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Nucleophilic boron strikes back*

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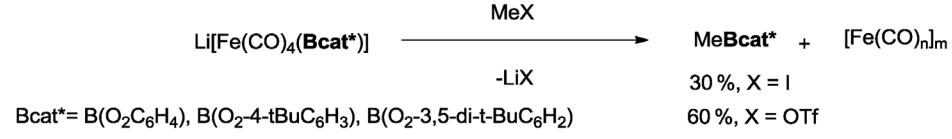
Abstract: It has been demonstrated that the interaction of a simple Lewis base with tetraalkoxydiboranes generates an unusual nucleophilic character in one of the boryl moieties. The interaction of amines, *N*-heterocyclic carbenes (NHCs), and alkoxides with a diboron reagent results in the formation of a Lewis acid–base adduct, in which the formally intact sp^2 boryl moiety becomes nucleophilic. We describe in this work the application of this new type of nucleophilic boron synthon in the selective preparation of organoboranes through β-boration and diboration reactions.

Keywords: nucleophilic boron; β-boration; boron conjugate addition; diboration.

INTRODUCTION

The electronic properties of the boron center in a three-coordinated borane reagent can be shifted from electrophilic to nucleophilic, depending on the substituents on the boron. When boron is bonded to specific transition-metal complexes, main group metals, and rare earth metals, the reactivity of the boryl moiety changes, showing a pronounced reactivity toward electrophilic centers of organic molecules. Hartwig and He described the synthesis of the first anionic boryl bound to iron carbonyl complexes [1]. These complexes reacted with MeI and MeOTf to yield methylcatecholborane in 30 and 60 % yield, respectively. Formally, this reaction involves addition of a boryl anion to an organic electrophile and is a rare example of the reactivity that would be characteristic of the catecholboryl anion (Scheme 1a).



Scheme 1 Formation of MeBcat* as a nucleophilic substitution of halide for a boryl group.

Sadighi and co-workers synthesized copper(I) boryl complexes modified with *N*-heterocyclic carbene (NHC) ligands and explored their reactivity toward CO_2 [2]. Complex (*IPr*)Cu(Bpin) abstracted oxygen from CO_2, resulting in the formation of (*IPr*)Cu(OBpin) and the release of CO as the byproduct (Scheme 2a). Subsequently Lin, Marder, and co-workers studied with the aid of density functional theory (DFT) the reaction mechanism in detail [3], and they found that the reaction occurs

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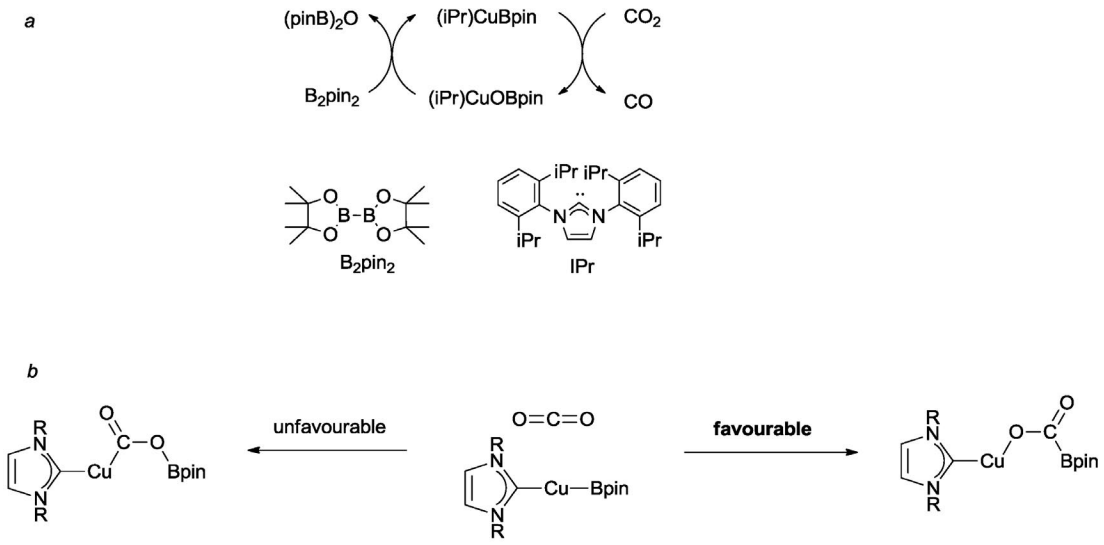


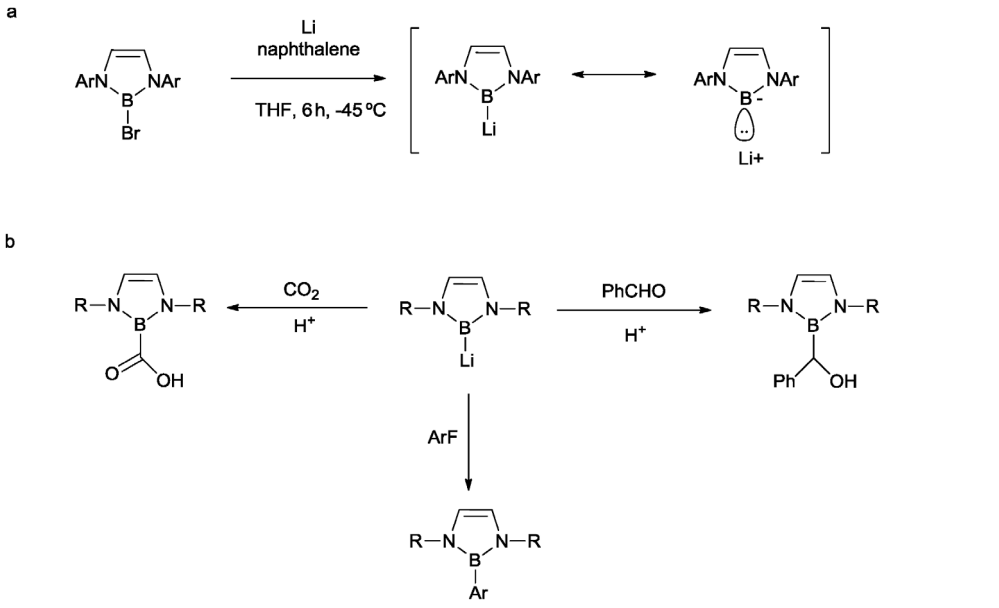
Scheme 2 (a) Catalytic reduction of CO_2 to CO with (IPr)CuBpin. (b) Favored insertion of CO_2 into Cu-Bpin linkage.

through CO_2 insertion into the Cu–B bond to give a Cu–OC(=O)-boryl species and subsequent boryl migration from C to O, followed by σ-bond metathesis between B_2pin_2 [bis(pinacolato)diboron] and (NHC)Cu(OBpin). Interestingly enough, they demonstrated that it is the nucleophilicity of the Cu–B bond rather than the oxophilicity of boron, that determines the direction of the CO_2 insertion process (Scheme 2b).

Alternatively, Schleyer, Nöth, and co-workers became interested in demonstrating, via both theoretical and experimental studies, that lithioboranes would serve as nucleophiles [4]. The same authors were inspired by an early observation where stannylated boranes were capable of reacting as nucleophiles with EtI (Scheme 3) [5]. The authors concluded that lithioboranes are moderately polar compounds, with a significant covalency in the Li–B bond. With the exception of the parent compound lithioborane, the boron atom remains positively charged and the partial negative charge of the boryl moiety is located on the boron substituents [4]. The potential nucleophilicity of these reagents was also demonstrated via addition reaction of lithioboranes to formaldehyde, which proceeded similarly to the addition of methyllithium [4].

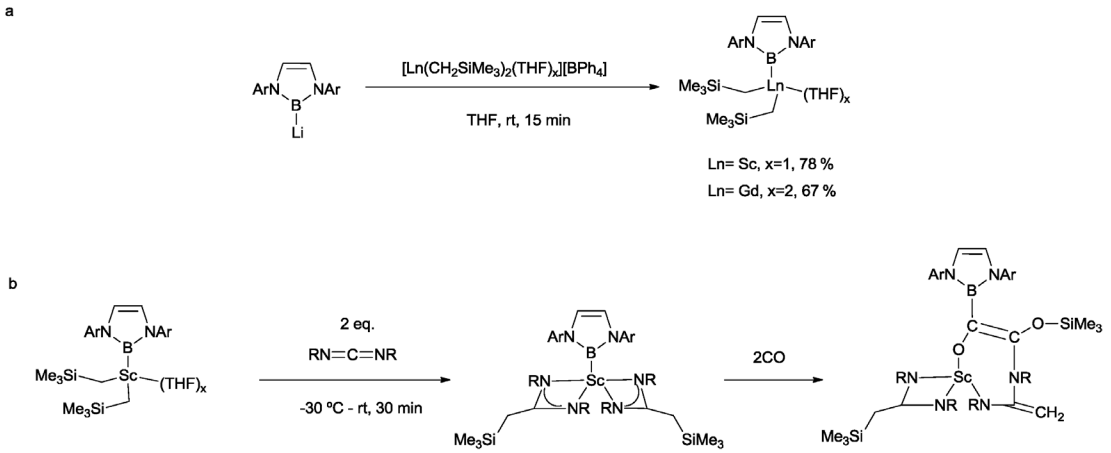
Scheme 3 Reactivity of stannylated boranes with alkyl halides.

The isolation and full characterization of a lithium salt of anionic boron moiety, (boryllithium), was first achieved by Segawa, Yamashita, and Nozaki. The application of a diamino-substituted boryl unit with bulky *N*-substituents guaranteed the stabilization of the negatively charged boron atom [6]. The synthetic route was also optimized with respect to the reduction of diaminohaloborane with Li (Scheme 4a). The B–Li bond of boryllithium can be drawn as a resonance between a covalent and an ionic bond, and the potential reactivity as nucleophile was well demonstrated via its reactions with different electrophiles (Scheme 4b) [7–9].



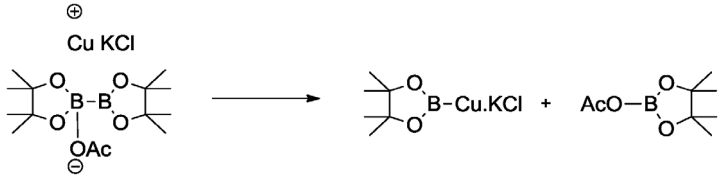
Scheme 4 (a) Synthesis of diaminoboryllithium. (b) Reactivity of diaminoboryllithium with a variety of electrophiles.

More recently, the synthesis of metal boryl complexes has been extended to include those in which boron is bonded to rare earth metals [10]. Toward this end, the authors treated diamidoboryllithium compounds described by Nozaki et al. [6] with rare earth metal alkyl ion-pair complex $[Ln(CH_2SiMe_3)_2(THF)_x][BPh_4]$, affording the corresponding boryl-ligated scandium and gadolinium dialkyl complexes (Scheme 5a) [10a]. Preliminary reactivity studies have shown that the Ln–B bonds can undergo insertion reactions with carbon monoxide to give a new B–C–O–Sc linkage (Scheme 5b). This reactivity resembles the insertion of CO_2 into Cu–B bond observed by Sadighi [2] and deeply studied by Lin and Marder [3], whereby the nucleophilicity of boron plays an important role in the insertion pathway.



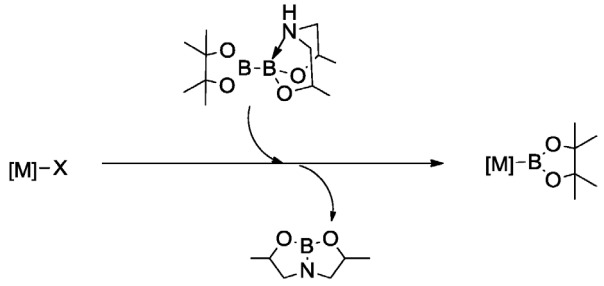
Scheme 5 (a) Synthesis of rare earth metal boryl dialkyl complexes. (b) Insertion reaction of CO into Sc–B bond.

In a new development, nucleophilic boron centers have been generated by the use of tetraalkoxydiboron reagents and a Lewis base that interacts with one of the boryl moieties, resulting in the formation of a Lewis acid–base adduct, where the formally intact sp^2 boryl unit becomes nucleophilic. An early inspiration of this type of interaction can be found in the first described transmetallation of Cu(I) salts with bis(pinacolato)diboron by Miyaura and co-workers (Scheme 6) [11], to generate copper-boryl species. They described that CuOAc·KCl could promote the heterolytic cleavage of the bis(pinacolato)diboron with the concomitant formation of two stable boryl species. Further studies on the reactivity of copper boryl complexes with activated olefins have pointed out the nucleophilic behavior of the boryl moiety [12] and lead to the elaboration of a great synthetic tool, namely, the copper-mediated β-boration of α,β-unsaturated carbonyl compounds [13].



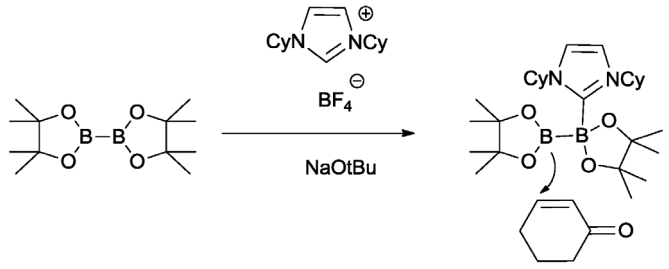
Scheme 6 First example of diboron activation with a base by Miyaura and co-workers.

Santos and co-workers have recently described an internally activated unsymmetrical diboron compound, named pinacolato diisopropanolaminato diboron (PDIPA diboron) (Scheme 7). This novel diboron with mixed sp^2-sp^3 hybridized boron atoms allows the transfer of pinacolboryl to copper, resulting in a facile transmetallation with CuCl systems to obtain Cu-Bpin moieties [14]. This is an interesting example of efficient intramolecular activation of diborons toward selective transfer of boryl units into organic molecules through Cu-mediated catalysis, particularly toward β-carbons of activated olefins [15].



Scheme 7 Chemoselective transfer of the pinacolate-protected sp^2-hybridized boron to CuCl.

In parallel work, Hoveyda and co-workers found that NHCs might associate with the Lewis acidic boron atoms of bis(pinacolato)diboron, and the resulting change of electron densities around the boron atoms could lead to the activation of the B–B bond, and reactions with an appropriate electrophilic site (Scheme 8) [16]. Thus, the transfer of Bpin from the adduct NHC-B_2pin_2 to cyclic and non-cyclic enones was efficiently performed, and constitutes the first example of a β-boration reaction conducted under transition metal-free conditions.



Scheme 8 Activation of bis(pinacolato)diboron with NHCs and interaction with enone.

With all these precedents in mind, our group sought a new methodology for the facile activation of diboron reagents to enhance the nucleophilic character of one of the boryl moieties, so that it can easily be transferred to electrophilic sites in organic molecules. We focused our preliminary studies on the nature of the activating agent, and we selected the simplest system based on Brønsted bases and alcohols.

ACTIVATION OF DIBORON REAGENTS WITH BRØNSTED BASES AND ALCOHOLS

Bis(pinacolato)diboron undergoes an important reorganization of the charges upon the interaction with MeO^-, generated from MeOH and bases. The B–B bond becomes considerably polarized toward the sp^2 boryl unit, because the sp^3 boron atom seems to lose negative charge density upon the charge transfer from the Lewis base, while the sp^2 boron atom unambiguously gains electron density with respect to its partial charge in the intact bis(pinacolato)diboron. The loss of electron density on the sp^3 boron atom, despite the direct charge transfer from the Lewis base, can be rationalized considering the fact that upon rehybridization the boron atom loses the π-symmetric electron donation from the oxygen atoms of the pinacolate moiety (Fig. 1). From a structural point of view, the B–B bond is elongated upon interaction with MeO^-, (from 1.701 Å in B_2pin_2 to 1.754 Å in $B_2pin_2 \cdot MeO^-$).

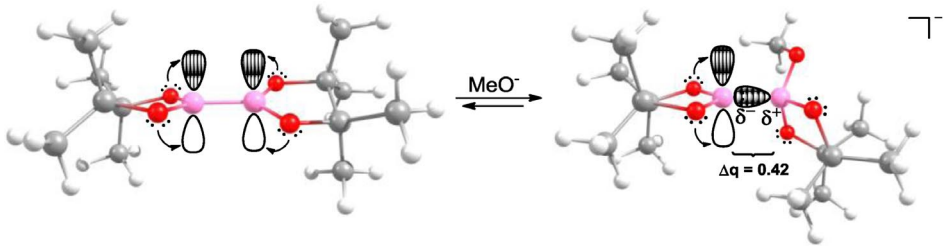
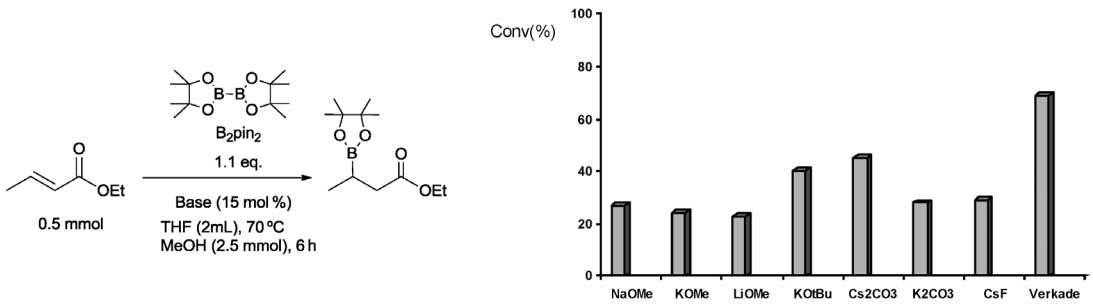


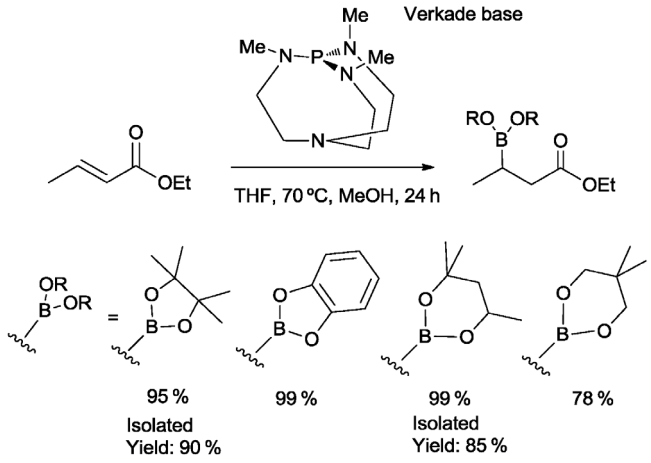
Fig. 1 Polarization of the B–B bond upon the formation of the Lewis acid-base adduct. Δq = difference between the Mulliken charges of the boron atoms of the adduct.

To demonstrate that the sp^2 boron atom gains a nucleophilic character in the Lewis-acid adduct, we intended to convert ethyl crotonate as a model substrate into the β-borated product in the presence of 10 % NaO^{t}Bu (Scheme 9), however, the observed converson was only 2 % at room temperature and 9 % at 70 °C. The sole addition of MeOH to the system facilitated the β-boration reaction up to 33 % conversion of ethyl crotonate, highlighting the importance of the alcohol to make the reaction catalytic. Alternative inorganic and organic bases were explored, such as NaO^{t}Bu, Cs_2CO_3, and Verkade's base, the latter being the most efficient.



Scheme 9 Brønsted base-methanol assisted the activation of B_2pin_2 and promoted the β-boration of ethyl crotonate.

The reaction of the bis(pinacolato)diboron with ethyl crotonate was complete within 24 h using Verkade base/methanol as catalytic system. The methodology could be applied to other diboron reagents such as bis(catecholato)borane (B_2cat_2), bis(hexyleneglycolato)diboron (B_2hex_2), and bis(neopentylglycolato)diboron (B_2neop_2) (Scheme 10).



Scheme 10 Verkade base/MeOH mediates the β-boration of ethyl crotonate with different diboron reagents.

To generalize the catalytic activation of bis(pinacolato)diboron with Verkade base/MeOH and the transfer of the pinacolboryl unit to the β-carbon of unsaturated conjugated substrates, we selected a series of activated olefins, with diverse structural features. α,β-Unsaturated esters, open-chain and cyclic α,β-unsaturated ketones were quantitatively β-borated (Fig. 2). The analogous α,β-unsaturated amide and phosphonate were also efficiently converted into the desired β-borated products.

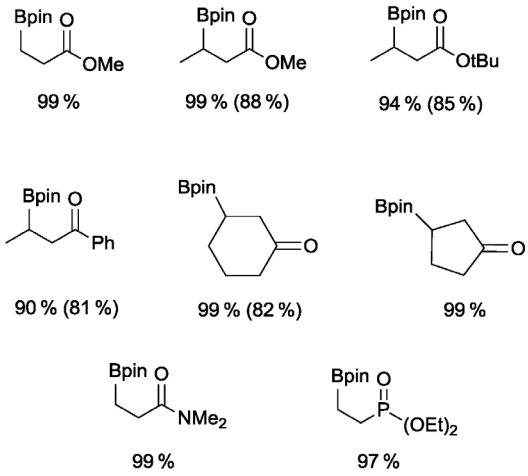
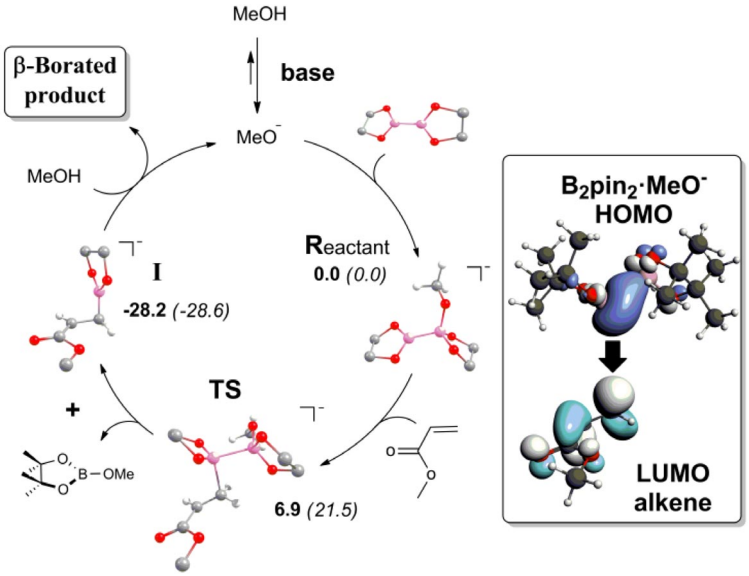


Fig. 2 Representative products arising from Verkade base/MeOH mediated β-boration of α,β-unsaturated ketones, esters, amides, and phosphonates.

To obtain a deeper insight into the reaction and postulate a plausible mechanism, the structures and stabilities of possible adducts formed within the alkene/diboron/alcohol/base system were investigated both computationally and experimentally. The molecular peak of the $B_2pin_2{\cdot}MeO^-$ adduct, *m*/*z* 285.1, was detected in an electrospray ionization-mass spectrometry (ESI-MS) experiment. In a theoretical study at the BP86 level, the electronic energies and Gibbs free energies (in parenthesis) have been computed for all the plausible intermediates in the β-boration reaction pathway, relative to the $B_2pin_2{\cdot}MeO^-$ adduct plus methyl acrylate (Scheme 11). A transition state (TS) was fully characterized and corresponded to the nucleophilic attack of the sp^2 boron moiety at the β-carbon of the methyl acrylate substrate. This interaction was identified as the overlap between the strongly polarized σ B–B bond (HOMO) of the activated diboron reagent and the antibonding π* orbital (LUMO) of the alkene. The



Scheme 11 Plausible mechanism for the organocatalytic β-boration of methyl acrylate.

TS structure releases the "(pin)B-OMe" by-product and directly leads to the formation of the anionic **I** intermediate, which will be further protonated in the presence of the excess of MeOH to provide the β-boration product, and to generate another MeO^- ion [18].

Next, we became interested in inducing asymmetry during the C–B bond formation through the organocatalytic β-boration reaction. The transition metal-catalyzed asymmetric β-boration of activated olefins has been addressed with great success since the first attempt by Yun and co-workers in 2006 [19a], using copper catalytic systems modified with chiral phosphines [13]. Our approach turned to phosphines as additives, and we found an early example by Hosomi and co-workers [19b], whereby it was shown that PBu_3 could induce a slight conversion of benzylideneacetophenone into the β-borated ketone, when the CuOTf precursor was not present in the reaction mixture [20]. We first optimized the reaction conditions using ethyl crotonate as a model substrate, B_2pin_2 as the boron source, and PPh_3 as the most common achiral phosphine as additive. The reactions were carried out in tetrahydrofuran (THF), at 70 °C external temperature. Conversions were moderate with 4 and 10 mol % of phosphine loading (54 and 63 % of conversion, respectively) in the presence of Cs_2CO_3 as base and MeOH. Almost complete conversion could be achieved at 20 % of PPh_3 loading. The substrate scope was then investigated under optimized reaction conditions using PPh_3 as additive (Fig. 3). The α,β-unsaturated esters showed a certain trend in the structure–reactivity relationship. Higher conversions were observed when the ester moieties represented lower steric hindrance. The α,β-unsaturated ketones were less sensitive to structural changes as they could all be converted readily with PPh_3/Cs_2CO_3/MeOH into the corresponding organoboranes.

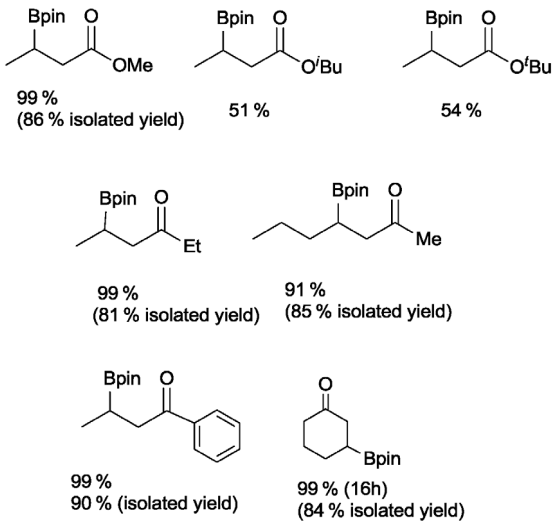


Fig. 3 Representative products arising from the organocatalytic β-boration of α,β-unsaturated esters and ketones with phosphine (4 mol %), Cs_2CO_3 (15 mol %), MeOH (2.5 mmol), THF, 70 °C, 6 h (if not indicated otherwise).

The beneficial effect of phosphine additives on the activity was clearly notable, thus next we focused our efforts on obtaining asymmetric induction in the model reaction. Chiral monophosphorus compounds as well as diphosphines were explored as catalysts, at 4 mol % loading, in the β-boration of ethyl crotonate. As can be seen in Fig. 4, the fairly basic (+)-neomenthyldiphenylphosphine provided good conversion but no asymmetric induction, however, chiral monodentate phosphoramidite ligands induced, to our delight, a certain degree of enantioselectivity (up to 35 % e.e.). Bidentate ligands *R*-3,5-Bu-4-MeO-MeOBIPHEP and *R*-binap were tested in the model reaction but only *R*-binap provided complete conversion, with 77 % e.e. Next we focused our efforts on exploring chiral ferrocenyl

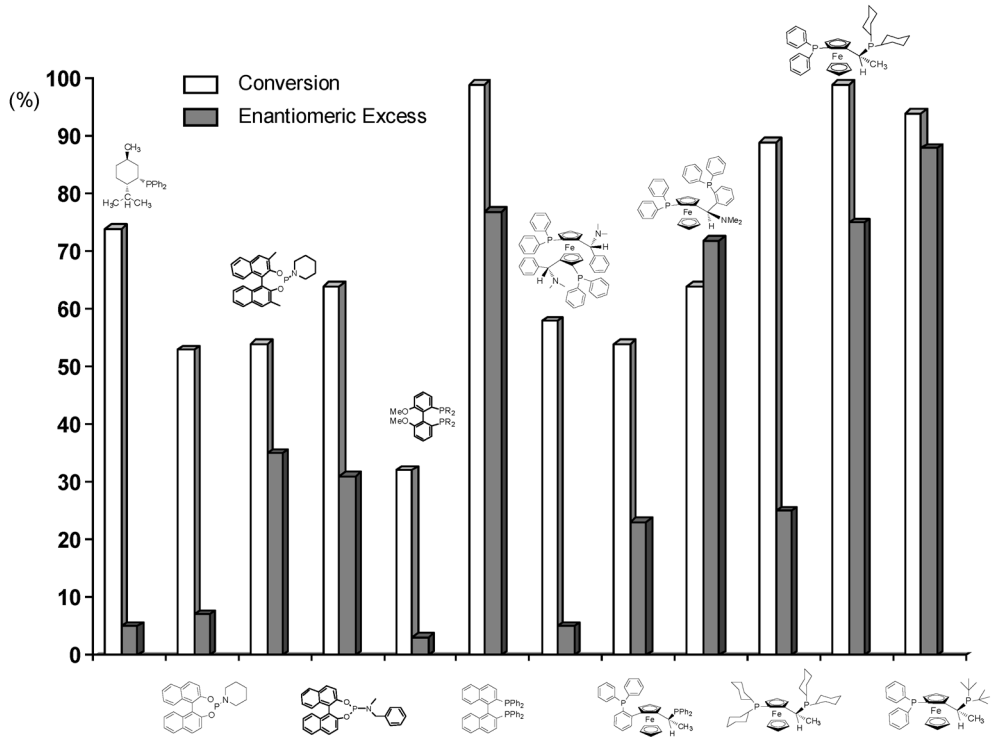


Fig. 4 Chiral phosphine (4 mol %) assisted the asymmetric β-boration of ethyl crotonate with different diboron reagents, Cs_2CO_3 base (15 mol %), MeOH (2.5 mmol) at 70 °C within 6 h.

diphosphines, which usually provide excellent enantioselectivities in copper-based catalytic systems. We found that when *R*,*S*-NMe_2-PPh_2-mandyphos, *R*,*R*-walphos-type, and *R*,*S*-taniaphos-type were used in the β-boration of ethyl crotonate, comparable activities were observed within 6 h, but only the taniaphos-type phosphine induced notable stereoselectivity (e.e. 72 %). Interestingly, *R*,*S*-josiphos-type ligands all provided much higher activities, but the asymmetric induction was very sensitive to the structure of the substituents of the phosphorus donor atoms. Under the applied conditions, the josiphos-type diphosphine with PPh_2 and $P(^tBu)_2$ units was capable of inducing enantioselectivities up to 88 %. Interestingly, upon applying smaller amount of base, the e.e. increased to 93 %, although 24 h reaction time was required for quantitative conversion. We selected the best performing phosphines, *R*-binap and the *R*,*S*-josiphos-type with ^{t}Bu substituents on P, to study the substrate scope of the asymmetric β-boration of α,β-unsaturated carbonyl compounds (Fig. 5), under optimized reaction conditions [phosphine (4 mol %), Cs_2CO_3 (15 mol %), MeOH (2.5 mmol), THF, 70 °C, 6 h]. In general, the enantioselectivities were comparable to the values we had observed for the model substrate. The organocatalysts were also very active for the transformation of α,β-unsaturated ketones, acyclic and cyclic, and we were pleased to see that the josiphos-type phosphine additive, combined with base and MeOH, β-borated hept-3-en-2-one with 95 % enantioselectivity [20].

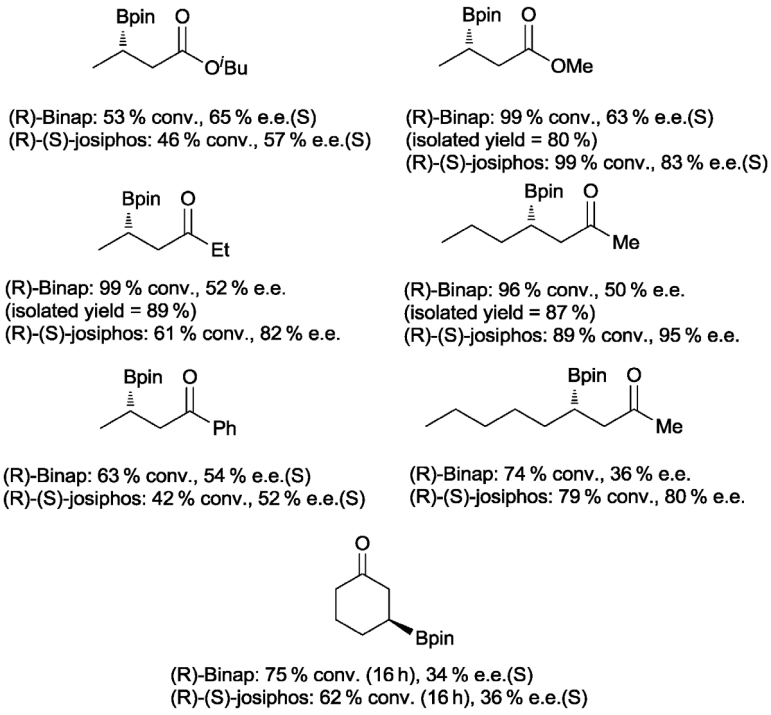
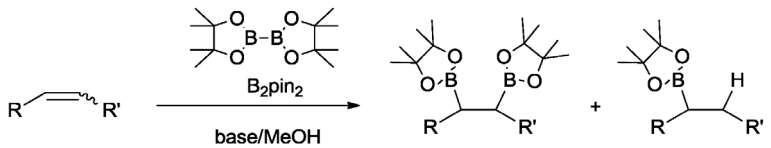


Fig. 5 Representative products arising from the organocatalytic β-boration of α,β-unsaturated esters and ketones with Cs_2CO_3 (15 mol %)/MeOH (2.5 mmol)/PPh_3 (4 mol %), at 70 °C within 6 h.

More recently, we have discovered that the in situ formed adducts $B_2pin_2 \cdot MeO^-$ can promote the nucleophilic attack on non-activated olefins [21]. Most importantly, although the reaction conditions are very similar to those we use for conjugate boron additions to activated olefins, the chemoselectivity is different. Despite the presence of the protic additive, usually MeOH, the electrophilic counterpart of the nucleophilic boryl unit also derives from the activated diboron reagent, resulting in the first example of Lewis-base-catalyzed diboration of alkenes (Scheme 12). This new approach involves at least three important points to be highlighted: (1) The product is formed via a reaction between a nucleophilic reagent and a substrate that also has a pronounced nucleophilic character, (2) both boryl units of the reagent are introduced to the substrate, resulting in an atom-economic addition reaction of great practical importance, and (3) to date, the only method to add tetralkoxydiborons to non-activated alkenes has been known to be the application of transition-metal complexes as catalysts.



Scheme 12 Nucleophilic diboration of non-activated olefins with diboron reagent, mediated with base/MeOH as catalyst.

A small library of substrates with carefully defined structural features was selected to study the scope and mechanism of this novel organocatalytic diboration reaction. The diboration of styrene

required milder reaction conditions than that of the aliphatic alkenes to obtain high selectivity (Fig. 6). The diboration of internal alkenes provided crucial information on the mechanism of the reaction. Unlike many of the classic electrophilic additions such as halogenation of alkenes, the nucleophilic diboration of non-activated olefins always occurs in *syn*-fashion. Thus, diboration of *trans*-hex-2-ene gives the diborated product in a 3:97 syn:anti ratio, while *cis*-hex-2-ene forms the corresponding diborated product in 95:5 syn:anti ratio. Similarly, the diboration of cyclohexene exclusively gives the cis diborated product. Another interesting finding is that nucleophilic diboration of allenes favors the formation of the 1,2-diborated product. This is in contrast to most transition-metal-catalyzed diborations of allenes, which usually provide the 2,3-diborated isomers as primary products [22–24].

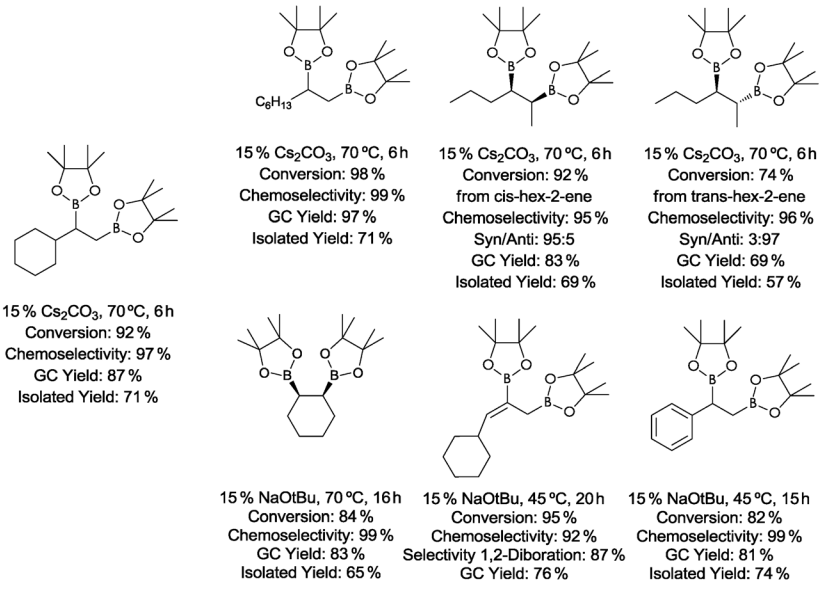
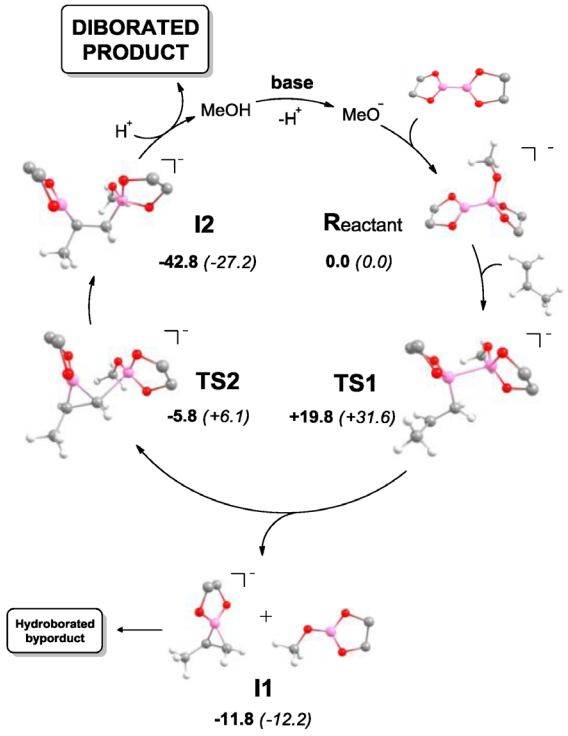


Fig. 6 Representative products arising from the organocatalytic diboration of alkenes and allenes with NaO^tBu or Cs_2CO_3 (15 mol %) and MeOH (2.5 mmol).

We have envisioned a mechanism for the organocatalytic diboration of olefins in which the methoxide anion, generated in situ from MeOH with catalytic amount of base, activates the diboron reagent forming the adduct $B_2pin_2 \cdot MeO^-$. A similar adduct formed from B_2pin_2 and KO^tBu has been previously reported by Marder and co-workers [25]. In order to find evidence for the subsequent steps of the catalytic cycle, we have studied the possible interactions between a model substrate, propylene, and the $MeO^- \rightarrow$ bis(pinacolato)diboron adduct using a variety of DFT methods. It has been possible to identify two TSs that can explain the formation of the diborated product and the "hydroborated" by-product (Scheme 13). In TS1, the sp^2 boron atom of the activated diboron reagent interacts with the non-substituted carbon atom (C_1) of the C=C double bond, while the B–B bond weakens, and the negative charge density on the C_2 (substituted carbon) increases. Importantly, we have found that the interaction leading to TS1 is the overlap between the strongly polarized B–B σ-bond (HOMO) of the activated diboron reagent and the antibonding π* orbital (LUMO) of the olefin. Hence, the reactivity between the reaction partners clearly is a nucleophilic attack of the reagent toward the substrate. The increased negative charge density on C_2 in TS1 results in a considerable kinetic lability, owing to the positive inductive effect of the alkyl substitutent. The negatively charged C_2 should be prone to attack any electrophilic site, and the closest one in TS1 is the attacking boron atom, which is losing the B–B



Scheme 13 Plausible mechanism of the organocatalytic diboration of propylene. Electronic energy (kcal mol^{-1}) and Gibbs free energy (kcal mol^{-1}) (in parenthesis) computed at the M06 level, relative to $B_2pin_2 \cdot MeO^-$ adduct plus propylene. Methyl groups of B_2pin_2 are omitted for clarity.

bond owing to the nucleophilic attack. The distribution of the negative charge density among C_1, C_2 and the boron atom, might explain the connection between TS1 and the intermediate I1, as well as the formation of the second transition state structure, TS2. Protonation of the intermediate I1 gives the "hydroborated" by-product.

In summary, we have reported a new methodology to activate diborons with simple Brønsted bases and alcohols to promote the nucleophilic character on the unaltered boryl unit. The heterolytic cleavage of the diboron and the consequent reactivity of nucleophilic boryl synthons have been demonstrated in the β-boration reaction of activated olefins and in the diboration reaction of non-activated olefins. In the organocatalytic β-boration reactions, it has been possible to increase activity and to induce asymmetry with catalytic amounts of chiral phosphines as additives. These examples constitute an unprecedented approach to activate tetraalkoxydiborons and apply them as reagents in organic synthesis. It is particularly interesting that although the reactivity arises from a strong nucleophilic character generated in the diboron reagents, it is apparently not limited to reactions with the classic organic electrophiles [26].

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REFERENCES

1. X. He, J. F. Hartwig. *Organometallics* **15**, 400 (1996).
2. D. S. Laitar, P. Müller, J. P. Sadighi. *J. Am. Chem. Soc*. **127**, 17196 (2005).
3. H. T. Zhao, Z. Lin, T. B. Marder. *J. Am. Chem. Soc*. **128**, 15637 (2006).
4. M. Wagner, N. J. R. v. E. Hommes, H. Nöth, P. v. R. Schleyer. *Inorg. Chem*. **34**, 607 (1995).
5. M. Wagner. Ph.D. Thesis (Doktorarbeit), Universitat Miinchen (1992).
6. (a) Y. Segawa, M. Yamashita, K. Nozaki. *Science* **314**, 113 (2006); (b) T. B. Marder. *Science* **314**, 64 (2006).
7. T. Kajiwara, T. Terabayashi, M. Yamashita, K. Nozaki. *Angew. Chem., Int. Ed*. **47**, 6606 (2008).
8. Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki. *J. Am. Chem. Soc*. **130**, 16069 (2008).
9. M. Yamashita, K. Nozaki. *Bull. Chem. Soc. Jpn*. **81**, 1377 (2008).
10. (a) S. Li, J. Cheng, Y. Chen, M. Nishiura, Z. Hou. *Angew. Chem., Int. Ed*. **50**, 6360 (2011); (b) L. M. A. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, P. Mountford. *J. Am. Chem. Soc*. **133**, 3836 (2011).
11. K. Takahashi, T. Isiyama, N. Miyaura. *J. Organomet. Chem*. **625**, 47 (2001).
12. (a) L. Dang, Z. Lin, T. B. Marder. *Organometallics* **27**, 4443 (2008); (b) L. Dang, H. Zhao, Z. Lin, T. B. Marder. *Organometallics* **27**, 1178 (2008).
13. For general reviews, see: (a) J. A. Schiffner, K. Müther, M. Oestreich. *Angew. Chem., Int. Ed*. **49**, 1194 (2010); (b) E. Hartmann, D. J. Vyas, M. Oestreich. *Chem. Commun*. **47**, 7917 (2011); (c) V. Lillo, A. Bonet, E. Fernández. *Dalton Trans*. 2899 (2009).
14. M. Gao, S. B. Thorpe, W. L. Santos. *Org. Lett*. **11**, 3478 (2009).
15. (a) M. Gao, S. B. Thorpe, Ch. Kleeberg, C. Slebodnick, T. B. Marder, W. L. Santos. *J. Org. Chem*. **76**, 3997 (2011); (b) S. B. Thorpe, X. Guo, W. L. Santos. *Chem. Commun*. 424 (2011).
16. (a) K. Lee, A. R. Zhugralin, A. H. Hoveyda. *J. Am. Chem. Soc*. **131**, 7253 (2009); (b) K. Lee, A. R. Zhugralin, A. H. Hoveyda. *J. Am. Chem. Soc*. Additions & Corrections, **132**, 12766 (2010).
17. For more examples of similar boron systems, see: (a) P. Nguyen, C. Daí, N. J. Taylor, N. P. Power, T. B. Marder. *Inorg. Chem*. **34**, 4290 (1995); (b) W. Clegg, C. Dai, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, N. L. Pickett, W. P. Power, A. J. Scott. *J. Chem. Soc. Dalton Trans*. 839 (1997).
18. C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyás, E. Fernández. *Chem.—Eur. J.* **18**, 1121 (2012).
19. (a) S. Mun, J.-E. Lee, J. Yun. *Org. Lett*. **8**, 4887 (2006); (b) H. Ito, H. Yamanaka, J. Tateiwa, A. Hosomi. *Tetrahedron Lett*. **41**, 6821 (2000).
20. A. Bonet, H. Gulyás, E. Fernández. *Angew. Chem., Int Ed.* **49**, 5130 (2010).
21. A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás, E. Fernández. *Angew. Chem., Int. Ed*. **50**, 7518 (2011).
22. F. Yu, Ch.-H. Cheng. *J. Am. Chem. Soc*. **123**, 761 (2001).
23. N. F. Pelz, A. R. Woodward, H. E. Burks, J. D. Sieber, J. P. Morken. *J. Am. Chem. Soc*. **126**, 16328 (2004).
24. A. R. Woodward, H. E. Burks, L. M. Chan, J. P. Morken. *Org. Lett*. **7**, 5505 (2005).
25. (a) C. Kleeberg, L. Dang, Z. Lin, T. B. Marder. *Angew. Chem., Int. Ed*. **48**, 5350 (2009); (b) T. B. Marder. Lecture at Euroboron 5, Edinburgh 2010; (c) C. Kleeberg. Lecture at Imeboron XIV, Niagara 2011.
26. J. Cid, H. Gulyás, J. J. Carbó, E. Fernández. *Chem. Soc. Rev.* **41**, 3558 (2012).

