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## Transition-metal-free diboration of non-activated olefins: A reaction mechanism revisited

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### ABSTRACT

Density functional theory (M06-2X/6-31+G\*) calculations were used to examine a mechanism (B<sub>2</sub>(1,1)) proposed by Fernández et al. (2011) that tries to rationalize the high SYN-stereoselectivity observed in their discovered transition-metal-free diboration of non-activated olefins. The results show that B<sub>2</sub>(1,1) incorrectly predicts ANTI-addition of bulky diboron esters, however correctly predicts less bulky and catecholic diboron esters. Alternative mechanisms (B<sub>2</sub>'(1,1), B<sub>2</sub>(1,2), and B<sub>3</sub>), which help rationalize the stereochemistry of all studied diboron esters were examined.

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### 1. Introduction

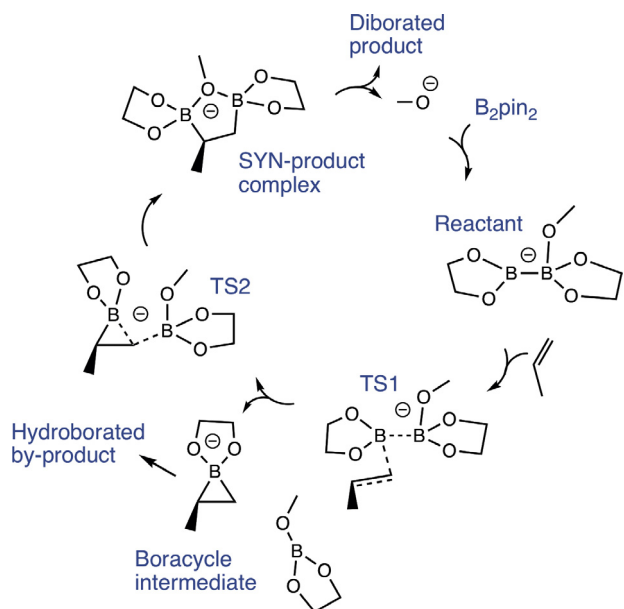
Since its discovery [1] in 1925 diboron compounds have become highly versatile compounds in synthetic chemistry [2]. A diverse set of diboron compounds in terms of structure and reactivity [3–5] are now available and used in various transition-metal catalyzed diborations of activated and non-activated olefins [6]. Inducing boron-centered nucleophilicity, necessary for the borylation reaction, was until recently a major hurdle, but with the realization that Lewis bases can promote this nucleophilicity by forming reactive sp<sup>2</sup>-sp<sup>3</sup> diborane-Lewis base complexes has simplified the chemical procedures and increased the synthetic applicability [7–10]. One example of such a sp<sup>2</sup>-sp<sup>3</sup> diborane-Lewis base complex was discovered by Hoveyda et al. where the formation of a *N*-heterocyclic carbene (NHC [11–12])-B<sub>2</sub>pin<sub>2</sub> complex engages in transition metal-free catalytic conjugate addition to acyclic or cyclic α,β-unsaturated carbonyls [13]. The NHC-B<sub>2</sub>pin<sub>2</sub> complex was later fully characterized by Marder et al. using X-ray crystallography, <sup>11</sup>B NMR and DFT-calculations [14]. A few years ago Fernández et al. presented an intriguing chemical transformation in which non-activated olefins are readily diborated by diboron esters in the absence of transition metals [15–17]. The reaction requires base, such as alkoxide or carbonate, and a small amount of methanol. It runs at 70 °C for 6 h in THF and results in high yield and is highly SYN-stereoselective. According to calculations done by them one of the sp<sup>2</sup>-hybridized boron centra of bis

(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) becomes nucleophilic when the reagent coordinates a methoxy anion [15]. Their calculations show that electron density shifts from the sp<sup>3</sup>-hybridized boron center, which coordinates the methoxide anion, towards the sp<sup>2</sup>-hybridized boron center, rendering it nucleophilic. A reaction mechanism (here denoted B<sub>2</sub>(1,1)) was suggested by them to rationalize the stereoselectivity, see Scheme 1. The diboronic ester, coordinating a methoxide anion (B<sub>2</sub>pin<sub>2</sub>(OMe<sup>-</sup>)) and a non-interacting olefin (propene) serve as the ground state of the reaction (Reactant in Scheme 1). B<sub>2</sub>pin<sub>2</sub>(OMe<sup>-</sup>) then reacts with propene forming an activated complex (TS1, Scheme 1) in which the B-B bond breaks and two C-B bonds form in an asynchronous and concerted process, which results in SYN-addition. Inspired by their work we decided to take a closer look at the reaction involving several of the experimentally examined diboron esters (see Fig. 1) using density functional theory (DFT) and *ab initio* methodology.

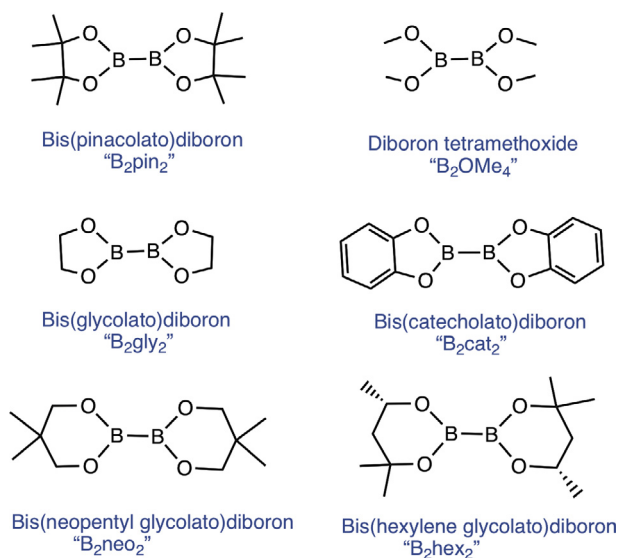
### 2. Results and discussion

The first part of this study involved computations on the B<sub>2</sub>(1,1)-mechanism, which aim was to, as closely as possible, reproduce the computations carried out by Fernández et al. They reported a Gibbs free energy of activation of 31.6 kcal/mol relative propene and a B<sub>2</sub>pin<sub>2</sub>(OMe<sup>-</sup>) anion in vacuum using different density functionals for geometry optimizations and energy computations [15]. We used the M06/TZVP method and got a similar value of 36.1 kcal/mol. However, when we repeated the calculations in THF-solvent the

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**Scheme 1.**  $B_2(1,1)$ -reaction mechanism proposed by Fernández et al. [15] Methyl groups of the pinacolato groups have been removed to improve clarity.



**Fig. 1.** Diboron ester substrates examined in this study.

activation barrier increased to 41.1 kcal/mol. According to transition state theory a Gibbs free energy of activation of 27 kcal/mol at 70 °C results in a half-life  $\tau = 4.2$  h for a 1st order kinetics reaction using the Eyring equation, which can be used as qualitative measure of the rate of their diboration reaction. Consequently, the activation barrier computed using computational methodology 1 (see Section 4) would result in a very slow reaction. By using intrinsic reaction coordinate (IRC) calculations we then monitored the collapse of the transition state TS1 on the potential energy surface (PES) leading to a solvent separated negatively charged boracycle intermediate and a Bpin(OMe) boronic ester (see Scheme 1). They suggest this boracycle intermediate is not part of the reaction coordinate towards the diborated product, however it is instead part of a competing hydroboration pathway [18]. They speculated that the reacting species, after passing TS1, channel through a valley-ridge inflection point, where the curvature of the PES changes from

concave to convex<sup>a</sup>, which then splits into a bifurcation forming either the SYN-product complex via TS2 (Scheme 1) or the boracycle leading to a hydroborated by-product [19]. However, our IRC-calculations leave no doubt that the reaction is non-concerted forming the boracycle intermediate as a minimum on the PES flanked by TS1 and TS2 (see Scheme 1). By using the separated boracycle intermediate and Bpin(OMe) two transition states (TS<sub>SYN</sub> and TS<sub>ANTI</sub>) were constructed and geometry optimized: one leading to SYN-addition and the other one to ANTI-addition (see Scheme 2 and Fig. 2).

The intrinsic activation energy of forming the ANTI-isomer is 26.5 kcal/mol, whereas that of the SYN-isomer is 29.1 kcal/mol (Scheme 2). Thus, if the reaction were under kinetic control the computations predict the ANTI-stereoisomer to be the major product, which contradicts experimental data [15]. The collapse of the transition states leads to SYN- and ANTI-product complexes. The formation of the ANTI-product complex is exergonic by –22.0 kcal/mol and that of forming the SYN-product complex is exergonic by –20.8 kcal/mol (Scheme 2). Consequently, thermodynamic control of the SYN/ANTI-addition process is also ruled out. The results of these calculations do not support their experimental data. The base promoted mechanism of  $B_2pin_2$  using NaOtBu/MeOH to generate a methoxide anion, that binds to one of the boron centra, has experimental support [20] and, hence, it seems a good starting point for deriving a mechanism describing the diboration reaction. There are several factors which affect the results of the computations and their comparison with experimental data, such as: choice of mechanism and model system, level of theory used, and how solvation and free energy computations are carried out. We decided to continue this investigation by studying these factors using the  $B_2(OMe)_5$  diboron complex, which is attractive because of its small size when carrying out time-demanding electron-correlated *ab initio* calculations. Diboron compounds are known to undergo both heterolytic and homolytic bond fission in certain chemical reactions [17,21]. Thus, we first investigated whether the B-B bond of the  $B_2(OMe)_5$  diboron complex is more prone to undergo hetero- or homolytic bond fission when reacting with propene. In the heterolytic bond fission a boryl  $B(OMe)_2^-$  anion and  $B(OMe)_3$  boronic ester would form and in the homolytic bond fission a neutral boryl  $B(OMe)_2$  radical and a  $B(OMe)_3$  radical anion would form. We geometry optimized these structures using restricted and unrestricted Møller-Plessett second-order perturbation theory (MP2) and DFT utilizing the 6-31+G\* basis set and the M06-2X density functional. We also studied the relative stability of these two pathways when reacting with propene forming either an anionic boracycle (heterolytic B-B bond cleavage) or a neutral boracycle radical (homolytic B-B bond cleavage). The results of both the MP2/6-31+G\* and M06-2X/6-31+G\* calculations predict heterolytic B-B bond fission of the  $B_2(OMe)_5$  complex to be the preferred pathway (see Table 1) in the gasphase and in THF-solution. The computed heat of reaction energies also demonstrate that the heterolytic pathway is favored when the  $B_2(OMe)_5$  diboron complex reacts with propene.

There are examples in the literature where both boron centra coordinate a charge neutral Lewis base and the B-B bond breaks homolytically [21]. We decided to investigate such a homolytic B-B bond fission process of the  $B_2(OMe)_5^{2-}$  dianion forming two  $B(OCH_3)_3^-$  radical anions. The reaction is, according to both the MP2- and DFT-results, strongly exothermic in the gas phase ( $\Delta H_{BDE} = -47.4$  (MP2/6-31+G\*) and  $\Delta H_{BDE} = -33.7$  (M06-2X/6-31+G\*)) kcal/mol, which is likely due to relief of Coulomb repulsion

<sup>a</sup> This point is characterized by a Hessian matrix having one zero-valued eigenvalue. A minimum on the potential energy surface, on the other hand, is characterized by a Hessian matrix having all positively valued eigenvalues. The Hessian of a 1st order saddle-point (transition state) has all its eigenvalues positively valued but one which is negatively valued.

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