Bond Activation

Boron–Ligand Cooperation: The Concept and Applications

Max Hasenbeck and Urs Gellrich[a]
Abstract: The term boron–ligand cooperation was introduced to describe a specific mode of action by which certain metal-free systems activate chemical bonds. The main characteristic of this mode of action is that one covalently bound substituent at the boron is actively involved in the bond activation process and changes to a datively bound ligand in the course of the bond activation. Within this review, how the term boron–ligand cooperation evolved is reflected on and examples of bond activation by boron–ligand cooperation are discussed. It is furthermore shown that systems that operate via boron–ligand cooperation can complement the reactivity of classic intramolecular frustrated Lewis pairs and applications of this new concept for metal-free catalysis are summarized.

Introduction

The concept of boron–ligand cooperation was coined to describe a specific mode of bond activation by boranes that is reminiscent of the concept of metal–ligand cooperation. However, these boranes can also be described as a specific class of intramolecular frustrated Lewis pairs (FLPs). We, therefore, commence this review with a brief reflection on metal–ligand cooperation and frustrated Lewis pairs.

Metal–ligand cooperation

Metal–ligand cooperation (MLC) has emerged as a powerful tool for bond activation and catalysis in the last decades. Whereas classic transition-metal complexes activate chemical bonds by an oxidative addition at the metal center, MLC denotes a situation where one of the ligands bound to the metal center is actively involved in the bond activation process. Prime examples for bond activation by MLC are the hydrogen activation by Noyori’s ruthenium catalyst 1 and by the ruthenium pincer complex 3 introduced by David Milstein and coworkers.[1, 2] In the course of the hydrogen activation by the Noyori system, the amide substituent is involved in the H2 activation. Hydrogen activation by the Milstein system is accompanied by the transfer of a proton to the benzylic position of the dearomatized pincer ligand, leading to a re-aromatization of the pyridine ring (Scheme 1).

In their comprehensive review on MLC from 2015,[3] Khusnutdinova and Milstein gave three criteria for MLC that read as:

1) Both the metal and the ligand participate in the bond cleavage or bond formation steps;
2) Both the metal and the ligand are chemically modified during bond activation.
3) The coordination mode of the cooperative ligand undergoes significant changes in the first coordination sphere as a result of bond activation."

In the context of this review, it is important to emphasize the third criterion, which stipulates that the “coordination mode of the cooperative ligand undergoes significant changes” during bond activation. An analysis of the examples given in the review by Khusnutdinova and Milstein reveals that this change in the coordination mode can usually be described as the transition of a covalently bound substituent to a datively bound ligand. For example, the amide substituent in the Noyori system becomes a datively bound amine ligand during bond activation. As a consequence of this change in the coordination sphere, the formal oxidation state of the ruthenium does not change. We note that inorganic chemists might prefer to describe this change in the coordination mode as the transi-
tion of an X-type ligand to an L-type ligand. However, we use the term “covalently bound substituent” here as equivalent to the notation X-type ligand to establish an analogy to transition-metal-free systems.

**Frustrated Lewis pairs**

The term frustrated Lewis pairs (FLPs) describes combinations of sterically encumbered Lewis bases and Lewis acids that are able to activate strong chemical bonds. Classic examples for intramolecular FLPs are the covalently linked phosphine–borane pairs 5 and 7 developed by the groups of Stephan and Erker (Scheme 2). The hydrogen activation by these intramolecular FLPs leads to the formation of borohydrides (6 and 8). Numerous metal-free catalytic reactions that are based on the FLP concept have been developed in recent years. 

![Scheme 2. Hydrogen activation by the intramolecular FLPs 5 and 7, which leads to the formation of the borohydrides 6 and 8.](image)

**Boron–ligand cooperation: The concept**

We and others recently reported bond activation by a specific class of intramolecular FLPs in which bond activation leads to a reorganization of π-electron density within the cooperative substituent. Furthermore, bond activation is associated with a transition of the involved substituent to a datively bound ligand (Scheme 3a). Thus, in contrast to classic FLPs, bond activation does not lead to a borate salt, but rather a borane complex. We note that the reorganization of π-electron density and the concomitant change in coordination mode of the cooperative substituent are reminiscent of hydrogen activation by Milstein’s established pyridine-based pincer complexes (Scheme 3b). In analogy, we propose the term boron–ligand cooperation (BLC) to describe the bond activation by these specific FLPs.

Thus, the BLC concept emphasizes a change in the valence sphere of the borane as a result of the bond activation. However, the systems that operate through BLC can in their reactive state before bond activation be classified as intramolecular FLPs. The three concepts of MLC, FLPs, and BLC have in common that the bond activation involves two active sites with Lewis basic and Lewis acidic character. These similarities were noted in recent reviews by Greb and Slootweg.

Within the second part of this review, we will discuss examples of bond activation by BLC with a special emphasis on changes in the bonding between the substituent involved in the bond activation and the borane. In the third part, we will discuss how the novel reactivity based on BLC can complement the reactivity of FLPs and show how the BLC concept can lead to new applications for transition-metal-free catalysis.

**Bond Activation by Boron–Ligand Cooperation**

In the following, we will discuss examples of bond activation that fulfill the criteria for BLC formally. We will focus on the question of whether experimental and computational data further support that the transition of a covalently bound substituent to a datively bound ligand is a real chemical event.

---

Max Hasenbeck studied chemistry at the universities of Cologne and Düsseldorf in Germany. For his master’s thesis, he worked on the computational investigation of reaction mechanisms under the supervision of Dr. Martin Breugst. After receiving his M.Sc. in 2017, he joined the group of Dr. Urs Gellrich at the Justus Liebig University Giessen for his doctoral studies working on the concept of boron–ligand cooperation and its application for catalysis.

Urs Gellrich studied chemistry at the University of Freiburg in Germany where he obtained his doctorate in 2013 for his work on supramolecular ligands under the guidance of Prof. Bernhard Breit. He then joined the group of Prof. David Milstein at the Weizmann Institute of Science as a postdoctoral researcher. In 2017, Urs started his independent career as a Liebig Fellow of the FCI at the Justus Liebig University Giessen where he is currently Emmy Noether Group Leader. His research focuses on the in silico design of novel metal-free systems for bond activation and catalysis.
Early examples of boron–ligand cooperation

In 2010, Tamm and co-workers reported the H₂ activation by the pyrazolylborane 9, which the authors described as a bifunctional FLP (Scheme 4). The authors reported the product 10 of the hydrogen activation as zwitterionic pyrazolium–borate. However, 10 can also be described as a pyrazol borane complex. The elongation of the N–B bond from 1.4281(16) Å in 9 to 1.5794(13) Å in 10, determined by single-crystal (SC)XRD, does support this description.

A similar bond elongation is observed upon CO₂ activation by 9, which yields 11. An alternative interpretation is that the N–B π-bonding in 9 is lost upon hydrogen activation, resulting in an elongation of this bond. However, the reported SCXRD structures further reveal that upon hydrogen activation the N1–C3 is shortened by 0.05 Å whereas the N2–C1 is elongated by 0.03 Å (Scheme 5). This change in the bond lengths, indicating a reorganization of π-electron density within the heterocycle upon hydrogen activation, is better described when 10 is depicted as a pyrazole borane complex.

A computational examination of boron–ligand cooperation

To mimic the reactivity of Milstein’s ruthenium pyridine pincer complex by metal-free systems, Wang, Schleyer, and colleagues investigated the activation of dihydrogen by model compound 12 (Scheme 6). From their computations, the authors concluded that hydrogen activation by 12 yielding 13 is kinetically feasible but that the reverse reaction is not possible. The computed nucleus independent chemical shifts (NICS(0)) further reveal an aromaticity gain upon hydrogen activation by 12, which is diagnostic for the formation of a dative bound pyridine ligand.

Although the authors did not use the term BLC, this computational study named MLC as a design principle for bond activation by a borane.

Boron–ligand cooperation by re-aromatization of a pyridine–borane complex

Inspired by the computational work by Schleyer and Wang, Milstein and co-workers attempted to realize bond activation by a dearomatized pyridine borane experimentally. Therefore, the amino-borane pyridine complex 14 was synthesized (Scheme 7). Upon moderate heating, hydrogen liberation from 14 and formation of the dearomatized aminoborane 15 was observed.

As indicated by the ¹H NMR chemical shifts of 14 and 15 and the computed NICS values, the de-aromatization event is in this case better described as a shift of the aromacity from the pyridine ring in 14 to the five-membered boracycle in 15. The reaction of 14 with benzylamine or benzoic acid leads to N-H activation and O-H cleavage and formation of 16 and 17, respectively. In both cases, the re-aromatization of the pyridine ring shows that the bond activation was accompanied by the change of the N–B bond from a covalent bond in 15 to a...
Borax–ligand cooperation by a pyridonate borane

In 2018, we reported reversible \( \text{H}_2 \) activation by the pyridonate borane complex 18 (Scheme 8).[13] The closed-form of the pyridonate borane 18 is in equilibrium with the open form 18', which can be regarded as an intramolecular FLP. Hydrogen activation by 18' yields 19. The hydrogen activation is reversible. Upon heating to 60 °C, 19 liberates dihydrogen and 18 is regenerated.

We became interested if 19 is better described as zwitterionic borate or as a pyridone borane complex. A comparison of the computed structures of 18' and 19 reveals an elongation of the O–B bond by 0.2 Å (Scheme 9). Furthermore, the C–O is shortened in course of the bond activation to 1.27 Å, a value that is typical for a C=O double bond. This indicates that the heterocycle in 19 is present as pyridone. In agreement with this interpretation, the C=O stretching vibration of 19 at 1643 cm\(^{-1}\) is similar to that observed for the “fixed” pyridone tautomer 1-methyl-2-pyridone.[14] The reduced aromaticity of 19 compared with 18, deduced from the computed NICS values, is further indicative of the formation of a pyridone.[15]

The disappearance of the covalent B–O upon dihydrogen activation of 18' to 19 is furthermore supported by the analysis of the Laplacian of the electron density (Figure 1). For covalent bonds, the Laplacian of the electron density should show a minimum along the bond axis.[16] In the case of pyridonate borane 18', this is clearly visible (“blue valley”, Figure 1, left side). This is not the case for pyridone borane 19 (Figure 1, right side), indicating a closed-shell interaction between O and B. An EDA-NOCV analysis further supports the change in the bonding mode of the pyridonate substituent upon hydrogen activation.[17]

Borax–ligand cooperation as a concept for metal-free catalysis

The IUPAC definition of a dative bond states that “The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the heterolytic bond cleavage path”.[19] To substantiate the presence of a dative bond in 19, we probed the heterolytic dissociation in a pyridone and borane (Scheme 10). As the equilibrium lies far on the side of the pyridone borane complex, there is no possibility to obtain direct spectroscopic evidence for such a dissociation. Therefore, we investigated if 19 is able to effect hydroboration, as hydroboration requires the presence of a trivalent borane.[20] Indeed, when 18' was reacted under an \( \text{H}_2 \) atmosphere with styrene, the formation of the pyridone alkylborane 20 was observed (Scheme 10).

![Figure 1. Analysis of the Laplacian of the electron density computed at PBE0(D3BJ)/def2-TZVP.][18] Left: pyridonate borane 18'; right: pyridone borane complex 19.

![Scheme 8. Reversible hydrogen activation by 18', leading to the formation of the pyridone borane complex 19.][19]

![Scheme 9. Computed bond lengths and NICS values for 18' and 19. The description of the pyridone borane complex is further supported by the experimentally determined IR stretching vibration of 19.][20]

![Scheme 10. Formation of the alkylborane 20, which shows that the pyridone borane complex 19 formed upon \( \text{H}_2 \) activation by 18' undergoes a heterolytic dissociation to pyridone 21 and Piers borane 22.][21]
Thus, the change of the B–O from a covalent bond to a dative bond during H₂ activation provides access to borane reactivity. Classic intramolecular FLPs rather show borohydride reactivity. In this regard, the concept of BLC complements the reactivity of classic FLPs.

**Semi-hydrogenation of alkynes**

Repo and co-workers showed that alkenylborate complexes are prone to undergo intramolecular protodeborylations in the presence of protic substituents. We, therefore, envisioned that a pyridone alkenylborane complex, formed analogously to 20 upon hydroboration of an alkyne, could undergo a protodeborylation yielding a cis alkene. This would enable the usage of 18’ as a potential hydrogenation catalyst in a sequence of H₂ activation, hydroboration, and protodeborylation. Using this strategy, several internal alkynes were hydrogenated in moderate to excellent yields under mild hydrogen pressure to the corresponding (Z)-alkenes (Scheme 11).[20, 22]

![Scheme 11. Semi-hydrogenation of internal alkynes to the corresponding (Z)-alkenes.](image)

Extended reaction times lead to the isomerization of the (Z)-alkenes to the corresponding (E)-alkenes for some substrates. We attributed this isomerization to the reversible hydroboration of alkenes by the Piers borane, which was reported earlier by the Du group.[22a] The reaction mechanism of the hydrogenation was investigated experimentally and computationally (Scheme 12). After hydrogen activation by the pyridone borane 18, the resulting pyridone borane complex 19 dissociates into the pyridone 21 and Piers borane 22. This endergonic reaction is rendered thermodynamically more favorable by the complexation of the pyridone 21 with the pyridonate borane 18’, yielding the bispyridone complex 23.[13, 23] After hydroboration of the alkyne by Piers borane 22, the resulting alkenylborane 24 has to re-coordinate to the pyridone 21 to undergo protonolysis. Therefore, the bispyridone complex 23 has to dissociate again into the pyridone 21 and Piers borane 22. The latter coordinates to alkenylborane 24, yielding the alkenylborane pyridone complex 25. Protodeborylation liberates the (Z)-alkene and regenerates the catalyst 18’.

The bispyridone complex 23 and the alkenylborane 24 were identified as the resting state of the catalytic transformation by NMR spectroscopy, whereas computations identified the protodeborylation as the turnover-determining transition state (TDTS). For 2-butyne as a model substrate, the computed kinetic barrier or energetic span of the catalytic cycle is 22.6 kcal mol⁻¹, which is in good agreement with the experimental reaction conditions (Scheme 13).[24]

![Scheme 12. Catalytic cycle of the semi-hydrogenation of internal alkynes to the corresponding (Z)-alkenes.](image)

![Scheme 13. Protoborylation of the alkenylborane and the computed energetic span of the catalytic cycle at revDSD-PBE96-D4/def2-QZVPP//PBEh-3c.](image)

Furthermore, several terminal alkynes could be hydrogenated in moderate to good yields although a higher catalyst loading had to be used (Scheme 14a). This is the first example of an FLP catalyst which is able to hydrogenate terminal alkynes. Other FLPs are deactivated by terminal alkynes because of an irreversible deprotonative borylation.[27] Although pyridonate borane 18’ reacts with terminal alkynes in such a deprotonative borylation, a competition experiment revealed that the C₉₋H cleavage is reversible, thus enabling the hydrogenation pathway (Scheme 14b).
Gem-dimerization of terminal alkynes

The ability of $^{18}$ to cleave the C$_{sp}$–H bond of terminal alkynes was used to develop a catalytic protocol for the first metal-free gem-dimerization of terminal alkynes.\(^{[28]}\) By heating a reaction mixture of a terminal alkyne with 20 mol\% of the pyridonate borane $^{18}$', several alkynes were dimerized to the respective enynes with exclusive gem-regioselectivity (Scheme 15). The active catalyst was formed in situ by dehydrogenation of $^{19}$.

Mechanistic investigations reveal that for the observed reactivity, the change in the B–O bonding from a covalent to a dative bond upon C$_{sp}$–H activation of the terminal alkyne by the pyridonate borane $^{18}$' is essential (Scheme 16). This change in the bond mode enables the dissociation of the pyridone alkynylborane complex $^{28}$ in the pyridone $^{21}$ and the trivalent alkynylborane $^{29}$, which undergoes an 1,2-carboboration reaction with another equivalent of the terminal alkyne.\(^{[29]}\) The resulting enynylborane $^{30}$ re-coordinates to the pyridone $^{21}$, forming $^{31}$. After protodeborylation, the gem-dimer is released and the catalyst $^{18}$ is regenerated. Computations and experiments showed that the alkynylborane pyridine complex $^{28}$ is the resting state whereas the 1,2-carboboration is the TDTS of the reaction. The energetic span for propyne as a model substrate was computed to be 25.0 kcal mol$^{-1}$.\(^{[25, 30]}\)

The 1,2-carboboration reaction was furthermore investigated by the reaction of the independently synthesized alkynylborane $^{32}$ with 3-phenylpropyne $^{33}$ (Scheme 17). The reaction yielded the enynylborane $^{34}$, which was fully characterized by NMR spectroscopy. The addition of one equivalent of pyridone $^{21}$ yielded the enyne $^{35}$ and the bispyridone complex $^{23}$ as the protodeborylation product. Computations showed that the 1,2-carboboration itself is concerted but highly asynchronous. The computed transition

![Scheme 14](image1.png)

**Scheme 14.** (a) Scope of the semi-hydrogenation of terminal alkynes, (b) competition experiment of the C$_{sp}$–H cleavage of terminal alkynes by $^{18}$'.

![Scheme 15](image2.png)

**Scheme 15.** Gem-dimerization of terminal alkynes by using pyridonate borane $^{18}$ as the catalyst.

![Scheme 16](image3.png)

**Scheme 16.** Catalytic cycle of the gem-dimerization of terminal alkynes. The energetic span was computed at TighPNO-DLPNO-CCSD(T)/def2-TZVP//PBE0-D3(BJ)/def2-TZVP.\(^{[25, 30]}\) The SMD model for toluene was used to implicitly account for solvent effects.\(^{[26]}\)

![Scheme 17](image4.png)

**Scheme 17.** 1,2-Carboboration of $^{33}$ by $^{32}$ and subsequent protodeborylation by the pyridone $^{21}$.\(^{[26]}\)
state structure shows that the formation of the new C–B bond is more advanced than the formation of the new C–C bond (Figure 2).

Figure 2. Computed transition state structure of the 1,2-carboboration with propyne as model substrate at PBE0(D3BJ)/def2-TZVP.14

Michael-addition of alkynylboranes to chalcones

Recently, Fountaine and co-workers reported the catalytic addition of \textit{in situ} generated alkynylboranes to chalcones.\cite{31} The active catalyst is formed by the transfer borylation of furanboronate 36 to the bifunctional mercaptoimidazole 37 (Scheme 18). The boronate moiety of 38 is transferred to a terminal alkyne (39), which changes the covalent N–B bond to a dative bond. This change to a dative bond enables the dissociation of the trivalent alkynylborane 40 and is thus essential for the observed reactivity. After dissociation, the free alkynylborane 40 adds to the chalcone\cite{32} in a 1,4-addition, yielding the intermediary enolboronate 41, which re-coordinates to imidazole 37, yielding 42. Protodeborylation liberates the product and regenerates the catalyst 38. The scope was thoroughly investigated by using different alkynes and chalcone derivatives (Scheme 19). The authors demonstrated that this protocol can be transferred to different nitrogen- and sulfur-containing heterocycles as nucleophiles.

![Scheme 19](image)

Scheme 19. Scope of the transfer borylation and the subsequent addition of alkynylboranes to chalcones.

Furthermore, potential deactivation pathways were investigated. By heating the catalyst 37 with trimethylsilylacetylene 43 and catecholboronate 36, the formation of the boron-containing zwitterionic heterocycle 44, which deactivates the catalyst, was observed (Scheme 20). The deactivation product is probably formed by thiboration of trimethylsilylacetylene by the \textit{in situ} formed imidazole boronate 38.

![Scheme 20](image)

Scheme 20. Deactivation pathway of catalyst 37 by addition of trimethylsilylacetylene to imidazol boronate 38.

Allylation of acetonitrile with \textit{in situ} formed allylboranes

The allylation of electrophiles by allylboranes is an important and frequently used reaction in organic synthesis.\cite{33, 34} Brown and co-workers described the synthesis of such allylboranes by the hydroboration of allenes.\cite{35} The approach for the synthesis of allylboranes by hydroboration of allenes in combination with BLC was used to realize a catalytic protocol for an allylation reaction requiring only catalytic amounts of an \textit{in situ} formed allylation reagent (Scheme 21).\cite{36} Hydrogen activation by the pyridonate borane 18 forms the pyridone borane com-
plex 19, which dissociates into the pyridone 21 and Piers borane 22. Adding an allene to the reaction mixture produces the allylborane 45, which undergoes an allylation reaction with acetonitrile as electrophile yielding the ketiminoborane 46. Re- coordination of the pyridone 21 to the ketiminoborane 46, followed by a virtually barrierless proton transfer, affords complex 47 (gray rectangle in Scheme 21). This intermediate is critical for the outcome of the reaction because two different reaction paths can be observed. In the presence of B(C₆F₅)₃ (BCF) as an additional Lewis acid, the allylimine moiety of 47 can dissociate and form the kinetically stable complex 48 with BCF, while simultaneously catalyst 18 is regenerated.

Without BCF, the pyridone moiety of 47 tautomerizes the allylimine to nucleophilic enamineborane 49, which dissociates and attacks a second equivalent of acetonitrile forming the β-diketiminate borane complex 50. This prevents further catalytic reactivity because the B(C₆F₅)₃ moiety of catalyst 18 is irreversible bound in 50.

Both, the β-diketiminate borane 50 and the allylamine BCF complexes 48 are air- and moisture-stable and can be isolated by column chromatography in moderate to excellent yields (Scheme 22).

The formation of nucleophilic allyboranes from dihydrogen and allenes is a conceptually new way to use dihydrogen for organic synthesis.

Transfer borylations

Fountaine and co-workers developed a catalytic protocol for the transfer borylation of 2-furylcatecholboran 36 to a wide range of heterocycles and terminal alkynes. They developed two different types of catalysts (Scheme 23). The transfer borylation with the first catalyst— mercaptopyridine 51—required relatively high catalyst loadings and five equivalents of the boron source catecholboranan 36 to borylate different N-, S-, and O-containing heterocycles. The mercaptoimidazole 37 as the second catalyst generation was significantly more
The authors could show that they only needed 5 mol% catalyst loading to borylate the same heterocycles under milder conditions by using only two equivalents of catecholboronate \(36\). Furthermore, by using \(37\) as the catalyst, they could expand the scope to terminal alkynes.

Both catalysts—mercaptopyridine \(51\) and mercaptoimidazole \(37\)—react through the same mechanism, which is in the following exemplified for \(37\) (Scheme 24). First, the nitrogen of the catalyst \(37\) coordinates to the catecholboronate, yielding \(52\). In a protodeborylation, the boron moiety of the furan boronate \(36\) is transferred to the catalyst, yielding \(38\). A concerted deprotonative borylation via \(\text{TS}_{38/37}\) transfers the boronate from the catalyst to the substrate. Here, the change from a covalent to dative \(\text{N}^-\text{B}\) bond enables the dissociation of the product and regenerates the catalyst. This change of the bond mode can again be described as BLC.

**Transfer hydrogenations with ammonia borane**

Another example of BLC was presented in a series of publications on enantioselective transfer hydrogenations catalyzed by an FLP-type system by using ammonia borane as a hydrogen source. Du and co-workers showed that by using a catalytic amount of a chiral sulfonamide borane complex \(53\), imines, indoles, enamines, and quinoxalines can be enantioselectively hydrogenated (Scheme 25).

**Scheme 24.** Catalytic cycle of the transfer borylation.

**Scheme 25.** Scope of the enantioselective transfer hydrogenation using \(53\) as the catalyst and ammonia borane as the hydrogen source.

Catalyst \(53\) is generated *in situ* by adding Piers borane \(22\) to the sulfonamide \(54\). To assess the structure of the Lewis adduct formed in this way, the authors investigated the adduct formation of Piers borane \(22\) with all three Lewis basics sites of sulfonamide \(54\) computationally (Scheme 26). Based on these results, the authors concluded that the \(\text{B}^-\text{O}\) coordinated form of \(53\) is the active catalyst.

**Scheme 26.** Comparison of the different free complexation enthalpies of \(54\) and \(22\) computed at M06-2X/6-31G(d). The PCM model for toluene was used to implicitly account for solvent effects.
Mechanistic investigations revealed that the hydrogenation itself is a concerted transfer of the hydridic B–H and protic N–H of 53 to the respective substrate. However, according to DFT computations by the authors, the active species of the hydrogenation transfer from the ammonia borane via $T S_{56/55}$ is the sulfamido borane 55 (Scheme 27). To regenerate the active catalyst 53, the Piers borane moiety of 56 has to dissociate and re-coordinate to the oxygen of the sulfamidamide, which is only possible because of the change in bonding mode between boron and nitrogen in the course of the hydrogen transfer from the ammonia borane to 55.

![Scheme 27. Regeneration of the active catalyst 53 by hydrogen transfer from ammonia borane to sulfamido borane 55.](image)

Acknowledgments

This work was supported by the FCI (Liebig Fellowship to U.G.) and the DFG (Emmy-Noether program, GE 3117/1-1). Continuous support by Prof. Dr. P. R. Schreiner, Prof. Dr. R. Göttlich, and Prof. Dr. H. A. Wegner is acknowledged. Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: bond activation - boron-ligand cooperation - dissociation - frustrated Lewis pair - homogeneous catalysis

[1] a) R. Noyori, T. Ohkuma, Angew. Chem. Int. Ed. 2001, 40, 40–73; Angew. Chem. 2001, 113, 40–75; b) T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 1995, 117, 2675–2676; c) P. A. Dub, J. C. Gordon, Nat. Rev. Chem. 2018, 2, 396–408.
[2] a) J. S. Zhang, G. Leitus, Y. Ben-David, D. Milstein, J. Am. Chem. Soc. 2005, 127, 10840–10841; b) C. Gunananthan, D. Milstein, Acc. Chem. Res. 2011, 44, 588–602; c) D. Milstein, Philos. T. R. Soc. A 2015, 372, 20140189.
[3] J. R. Khusnutdinova, D. Milstein, Angew. Chem. Int. Ed. 2015, 54, 12236–12273; Angew. Chem. 2015, 127, 12406–12445.
[4] R. H. Crabtree, The Organometallic Chemistry of the Transition Metals, 4th ed., Wiley, New York, 2005, pp. 32–35.
[5] For examples of bond activation by intramolecular boron-based FLPs, see: a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, Science 2006, 314, 1124; b) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimmel, D. W. Stephan, Chem. Commun. 2007, 5072; c) Z. Jian, G. Kehr, C. G. Daniliuc, B. Wibbeling, G. Erker, Dalton Trans. 2017, 46, 11715; d) K. Chernichenko, M. Niegier, M. Leskela, T. Repo, Dalton Trans. 2012, 41, 9029; e) K. Chernichenko, B. Kötä, K. Pajä, V. Zhivonitko, M. Niegier, M. Leskela, T. Repo, Angew. Chem. Int. Ed. 2015, 54, 1749; Angew. Chem. 2015, 127, 1769; f) M.-A. Légare, M.-A. Couttemanche, E. Rochette, F.-G. Fontaine, Science 2015, 349, 513; g) C. M. Mörmmling, E. Otten, G. Kehr, R. Fröhlich, S. Grimmel, D. W. Stephan, G. Erker, Angew. Chem. Int. Ed. 2009, 48, 6643; Angew. Chem. 2009, 121, 6770; h) Z. Mo, E. L. Kolychev, A. Rit, J. Campos, H. Niu, S. Aldridge, J. Am. Chem. Soc. 2015, 137, 12227.
[6] For recent reviews about FLPs, see: a) J. Lamm, K. M. Szpko, E. Mosafner, D. W. Stephan, Chem. Soc. Rev. 2019, 48, 3592; b) D. W. Stephan, J. Am. Chem. Soc. 2015, 137, 10018; c) D. W. Stephan, Organ. Biomol. Chem. 2012, 10, 5740; d) D. W. Stephan, Science 2016, 354, 4a72229; e) D. W. Stephan, G. Erker, Chem. Sci. 2014, 5, 2625; f) D. W. Stephan, G. Erker, Angew. Chem. Int. Ed. 2015, 54, 6400; Angew. Chem. 2015, 127, 6498; g) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch, M. Ulbrich, Inorg. Chem. 2011, 50, 12338; h) J. Paradies, Eur. J. Org. Chem. 2019, 283.
[7] a) L. Greb, F. Ebner, Y. Ginzburg, L. M. Sigmund, Eur. J. Inorg. Chem. 2020, 3030; b) E. R. M. Habranen, A. R. Jupp, M. B. Brands, M. Niegier, A. W. Ehlers, J. C. Slotteow, Eur. J. Inorg. Chem. 2019, 2436.
[8] E. Theuergartner, D. Schlüns, J. Grünenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, Chem. Commun. 2010, 46, 8561.
[9] E. Theuergartner, J. Schlösser, D. Schlüns, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, Dalton Trans. 2012, 41, 9101.
[10] G. Lu, H. Li, L. Zhao, F. Huang, P. von R. Schleyer, Z.-X. Wang, Chem. Eur. J. 2011, 17, 2038.
[11] P. V. R. Schleyer, C. Maereker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, J. Am. Chem. Soc. 1996, 118, 6317.
[12] U. Gellrich, Y. Diskin.Posner, L. W. Shimon, D. Milstein, J. Am. Chem. Soc. 2016, 138, 13307.
[13] U. Gellrich, Angew. Chem. Int. Ed. 2018, 57, 4779; Angew. Chem. 2018, 130, 4869.
[14] A. R. Katsritzky, R. A. Jones, J. Am. Chem. Soc. 1960, 82, 2947.
[26] A. V. Marenich, C. J. Cramer, D. G. Truhlar, Angew. Chem. Int. Ed. 2010, 49, 2414; Angew. Chem. 2010, 122, 2464; e) T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan, G. Erker, Organometallics 2012, 31, 2367.

[27] M. Hasenbeck, T. Müller, U. Gelrich, Catal. Sci. Technol. 2019, 9, 2438.

[28] For different examples of 1,2-carboration reactions, see: a) M. Devilard, R. Brousses, K. Miqueu, G. Boughadir, D. Bourissou, Angew. Chem. Int. Ed. 2015, 54, 5722; Angew. Chem. 2015, 127, 5814; b) I. A. Cade, M. J. Ingleson, Chem. Eur. J. 2014, 20, 12874; c) Y. Shoji, N. Tanaka, S. Muranaka, N. Shigeno, H. Sugiyama, K. Takenouchi, H. Fujishita, Nat. Commun. 2016, 7, 12074; d) M. F. Lappert, B. Prokai, J. Organomet. Chem. 1964, J, 384; e) Y. Cheng, C. Mück-Lichtenfeld, A. Studer, J. Am. Chem. Soc. 2018, 140, 6221.

[29] a) C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, J. Chem. Phys. 2013, 139, 134101; b) F. Neese, WIREs Comput. Mol. Sci. 2012, 2, 73.

[30] V. Desrosiers, C. Z. Garcia, F.-G. Fontaine, ACS Catal. 2020, 10, 11046.

[31] T. R. Wu, J. M. Chong, J. Am. Chem. Soc. 2005, 127, 3244.

[32] W. R. Roush, Comprehensive Organic Synthesis, Vol. 2 (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, 1991, pp. 1–53.

[33] a) H. C. Brown, P. K. Jadhav, J. Am. Chem. Soc. 1983, 105, 2092; b) H. C. Brown, K. S. Bhat, J. Am. Chem. Soc. 1986, 108, 5919; c) U. S. Racherla, H. C. Brown, J. Org. Chem. 1991, 56, 401; d) W. R. Roush, A. D. Palkovitz, K. Ando, J. Am. Chem. Soc. 1990, 112, 6348.

[34] G. W. Kramer, H. C. Brown, J. Organomet. Chem. 1977, 132, 9.

[35] M. Hasenbeck, S. Ahles, A. Averdunk, J. Becker, U. Gelrich, Angew. Chem. Int. Ed. 2020, 59, 23885; Angew. Chem. 2020, 132, 24095.

[36] E. Rochette, V. Desrosiers, Y. Solfrani, F.-G. Fontaine, J. Am. Chem. Soc. 2019, 141, 12305.

[37] a) W. Zhao, Z. Zhang, X. Feng, J. Yang, H. Du, Org. Lett. 2020, 22, 5850; b) S. Li, W. Meng, H. Du, Org. Lett. 2017, 19, 2604; c) S. Li, G. Li, W. Meng, H. Du, J. Am. Chem. Soc. 2016, 138, 12956; d) W. Zhao, X. Feng, J. Yang, H. Du, Tetrahedron Lett. 2019, 60, 1193.

[38] a) Y. Zhao, D. G. Truhlar, Acc. Chem. Res. 2008, 41, 157; b) Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 2008, 120, 215; c) R. Ditchfield, W. J. Hether, J. A. Pople, J. Chem. Phys. 1971, 54, 724; d) W. J. Hether, R. Ditchfield, J. A. Pople, J. Chem. Phys. 1972, 56, 2257.

[39] G. Scalmani, M. J. Frisch, J. Chem. Phys. 2010, 132, 114110.

Manuscript received: October 13, 2020
Revised manuscript received: December 2, 2020
Accepted manuscript online: December 9, 2020
Version of record online: January 28, 2021