2cat_2 but also deliver the boryl units on alkenes with total chemoselectivity.¹⁴² The gold nanoparticles were estimated to have a mean crystallite size of $10.5 \pm 0.3\text{nm}$. The gold nanoparticles were stabilized by 2,2'-bis-(diphenylphosphino)-1-1'-binaphthyl (BINAP), diphenylphosphinoethane (DPPE) and L-glutathione. The core size and size distribution of binap–gold nanoparticles were examined by transition electron microscopy (TEM), and the image shows disperse nanoparticles $6.9 \pm 3.0\text{ nm}$ in diameter, (Figure 6).

Insert **Figure 6** here

Pure BINAP-Au nanoparticles with smaller diameter (1.7 ± 0.3 nm) were alternatively synthesized following the Fujihara protocol,¹⁴³ from $\text{HAuCl}_4 + \text{BINAP}$ in the presence of NaBH_4 , and eventually used in the catalytic diboration reaction. The activity and chemoselectivity observed, were similar to those of the “*in situ*” BINAP-stabilized gold nanoparticles. Interestingly, the recovered reddish solid BINAP-stabilized gold nanoparticles, was reused in a new catalytic diboration reaction of styrene. Conversion and total chemoselectivity towards the diborated product maintained high.. This shows that the catalytic system was stable and that it could be recycled to activate new diborons and promote diboration on olefins. Unfortunately, the use of chiral stabilizers of the gold nanoparticles, did not contributed to induce asymmetry in the new C-B bond formed.

It was suggested that the activation of the B_2cat_2 could be involved in a base-mediated σ -bond metathesis instead of oxidative addition. This hypothesis gained support from the cross addition experiment, in which B_2cat_2 and $\text{B}_2((4\text{-Me})\text{cat})_2$ were simultaneously added to styrene and cross-diborated product was observed.

Further work in this area came from Corma et al.¹⁴⁴ about magnesia-supported Cu(II) or copper oxide nanoparticles which exhibited a unique regio and stereoselectivity in the catalyzed monoborylation of alkynes with bis(pinacolato)diboron, assisted by triphenylphosphine. In the same work, supported platinum on magnesia exhibited higher catalytic activities even in the absence of triphenylphosphine, but the products formed were the bis-boronated alkenes. Ceria was also a suitable support for the platinum nanoparticles. Because the organoborate products obtained with CuO/MgO and Pt/MgO were different, it was proposed that activation of B_2pin_2 took place in a different way. The active sites formed by platinum atoms of the metal nanoparticles on the solid surface could intercat with B_2pin_2 to promote the oxidative addition (Scheme 39a). The supported copper catalyst only leads to one C-B bond and it is particular relevant that requires the assistance of triphenylphosphine as promoter. In that case a Lewis acid

(boron)/base(phosphorous) adduct was suggested to participate in the activation process (Scheme 39b).

Insert **Scheme 39** here

Braunschweig et al., also reported that Pt sponge- or Pd/C-activated borametalloarenophanes to conduct catalyzed diboration of propyne and 2-butyne in a heterogenous fashion.¹³⁷ More recently, Jin et al, prepared PtNPore from Pt-Cu alloy and conducted the activation of B₂pin₂ towards the catalytic diboration of terminal alkynes affording the corresponding 1,2-diborylalkene as *cis*-adduct in 99% yield within 40 h.¹⁴⁵ However, the leaching experiments and inductively coupled plasma (ICP-MS) showed that Pt atoms in PtNPore catalyst were leached to the reaction solution. The same authors prepared the analogue AuNPore system from Au₃₀Ag₇₀ forming a thin film that possesses a bicontinuous porous structure with an average diameter of 30 nm for both ligaments and nanopores. When the authors studied the activation of B₂pin₂ and the catalytic diboration of terminal alkynes, they found a remarkably increased activity with completed diborated reactions in 1.5 h, giving the corresponding *cis*-adduct as the major isomer with a small amount of *trans*-adduct. It is worth noting that AuNPore was active only in toluene as solvent. The leaching experiments and ICP-MS analysis indicated that no gold catalyst was leached. The recovered AuNPore catalyst exhibited high recyclability without decreasing the catalytic activity after reusing for two more cycles. However, other diboranes such as bis(neopentylglycolato)diboron (B₂neop₂) and bis(catecholato)diboron (B₂cat₂) were not activated by AuNPore.

Other nanoporous metal catalysts such as nanoporous palladium (PdNPore), nanoporous copper (CuNPore) and nanoporous silver (AgNPore) were totally inactive for the studied diboration.

From a mechanistic perspective of the activation mode, as it happened previously with the stabilized gold nanoparticles described by Fernández, a cross-addition experiment of B₂pin₂ and B₂hex₂ to phenylacetylene showed the formation of a cross-addition product, suggesting that the reaction did not involve the oxidative addition of diborons to Au(0). Although the detailed

driving force for the cleavage of the B-B bond in B_2pin_2 by the AuNPore surface remains uncertain, on the basis of the experimental observations, the authors suggested that B_2pin_2 gets absorbed onto the low coordinated Au atoms on the stepped surface of AuNPore. The B-B bond is cleaved on the surface of AuNPore to give [Au-Bpin] species under the reaction conditions. Next, the adsorbed alkyne reacts rapidly with two [Au-Bpin] species either through the simultaneous addition path to form the corresponding cis-adduct (Scheme 40) or through the stepwise addition, in which the formation of a vinyl cation intermediate is involved. There might exist an interaction between the vinyl cation and the electron-rich Au atoms.

Insert **Scheme 40** here

Commercially available and inexpensive $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles (particle size 58 nm), also efficiently activate B_2pin_2 and promote a direct borylation of alkenes.¹⁴⁶ The mechanism of this unusual nano- Fe_2O_3 -catalyzed aromatic borylation reaction is not clear. The kinetic isotope effect was measured to be 1.3, indicating that a C-H bond activation by oxidative addition to the iron catalyst is not likely. An electrophilic metalation by Fe-B species, followed by reductive elimination seems conceivable.

3 Precise activation of unsymmetrical dialkoxy-diamino-diboron compounds

The number of examples of unsymmetrical diboron reagents containing $B(OR)_2$ and $B(NR_2)_2$ moieties is less abundant than the corresponding tetra(alkoxy)diborons. However, the possibility of synthesizing mixed $(RO)_2B-B(NR_2)_2$ compounds increases the potential application towards difunctionalized organoboranes. Suginome was a pioneer in this issue and he was able to prepare the unsymmetrical diboron (pin)B-B(dan) compound,¹⁴⁷ in which one of the two boron atoms carries the naphthalene-1,8-diaminato (dan) ligand, that behaves as an effective protecting group for the boronyl group.¹⁴⁸⁻¹⁵¹ Several transition metal complexes, such as $Pt(dba)_2$, $Pd(dba)_2$, $Ni(cod)_2$, $[RhCl(cod)]_2$ and $[IrCl(cod)]_2$, were used to activate (pin)B-

B(dan). Despite the lack of information about the metal boryl species resulting from this activation, their application in the regioselective diboration of alkynes lead to the addition of the Bpin moiety in the internal position (Scheme 41).

Insert **Scheme 41** here

A recent paper by Borner and Kleeberg discussed the synthesis and reactivity of unsymmetrical diborane(4) compounds (pin)B-B(dmab) (dmab = 1,2-di(methylamino)benzene) and (pin)B-B(dbab) (dbab = 1,2-di(benzylamino)benzene) also derived from diaminoboryl ligands.¹⁵² They found that reactions of $[\text{Pt}(\eta^2\text{-CH}_2\text{=CH}_2)(\text{PPh}_3)_2]$ with these new diborane(4) species gave selective and unprecedented formation of unsymmetrical bis(boryl)platinum(II) complexes (Scheme 42).

Insert **Scheme 42** here

In the same study, (pin)B-B(dmab) and (pin)B-B(dbab) could be activated by s-bond metathesis with IDippCu(I)-O*t*Bu complexes (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) (Scheme 43). The selectivity of the B–B bond cleavage reaction in favor of the formation of diaminoboryl complexes may be explained by the higher Lewis acidity of the Bpin moiety, which favored the formation of pinB–O*t*Bu and the diaminoboryl Cu(I) complexes.

Insert **Scheme 43** here

In this context, an internally activated, $\text{sp}^2\text{-sp}^3$ hybridized diboron compound, PDIPA diboron (pinacolato diisopropanolaminato diboron) prepared by Santos et al, has shown to easily interact with CuCl salts to favor the B-B cleavage and form the corresponding Cu-Bpin species (Scheme 44) which were very active in the copper-catalyzed, β -borylation of α,β -unsaturated conjugated compounds,^{153,154} and allenoates.¹⁵⁵

Insert **Scheme 44** here

4. Summary and outlook

Symmetrical and unsymmetrical diboron compounds have become useful reagents for organic synthesis.¹⁵⁶⁻¹⁶⁶ The mode of activation depends on the nature of the diboron compound and the inherent Lewis acid properties. From tetrahalide diboron compounds to tetra(alkoxy)diboron compounds the reactivity diminishes significantly at the same time that stability of the resulting organoboron compounds increases. Taking advantage of this trend, chemists chose to use tetra(alkoxy)diboron reagents in organic synthesis and in particular to be added to unsaturated hydrocarbons. To accomplish the activation of the B-B bond an extra component is required, which in mostly of the cases is based on transition metal complexes in low oxidative states.¹⁶⁷ In principal, the metal complexes modified or not by ligands, interact with the diboron to promote the B-B cleavage through oxidative addition or σ -bond metathesis. Sometimes, the unsaturated substrate interacts first with the metal complex and the new metal species reacts further with the diboron reagents. Even heterogeneous activation of the diboron reagents can be exerted by nanoparticles, with the concomitant recovery and reuse of the active sites.

It seems that all the efforts to activate tetra(alkoxy)diboron compounds are justified since the model $\text{Cl}_2\text{B}-\text{BCl}_2$ reagent, which develops borylation without metal activation, is too difficult to handle. However, the progress in this field has opened a new window towards the activation of tetra(alkoxy)diboron compounds in a metal-free context, by the formation of Lewis acid-base adducts¹⁶⁸⁻¹⁷⁶ and their addition to unsaturated substrates can be performed with total chemo-, regio- and stereoselectivity.

Therefore this historical prospection towards the activation of diboron has moved from direct reaction of $\text{Cl}_2\text{B}-\text{BCl}_2$ with alkenes to the current methodology that circumvent the activation of tetra(alkoxy)diboron reagents with simple Lewis bases. But metal activation has been and still is a guarantee of precise activation and delivery of the boryl moieties. The need for simple but

efficient methodologies is the driving force of this exciting field, in which the boron atom becomes the real protagonist.

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6. References

1. Urry G, Kerrigan J, Parsons TD, Schlesinger HI. Diboron tetrachloride B_2Cl_4 as a reagent for the synthesis of organoboron compounds. *J Am Chem Soc.* 1954;76:5299-5301.
2. Brown HC; Rao, BCS. Hydroboration of olefins. A remarkable fast room-temperature addition of diborane to olefins. *J Org Chem.* 1957;22:1136-1137.
Ceron P, Finch A, Frey J, Kerrigan J, Parsons T, Urry G, Schlesinger H. I. Diboron tetrachloride and tetrafluoride as reagents for the synthesis of organoboron compounds.
II. The behavior of the diboron tetrahalides toward unsaturated organic compounds. *J Am Chem Soc.* 1959;81:6368-6371.
3. Chambers C, Holliday AK. The reactions of diboron tetrahalides with acetylene. The preparation and properties of 1,2-bisdichloroborylethylene. *J Chem Soc.* 1965;3459-3462.
4. Feeney J, Holliday AK, Marsden FJ. Diboron tetrachloride-olefin compounds. *J Chem Soc.* 1961;356-360.
5. Fox WB, Wartik T. Reaction of diboron tetrachloride with aromatic substances. *J Am Chem Soc.* 1961;83:498-499.

6. Zeldin M, Wartik T. The addition of B_2Cl_4 to 1,3-cyclohexadiene and the structural similarity of the adduct to that formed between B_2Cl_4 and naphthalene. *J Am Chem Soc.* 1966;88:1336-1337.
7. Rudolph RW. The mechanism of addition of diboron tetrachloride to unsaturated organic compounds. *J Am Chem Soc.* 1967;89:4216-4217.
8. Zeldin M, Gatti AR, Wartik T. Stereochemical investigations of the addition of diboron tetrachloride to unsaturated organic molecules. *J Am Chem Soc.* 1967;89:4217-4218.
9. Geanangel RA. Orbital overlap in the reactions of diboron compounds. *J Inorg Nucl Chem.* 1972;34:1083-1086.
10. Gunn SR, Green LG, Von Egidy AI. The heat of chlorination of diboron tetrachloride. *J Phys Chem.* 1959;63:1787-4218.
11. Kotz JC, Post EW. Ferrocenylboranes: the preparation and properties of ferrocenyldichloroboranes. *Inorg Chem* 1970;9:1661-1669.
12. Ritter JJ, Coyle DD. Reactions of diboron tetrahalides with haloolefins. Formation of poly(dihaloboryl)ethanes. *J Organomet Chem* 1971;29:175-184.
13. Rosen A, Zeldin M. The chemistry of tetrachlorodiborane(4): Reactions with cyclic olefins. *J Organomet Chem* 1971;31:319-328.
14. Haubold W, Stanzl K. Addition of diborontetrahalides to unsaturated hydrocarbons. *Chem Ber* 1978;111:2108-2112.
15. W. Haubold, K. Stanzl. Die addition von tetrahalogeno-diboran(4)-molekülen an diene. *J Organomet Chem.* 1979;174:141-147.
16. Coyle DD, Ritter JJ. Organometallic aspects of diboron chemistry. *J Organomet Chem.* 1972;10:237-243.
17. Morrison JA, Chemistry of the polyhedral boron halides and the diboron tetrahalides. *Chem Rev.* 1991;91:35-48.
18. Stock A, Brant A, Fischer H. Der zink-lichtbogen als reduktionsmittel. *Chem Ber.* 1925;58:643.

19. Wartik T, Moore RE, Schlesinger HI. Derivatives of diborane. *J Am Chem Soc.* 1949;71:3265-3266.
20. Urry G, Wartik T, Moore RE, Schlesinger, HI. The preparation and some of the properties of diboron tetrachloride, B₂Cl₄. *J Am Chem Soc.* 1954;76:5293-5298.
21. Timms PL. The chemistry of transition-metal vapours. Part II. The preparation of diboron tetrachloride from copper vapour and boron trichloride. *J Chem Soc Dalton Trans.* 1972;830-832.
22. Timms PL, Ittel SD, Kuck M. Tetrachlorodiborane(4). *Inorg Synth.* 1979;19:74-78.
23. Biffar W, Nöth H, Pommerening H. Stabilization of diborane(4) derivatives by *tert*-butyl groups: The first tetraalkyldiborane(4). *Angew Chem Int Ed.* 1980;19:56-57
24. Schlüter K, Berndt A. Persistent tetraalkyldiboranes(4). *Angew Chem Int Ed.* 1980;19:57-58.
25. Hommer H, Nöth H, Knizek J, Ponikvar W, Schwenk-Kircher H. Synthesis and structures of dimesityldiboranes(4). *Eur J Inorg Chem.* 1998;1527-1529.
26. Brotherton RJ, McCloskey AL, Petterson LL, Steinberg H. The tetra(amino)diboron. *J Am Chem Soc.* 1960;82:6242-6245.
27. Abu AH, Goldberg I, Srebnik M. Tetra(pyrrolidino)diborane(4), [(C₄H₈N)₂B]₂, as a new improved alternative synthetic route to bis(pinacolato)diborane(4)- Crystal Structures of the Intermediates. *Eur J Inorg Chem.* 2002;73-78.
28. Wiberg E, Ruschmann W. *Chem Ber.* 1937;70b:1393-1395.
29. Brotherton RJ, McCloskey AL, Boone JL, Manasevi HM. The preparation and properties of some tetraalkoxydiborons. *J Am Chem Soc.* 1960;82:6245-6247.
30. Anastasi NR, Waltz KM, Weerakoon W L, Hartwig JF. A short synthesis of tetraalkoxydiborane(4) reagents. *Organometallics.* 2003;22:365-369.
31. Braunschweig H, Guethlein F. Transition-metal catalyzed synthesis of diboranes(4). *Angew Chem Int Ed* 2011;50,12613-12616.
32. Malhotra SC. The chemistry of tetrakis(dimethylamino)diboron, *Inorg Chem.* 1964;862-866.

33. Welch CN, Shore SG. *Inorg Chem.* 1968;7:225-230.
34. Nöth H. The crystal and molecular structure of a 1.3.2-dioxaborolan-2-yl-1'.3'.2'-dioxaborolane *Z. Naturforsch Teil B.* 1984;39:1463-1464.
35. Coyle TD, Ritter JJ. *Organometallic aspects of diboron chemistry. Advances in Organometallic Chemistry.* 1972 – Elsevier
36. Abu Ali H, Dembitsky VM, Srebnik M. *Contemporary Aspects of Boron: Chemistry and Biological Applications.* 2005- Elsevier
37. Finch A, Gardner PJ, Webb AF. The standard enthalpy of formation of tetramethoxydiboron. *J Chem Thermodynamics.* 1972;4:495–498.
38. Deutsch PW, Curtiss LA, Pople JA. Boron dimer: dissociation energy and ionization potentials. *Chem Phys Lett.* 1990;174:33-36.
39. Ishiyama T, Matsuda N, Miyaura N, Suzuki A. Platinum(0)-catalyzed diboration of alkynes. *J Am Chem Soc.* 1993;115:11018-11019.
40. Ishiyama T, Matsuda N, Murata M, Ozawa F, Suzuki A, Miyaura N. Platinum(0)-catalyzed diboration of alkynes with tetrakis(alkoxo)diborons: An efficient and convenient approach to *cis*-bis(boryl)alkenes. *Organometallics.* 1996;15:713-720.
41. Iverson CN, Smith III MR. Reactivity of organoplatinum complexes with C₆H₄O₂B-BO₂C₆H₄: Synthesis of a platinum diboryl complex with, and without, metathesis of boron-boron and metal-carbon bonds. *J Am Chem Soc.* 1995;117:4403-4404.
42. Iverson CN, Smith III MR. Mechanistic investigation of stoichiometric alkyne insertion into Pt-B bonds and related chemistry bearing on the catalytic diborylation of alkynes mediated by platinum(II) diboryl complexes. *Organometallics.* 1996;15:5155-5165.
43. Lesley G, Nguyen P, Taylor NJ, Marder TB, Scott AJ, Clegg W, Norman NC. Synthesis and characterization of platinum(II)-bis(boryl) catalyst precursors for diboration of alkynes and diynes: Molecular structures of *cis*-[(PPh₃)₂Pt(B-4-Bu'cat)₂], *cis*-[(PPh₃)₂Pt(Bcat)₂], *cis*-[(dppe)Pt(Bcat)₂], *cis*-[(dppb)Pt(Bcat)₂], (*E*)-(4-MeOC₆H₄)C(Bcat)=CH(Bcat), (*Z*)-(C₆H₅)C(Bcat)=C(C₆H₅)(Bcat), and (*Z,Z*)-(4-

- MeOC₆H₄)C(Bcat)=C(Bcat)C(Bcat)=C-(4-MeOC₆H₄)(Bcat) (cat = 1,2-O₂C₆H₄; dppe = Ph₂PCH₂CH₂PPh₂; dppb = Ph₂P(CH₂)₄PPh₂). *Organometallics*. 1996;15:5137-5154.
44. Curtis D, Lesley MJG, Norman NC, Orpen AG, Starbuck J. Phosphine exchange reactions involving *cis*-[Pt(PPh₃)₂(Bcat)] (cat = 1,2-O₂C₆H₄) and the oxidative addition of 1,2-B₂Cl₂(NMe₂)₂ to Pt^{II}. *J Chem Soc Dalton Trans*. 1999:1687-1694
 45. Charmant JPH, Fan C, Norman NC, Pringle PG. Synthesis and reactivity of dichloroboryl complexes of platinum(II). *Dalton Trans*. 2007:114-123.
 46. Ishiyama T, Yamamoto M, Miyaura N. Diboration of alkenes with bis(pinacolato)diboron catalysed by a platinum(0) complex. *Chem Commun*. 1997:689-690.
 47. Iverson CN, Smith III MR. Efficient olefin diboration by a base-free platinum catalyst. *Organometallics*. 1997;16:2757-2759.
 48. Mann G, John KD, Baker RT. Platinum catalyzed diboration using a commercially available catalyst: diboration of aldimines to α -aminoboronate esters. *Org Let*. 2000;2:2105-2108.
 49. Cui Q, Musaev DG, Morokuma K. Molecular orbital study of the mechanism of platinum(0)-catalyzed alkene and alkyne diboration reactions. *Organometallics*. 1997;16:1355-1365.
 50. Sakaki S, Kikunot T. Reaction of BX₂-BX₂ (X = H or OH) with M(PH₃)₂ (M = Pd or Pt). A theoretical study of the characteristic features. *Inorg Chem*. 1997;36:226-229.
 51. Coombs JR, Haeffner F, Kliman LT, Morken JP. Scope and mechanism of the Pt-catalyzed enantioselective diboration of monosubstituted alkenes. *J Am Chem Soc*. 2013; 135:11222-11231.
 52. Ishiyama T, Yamamoto M, Miyaura N. Platinum(0)-catalysed diboration of alka-1,3-dienes with bis(pinacolato)diboron. *Chem Commun*. 1996:2073-2075.
 53. Clegg W, Johann TRF, Marder TB, Norman NC, Orpen AG, Peakman TM, Quayle MJ, Rice CR, Scott AJ. Platinum-catalysed 1,4-diboration of 1,3-dienes. *J Chem Soc Dalton Trans*. 1998:1431-1438.

54. Lawson YG, Lesley MJG, Marder TB, Norman NC, Rice CR. Platinum catalysed 1,4-diboration of α,β -unsaturated ketones. *Chem Commun.* 1997:2051-2052.
55. Ali HA, Goldberg I, Srebnik M. Addition reactions of bis(pinacolato)diborane(4) to carbonyl enones and synthesis of (pinacolato)₂BCH₂B and (pinacolato)₂BCH₂CH₂B by insertion and coupling. *Organometallics.* 2001;20:3962-3965.
56. Bell NJ, Cox AJ, Cameron NR, Evans JSO, Marder TB, Duin MA, Elsevier CJ, Baucherel X, Tulloch AAD, Tooze RP. Platinum catalysed 3,4- and 1,4-diboration of α,β -unsaturated carbonyl compounds using *bis*-pinacolatodiboron. *Chem Commun.* 2004:1854-1855.
57. Liu B, Gao M, Dang L, Zhao H, Marder TB, Lin Z. DFT studies on the mechanisms of the platinum-catalyzed diboration of acyclic α,β -unsaturated carbonyl compounds. *Organometallics.* 2012;31:3410-3425.
58. Ali HA, Goldberg I, Kaufmann D, Burmeister Ch, Srebnik M. Novel C1-bridged bisboronate derivatives by insertion of diazoalkanes into bis(pinacolato)diborane(4). *Organometallics.* 2002;21:1870-1876.
59. Wommack AJ, Kingsbury JS. On the scope of the Pt-catalyzed Srebnik diborylation of diazoalkanes. An efficient approach to chiral tertiary boronic esters and alcohols via B-stabilized carbanions. *Tetrahedron Lett.* 2014;55:3163-3166.
60. Braunschweig H, Bertermann R, Brenner P, Burzler M, Dewhurst RD, Radacki K, Seeler F. *trans*-[Pt(BCat')Me(PCy₃)₂]: An experimental case study of reductive elimination processes in Pt-boryls through associative mechanisms. *Chem Eur J.* 2011;17:11828-11837.
61. Cui Q, Musaev DG, Morokuma K. Why do Pt(PR₃)₂ complexes catalyze the alkyne diboration reaction, but their palladium analogs do not? A density functional study. *Organometallics.* 1998;17:742-751.
62. Burks HE, Liu S, Morken JP. Development, mechanism, and scope of the palladium-catalyzed enantioselective allene diboration. *J Am Chem Soc.* 2007;129:8766-8773.

63. Pelz NF, Woodward A R, Burks HE, Sieber JD, Morken JP. Palladium-catalyzed enantioselective diboration of prochiral allene. *J Am Chem Soc.* 2004;126: 16328-16329.
64. Zhu Y, Chen C-H, Farard CM, Foxman BM, Ozerov OV. Net heterolytic cleavage of B-H and B-B bonds across the N-Pd bond in a cation (PNP)Pd fragment. *Inorg Chem.* 2011;50:7980-7987.
65. Lillo V, Mas-Marza E, Segarra AM, Carbo JJ, Bo C, Peris E, Fernandez E. Palladium–NHC complexes do catalyse the diboration of alkenes: mechanistic insights *Chem Commun.* 2007;3380-3382.
66. Yang FY, Cheng Ch-H. Unusual diboration of allenes catalyzed by palladium complexes and organic iodides: a new efficient route to biboronic compounds. *J Am Chem Soc.* 2001;123:761-762.
67. Yang FY, Shanmugasundaram M, Chuang Sy, Ku PJ, Wu MY, Cheng Ch-H. Highly regio- and stereoselective acylboration, acylsilylation, and acylstannation of allenes catalyzed by phosphine-free palladium complexes: □ An efficient route to a new class of 2-acylallylmetal reagents. *J Am Chem Soc.* 2003;125:12576-12583.
68. Raducan M, Alam R, Szabó KJ. Palladium-catalyzed synthesis and isolation of functionalized allylboronic acids: selective, direct allylboration of ketone. *Angew Chem Int Ed.* 2012;51:13050–13053.
69. Böse D, Niesobski P, Lübcke M, Pietruszka J. A diastereoselective one-pot, three-step cascade toward α -substituted allylboronic esters. *J Org Chem.* 2014;79:4699-4703.
70. Ishiyama T, Ahiko T, Miyaura N. A synthesis of allylboronates via the palladium(0)-catalyzed cross-coupling reaction of bis(pinacolato)diboron with allylic acetates *Tetrahedron Lett.* 1996;37:6889-6892.
71. Zhang P, Roundtree IA, Morken JA. Ni- and Pd-Catalyzed synthesis of substituted and functionalized allylic boronates. *Org Lett.* 2012;14:1416-1419.
72. Lillo V, Geiger MJ, Westcott SA, Fernández E. Ni and Pd mediate asymmetric organoboron synthesis with ester functionality at the β position. *Org Biom Chem.* 2009;7:4674-4676.

73. Hirano K, Yorimitsu H, Oshima K. Nickel-catalyzed β -boration of α,β -unsaturated esters and amides with bis(pinacolato)diboron. *Org Lett.* 2007;9:5031-5033.
74. Ely RJ, Morken JP, Ni(0)-catalyzed 1,4-selective diboration of conjugated dienes, *Org. Lett.* 2010;12:4348-4351.
75. Adhikari D, Mossin S, Basuli F, Dible BR, Chipara M, Fan H, Huffman JC, Meyer K, Mindiola DJ. A dinuclear Ni(I) system having a diradical Ni₂N₂ diamond core resting state: Synthetic, structural, spectroscopic elucidation, and reductive bond splitting reactions. *Inorg Chem.* 2008;47,10479-10490.
76. Tran AL, Adhikari D, Fan H, Pink M, Mindiola DJ. Facile entry to 3d late transition metal boryl complexes. *Dalton Trans.* 2010;39:358–360.
77. Takahashi K, Isiyama T, Miyaura N. Addition and coupling reactions of bis(pinacolato)diboron mediated by CuCl in the presence of potassium acetate. *Chem Lett.* 2000;982-983.
78. Takahashi K, Isiyama T, Miyaura N. A borylcopper species generated from bis(pinacolato)diboron and its additions to α,β -unsaturated carbonyl compounds and terminal alkyne. *J Organomet Chem.* 2001;625:47-53
79. Ito H, Yamanaka H, Tateiwa J, Hosomi, A. Boration of an α,β -enone using a diboron promoted by a copper(I)-phosphine mixture catalyst. *Tetrahedron Lett.* 2000;41:6821-6825.
80. Ramachandran PV, Pratihari D, Biswas D, Srivastava A, Venkat Ram Reddy R. Novel functionalized trisubstituted allylboronates via Hosomi–Miyaura borylation of functionalized allyl acetates. *Org Lett.* 2004;6:481-485.
81. Laitar DS, Müller P, Sadighi JP. Efficient homogeneous catalysis in the reduction of CO₂ to CO. *J Am Chem Soc.* 2005;127:17196-17197.
82. Zhao HT, Lin Z, Marder TB. Density Functional Theory studies on the mechanism of the reduction of CO₂ to CO catalyzed by copper(I) boryl complexes. *J Am Chem Soc.* 2006;128:15637-15643.

83. Laitar DS, Tsui, Sadighi JP. Catalytic diboration of aldehydes via insertion into the copper-boron bond. *J Am Chem Soc.* 2006;128:11036-11037.
84. Laitar DS, Tsui EY, Sadighi JP. Copper(I) β -boroalkyls from alkene insertion: Isolation and rearrangement. *Organometallics.* 2006;25:2405-2408.
85. Ito H, Kawakami C, Sawamura M. Copper-catalyzed γ -selective and stereospecific substitution reaction of allylic carbonates with diboron: Efficient route to chiral allylboron compounds. *J Am Chem Soc.* 2005;127:16034-16035.
86. Mun S, Lee JE, Yun J. Copper-catalyzed β -boration of α,β -unsaturated carbonyl compounds: Rate acceleration by alcohol additives. *Org Lett.* 2006;8:4887-4889.
87. Lee JL, Kwon J, Yun J. Copper-catalyzed addition of diboron reagents to α,β -acetylenic esters: efficient synthesis of β -boryl- α,β -ethylenic esters. *Chem Commun.* 2008, 733-735.
88. Lee JL, Yun J. Catalytic asymmetric boration of acyclic α,β -unsaturated esters and nitriles. *Angew Chem Int Ed.* 2008;47:145-147.
89. Dang L, Lin Z, Marder TB. DFT studies on the borylation of α,β -unsaturated carbonyl compounds catalyzed by phosphine copper(I) boryl complexes and observations on the interconversions between O- and C-bound enolates of Cu, B, and Si. *Organometallics.* 2008;27:4443-4454.
90. Kleeberg C, Dang L, Lin Z, Marder TB. A facile route to aryl boronates: Room-temperature, copper-catalyzed borylation of aryl halides with alkoxy diboron reagents. *Angew Chem Int Ed.* 2009;48:5350–5354.
91. Thorpe SB, Calderone JA, Santos WL. Unexpected copper(II) catalysis: Catalytic amine base promoted β -borylation of α,β -unsaturated carbonyl compounds in water. *Org Lett.* 2012;14:1918-1921.
92. Kitanosono T, Xu P, Kobayashi S. Heterogeneous versus homogeneous copper(II) catalysis in enantioselective conjugate-addition reactions of boron in water. *Chem Asian J.* 2014;9:179-188.

93. Lillo V, Fructos MR, Ramírez J, Braga AAC, Maseras F, Díaz Requejo MM, Pérez PJ, Fernández E. Valuable, inexpensive Cu^I/N-heterocyclic carbene catalyst for the selective diboration of styrene. *Chem Eur J*. 2007;13:2614-2621.
94. Dang L, Lin Z, Marder TB. Understanding the higher reactivity of B₂cat₂ versus B₂pin₂ in copper(I)-catalyzed alkene diboration reactions. *Organometallics*. 2008;27:1178-1186.
95. Meng F, Haeffner F, Hoveyda AH. Diastereo- and enantioselective reactions of bis(pinacolato)diboron, 1,3-enynes, and aldehydes catalyzed by an easily accessible bisphosphine–Cu complex. *J Am Chem Soc*. 2014;136:11304-11307.
96. Ramírez J, Corberán R, Sanaú M, Peris E, Fernández E. Unprecedented use of silver(I) N-heterocyclic carbene complexes for the catalytic preparation of 1,2-bis(boronate) esters. *Chem Commun*. 2005;3056-3058.
97. Corberán R, Ramírez J, Poyatos M, Peris M, Fernández E. [Coinage metal complexes with N-heterocyclic carbene ligands as selective catalysts in diboration reaction.](#) *Tetrahedron:Asymmetry*. 2006;17,1759-1762.
98. Yoshida H, Kageyuki I, Takaki K. Silver-catalyzed highly regioselective formal hydroboration of alkynes. *Org Lett*. 2014;16:3512-3515.
99. Baker RT, Nguyen P, Marder TB, Westcott SA. Transition metal catalyzed diboration of vinylarenes. *Angew Chem Int Ed Engl*. 1995;34:1336-1338.
100. Morgan JB, Miller SP, Morken JP, Rhodium-catalyzed enantioselective diboration of simple alkenes. *J Am Chem Soc*. 2003;125:8702-8703.
101. Trudeau S, Morgan JB, Shrestha M, Morken JP. Rh-catalyzed enantioselective diboration of simple alkenes: □ Reaction development and substrate scope. *J Org Chem*. 2005;70:9538-9544.
102. Ramírez J, Segarra AM, Fernández E. [Metal promoted asymmetry in the 1,2-diboroethylarene synthesis: diboration versus dihydroboration.](#) *Tetrahedron: Asymmetry*. 2005;16:1289-1294.
103. Nguyen P, Lesley G, Taylor NJ, Marder TB, Pickett NL, Clegg W, Elsegood MRJ, Norman NC. Oxidative addition of B-B bonds by Rh(I) phosphine complexes: Molecular

- structures of B_2cat_2 (cat = 1,2- $O_2C_6H_4$) and its 4-Bu^t and 3,5-Bu^t₂ analogs. *Inorg Chem.* 1994;33:4623-4624.
104. Baker RT, Calabrese JC, Westcott SA, Nguyen P, Marder TB. Insertion of alkenes into Rh-B bonds. *J Am Chem Soc.* 1993;115:4361-4368.
105. Dai C, Stringer G, Marder TB, Scott AJ, Clegg W, Norman NC. Synthesis and characterization of rhodium(I) boryl and rhodium(III) tris(boryl) compounds: Molecular structures of $[(PMe_3)_4Rh(B(cat))]$ and *fac*- $[(PMe_3)_3Rh(B(cat))_3]$ (cat = 1,2- $O_2C_6H_4$). *Inorg Chem.* 1997;36:272-273.
106. Lam KC, Lam WH, Lin Z, Marder TB, Norman NC. Structural analysis of five-coordinate transition metal boryl complexes with different d-electron configurations. *Inorg Chem.* 2004;43:2541-2547.
107. Câmpian MV, Harris JL, Jasim N, Perutz RN, Marder TB, Whitwood AC. Comparisons of photoinduced oxidative addition of B-H, B-B, and Si-H bonds at rhodium(η^5 -cyclopentadienyl)phosphine centers. *Organometallics.* 2006;25:5093-5104.
108. Kalläne SI, Braun T, Braun B, Mebs S. Versatile reactivity of a rhodium(I) boryl complex towards ketones and imines. *Dalton Trans.* 2014;43:6786-6801.
109. Kalläne SI, Braun T. Catalytic borylation of SCF_3 -functionalized arenes by rhodium(I) boryl complexes: Regioselective C-H activation at the ortho position. *Angew Chem Int Ed.* 2014;53:9311-9315.
110. Kabalka GW, Das BC, Das S. Rhodium-catalyzed 1,4-addition reactions of diboron reagents to electron deficient olefins. *Tetrahedron Letters.* 2002;43:2323-2325.
111. Shiomi T., Adachi, T., Toribatake K., Zhou, Li., Nishiyama, H. [Asymmetric \$\beta\$ -boration of \$\alpha,\beta\$ -unsaturated carbonyl compounds promoted by chiral rhodium-bisoxazolinylphenyl catalysts.](#) *Chem Commun.* 2009;5987-5989.
112. Toribatake K, Nishiyama H. Asymmetric diboration of terminal alkenes with a rhodium catalyst and subsequent oxidation: enantioselective synthesis of optically active 1,2-diols, *Angew Chem Int Ed.* 2013;52:11011-11015.

113. Pubill-Ulldemolins C, Poyatos M, Bo C, Fernández E. Rhodium-NHC complexes mediate diboration versus dehydrogenative borylation of cyclic olefins: a theoretical explanation. *Dalton Trans.* 2013;14:746-752.
114. Clegg W, Lawlor FJ, Marder TB, Nguyen P, Norman NC, Orpen AG, Quayle MJ, Rice CR, Robins EG, Scott AJ, Souza FES, Stringer G, Whittell GR. Boron-boron bond oxidative addition to rhodium(I) and iridium(I) centres. *J Chem Soc Dalton Trans.* 1998:301-309.
115. Dai C, Stringer G, Marder TB, Baker RT, Scott AJ, Clegg W, Norman NC. Oxidative addition of a B-B bond by an iridium(I) complex: Molecular structure of *mer-cis*-[Ir(PMe₃)₃Cl(Bcat)₂]. *Can J Chem.* 1996;74:2026-2031.
116. Tamura H, Yamazaki H, Sato H, Sakaki S. Iridium-catalyzed borylation of benzene with diboron. Theoretical elucidation of catalytic cycle including unusual iridium(V) intermediate. *J Am Chem Soc.* 2003;125:16114-16126.
117. Vanchura BA, Preshlock SM, Roosen PC, Kallepalli VA, Staples RJ, Maleczka, RE Jr, Singleton DA, Smith MR III. Electronic effects in iridium C-H borylations: insights from unencumbered substrates and variation of boryl ligand substituents. *Chem Commun.* 2010;46:7724-7726.
118. Nguyen P, Blom HP, Westcott SA, Taylor NJ, Marder TB. Synthesis and structures of the first transition-metal tris(boryl) complexes: (η^6 -arene)Ir(BO₂C₆H₄)₃. *J Am Chem Soc.* 1993;115:9329-9330.
119. Dai C, Stringer G, Corrigan JF, Taylor NJ, Marder TB, Norman NC. Synthesis and molecular structure of paramagnetic Co(II) bis(boryl) complex [Co(PMe₃)₃(Bcat)₂] (cat = 1,2-O₂C₆H₄). *J Organomet Chem.* 1996;513:273-275.
120. Adams CJ, Baber RA, Batsanov AS, Bramham G, Charmant JPH, Haddow MF, Howard JAK, Lam WH, Lin Z, Marder TB, Norman NC, Orpen AC. Synthesis and reactivity of cobalt boryl complexes. *Dalton Trans.* 2006;1370-1373.

121. Lam KCh, Lam WH, Lin Z, Marder TB, Norman NC, Structural analysis of five-coordinate transition metal boryl complexes with different d-electron configurations. *Inorg Chem.* 2004;43:2541-2547.
122. He X, Hartwig JF. Boryls bound to iron carbonyl. Structure of a rare bis(boryl) complex, synthesis of the first anionic boryl, and reaction chemistry that includes the synthetic equivalent of boryl anion transfer. *Organometallics.* 1996;15:400-407.
123. Rickard CEF, Roper WR, Williamson A, Wright LJ. Synthesis and structures of *cis*- and *trans*-[Os(Bcat)(aryl)(CO)₂(PPh₃)₂]: Compounds of relevance to the metal-catalyzed hydroboration reaction and the metal-mediated borylation of arenes. *Angew Chem Int Ed.* 1999;38:1110-1113.
124. Rickard CEF, Roper WR, Williamson A, Wright LJ. Reaction of *cis* and *trans* Bcat, aryl osmium complexes (cat = 1,2-O₂C₆H₄). Bis(Bcat) complexes of osmium and ruthenium and a structural comparison of *cis* and *trans* isomers of Os(Bcat)I(CO)₂(PPh₃)₂. *Organometallics.* 2000;19:4344-4355
125. Esteruelas MA, Fernández I, López AM, Mora M, Oñate E. Preparation, structure, bonding, and preliminary reactivity of a six-coordinate d⁴ osmium-boryl complex. *Organometallics.* 2012;31:4646-4649.
126. Kerr A, Marder TB, Norman NC, Orpen AG, Quayle MJ, Rice CR, Timms PL, Whittell GR. Preparation and structure of *cis*-[Pt(BF₂)(PPh₃)₂]: The first crystallographically characterised complex containing the BF₂ ligand. *Chem Commun.* 1998:319-320.
127. Lu N, Norman NC, Orpen AG, Quayle MJ, Timms PL, Whittell GR. Transition metal complexes incorporating the BF₂ ligand formed by oxidative addition of the B–B bond in B₂F₄. *J Chem Soc Dalton Trans.* 2000:4032-4037.
128. Curtis D, Lesley MJG, Norman NC, Orpen AG, Starbuck J. [Phosphine exchange reactions involving *cis*-\[Pt\(PPh₃\)₂\(Bcat\)₂\] \(cat=1,2-O₂C₆H₄\) and the oxidative addition of 1,2-B₂Cl₂\(NMe₂\)₂ to Pt\(0\)](#). *T J Chem Soc Dalton Trans.* 1999;1687-1694.

129. Braunschweig H, Damme A, Kupfer T. Unexpected bonding mode of the diboran(4)yl ligand: Combining the boryl motif with a dative Pt-B interaction. *Angew Chem Int Ed.* 2011;50:7179-7182.
130. Braunschweig H, Damme A, Kupfer T. Conversion of *trans*-diboran(4)yl platinum complexes into their *cis*-bisboryl analogues. *Chem Eur J.* 2013;19:14682-14686.
131. Brand J, Braunschweig H, Sen SS. B=B and B≡E (E = N and O) multiple bonds in the coordination sphere of late transition metals. *Acc Chem Res.* 2014;47:180-191.
132. Braunschweig H, Bertermann R, Damme A, Kupfer T. A dinuclear platinum complex featuring the diboran(4)-1,2-diyl ligand in a μ_2 -bridging coordination mode. *Chem Commun.* 2013;49:2439-2441.
133. Braunschweig H, Damme A, Kupfer T. Biboran(4)yl platinum(II) complexes. *Inorg Chem.* 2013;52:7822-7824.
134. Braunschweig H, Damme A. Thermodynamic control of oxidative addition and reductive elimination processes in *cis*-bis(dimethoxyboryl)-bis(tricyclohexylphosphine)-platinum(II). *Chem Commun.* 2013;49:5216-5218.
135. Braunschweig H, Lutz M, Radacki K. Synthesis of *ansa*-[2]boracyclopentadienyl-cycloheptatrienylchromium and its reaction to the *ansa*-platinumbis(boryl) complex by oxidative addition of the boron-boron bond. *Angew Chem Int Ed.* 2005;44:5647-5651.
136. Braunschweig H, Kupfer T, Lutz M, Radacki K, Seeler F, Sigritz R. Metal-mediated diboration of alkynes with [2]bormetalloarenophanes under stoichiometric, homogeneous, and heterogeneous conditions. *Angew Chem Int Ed.* 2006;45:8048-8051.
137. Braunschweig H, Fuß M, Mohapatra SK, Kraft K, Kupfer T, Lang M, Radacki K, Daniliuc CG, Jones PG, Tamm M. Synthesis and reactivity of boron-, silicon, and tin-bridged *ansa*-cyclopentadienyl-cycloheptatrienyl titanium complexes (troticenophanes). *Chem Eur J.* 2010;16:11732-11743.
138. Braunschweig H, Koster M. Diborane(4)yl and bridged borylene complexes from 1,2-dipyrrolidino- and 1,2-dipiperidinodiborane(4) derivatives. *J Organomet Chem.* 1999;588:231-234

139. Wagner A, Kaifer E, Himmel H-J. Diborane(4)-metal bonding: Between hydrogen bridges and frustrated oxidative addition. *Chem Commun.* 2012;48:5277-5279.
140. Wagner A, Kaifer E, Himmel H-J. Bonding in diborane-metal complexes: A quantum-chemical and experimental study of complexes featuring early and late transition metals. *Chem Eur. J.* 2013;19:7395-7409.
141. Ramírez J, Sanaú M, Fernández E. Gold(0) nanoparticles for selective catalytic diboration, *Angew Chem Int Ed*, 2008;47:5194-5197.
142. Tamura M, Fujihara H. Chiral Bisphosphine BINAP-stabilized gold and palladium nanoparticles with small size and their palladium nanoparticle-catalyzed asymmetric reaction. *J Am Chem Soc.* 2003;125:15742-15743.
143. Grirrance A, Corma A, Garcia H. Stereoselective single (copper) or double (platinum) boronation of alkynes catalyzed by magnesia-supported copper oxide or platinum nanoparticles. *Chem Eur J.* 2011;17:2467-2478.
144. Chen Q, Zhao J, Ishikawa N, Yamamoto Y, Jin T. Remarkable catalytic property of nanoporous gold on activation of diborons for direct diboration of alkynes. *Org Lett.* 2013;15:5766-5769.
145. Yan G, Jiang Y, Kuang CH, Wang S, Liu H, Zhangb Y, Wang J. Nano-Fe₂O₃-catalyzed direct borylation of arenes. *Chem Commun.* 2010;46:3170-3171.
146. Iwadata N, Suginome M. Differentially protected diboron for regioselective diboration of alkynes: Internal-selective cross-coupling of 1-alkene-1,2-diboronic acid derivatives. *J Am Chem Soc.* 2010;132:2548-2549.
147. Noguchi H, Shioda T, Chou CM, Suginome M. Differentially protected benzenediboronic acids: □ Divalent cross-coupling modules for the efficient synthesis of boron-substituted oligoarenes. *Org Lett.* 2008;10:377-380.
148. Noguchi H, Hojo K, Suginome M. Boron-masking strategy for the selective synthesis of oligoarenes via iterative Suzuki–Miyaura coupling. *J Am Chem Soc.* 2007;129:758-759.

149. Iwadate N, Suginome M. Synthesis of masked haloareneboronic acids via iridium-catalyzed aromatic C–H borylation with 1,8-naphthalenediaminatoborane (danBH). *J Organomet Chem.* 2009;694:1713-1717.
150. Iwadate N, Suginome M. Synthesis of B-protected β -styrylboronic acids via iridium-catalyzed hydroboration of alkynes with 1,8-naphthalenediaminatoborane leading to iterative synthesis of oligo(phenylenevinylene)s. *Org Lett.* 2009;11:1899-1902.
151. Borner C, Kleeberg Ch. Selective synthesis of unsymmetrical diboryl Pt^{II} and diamino-boryl CuI complexes by B–B activation of unsymmetrical diboranes(4) {pinB–B[(NR)₂C₆H₄]}. *Eur J Inorg Chem.* 2014;2486–2489.
152. Gao M, Thorpe SB, Santos WL. sp²-sp³ Hybridized mixed diboron: Synthesis, characterization, and copper-catalyzed β -boration of α,β -unsaturated conjugated compounds. *Org Lett.* 2009;11:3478-3481.
153. Gao M, Thorpe SB, Kleeberg Ch, Slebodnick C, Marder TB, Santos WL. Structure and reactivity of a preactivated sp²-sp³ diboron reagent: Catalytic regioselective boration of α,β -unsaturated conjugated compounds. *J Org Chem.* 2011;76:3997–4007.
154. Thorpe SB, Guo X, Santos WL. Regio- and stereoselective copper-catalyzed β -borylation of allenolates by a preactivated diboron. *Chem Commun.* 2011;47:424–426.
155. Hall DG. *Boronic Acids – Preparation, Applications in Organic Synthesis and Medicine.* Weinheim:Wiley-VCH; 2005.
156. Mkhaliid IAI, Barnard JH, Marder TB, Murphy JM, Hartwig JF. C-H activation for the construction of C-B bonds. *Chem Rev.* 2010;110:890-931
157. Marder TB, Norman NC, Transition metal catalyzed diboration *Top. Catal.*, 1998;5:63-73
158. T. Ishiyama and N. Miyaura. Metal-catalyzed reactions of diborons for synthesis of organoboron compounds. *Chem Rec.* 2004;3:271-280.
159. Takaya J, Iwasawa N. Catalytic, direct synthesis of bis(boronate)compounds, *ACS Catalysis.* 2002;2:1993-2006.
160. Schiffner JA, Müther K, Oestreich M. Enantioselective conjugate borylation. *Angew Chem Int Ed.* 2010;49:1194-1196.

161. Hartmann, E, Vyas DJ, Oestreich M. Enantioselective formal hydration of α,β -unsaturated acceptors: Asymmetric conjugate addition of silicon and boron nucleophiles. *Chem Commun.* 2011, 7917-7930.
162. Lillo V, Bonet A, Fernández E. Asymmetric induction on β -boration of α,β -unsaturated compounds: an inexpensive approach. *Dalton Trans.* 2009;2899-2908.
163. Dang L, Lin, Z, Marder TB. Boryl ligands and their roles in metal-catalysed borylation reactions. *Chem Commun.* 2009;3987-3995.
164. Mantilli L, Mazet C. Copper-catalyzed asymmetric β -boration of α,β -unsaturated carbonyl derivatives. *ChemCatChem.* 2010;2:501-504.
165. Calow ADJ, Whiting A. Catalytic methodologies for the β -boration of conjugated electron deficient alkenes. *Org Biomol Chem.* 2012,29:5485-5497.
166. Beletskaya I, Moberg C. Element–element additions to unsaturated carbon–carbon bonds catalyzed by transition metal complexes. *Chem Rev.* 2006;106:2320-2354.
167. Lee K, Zhugralin AR, Hoveyda AH. Efficient C–B bond formation promoted by N-heterocyclic carbenes: Synthesis of tertiary and quaternary B-substituted carbons through metal-free catalytic boron conjugate additions to cyclic and acyclic α,β -unsaturated carbonyls. *J. Am. Chem. Soc.* 2009;131:7253-7255.
168. Bonet A, Gulyás H, Fernández E. Metal-free catalytic boration at the β -position of α,β -unsaturated compounds: A challenging asymmetric induction. *Angew Chem Int Ed.* 2010;49:5130-5134.
169. Bonet A, Pubill-Ulldemolins C, Bo C, Gulyás H, Fernández E. Transition-metal-Free diboration reaction by activation of diboron compounds with simple Lewis Bases. *Angew Chem Int Ed.* 2011;50:7158-7161.
170. Ibrahim I, Breistein P, Córdova A, One-pot three-component highly selective synthesis of homoallylboronates by using metal-free catalysis *Chem.–Eur. J.*, 2012,;18:5175-5179.
171. Wu H, Radomkit S, O'Brien JM, Hoveyda AH, Metal-free catalytic enantioselective C–B bond formation: (Pinacolato)boron conjugate additions to α,β -unsaturated ketones, esters,

Weinreb amides, and aldehydes promoted by chiral N-heterocyclic carbenes. *J. Am. Chem. Soc.* 2012;134:8277-8285.

172. Sole C, Gulyás H, Fernández E, Asymmetric synthesis of α -amino boronate esters via organocatalytic pinacolboranyl addition to tosylaldimines *Chem. Commun.*, 2012;48:3769-3771.
173. Kleeberg C, Crawford AG, Batsanov AS, Hodgkinson P, Apperley DC, Cheung MS, Lin ZY, Marder TB, Spectroscopic and structural characterization of the CyNHC adduct of B_2pin_2 in solution and in the solid state. *J. Org. Chem.* 2012;77:785-789.
174. Cid J, Carbó, JJ, Fernández E, A clear-cut example of selective Bpin-Bdan activation and precise Bdan transfer on boron conjugate addition, *Chem Eur J*, 2014;20:3616-3620.
175. Braunschweig H, Damme A, Dewhurst RD, Kramer T, Kupfer T, Radacki K, Siedler E, Trumpp A, Wagner K, Werner C. Quaternizing diboranes(4): Highly divergent outcomes and an inorganic Wagner-Meerwein rearrangement. *J. Am. Chem. Soc.*, 2013, 135, 8702-8707.

Figure and scheme legends

Figure 1. Suggested concerted interaction of Cl_2B-BCl_2 with olefins.

Figure 2. Relative Lewis acidity of Cl_2B-BCl_2 and tetra(alkoxy)diboron compounds B_2cat_2 , and B_2pin_2 .

Figure 3. Formation of the sigma adduct $[Cu(NHC)(\sigma-catB-Bcat)]^+$

Figure 4. Calculated σ -bond metathesis barriers involving B_2cat_2 and B_2pin_2 .

Figure 5. Energy profile for the formation of cationic bisboryl Rh(III)-NHC complex. Electronic energy as $kcal.mol^{-1}$. Distances between B atoms are given in Å.

Figure 6. In situ BINAP-stabilized gold nanoparticles: TEM micrograph (x 500000) and core size distribution.

Scheme 1. Postulated activation of $\text{Cl}_2\text{B}-\text{BCl}_2$ with olefins towards diboration reaction.

Scheme 2. Unlikely heterolytic cleavage of $\text{Cl}_2\text{B}-\text{BCl}_2$.

Scheme 3. Activation of $\text{Cl}_2\text{B}-\text{BCl}_2$ with ferrocene.

Scheme 4. Selected synthetic applications of B_2pin_2 .

Scheme 5. Activation modes for B_2pin_2 .

Scheme 6. Proposed mechanism for the $\text{Pt}(0)$ -diboration of alkynes with B_2pin_2 .

Scheme 7. Multiple strategies to activate tetra(alkoxy)diboron with $\text{Pt}(0)$ and related transformations.

Scheme 8. Diboration of olefins with B_2cat_2 by $\text{Pt}(0)$ -olefin complexes.

Scheme 9. Diboration of aldimines with B_2cat_2 activated by $[\text{Pt}(\text{COD})\text{Cl}_2]$ complex.

Scheme 10. Activation of chiral diboron compounds by $\text{Pt}(0)$ -olefin complexes.

Scheme 11. Influence of ligand nature on Pt(0) complex to activate diboron and add to α,β -unsaturated esters.

Scheme 12. Postulated diboration of methylacrylate and acrolein with Pt.

Scheme 13. Activation of B_2pin_2 by $[Pt(PPh_3)_4]$ and further mechanistic proposal for formal carbon insertion.

Scheme 14. Activation of B_2cat_2 by *trans*- $[Pt(B(4-Bu^tcat))(Me)(PCy_3)_2]$ and further mechanistic proposal for MeBcat and Me B(4-Bu^tcat) formation.

Scheme 15. Activation of B_2cat_2 by σ -bond metathesis with *cis*- $[Pt(CH_2)_4(PPh_3)_2]$.

Scheme 16. Activation of B_2cat_2 by $[Pd(II)(PNP)]^+$.

Scheme 17. Activation of B_2cat_2 by $[Pd(II)(NHC)(Br)]^+$ and $[Pd(II)(NHC)]^{2+}$.

Scheme 18. 1,2 Diboration of allenes with B_2pin_2 by phosphine-free Pd complexes.

Scheme 19. Proposed mechanism for Ni(0) activation of B_2pin_2 throughout Ni-olefin species.

Scheme 20. Proposed mechanism for activation of B_2cat_2 through a) binuclear oxidative addition reaction and b) σ -bond metathesis.

Scheme 21. Suggested copper (I) activation of B_2pin_2 via σ -bond metathesis.

Scheme 22. Influence of ligands in copper (I) activation of B_2pin_2 via σ -bond metathesis.

Scheme 23. Activation of B₂pin₂ with Cu(II) in water.

Scheme 24. Activation of B₂pin₂ via σ -bond metathesis with Ag(I) complexes.

Scheme 25. Activation of B₂cat₂ and its 4-Bu^t and 3,5-Bu^t analogs by oxidative addition to [RhCl(PPh₃)₃].

Scheme 26. Activation of B₂cat₂ with [RhMe(PMe₃)₄].

Scheme 27. Activation of B₂pin₂ with [Rh(η^5 -C₅H₅)(PR₃)(C₂H₄)].

Scheme 28. Activation of B₂pin₂ with a rhodium aryl species.

Scheme 29. Activation of B₂pin₂ with [Rh(III)(OAc)₂(H₂O)(Phebox)].

Scheme 30. Activation of B₂cat₂ with [IrCl(PEt₃)₃] through oxidative addition.

Scheme 31. The activation of B₂cat₂ with [Co(PMe₃)₄] to generate bis(boryl)cobalt complex.

Scheme 32. The activation of B₂cat₂ with [Co(Me)(PMe₃)₄] through σ -bond metathesis.

Scheme 33. The activation of B₂pin₂ with [Co(PNP)(O^tBu)] through σ -bond metathesis.

Scheme 34. The activation of B₂cat₂ with [Fe(CO)₅] through oxidative addition.

Scheme 35. Formation of the bis(boryl) complex *trans,cis,cis*-[Os(CO)₂(PPh₃)₂(Bcat)₂] (**32**) and *trans,cis,cis*-[Ru(CO)₂(PPh₃)₂(Bcat)₂] (**32**).

Scheme 36. Activation of F_2B-BF_2 through oxidative addition with $Pt(\eta^2-C_2H_4)(PPh_3)_2$, $[Pt(dppb)(\eta^2-C_2H_4)]$ and *trans*- $[IrCl(CO)(PPh_3)_2]$.

Scheme 37. Activation of [2]borametalloarenophanes with platinum(0) phosphine complexes.

Scheme 38. Activation of doubly-base stabilized diborane(4) $[HB(hpp)]_2$.

Scheme 39. Suggested mechanism for B_2pin_2 activation and reactivity with alkynes, by Pt and Cu nanoparticles.

Scheme 40. Suggested mechanism for B_2pin_2 activation and reactivity with alkynes, by AuNPore.

Scheme 41. Activation of unsymmetrical diboron (pin)B-B(dan) with Ir(I) complex and further regioselective diboration.

Scheme 42. Activation of unsymmetrical diboron (pin)B-B(dmab) and (pin)B-B(dbab) with $[Pt(\eta^2-CH_2=CH_2)(PPh_3)_2]$.

Scheme 43. Activation of unsymmetrical diboron (pin)B-B(dmab) and (pin)B-B(dbab) with IDippCu(I)-O^tBu complexes.

Scheme 44. Activation of unsymmetrical diboron PDIPA diboron with CuCl.