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Rhodium–NHC complexes mediate diboration *versus* dehydrogenative borylation of cyclic olefins: a theoretical explanation†

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In rhodium catalysed borylation of cyclic olefins, the synergy between bidentate NHC ligands, that modify cationic Rh(I) species, and the use of non-polar solvents, such as cyclohexane, is the key factor to favour a less energetically demanding route towards the formation of diborated products *versus* allyl boronate esters.

Introduction

Dehydrogenative borylation of olefins, in which a vinylic C–H bond is replaced with a C–B bond, is an efficient approach towards the synthesis of the useful vinyl boronate esters.[1] However, the extension of this methodology to cyclic olefins has been much less explored and can be classified by the nature of the reagent (HBpin or B_2pin_2) or the transition metal complex involved in the activation of the borane reagent. Scheme 1 summarizes the limited examples of cyclic olefins that underwent dehydrogenative borylation, illustrating the reaction conditions and the selectivity of the reaction products. When Sabo-Etienne and co-workers activated pinacolborane by means of $RuH_2(H_2)_2(PCy_3)_2$,[2] the hydroboration of cyclohexene seemed to be highly favored, whereas for cyclodecene, vinylboronate was produced with only traces of allylboronate. Cyclooctene provided the vinyl- and allylboronate in a 1 : 3 ratio, whereas only allylboronate was obtained from cycloheptene (Scheme 1a). Szabó and co-workers were the first to use B_2pin_2 in the dehydrogenative borylation of cyclic olefins and towards the activation of the diboron reagent, the iridium precursor $[Ir(\mu\text{-}Cl)(COD)]_2$ was selected.[3] Heating at 70 °C, cyclohexene gave a 1 : 1 ratio of allylic and vinylic borylation products while addition of 0.5 equiv. of 1,8-diazabicyclo[5.4.0]-undecane (DBU) led to an increase in the ratio of allylic to vinylic products although the proportion of the vinylic product increased with prolonged heating (Scheme 1b). Miyaura and co-workers further reported the borylation of vinyl C–H bonds in cyclic vinyl ethers by B_2pin_2 catalyzed by $[Ir(\mu\text{-}OMe)(COD)]_2$ and dtbpy.[4] Borylation of 1,4-dioxene with 0.5 equiv. of B_2pin_2 provided the vinylboronate ester product in 81% yield. Substrates containing substituents at the γ-position in dihydropyrans reacted with higher regioselectivity where borylation occurred solely at the α-position (Scheme 1c). In subsequent work, Marder and co-workers explored the dehydrogenative borylation catalysed by *trans*-$[RhCl(CO)(PPh_3)_2]$ and the borylation of indene with B_2pin_2.[5] They observed the selective formation of the vinylboronate ester with borylation occurring at the 2-position, however only 19% conversion was achieved after 6 days at 80 °C (Scheme 1d).[5] Finally, Jamison and co-workers reported the benefits of xantphos on the rhodium precursor $[Rh(\mu\text{-}Cl)(COD)]_2$ towards the dehydrogenative borylation of cyclic alkenes with B_2pin_2, forming the corresponding cyclic 1-alkenylboronic acid pinacol esters (Scheme 1e).[6]

We were surprised by the fact that in all the examples where B_2pin_2 was the boron reagent used, the 1,2-diborated product was not observed, even in the presence of rhodium complexes modified with phosphines.[7] We also noticed that apart from phosphines and amines,[8] no other ligands have been studied to modify the catalytic systems in order to promote the dehydrogenative borylation reactions. In that context, we planned to focus our efforts on exploring the catalytic activity of rhodium complexes modified with *N*-heterocyclic carbenes (NHC), towards the borylation of cyclic olefins in the presence of B_2pin_2. But also, in view of the lack of detailed studies concerning the mechanism of rhodium-mediated borylation of cyclic alkenes, we became interested to rationalise the experimental data with theoretical data and propose a plausible mechanism based on the reaction energy profile. We selected cyclohexene as the model substrate to undergo the borylation

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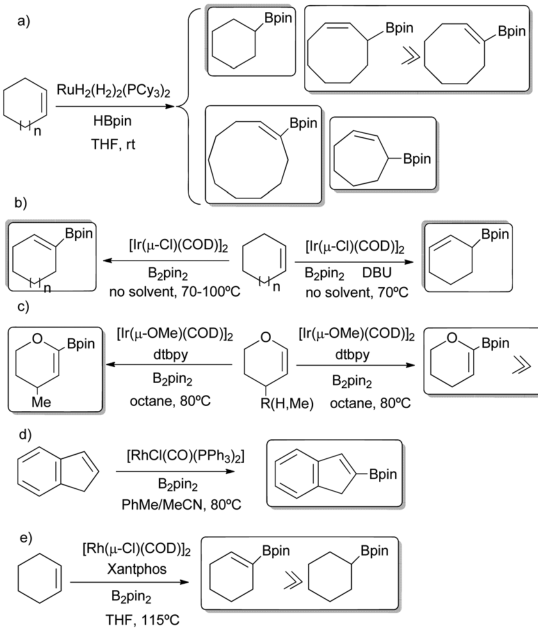
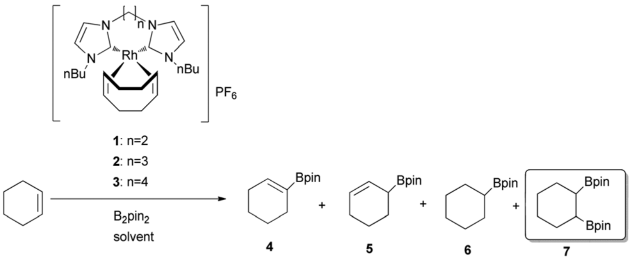


Scheme 1 Updated strategies on metal mediated dehydrogenative borylation reactions of cyclic alkenes.



Scheme 2 Model borylation reaction of cyclohexene and B_2pin_2 with Rh–NHC complexes.

reaction with B_2pin_2 and Rh(I)–NHC complexes (Scheme 2). NHC-based rhodium complexes **1–3** are well known complexes, first reported by Crabtree *et al.*,[9] which have been prepared by transmetallation from the corresponding silver carbene derivatives by a two-step procedure. The first step involves the deprotonation of the corresponding chelating bis(imidazolium) salt with Ag_2O. The so generated Ag(I)–NHC complexes were reacted *in situ* with $[Rh(\mu\text{-}Cl)(COD)]_2$ giving the desired chelating complexes in moderate yields.[9]

Results and discussion

The borylation of cyclohexene in THF, when the rhodium complex **1** was used, provided moderate conversions of a mixture of borylated products where the vinyl boronate ester **4** was the major one (49%) (Table 1, entry 1). In addition, certain amounts of allyl boronate ester and hydroborated product were also observed, but the diborated product **7** was not identified among the mixture of products. Similar results were observed using complexes **2** and **3** (Table 1, entries 2 and 3), but to our surprise, complex **2** allowed us to achieve the 1,2-diborated product in a modest percentage (25%), as the *cis*-1,2-diborated product. Exploring in detail the catalytic behaviour of complex **2** in less polar solvents like cyclooctane, we found that despite the fact that the conversion was still low, the percentage of diborated product increased significantly, becoming the major product (45%) (Table 1, entry 4). The beneficial influence of this type of solvent was enhanced when the borylation of cyclohexene took place in pentane, hexane and cyclohexane, obtaining better conversions and quantitative formation of the 1,2-diborated product (Table 1, entries 5–7). Increasing the temperature from 70 °C to 120 °C improved the conversion of the reaction (89%) keeping constant the quantitative formation of the diborated product **7** (Table 1, entry 8). Rhodium complexes **1** and **3** were less selective (Table 1, entries 9 and 10) towards the diborated product relative to the partial formation of the vinyl boronate ester **4**. A direct comparison with an unmodified Rh complex $[Rh(\mu\text{-}Cl)(COD)]_2$ and modified Rh complexes with phosphines confirmed the previously observed experimental trend by Jamison and coworkers[7] where dehydrogenative borylation of the cyclic olefins is the major process (Table 1, entries 11–13). However, under our reaction conditions, and using cyclohexane as the solvent of choice, a representative amount of 1,2-diborated product could be observed.

Table 1 Rhodium complexes modified with NHC ligands catalysed the borylation of cyclohexene[a]

Entry	Rh complex	Solvent	Conv[b] (%)	**4**/**5**/**6**/**7**[b] (%)
1	**1**	THF	30	49/29/23/—
2	**2**	THF	9	17/40/18/25
3	**3**	THF	18	30/30/40/—
4	**2**	Cyclooctane	27	30/8/17/45
5	**2**	Pentane	64	1/—/—/99
6	**2**	Hexane	54	1/—/—99
7	**2**	Cyclohexane	68	1/—/—99
8[c]	**2**	Cyclohexane	89	1/—/—99
9	**1**	Cyclohexane	52	14/—/—/86
10	**3**	Cyclohexane	68	28/3/3/66
11[d]	$[Rh(\mu\text{-}Cl)(COD)]_2$	Cyclohexane	17	78/6/4/13
12[d]	$[Rh(\mu\text{-}Cl)(COD)]_2PPh_3$ (1 : 2)	Cyclohexane	24	61/17/14/8
13[d]	$[Rh(\mu\text{-}Cl)(COD)]_2PPh_3$ (1 : 4)	Cyclohexane	33	62/14/9/14

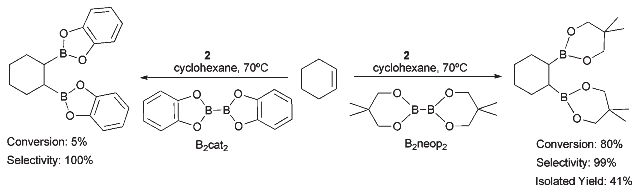
[a] Standard conditions: Rh–NHC complex (4 mol%), substrate (0.2 mmol), B_2pin_2 (1.0 equiv.), 70 °C, 16 h. [b] Conversion and selectivity calculated using ^1H NMR spectroscopy and GC. [c] *T*: 120 °C. [d] Rh complex (2 mol%), phosphine (4 or 8 mol%), substrate (0.2 mmol), B_2pin_2 (1.0 equiv.), 70 °C, 16 h.

With all these data in mind we concluded at this point that the synergy between the catalytic system **2** and the solvent cyclohexane favoured the diboration process *versus* the dehydrogenative borylation of cyclic olefins, in the presence of B_2pin_2. To generalise the methodology, we explored alternative tetraalkoxydiboron reagents such as bis(catecholato)diboron (B_2cat_2) and bis(neopentylglycolato)diboron (B_2neop_2) to borylate cyclohexene with complex **2**, using cyclohexane as a solvent. In both cases, after 16 h at 70 °C, the catalytic

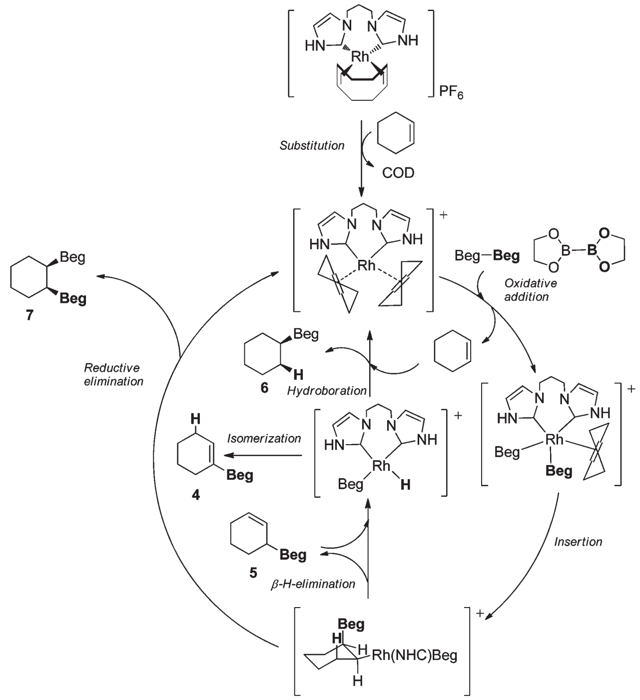
1,2-diboration was the preferred borylation process with quantitative formation of the corresponding 1,2-diborated product, despite the fact that conversion values were significantly different depending on the diboron reagent used (Scheme 3). When B_2neop_2 was involved, the conversion reached 80%. The oxidative work-up of the 1,2-diborated product confirmed the *cis*-1,2-cyclohexanediol formation, in all the cases.

The scope of the Rh–NHC mediated diboration of cyclic alkenes was also explored. In all the studied cases, exclusive formation of the 1,2-diborated product could be observed, with high conversion in the case of cyclopentene even at 50 °C (Table 2, entry 2). The beneficial influence of *N*-heterocyclic carbenes as ligands in the catalytic diboration of olefins has been previously demonstrated with Pd,[10] Pt,[11] Ir,[12] Ag[13] and Au[14] complexes, with complete chemoselectivity towards the 1,2-diborated product. However, in this case where NHC modifies rhodium complexes, it has an added value because the dehydrogenative borylation of olefins was usually favoured in the presence of rhodium complexes modified with phosphines.[15]

In this particular case, we became interested to know more details about the mechanism of the rhodium mediated boron addition reaction in order to identify the elements that could favour the 1,2-diboration *versus* the dehydrogenative borylation. For this purpose, using DFT based methods, we determined the reaction energy profile for the formation of the diborated product **7** and the allyl boronate ester **5**. Scheme 4 shows the general mechanistic pathways that we have considered to perform the theoretical study. This proposed mechanism resembles the mechanism previously suggested by Szabó[3] and Jamison,[6] where the conformational flexibility of a model cyclic alkene was already considered. In our DFT calculations we used Beg (eg = ethylenglycolato = OCH_2CH_2O) as a suitable model for the boryl moiety[16] and $[Rh(COD)(NHC)]^+$ (**2**) as the metal complex simplifying the *n*Bu groups of the NHC ligand by hydrogen atoms. Cyclohexene was selected as the model cyclic olefin.

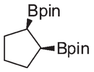
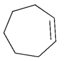
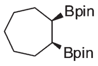
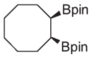
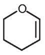
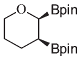
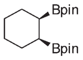


Scheme 3 1,2-Diboration of cyclohexene with bis(catecholato)diboron and bis(neopentylglycolato)diboron.



Scheme 4 General proposed catalytic pathways for the formation of products **4–7**.

Table 2 Substrate scope of the Rh–NHC mediated 1,2-diboration reaction with B_2pin_2[a]

Entry	Substrate	Product	T (°C)	Conv[b] (%)	1,2-Diborated[b] (%)	Isolated yield (%)
1			70	99	100	89
2	“	“	50	95	100	77
3			70	70	100	62
4			70	68	100	61
5			70	63	100	57
6			70	68	99	65

[a] Standard conditions: Rh–NHC complex (4 mol%), substrate (0.2 mmol), B_2pin_2 (1.0 equiv.), 16 h. [b] Conversion and selectivity calculated using ^1H NMR spectroscopy and GC.

We first focussed our study on the formation of the diborated product. The most accepted mechanism for the alkene diboration reaction involves oxidative addition of the diboron reagent to the metal centre, followed by insertion of the alkene and reductive elimination to generate the *syn*-organodiboron product. Generation of the cationic metal species [Rh(cyclohexene)$_2$(NHC)]$^+$ is an endothermic process (ΔE = 17.8 kcal mol^{-1}) that takes place by substitution of the labile 1,5-cyclooctadiene (COD) by two molecules of cyclohexene (see ESI†). Concerning the oxidative addition pathway, it has experimentally been demonstrated that diboron reagents such as B_2cat_2 and B_2pin_2 can be activated by late transition metal complexes[17,18] promoting the homolytic cleavage of the B–B bond. The resulting bisboryl Rh(III) complexes have been completely characterized and in the case of Bcat moieties the crystal structure has also been determined.[17] The oxidative addition of diboron reagents to neutral Rh(I) complexes modified with phosphines has been studied by means of computational studies.[19] However to the best of our knowledge, the oxidative addition of diboron reagents to cationic Rh(I) complexes modified with NHC ligands has not been previously reported. In the present work, we have been able to characterise the structure for the resulting species of the oxidative addition of B_2eg_2 to the cationic [Rh(cyclohexene)$_2$(NHC)]$^+$.

After a conformational study of the resulting Rh(III) diboryl species [Rh(Beg)$_2$(cyclohexene)(NHC)]$^+$, we found that the most stable conformation was characterised as a distorted square planar pyramidal structure with one boryl moiety occupying the apical site and the other boryl moiety in the basal site (Fig. 1). The bond angles about the rhodium centre support the description of the mentioned distorted square planar pyramidal geometry since C(1)–Rh–B(1) is 166.47° and C(2)–Rh–C(3) is 168.61, both values are similar and reasonably close to linear. Remarkably, angles between the basal B(1) and the apical B(2) are 84.87°, thus the two boryl moieties adopt a mutually perpendicular relative orientation, as was found in some Rh(III) bisboryl species with B_2cat_2.[17] Also, the B(1)–Rh–B(2) angle results in a B···B separation of 2.89 Å which differs by 1.19 Å relative to the B–B distance in B_2eg_2 (1.70 Å). Consequently, any residual B···B interaction must be weak. This newly characterized rhodium(III) complex, [Rh(Beg)$_2$(cyclohexene)(NHC)]$^+$, has been chosen as the origin of energies in our reaction energy profile (Scheme 5).

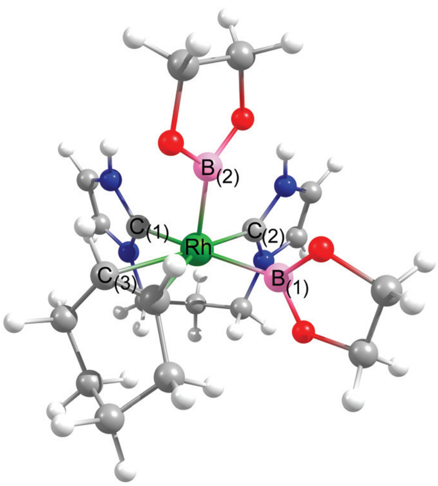
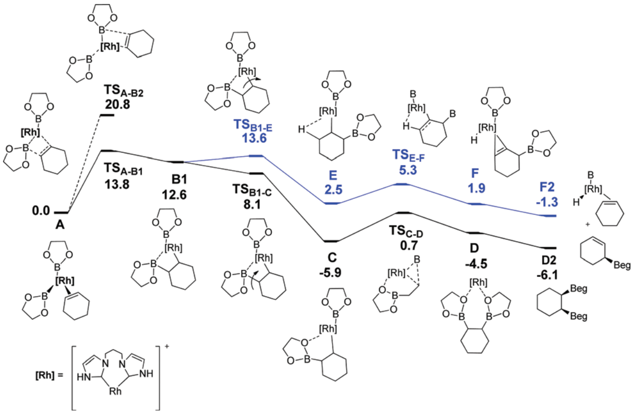


Fig. 1 Model structure for the cationic bisboryl Rh(III)–NHC species [Rh(Beg)$_2$(cyclohexene)(NHC)]$^+$ (**A**).



Scheme 5 Comparative energy profiles for the formation of the diborated and allyl boronate ester compounds computed at the BP86 level. Gibbs free energy is given in kcal mol^{-1}.

As has been depicted in Scheme 4, once the oxidative addition has taken place, the second step is defined as the insertion of the alkene in the Rh–B bond. Two plausible mechanisms for the insertion pathway can be considered (Scheme 5): apical insertion when the alkene binds the apical boryl (**TS$_{A-B2}$**) and basal insertion when the reaction occurs in the basal plane of the distorted square-based pyramid (**TS$_{A-B1}$**). According to our DFT results, it is clear that basal insertion is less energetically demanding (ΔG = 7.0 kcal mol^{-1} lower than the apical one). The resulting **B1** species can further undergo a rearrangement in order to occupy the vacancy generated in the coordination sphere of the metal. This process involves the rotation of the B(1)–C$_{\text{cyclohexene}}$ bond to afford a more stable species **C**, in which an interaction of the oxygen of the boryl unit with the metal centre has been established. Note that this process is barrierless (TS_{B-C} = −4.5 kcal mol^{-1}). In the following step, reductive elimination takes place recovering a Rh(I) **D** species in which the diborated product is coordinated through the oxygens of the Beg moiety to the metal centre (**D** species). Dissociation of the diborated product is characterized as an exothermic process (ΔG = −5.0 kcal mol^{-1}). Next, we evaluated the energy profile for the formation of the allyl boronate ester (Scheme 5, blue line). Once the **B** intermediate was formed, an alternative rearrangement could take place through rotation of the Rh–C$_{\text{cyclohexene}}$ bond. Although the energy barrier for this rotation was found to be very low (ΔG = 1.0 kcal mol^{-1}), it was less favoured than the B(1)–C$_{\text{cyclohexene}}$ rotation. The resulting **E** species could favour an agostic interaction between the Rh centre and the *ortho* hydrogen of the cyclohexene, promoting the β-hydride-elimination towards the Rh–allylboronate complex (**F**). Further dissociation of the allylboronate provides a Rh–hydride species, which is a key intermediate to obtain the rest of the observed organoborated byproducts (vinylic and hydroborated compounds). It is noteworthy to mention that the overall formation process is only slightly exothermic (ΔG = −1.3 kcal mol^{-1}) for the allyl boronated ester product and much more exothermic for the diborated one (ΔG = −6.1 kcal mol^{-1}). Both experimental and theoretical calculations seem to be in agreement with the favoured formation of the diborated product over the β-borated one.

Differences between the two reaction pathways are not very large, thus subtle changes in the solvent and in the ligands can switch reactivity. Indeed, polarity and coordination ability of the solvent are key factors to explain the differences observed in selectivity (Table 1). But the nature of the bidentate ligand NHC is of crucial importance, because when the borylation of cyclohexene was performed with the analogous cationic rhodium system $[Rh(COD)(BINAP)]BF_4$ under the same reaction conditions as with the precursor of catalyst **2** (Table 1, entry 7), less than 20% of conversion was observed and only 57% of selectivity towards the diborated product was achieved.

Conclusions

Although it has been well established that rhodium complexes modified with phosphines favoured the dehydrogenative borylation reaction in borylation of cyclic olefins, we have found that Rh(I) cationic complexes modified with bidentate *N*-heterocyclic carbene ligands selectively promote the diboration reaction. The use of non-polar solvents, such as pentane, hexane or cyclohexane, is also of crucial importance to guarantee the selective organodiboronate product formation. Theoretical calculations carried out to determine the key pathways that might favour the diboration mechanism *versus* the dehydrogenative borylation mechanism have demonstrated the more energetically demanding β-H-elimination pathway *versus* the reductive elimination step. We are currently evaluating the influence of similar ligands and solvents from a theoretical and experimental point of view. Making the methodology more general for non-cyclic substrates is also a matter of our current interest.

Experimental data

General aspects

All reactions and manipulations were carried out under an argon atmosphere by using Schlenk-type techniques. The solvents were distilled over dehydrating reagents and were deoxygenated before use. Bis(pinacolato)diboron was provided from Allychem. Substrates, bases and other diboron reagents were used as purchased from Sigma-Aldrich and Alfa Aesar. Rh(I)–NHC complexes (**1–3**) were prepared following the literature protocol.[9] NMR spectra were obtained on a Varian Mercury 400 spectrometer. ^1H NMR and ^{13}C $\{^1H\}$ NMR chemical shifts are reported in ppm (δ) relative to the chemical shifts of tetramethylsilane or residual solvent resonances. ^{11}B $\{^1H\}$ NMR chemical shifts are reported in ppm (δ) relative to $BF_3(CH_3)_2O$. Gas chromatography was equipped with an HP-5 column with a FID or MS detector.

General procedure for the NHC–Rh catalysed diboration of cyclohexene with B_2pin_2

Rh complexes (**1–3**) (4 mol%, 0.008 mmol), or $[Rh(\mu\text{-}Cl)(COD)]_2$ (2 mol%, 0.004 mmol)/phosphine (4–8 mol%), and bis(pinacolato)diboron (1.0 equiv., 51.0 mg, 0.2 mmol) were transferred into an oven-dried Schlenk tube under argon. Dried and deoxygenated solvent (2 mL) was added. The mixture was stirred for 10 min at room temperature to dissolve the diboron reagent completely. Cyclohexene (0.2 mmol) was added, and the reaction mixture was stirred at 70 °C oil bath temperature for 16 h. The reaction mixture was cooled to room temperature. An aliquot of 0.2 mL was taken from the solution. It was diluted with CH_2Cl_2 (1 mL) and analysed by GC/GC-MS to determine conversion. After the GC analysis, the aliquot was analysed by ^1H-NMR to confirm the conversion previously observed by gas chromatography. The analytical samples were combined with the rest of the reaction mixture, all the volatiles were removed in vacuum, and the crude product was purified by column chromatography (deactivated silica, petroleum ether–EtOAc, 15 : 1). White solid. Yield: (65%). R_f = 0.3 (silica TLC, petroleum ether–EtOAc, 15 : 1). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.67–1.50 (m, 5H), 1.48–1.34 (m, 5H), 1.23 (s, 12H, B(pin)), 1.22 (s, 12H, B(pin)). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 82.96, 28.29, 27.07, 25.12, 25.04. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.35. HRMS (ESI^+) *m*/*z* found for $C_{18}H_{34}B_2O_4$ $[M + H]^+$ = 337.2713.

General procedure for the catalysed diboration of cyclohexene with B_2neop_2

Rhodium complex **2** (4 mol%, 1.0 mg, 0.008 mmol) and bis(neopentylglycolato)diboron (1.0 equiv., 0.2 mmol) were transferred into an oven-dried Schlenk tube under argon. Dried and deoxygenated cyclohexane (2 mL) was added. The mixture was stirred for 10 min at room temperature. The substrate cyclohexene (21 μL, 0.2 mmol) was added, and the reaction mixture was stirred at 70 °C oil bath temperature for 16 h. The reaction mixture was cooled to room temperature. An aliquot of 0.2 mL was taken from the solution. It was diluted with CH_2Cl_2 (1 mL) and analysed by NMR to determine conversion of the reaction. The analytical samples were combined with the rest of the reaction mixture, all the volatiles were removed in a vacuum, and the crude product was purified by column chromatography (deactivated silica, petroleum ether–EtOAc, 15 : 1). White solid. Yield: (41%). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.95 (s, 12H), 1.26–1.14 (m, 2H) 1.40–1.34 (m, 4H), 1.60–1.50 (m, 4H), 3.56 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 72.11, 31.76, 27.7, 27.06, 22.14. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.9. HRMS (ESI^+) *m*/*z* found for $C_{16}H_{30}B_2O_4$ $[M + H]^+$ = 309.236.

General procedure for the catalysed diboration/oxidation of cyclohexene with B_2cat_2

Rhodium complex **2** (4 mol%, 1.0 mg, 0.008 mmol) and bis(catecholato)diboron (1.0 equiv., 0.2 mmol) were transferred into an oven-dried Schlenk tube under argon. Dried and deoxygenated cyclohexane (2 mL) was added. The mixture was stirred for 10 min at room temperature. The substrate cyclohexene (21 μL, 0.2 mmol) was added, and the reaction mixture was stirred at 70 °C oil bath temperature for 16 h. The reaction mixture was cooled to room temperature. An aliquot of 0.2 mL was taken from the solution. It was diluted with CH_2Cl_2 (1 mL) and analysed by NMR to determine conversion of the reaction.[20] The aliquot was returned to the reaction mixture and the solvent was removed under vacuum. 1 mL of THF was added and it was cooled at 0 °C. NaOH (2 mL, 3 M) and H_2O_2 (1 mL, 33%) were added to the reaction mixture and the entire sample was stirred from 0 °C to room temperature, overnight. Then, a saturated solution of $Na_2S_2O_3$ was added to the mixture and the product was extracted with ethyl acetate (3 × 25 mL). A combination of the organic phases was gently concentrated on a rotary evaporator and chemoselectivity of the alcohol products was determined by ^{1}H NMR in comparison with reported data.[21]

Characterisation of the products from the NHC–Rh catalysed diboration of cycloalkenes with B_2pin_2

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane. This product was purified by column chromatography (deactivated silica, petroleum ether–EtOAc, 15 : 1). White solid. Yield: (89%). ^{1}H NMR ($CDCl_3$, 400 MHz): 1.70–1.90 (m, 2H), 1.60–1.52 (4H, m), 1.48–1.40 (2H, m), 1.21 (s, 12H), 1.20 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): 88.8, 29.3, 32.0, 27.5, 24.7, 22.1. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.0. These spectroscopic data are in agreement with that previously reported.[22]

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cycloheptane. This product was purified by column chromatography (deactivated silica, petroleum ether–EtOAc, 15 : 1). Yellow pale solid. Yield: (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76–1.70 (m, 2H), 1.65–1.50 (m, 3H), 1.52–1.43 (m, 5H), 1.40–1.31 (m, 2H), 1.22 (s, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 82.4, 30.45, 28.25, 27.61, 24.89. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.6. HRMS (ESI$^+$) *m*/*z* calculated for $C_{19}H_{36}B_2O_4$ $[M + H]^+$ = 351.288.

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclooctane. The product was purified by column chromatography (deactivated silica, petroleum ether–EtOAc, 15 : 1). White solid. Yield: (72%). ^{1}H NMR ($CDCl_3$, 400 MHz): 1.72–1.68 (m, 2H), 1.58–1.40 (m, 10H), 1.39–1.37 (m, 2H), 1.22 (s, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 82.84, 28.21, 27.70, 26.58, 24.88, 24.79. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.9. HRMS (ESI$^+$) *m*/*z* calculated for $C_{20}H_{38}B_2O_4$ $[M + H]^+$ = 365.304.

1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-tetrahydro-2*H*-pyran. The product was purified by column chromatography (deactivated silica, petroleum ether–EtOAc, 15 : 1). Colorless oil. Yield: (57%). ^{1}H NMR ($CDCl_3$, 400 MHz): 1.20 (s, 12H), 1.24 (s, 12H), 1.38–1.50 (m, 2H), 1.53–1.72 (m, 3H), 3.5–3.7 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 88.8, 71.9, 70.4, 28.4, 26.3, 24.7, 17.5. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 36.2.

Computational details

Molecular structures for all the species were optimized without constraints by using Density Functional Theory (DFT) based methods as implemented in the Amsterdam Density Functional (ADF v2007.01) package.[23,24] A triple-ζ plus polarization Slater basis set was used on all atoms. Relativistic corrections were introduced by scalar-relativistic zero-order regular approximation (ZORA).[25] For geometry optimizations we used the local VWN correlation potential[26] together with the Becke's exchange[27] and the Perdew's correlation[28,29] (BP86) generalized gradient corrections. Stationary points in the potential energy hypersurface were characterized either as minima or transition states by means of harmonic vibrational frequencies calculations. Standard corrections to Gibbs free energy at 298 K were evaluated too.

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