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A Valuable, Inexpensive Cu^I/N-Heterocyclic Carbene Catalyst for the Selective Diboration of Styrene

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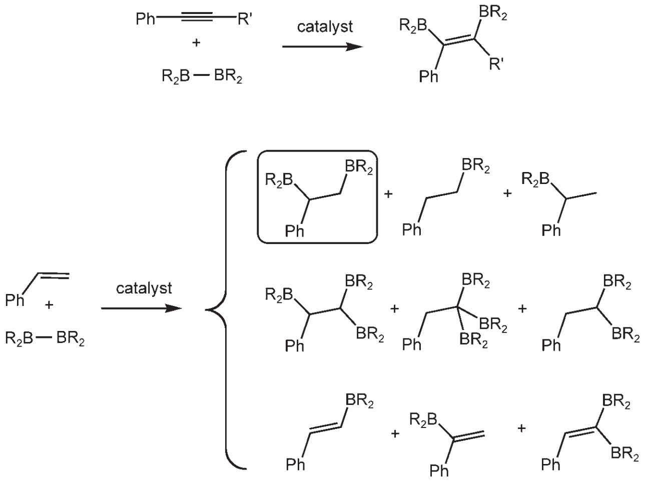
Abstract: The complexes [Cu(NHC)(NCMe)]BF_4 (NHC = N-heterocyclic ligand), with bis(catecholato)diboron ($B_2(cat)_2$) as the boron source, efficiently catalyze the diboration of styrene with very high degrees of conversion. With the appropriate NHC ligand, the reaction proceeds quantitatively toward the diborated derivative PhCH(Bcat)−CH_2(Bcat). The [styrene]/[$B_2(cat)_2$] ratio also has a strong effect on the selectivity: the use of an excess of styrene allows modification of the selectivity toward the formation solely of the monoborated derivative, $PhCH_2$−CH_2(Bcat). DFT calculations suggest that no oxidative addition processes take place at copper, but that intermediates containing coordinated σ-bonds are involved in the catalytic cycle.

Keywords: boranes · boron · copper · nitrogen heterocycles · reaction mechanisms

Introduction

The difunctionalization of multiple carbon–carbon bonds with boron-containing reagents to generate suitable organoboron intermediates is a powerful tool in organic synthesis.[1] This is a consequence of the existence of well-established procedures to convert such vicinal C−B bonds into valuable functional groups by replacement of the boron atom.[2] Probably the most convenient mode for organodiboron preparation involves the metal-mediated addition of a diboron reagent to an unsaturated carbon–carbon bond.[3] The diboration of alkynes provides the *syn* addition of the B−B bond to afford diborylalkene products (Scheme 1) by a well-established protocol based on monophosphane, platinum-containing catalysts.[4] However, the related alkene diboration seems to be more complex, judging from the mixtures of products commonly observed when alkenes and diborons react in the presence of the appropriate transition-metal catalyst (Scheme 1).[3]



Scheme 1. Metal-catalyzed addition of boranes to unsaturated C−C bonds. a) Alkyne diboration; b) styrene diboration, showing the different products that may be formed.

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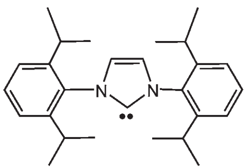
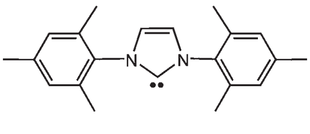
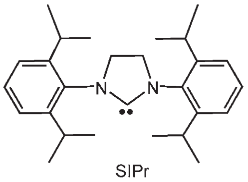
The availability of a very selective catalyst for the exclusive diboration of alkenes,[5] thus avoiding the drawback of low selectivity, is very desirable, particularly for the subsequent development of chiral systems to induce the appearance of enantiomeric excesses.[6] Substantial efforts have focused mainly on phosphane-containing Rh^I and Pt^0 catalyst precursors, and only a few examples of selective conversion into the diborated (Scheme 1) product have been reported to date. They include the zwitterionic rhodium complex [Rh(dppm)(η^6-catBcat)] (dppm = $Ph_2P(CH_2)PPh_2$ (1,2-bis(diphenylphosphino)ethane), catBcat = 1,2-$O_2C_6H_4$) prepared in situ,[7] and the phosphane-free Pt-catalyst precursors.[5a,b,d] In addition to rhodium and platinum, two other precious metals, gold and silver, are also known to promote this transformation. Diphosphane–gold complexes have been reported to catalyze the addition of diborons to alkenes, although in moderate yields.[8] Very recently, one of our groups described Ag^I and Pt^0 complexes containing an NHC ligand (NHC = N-heterocyclic carbene) that catalyzed this process with a high degree of selectivity and moderate activity, opening a new perspective for catalyst precursors.[9] With the goal of developing both active and selective catalysts for this transformation, we have turned our attention to copper, the remaining Group 11 metal still not known to catalyze the diboration of alkenes.[10] We have investigated the potential of several complexes containing the (NHC)Cu core as the catalyst for this reaction, given the success of such compounds in other catalyses.[11,12]


IPr

1: [CuCl(IPr)]
2: [Cu(IPr)(NCCH$_3$)]BF$_4$


IMes

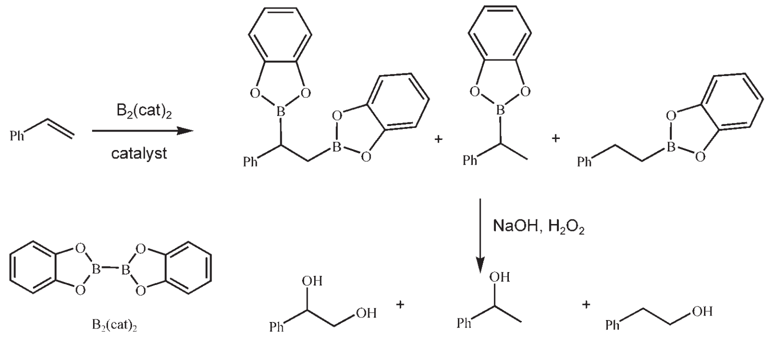
3: [CuCl(IMes)]
4: [Cu(IMes)(NCCH$_3$)]BF$_4$


SIPr

5: [CuCl(SIPr)]
6: [Cu(SIPr)(NCCH$_3$)]BF$_4$

Results and Discussion

Development of the catalytic system for diboron addition to unsaturated C−C bonds: In a first screening, the previously described[12] Cu^I(NHC) compounds **1**–**6** were tested as catalyst precursors in the reaction of styrene and bis(catecholato)diboron, B_2cat_2. The latter was added to a solution of the catalyst precursor (5 mol %, 0.025 mmol) in tetrahydrofuran under argon and stirred for 5 min before styrene addition (the reverse order of addition has no influence on the course of the reaction); the catalyst/styrene/B_2cat_2 molar ratio was 0.025:0.5:0.55. The mixture was stirred for 4 h at RT or solvent refluxing temperature. At 4 h the reaction mixtures were investigated by NMR spectroscopy (see the Experimental Section). The products were oxidized to the corresponding alcohols with H_2O_2 in a basic medium (Scheme 2) and the product distribution was then determined by GC and NMR spectroscopy.



Scheme 2. Catalytic diboration of styrene with Cu^I(NHC) complexes.

In the first series of experiments, the IPr ligand (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) was used in four different catalyst precursors: the neutral complex [CuCl(IPr)] (**1**), the isolated cationic species [Cu(IPr)(NCCH$_3$)]BF$_4$ (**2**), and mixtures of **1** with NaBAr'$_4$[13] (BAr'$_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) or AgBF$_4$ for the in-situ generation of cationic species (Table 1). Use of the neutral complex **1** did not induce the transformation at room temperature, the conversions being very low in refluxing THF. Addition of NaBAr'$_4$ as the halide scavenger was not effective (entry 3), but moderate conversions (53 %) were observed when AgBF$_4$ was used instead (entry 4): the nature of the salt seems to play a significant role in cationic catalyst formation in situ. However, when the well-defined, previously isolated complex **2** was employed as the catalyst precursor, moderate (50 %) conversion was obtained at room temperature, and nearly quantitative conversion (94 %) was achieved at refluxing THF temperature (entries 5 and 6, respectively). The previous literature on the use of Cu^I catalysts for alkene diboration did not report any transformation; only monoboration of α,β-

Table 1. Catalytic diboration/oxidation of styrene with Cu^I(NHC).[a]

Entry	Catalyst	Solvent, *T*	Conv. [%][b]	Diol [%][c]	Linear [%][c]
1	**1**	THF, 22 °C	0	0	0
2	**1**	THF, reflux	11	>99	0
3	**1**/NaBAr'$_4$	THF, reflux	5	>99	0
4	**1**/AgBF$_4$	THF, reflux	53	63	37
5	**2**	THF, 22 °C	50	80	20
6	**2**	THF, reflux	94	89	11
7	**2**	CH$_3$CN, reflux	12	>99	0
8	**2**	toluene, reflux	59	22	54[d]
9	**2**[e]	THF, reflux	74	20	80
10	**2**[f]	THF, reflux	43	0	>99
11	**3**	THF, reflux	25	59	41
12	**4**	THF, reflux	53	42	58
13	**5**[g]	THF, reflux	>99	>99	0
15	**6**	THF, reflux	41	58	42

[a]Standard conditions: 5 mol% Cu^I(NHC) precatalyst, styrene/diboron = 1:1.5, diboron = B$_2$(cat)$_2$ = bis(catecholato)diboron, reaction time 4 h. [b] Conversions determined by ^{1}H NMR. [c] Selectivity based on ^{1}H NMR spectroscopy and GC. [d] Branched alcohol observed (24%). [e] Diboron = B$_2$(pin)$_2$ = bis(pinacolato)diboron. [f] A [styrene]/[B$_2$cat$_2$] ratio of 3:1 was employed. [g] $t = 10$ h.

unsaturated ketones was successful with this metal.[14] The main advantage of using **2** is the good selectivity toward the diboration product (89%), with minor amounts of the linear monoborated derivative as a byproduct (11%), accompanied by none of the branched isomer or any other borated compounds (Scheme 2).

The reaction conditions can induce effects on both the activity and the selectivity. For instance, the selection of the solvent is important: as shown in entries 6, 7, and 8 in Table 1, it affected the conversion as well as the distribution of products. In the case of toluene, the monoalcohol was the major product, and some branched isomer is observed (24%). Another variable is the nature of the diboron reagent. The use of B$_2$(pin)$_2$, (bis(pinacolato)diboron) not only diminished the yields of the diboration product, but gave the linear monoalcohol as the main product (80%, entry 9). Perhaps the most intriguing result was obtained upon varying the [styrene]/[B$_2$cat$_2$] ratio. The above results were obtained with a slight excess of B$_2$cat$_2$ (10%) with respect to styrene. However, when a [styrene]/[B$_2$cat$_2$] ratio of 3:1 was employed, *only* the linear monoalcohol, and no other borated product, was observed at the end of the reaction. This result suggests the possibility of controlling the selectivity of the reaction just by modifying this ratio. Use of the inverse ratio ([styrene]:[B$_2$cat$_2$] = 1:3) provided the same selectivity as the nearly equimolar one.

These copper-based catalysts provide the opportunity to readily modify the nature of the groups bonded to the NHC N atoms as well as that of the backbone. Thus, use of mesityl instead of 2,6-diisipropylphenyl groups as the N substituents seems to increase the amount of the linear monoalcohol (entries 11 and 12). Another variable is the saturation of the backbone, which also influences the course of the reaction. When the neutral ligand SIPr was employed in the neutral precatalyst **5**, 68% conversion was observed (after the standard 4 h reaction time), a value substantially higher than that found with complex **1** (11%). Such conversion was improved to >99% by prolonging the reaction time to 10 h: only the diborated product was observed at the end of the reaction, in a completely quantitative and selective transformation. However, the cationic analogue **6** did not provide such a quantitative selectivity.

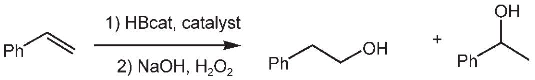
These results are worthy of comment since both activity and selectivity values are, at least, comparable with the previously reported data in the literature. The exclusive formation of the difunctionalized product has been reported with Au^I and Ag^I, but in our case catalyst **5** was more active on the basis of the shorter reaction times required for total conversion (10 h with 5 mol% of **5**, instead of 48 h with 8 mol% of Au^I–diphosphane[8] or 60 h with 5 mol% of [Ag(mentimid)$_2$][AgCl$_2$] mentimid = 1-methyl-e-(+)-methylmenthoxide imidazolium).[9] Only the very active [Rh(dppb)(η^6-catBcat)] (dppb = Ph$_2$P(CH$_2$)$_4$PPh$_2$),[7] the monophosphine Pt^0 complexes,[4h] and the base-free platinum catalyst precursors [Pt(dba)$_2$],[5a] [Pt(nbe)$_3$],[5b] [Pt(cod)$_2$],[5b] and [Pt(cod)Cl$_2$][5d] seem to be comparable with this Cu^I(NHC) system (dba = dibenzylideneacetone, nbe = norbornene, cod = cyclooctadiene). However, the Cu^I(NHC) system offers two advantages: the use of an inexpensive metal and the tunability of the ligand, which allows development of the asymmetric version of the catalytic reaction.

We have also studied the separate capabilities of these Cu^I(NHC) complexes in the alkene hydroboration reaction, since the terminal monoborated product was also formed in the transformation described above. Thus, when catecholatoborane (HBcat) was added to styrene in a solution of the complexes **1**–**6** in THF at room temperature, a smooth reaction took place. After 4 h at room temperature and the corresponding workup, the predominant compound was the linear monoalcohol in all cases (Table 2), the branched isomer being obtained as the minor product in all cases (Scheme 3), presumably as a consequence of the steric hindrance of the NHC ligands. To our knowledge, there is only one previous related example in the literature, the metal-

Table 2. Catalytic hydroboration/oxidation of styrene with Cu^I(NHC).[a]

Entry	Catalyst	Conv. [%][b]	PhCH(OH)CH$_3$[c]	PhCH$_2$CH$_2$OH[c]
1	**1**	95	27	73
2	**2**	73	30	70
3	**3**	85	16	84
4	**4**	77	12	88
5	**5**	73	28	72
6	**6**	78	19	81

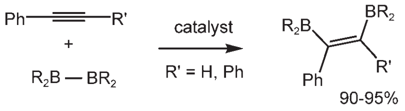
[a] Standard conditions: 5 mol% Cu^I(NHC) precatalyst, [styrene]/[catecholatoborane] = 1:1.5, 4 h, 25 °C, THF. [b] Conversions determined by ^{1}H NMR spectroscopy. [c] Selectivity based on ^{1}H NMR spectroscopy and GC.



Scheme 3. Styrene hydroboration (and subsequent oxidation) catalyzed by (NHC)Cu complexes.

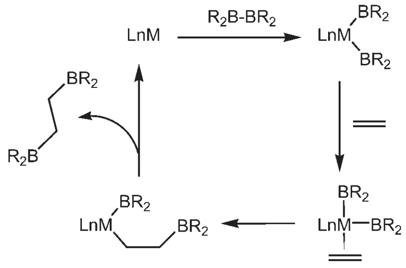
catalyzed hydroboration of imines with Cu^{I} containing bulky, chelating bisphosphane ligands.[15]

To broaden the scope of diboration by Cu^{I}(NHC), alkynes were also transformed into the corresponding 1,2-bis-(alkenyl)diboronate esters. Both phenylacetylene and diphenylacetylene (Scheme 4) were diborated with B_2cat_2 in THF at refluxing temperature for 4 h, with conversions between 90 and 95 % when complexes **2** and **4** were used as the catalyst precursor. Selectivity to the diborated product was completely toward the *cis* isomer.



Scheme 4. Alkyne diboration catalyzed by (NHC)Cu complexes.

Mechanistic considerations: When complex **2** and styrene (3 equiv) were dissolved in [D$_8$]THF, the resonances due to **2** did not vary at either 22 °C or 50 °C. In a separate experiment, addition of B_2cat_2 (2 equiv) to a solution of **2** in [D$_8$]THF gave an immediate change from colorless to brownish. The ^{1}H NMR spectrum revealed minor changes in the chemical shifts of the NHC ligand resonances, as well as some broadening in the aromatic resonances of the catechol units. However, we have not been able to isolate or identify the resulting product, since decomposition took place unless styrene was added to the mixture. In that case, even at room temperature, the catalytic diboration reaction started immediately, at a low rate which was accelerated when the temperature was raised to 50 °C. Only one Cu^{I}(NHC) species was detected during catalysis, with resonances identical to those observed when **2** and B_2cat_2 were mixed. No evidence for styrene coordination was obtained. Interestingly, when the same set of experiments was performed in [D$_3$]acetonitrile, no reaction was observed between **2** and styrene or between **2** and B_2cat_2 at 50 °C. We believe this to be in accord with the existence of a dissociation preequilibrium of the CH_3CN ligand to generate an unsaturated species which is reactive toward B_2cat_2, but not toward styrene. That dissociation takes place readily in THF, but it is disfavored in acetonitrile. As mentioned above, previous work in the literature has mainly focused on rhodium- and platinum-based catalysts,[3,5,16] for which mechanisms have been proposed. It is well established that the first step in these transformations consists of the oxidative addition of the B–B bond to the metal center (Scheme 5). Subsequent insertion of the olefin into one M–B bond and reductive elimination would afford the final diborated product. In our case, it seems clear that the reaction is not initiated by olefin coordination but by an interaction with the B_2cat_2, although we have no evidence of oxidative addition products. The broadening of the NMR spectra of the mixtures of **2** and B_2cat_2 seems to indicate the existence of equilibria among several species.



Scheme 5. Classical mechanism for the Rh- or Pt-catalyzed diboration of olefins.

To gain information about the nature of the interaction between the unsaturated [Cu^{I}(NHC)]$^+$ complex and B_2cat_2, we have carried out a theoretical DFT study with the B3LYP functional. The system chosen was [(IMes)Cu"catB–Bcat"]$^+$; the IMes ligand IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was used because it is conformationally simpler. To our surprise, the results excluded an oxidative addition process; instead, they were conclusively in favor of a [Cu(NHC)(σ-catB–Bcat)]$^+$ description, in which the unbroken B–B bond coordinates Cu as a B–B σ adduct (SA-BB). In fact, this was the only local minimum we could optimize for this system, as all attempts to optimize the expected diboryl complex failed. The Cu^{I} species SA-BB is logically a singlet, but both the singlet and triplet spin states were explored in a search for the diboryl. Within the singlet spin state, the energy of a hypothetical diboryl species derived from B–B oxidative addition (OA-BB) was estimated from a constrained geometric optimization in which the B-Cu-B and C-Cu-B bond angles were frozen at 120°. The energy of OA-BB is 69.2 kcal mol^{-1} above that of SA-BB. The optimized geometries are shown in Figure 1. An additional attempt was made to optimize a singlet diboryl geometry OA-BB′ with a T-shape around Cu, constraining the C-Cu-B angles to 90° and the B-Cu-B angle to 180°. The energy was even higher, 85.6 kcal mol^{-1} above OA-BB. As the three-coordinate Cu^{III} species could also be a triplet, we considered this spin state. The only local minimum in the triplet state is also a σ complex, SA-BB triplet, albeit with an energy 53.8 kcal mol^{-1} above that of the singlet. The corresponding OA-BB triplet species, also obtained by constraining the bond angles around Cu, was 81.5 kcal mol^{-1} above the singlet minimum. We think that the significant differences of more than 50 kcal mol^{-1} in favor of the most stable singlet SA-BB species are conclusive. Although the accuracy of DFT methods is certainly not perfect, there is very unlikely to be an error of more than 50 kcal mol^{-1} for relatively stable species like the present ones.

After these calculations, and given the observed catalytic activity in the hydroboration reactions of this family of complexes, we carried out similar theoretical calculations regarding the stability of the[Cu(NHC)(HBcat)]$^+$ species contain-

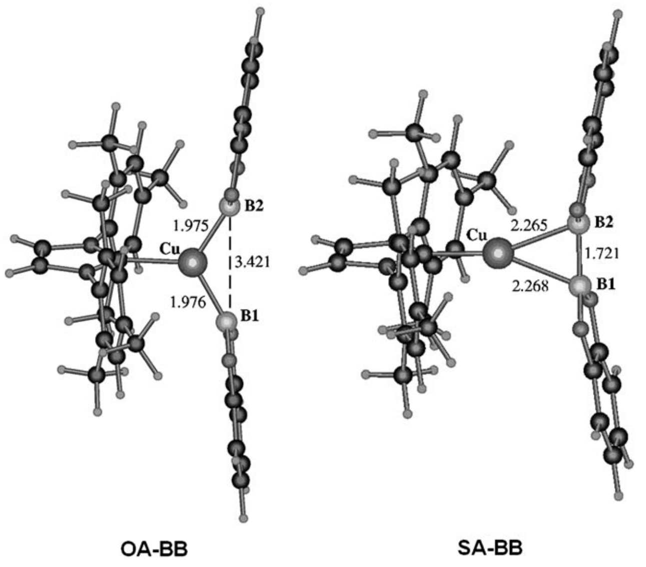


Figure 1. B3LYP-optimized structures of OA-BB (oxidative addition) and SA-BB (σ adduct) for $[(NHC)Cu(catB{-}Bcat)]^+$. Selected distances are in Å.

ing a borane ligand with a coordinated H–B bond. In good accord with the previous results, the $[Cu(NHC)(\sigma\text{-}H\text{-}Bcat)]^+$ structure was the only local minimum. Figure 2 shows the optimized geometries for the σ adduct (SA-BH) and the hydridoboryl species (OA-BH) that was obtained through a constrained geometric optimization.

The energy difference between the two structures is even larger, at 86.5 $kcal\,mol^{-1}$ above SA-BH. Again, these data suggest that the existence of the Cu^{III} hydridoboryl species is very unlikely. We have not been able to isolate any product from the reaction of **2** and HBcat: although an immediate change in colour took place, some decomposition was also observed, unless styrene was added. In this case, styrene hydroboration was observed, with the results shown in Table 2.

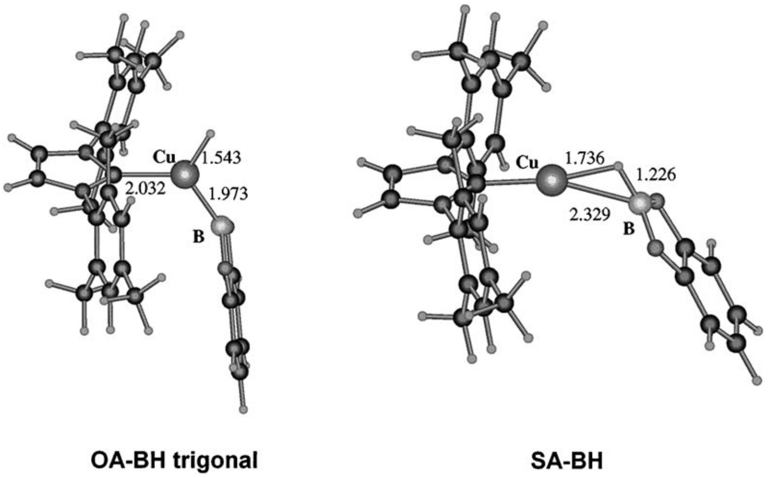
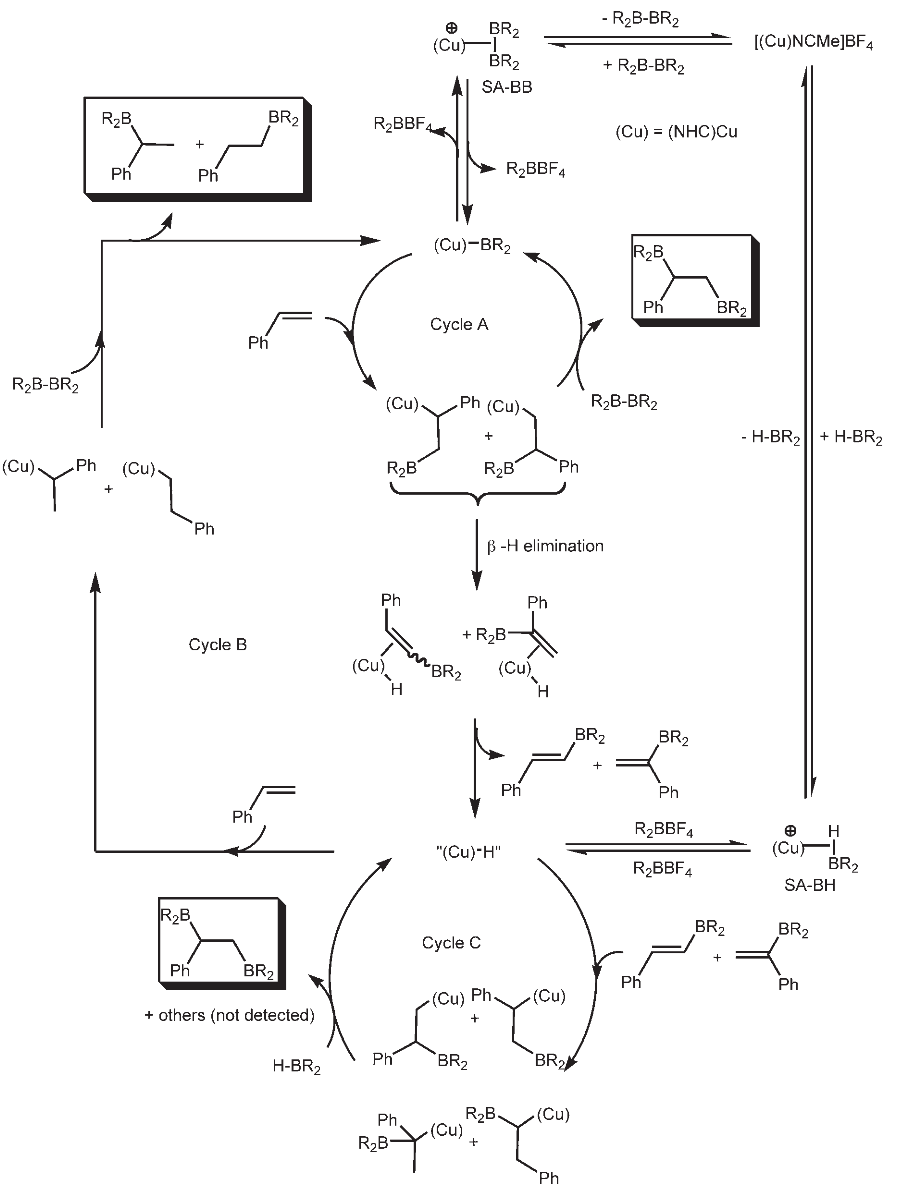


Figure 2. B3LYP-optimized structures of OA-BH and SA-BH for $[(NHC)Cu(HBcat)]^+$. Selected distances are in Å.

Thus, the above experimental and calculated data indicate that: 1) no olefin adduct is detected during the catalytic reaction; 2) **2** interacts with added B_2cat_2 or HBcat, so the catalytic reaction could start at this point; and 3) the products due to the oxidative additions of the borane reagents (B_2cat_2 or HBcat) are quite unstable in terms of energy compared with the related σ-borane complexes. We are not aware of any reports of experimental evidence of the diboron or borane adducts with copper as the metal center. The HBR_2 adducts have been reported for few other metals,[17,18] so far as we know, the $R_2B{-}BR_2$ adducts being as yet unknown.[18d]

With the above information, we propose a mechanism for the diboration reaction (Scheme 6). The first step would consist of an equilibrium between the cationic catalytic precursor $[Cu(NHC)(NCMe)]BF_4$ and the adduct $[Cu(IPr)(\sigma\text{-}catB{-}Bcat)]^+$. This explanation is not based on the oxidative addition pathway commonly employed for Rh- and Pt-based catalysts and already mentioned; it supposes a new approach to this type of transformation. Some examples of related reactions support our proposal. Baker et al. described the use of Cu-, Ag-, and Au-based catalysts for the hydroboration of imines, in a process in which no oxidative addition of the HBcat was observed.[15] Hosomi and coworkers later reported[14a] a similar result during the copper-catalyzed boration of α,β-enones, in which no reaction of the borane and the metal center was found. However, some early metal-based catalysts for alkene hydroboration were also described as inducing such a transformation without the oxidative addition step.[19]

The interaction of the diboron adduct with the Lewis base BF_4 would lead to the formation of a neutral copper-boryl species $[Cu(NHC)(BR_2)]$ with one equivalent of $R_2B{\cdot}BF_4$. This transmetalation reaction finds precedent in the previous work by Miyaura and co-workers,[20] in which a copper–boryl species was generated in situ from $B_2(pin)_2$ and copper acetate. More recently, Sadighi and co-workers have reported the synthesis of a related complex [Cu(IPr)(Bpin)] through direct reaction of [Cu(IPr)(O*t*Bu)] and $B_2(pin)_2$.[21] The $[Cu(NHC)(BR_2)]$ species in Scheme 6 would then react with styrene to give Cu^I–alkyl intermediates which undergo further interaction with another diboron molecule to afford the desired diborylated product and to regenerate the real catalytic species, $[Cu(NHC)(BR_2)]$. The reactivity of a $(NHC)Cu^I$–boryl complex toward styrene has also been described by Sadighi and co-workers, who demonstrated the clean insertion of styrene into the Cu–B bond to give a β-boroalkyl intermediate, which can be converted into the α-derivative upon heating. This step has been proposed to pro-



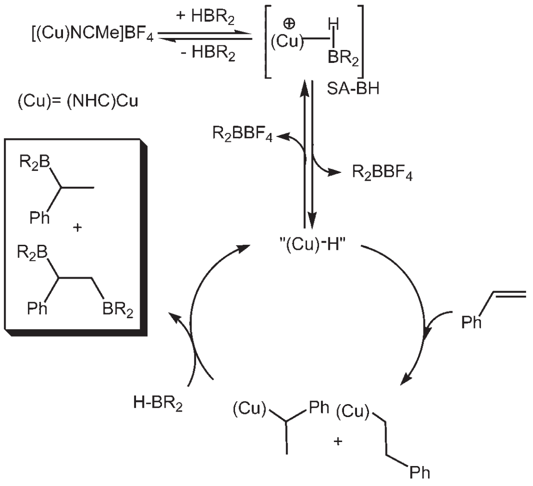
Scheme 6. Proposed mechanism for the copper-catalyzed diboration of styrene.

ceed through a β-hydride elimination/reinsertion sequence.[22]

The above explanation, represented by Cycle A in Scheme 6, would only explain the formation of the diboration product, which is the major product in most of the experiments shown in Table 1. It has already been proposed that neutral catalytic precursors undergo halide exchange in the presence of donor substrates, so an additional pre-equilibrium should be included.[12a] However, the formation of the hydroboration products cannot be explained by Cycle A. The reversible β-elimination reactions observed in [Cu(IPr){(Bpin)H−CH$_2$Ph}] (mentioned already) can be invoked to account for the appearance of these byproducts.[22] Such elimination from the alkyl intermediates in Cycle A would lead to hydridoalkene compounds that could undergo olefin dissociation to generate an unsaturated hydridocopper(I) species. The interaction of this [CuH^I(NHC)] intermediate with styrene and further transmetalation with a diboron molecule would provide the monoborated byproducts before the [Cu(NHC)(BR$_2$)] catalytic species is regenerated, closing this Cycle B Scheme 6.

The formation of the CuH species also promotes the appearance of two different alkenylboron compounds that we have not detected in any of the in-situ NMR monitoring of catalytic experiments. However, in a separate experiment, PhCH=CHBcat, a feasible intermediate in our reaction scheme, was employed as the substrate in a diboration experiment with B$_2$cat$_2$ as the boryl source and **2** as the catalyst precursor, at 50 °C in [D$_2$]THF. Very fast, complete conversion into the diborated product Ph−C(Bcat)H−C(Bcat)H$_2$ was observed, showing that these substrates, when formed, are also consumed during the catalytic cycle.[23,24] To account for this behavior, we propose a third cycle, Cycle C, consisting of insertion of the alkenylboron molecule into the Cu−H bond, followed by interaction of the Cu–alkyl intermediates with HBcat. This hydroboron molecule appears as a consequence of an equilibrium between the Cu−H species and the R$_2$B−BF$_4$ formed at the beginning of the reaction, which would lead to formation of the SA-BH adduct, and subsequent decoordination. This proposed mechanism also ensures the mass balance, since the hydrogen source for the monoborated product is the styrene. No incorporation of deuterium was observed in NMR studies to check this statement. A similar result was obtained when the reaction was performed in the presence of added D$_2$O: all the products obtained contained H atoms exclusively, within the NMR detection scale. Scheme 6 shows all the possible intermediates for a general NHC ligand. The results in Table 1 indicate that the ligand, the precatalyst charge, and the solvent exert a perceptible influence on the activity and the selectivity; therefore in some cases not all the cycles or intermediates would exist. The use of complex **5** is the best example: the results are explained by Cycle A exclusively.

As remarked above, these (NHC)Cu complexes catalyze the hydroboration of styrene also. However, comparison of the regioselectivities of the linear and branched alcohols in Tables 1 and 2 clearly indicates that the formation of the monoborated compounds must take place along two different pathways. We have proposed that in the case of the diboration system, the monoborated products are formed as in Cycle B in Scheme 6. For the hydroboration of styrene with HBcat, a cycle related to Cycle C is shown in Scheme 7. The catalyst precursor with HBcat initiates the reaction upon forming the stable adduct SA-BH discussed already. This adduct would then interact with the Lewis base BF_4 to give catB$-BF_4$ and CuH(NHC), which is the real catalyst. Styrene insertion followed by transmetalation with HBcat would provide the desired monoborated product and would close the cycle.



Scheme 7. Proposed mechanism for the copper-catalyzed hydroboration of styrene.

It is worth noting that 1) the proposed mechanisms based on both experimental and theoretical studies do not include the oxidative addition of the diboron reagents, which differ in this way from other Rh- and Pt-based catalysts which have been reported already; and 2) all the intermediates correspond to Cu^I species, no other oxidation state being invoked along the reaction pathway.

Conclusion

We have found that complexes of composition CuCl(NHC) or $[Cu(NHC)(NCMe)]BF_4$ catalyze the diboration as well as the hydroboration of styrene. With appropriate selection of the ligand, very efficient, nearly quantitative conversions to the diborated derivative have been achieved in moderate reaction times and mild conditions. The [styrene]/[diboron] ratio has a remarkable effect on the selectivity of the reaction, in that the modification of this sole variable leads to very high yields of either the diborated or the monoborated product. A mechanism has been proposed based on the existence of three cycles for the formation of the di- and the monoborated products. Theoretical calculations have predicted the absence of the oxidative addition of the borane reagent, and the presence of σ-borane adducts.

Experimental Section

General: All reactions and manipulations were carried out under an atmosphere of dry nitrogen. All organic solvents were dried, distilled, and degassed before use. The copper complexes were prepared by reported methods.[12] Styrene, bis(catecholato)diboron, and cathecolatoborane were purchased from Aldrich. NMR spectra were recorded on Varian Gemini 300 and Mercury 400 spectrometers. Chemical shifts were reported relative to tetramethylsilane for ^1H and ^{13}C, using $CDCl_3$ or $[D_2]THF$ as solvents. GC analyses were performed on a Hewlett–Packard 5890 II with a flame ionization detector equipped with a FS-Cyclodex B-IP column (50 m × 0.25 mm).

Typical catalytic diboration of styrene: Bis(catecholato)diboron (0.55 mmol) was added to a solution of the catalyst (5 mol%, 0.025 mmol) in THF (2 mL) under argon. The solution was stirred for 5 minand styrene (0.5 mmol) was then added. The mixture was stirred for 4 h at refluxing temperature, after which a solution aliquot was taken from the reaction mixture to determine, from the ^1H NMR spectrum, the degree of conversion and the nature of the organoboron reaction. An identical experiment carried out in $[D_2]THF$ gave identical results. [**Caution**: *Workup must be carried out carefully due to the risk of explosion when using peroxides with THF.*] NaOH (3 M, 800 mL) and H_2O_2 (800 mL) were added to the mixture, which was then stirred for 3 h. After this time, saturated brine (1 mL) was added, followed by NaOH (1 M, 10 mL). The reaction mixture was treated with AcOEt (3 × 25 mL), and the organic layer was washed with brine and dried over $MgSO_4$. The hydroxylated products contained in the resulting solution were identified by GC and ^1H NMR spectroscopy. The conversions and distribution of products corresponded to those of the organoboron precursors previously determined by NMR at the end of the reaction.

Typical catalytic hydroboration of styrene with catecholatoborane: Styrene (0.5 mmol) was added to a solution of catalyst (5 mol%, 0.025 mmol) in THF (2 mL) under nitrogen. The solution was stirred for 5 min and freshly distilled catecholatoborane (0.75 mmol) was then added. The mixture was stirred at room temperature for 4 h. Conversions were calculated on the basis of the borated products in the ^1H NMR spectrum and then quenched with EtOH (2 mL). [**Caution**: *Workup must be carried out carefully because of the risk of explosion when using peroxides with diethyl ether and THF.*] NaOH (2 M, 2 mL) and H_2O_2 (2 mL) were added and the mixture was stirred for several hours. The reaction mixture was extracted into Et_2O, then washed (2 M NaOH, H_2O, saturated brine), the organic layer was dried over $MgSO_4$, and the products were identified by GC and ^1H NMR spectroscopy. The conversions and distribution of products corresponded to those of the organoboron precursors previously determined by NMR spectroscopy at the end of the reaction.

Computational details: Calculations were performed at the DFT level, by means of the hybrid Becke3LYP[25–27] functional as implemented in Gaussian 03.[27] Cu atoms were described by using an effective core potential (LANL2DZ) for the inner electrons,[28,29] and its associated double-zeta ζ basis set for the outer ones. In the case of Cu an additional f polarization shell was added, with exponent 3.525.[30] The 6-31G(d) basis set was used for the C, N, H, and B atoms.[31]

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