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Cobalt pincer-type complexes demonstrating unique selectivity for the hydroboration reaction of olefins under mild conditions†

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The hydroboration of alkenes catalyzed using an inexpensive and easily accessible Earth-abundant cobalt pincer complex based on a PN5P triazine backbone is reported. The presented protocol allows efficient anti-Markovnikov functionalization of alkenes bearing a wide range of functional groups (unsaturated amines, carbonates, ethers, vinylarenes, vinylsilanes, and natural products) under mild conditions with high yields. Moreover, the presented procedure exhibits unique selectivity distinguishing vinylsilyl groups from other alkenyl or alkyne groups, leading to an interesting class of bifunctional compounds that have potential application in the synthesis of advanced materials. Their application potential was demonstrated by several model transformations.

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Introduction

Hydroboration, the addition of a boron–hydrogen bond to an unsaturated carbon–carbon or carbon–heteroatom bond, was discovered in 1956 by H. C. Brown.¹ Since its discovery, it has become an important tool used in organic chemistry, as evidenced by the numerous investigations published each year focused on the synthesis and transformation of the boron group.^{2–7}

Organoboron compounds can be synthesized directly from unsaturated substrates in the presence of more reactive boron hydrides such as trihydridoboron (BH₃) and dialkyl boron hydrides (HBR₂) without the need for a catalyst, but the use of these reactants is associated with safety hazards and the high instability of the resulting products.^{8–10} As a result, in practice, less reactive dioxaborolane derivatives (pinacolborane, catecholborane) are commonly used, which usually require the assistance of a catalyst.⁴

In recent years, researchers have developed a variety of catalysts for hydroboration reactions, many of which use noble metals like rhodium and iridium.^{11,12} However, there is now a growing focus on using first-row d-block metals for catalysis.^{13–15} Specifically, there is significant interest in cobalt catalysts that utilize pincer ligands, which have shown promise as an alternative to traditional precious metal catalysts.¹⁶

Recently, there have been several articles highlighting the exceptional catalytic performance of cobalt complexes in olefin hydroboration reactions, particularly when used in low catalyst concentrations.^{17–22} These studies are headlined by unprecedented research by Huang's group. In their work, they reported a highly efficient Co-complex [(ⁱPrPNN)CoCl₂] with high activity and exhibiting excellent regio- and chemo-selectivity toward anti-Markovnikov products.²³ Similarly, Zheng's team demonstrated the possibility of hydroboration of vinylarenes using a cobalt(II) coordination polymer (CP) based on the pincer moiety for achieving excellent activity and observing the Markovnikov selectivity.²⁴ This unusual hydroboration selectivity has also been reported for the bipyridyl-oxazoline cobalt catalyst [(^tBuBPO)CoCl₂].²⁵ Moreover, an interesting example of the pincer cobalt complex utility is their use as catalysts in asymmetric hydroboration reactions.^{14,26–30} Exciting developments have emerged from Prof. Lu's group, who have achieved control over the enantioselectivity of hydroboration reactions by introducing a rigid imine group in place of a flexible amine group in the ligand structure.³¹ Additionally, other promising methods for synthesizing organoboron compounds include the sequential hydrosilylation–hydroboration reaction of terminal acetylenes^{32–34} and the use of the cobalt-catalyzed isomerization–hydroboration reaction of internal alkenes.^{35–37}

In the case of bifunctional terminal olefins or unconjugated (1,*n*-) dienes, there are known reports of dihydroboration^{38–40} or hydroboration with the retention of the internal double bond,^{17,18,41,42} as well as the synthesis of *gem*-bis(boryl)alkanes using a chain-walking mechanism.⁴³ As far as we know, there is a lack of examples allowing regioselective monohydrobora-

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tion of terminal uncoupled dienes as well as uncoupled enynes.

Therefore, we decided to examine how pincer cobalt complexes based on the triazine backbone would perform in olefin hydroboration reactions with a strong focus on chemoselectivity. Recently, we have shown the possibility of their use in the dehydrogenative silylation reactions of silylacetylenes⁴⁴ or dehydrogenative coupling of silanes with alcohols.⁴⁵ Moreover, we have demonstrated the possibility of controlling the direction of the reaction of silylacetylenes with pinacolborane toward hydroboration or dehydrogenative borylation products depending on the substituents at the triazine ring.⁴⁶ Now we present an efficient anti-Markovnikov selective protocol for the hydroboration of a broad range of alkenes (amines, carbonates, ethers, vinylarenes, vinylsilanes, natural products) under mild conditions using an inexpensive and Earth-abundant cobalt complex as a catalyst. Moreover, the presented procedure allows selective functionalization of alkenyl(vinyl) silanes and alkynyl(vinyl)silanes with the retention of the alkenyl or vinyl group, respectively, leading to interesting bifunctional precursors of modern materials, in which the free alkenyl group allows further modification of the obtained polymers or their crosslinking.

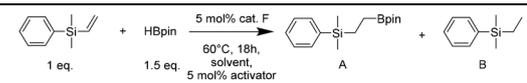
Results and discussion

In a two-step synthesis, a series of PNP ligands based on the triazine ring were obtained from commercially available substrates. Subsequently, they were utilized in the synthesis of the corresponding complexes from the cobalt chloride precursor (Scheme 1).

First, we checked the activity of the most promising cobalt precatalyst **F** in a model hydroboration reaction of dimethylphenylvinylsilane with pinacolborane (Table 1).

In the initial reaction carried out in chlorobenzene, using pinacolborane as the substrate and simultaneous precatalyst activator, we obtained 66% conversion of vinylsilane (entry 1).

Table 1 Preliminary tests for the cobalt catalyzed hydroboration of dimethylphenylvinylsilane (best reaction conditions indicated in bold)

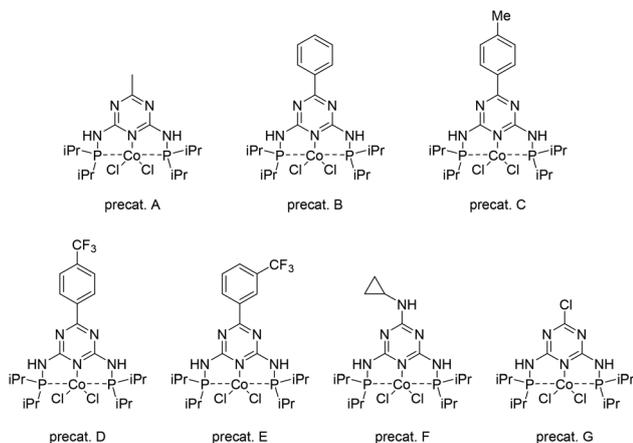


Entry	Activator	Solvent	Conversion ^a	Selectivity ^b A : B
1	—	Chlorobenzene	66%	99 1
2	Cs ₂ CO ₃	Chlorobenzene	98%	99 1
3	Cs ₂ CO ₃	Chlorobenzene	80% ^c	99 1
4	Cs ₂ CO ₃	Chlorobenzene	26% ^d	84 16
5	—	Chlorobenzene	Trace ^e	— —
6	Cs ₂ CO ₃	Chlorobenzene	Trace ^e	— —
7	—	THF	95%	98 2
8	Cs ₂ CO ₃	THF	99%	90 10
9	—	Toluene	16%	94 6
10	Cs ₂ CO ₃	Toluene	98%	91 9
11	—	Solvent-free	97%	99 1
12	—	Solvent-free	Trace ^f	— —

^a Conversion of vinylsilane determined by GC with *n*-dodecane as an internal standard. ^b Selectivity of [A]:[B] products determined by GC. ^c Reaction performed at 40 °C. ^d Reaction performed at 25 °C. ^e CoCl₂ instead of cat. F. ^f Catalyst-free.

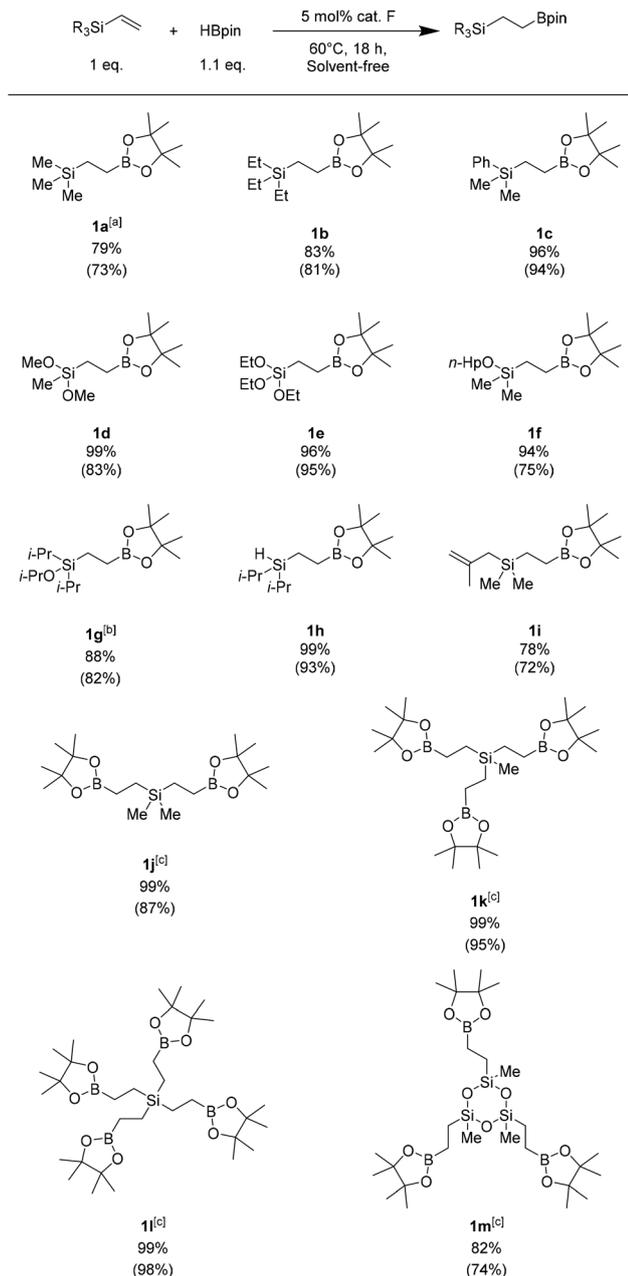
Therefore, to increase the conversion we added cesium carbonate as an additional activator, which allowed us to achieve a full conversion of the substrate (entry 2). Decreasing the reaction temperature to 40 °C (entry 3) or room temperature (entry 4) reduced the conversion rate, leading to 80% and 26% transformation of dimethylphenylvinylsilane, respectively. Experiments in other solvents (entries 7–10) gave results analogous to the model reaction in chlorobenzene. However, a reaction carried out under solvent-free conditions (entry 11) showed the possibility of running the process without the addition of an activator, giving a selectively anti-Markovnikov hydroboration product. A catalyst-free and solvent-free control experiment yielded only trace amounts of the product (entry 12). Consequently, in the next step, we decided to check the catalytic activity of other synthesized cobalt precatalysts (ESI Table S1†) under solvent-free conditions. Among them, the best results were obtained using complex **F** (ESI Table S2†), for which we also optimized the amount of used pinacolborane to 1.1 equivalents.

With the optimized reaction conditions in hand, we decided to investigate other vinylsilanes in the hydroboration reaction with pinacolborane (Scheme 2). Experiments with vinylsilanes having both aliphatic (**1a** and **1b**) and aromatic (**1c**) substituents afforded the desired products with high conversions and yields. The developed method also allows selective functionalization of sensitive alkoxy silanes (**1d–1g**), belonging to a group of important polymer precursors commonly used in materials science. The proposed procedure is fully compatible with vinylsilanes having the Si–H group (**1h**) capable of further use of the obtained products in hydrosilylation reactions. Interestingly, in the case of 2-methylallyldimethyl(vinyl)silane, the developed catalytic system permitted an exclusive functionalization of the vinyl group (**1i**), indicating the lack of activity of the presented protocol towards



Scheme 1 Structures of the obtained pincer cobalt complexes.





Scheme 2 Cobalt-catalyzed solvent-free hydroboration of vinylsilanes. ^aConversion of vinylsilane determined by GC with *n*-dodecane as an internal standard; the isolated yields are given in parentheses. ^bReaction performed at 80 °C. ^c5 mol% of catalyst per vinyl group.

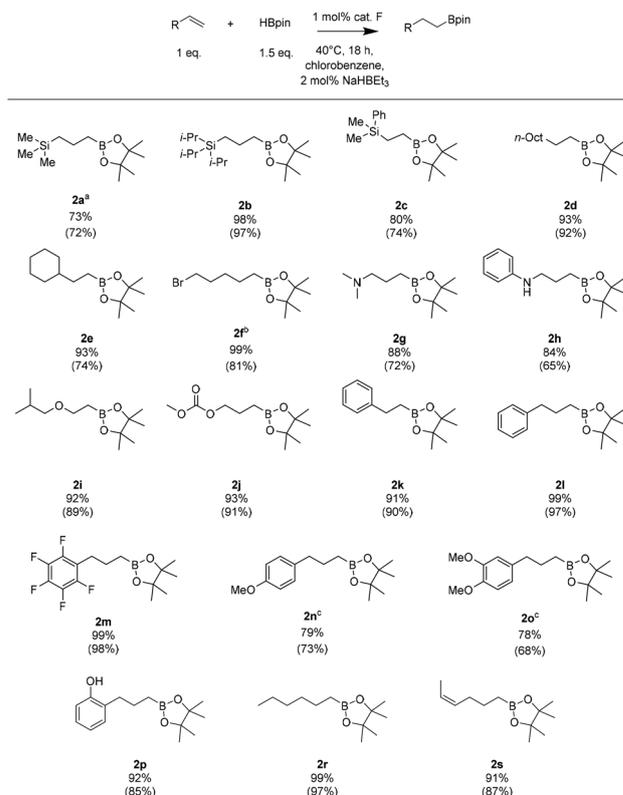
the functionalization of 2-methylallyl derivatives. Moreover, using multi-vinyl substituted silanes we were able to obtain branched derivatives (**1j–1m**) which are interesting building blocks for the synthesis of dendrimers.

Unfortunately, attempts to hydroborate allyltrimethylsilane or allyltriisopropylsilane resulted in low conversions (<7%). Similarly, in the case of non-silylated alkenes (allylbenzene and decene), we observed only partial conversions of the substrate, suggesting a strong influence of the β-silicon effect on the performed reaction.

As a consequence, we changed our strategy and used the addition of an activator (NaHBET₃). Preliminary results for the model hydroboration reaction of triisopropylallylsilane provided the desired product with full conversion (ESI Table S4†). For this reason, we conducted an optimization process, the details of which are provided in the ESI (Tables S4–S8†). Among the tested activators, all of them allowed the successful activation of the complex. Finally, we decided to use sodium triethylboron hydride solution due to its commercial availability and ease of handling. Ultimately, optimal conditions were achieved by running the reactions at 40 °C and reducing the amount of precatalyst F used to 1 mol% and the activator to 2 mol%.

Under such developed conditions, we tested a wide range of alkenes in the hydroboration reaction (Scheme 3). As a result, we functionalized with good yields of allylsilanes (**2a** and **2b**), vinylsilanes (**2c**), aliphatic alkenes (**2d** and **2e**), haloalkenes (**2f**), unsaturated amines (**2g** and **2h**), ethers (**2i**), carbonates (**2j**), or vinylarenes (**2k**).

Moreover, the excellent results of the hydroboration of allylbenzene (**2l**) and pentafluoroallylbenzene (**2m**) prompted us to investigate other naturally occurring derivatives of allylbenzenes such as estragole (**2n**) and methyl eugenol (**2o**). These compounds, due to their biological activity, are often a moiety of newly designed drugs^{47–50} and for these reasons, the



Scheme 3 Cobalt-catalyzed hydroboration of alkenes with sodium triethylboron hydride as a precatalyst activator. ^aConversion of olefin determined by GC with *n*-dodecane as an internal standard; the isolated yields are given in parentheses. ^b5 mol% cat. ^c2.5 mol% cat.



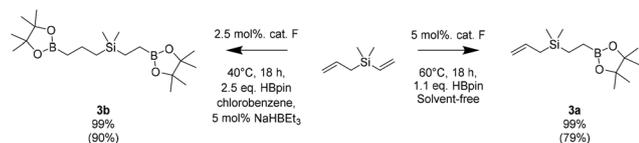
obtained products provide interesting biorelevant scaffolds for the synthesis of pharmaceuticals. Interestingly, under the developed conditions, we selectively functionalized 2-allylphenol (**2p**), leaving the hydroxyl group free, while there are scientific reports of catalyst-free dehydrocoupling of pinacol with nucleophiles (including phenols).⁵¹

To test the limitations of the developed method, we performed reactions with four unsaturated hexane derivatives under the optimized conditions. The reaction involving 1-hexene (**2r**) achieved a complete conversion of the substrate into the desired product. However, for *trans*-3-hexene and *cis*-3-hexene, no product formation was observed. This indicates that the described method enables only the functionalization of terminal olefins, which eventually allowed us to selectively functionalize mono hydroborate *cis*-1,4-hexadiene (**2s**).

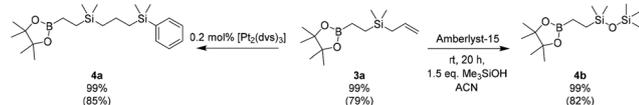
Interestingly, the different activities of the presented catalytic systems allow selective functionalization of the vinyl group in alkenyl(vinyl)silane derivatives. To confirm this concept, we carried out the hydroboration of allyldimethyl(vinyl)silane under the two developed conditions (Scheme 4). When the reaction was carried out under solvent- and activator-free conditions, we selectively modified the vinyl group leaving the allyl double bond intact (**3a**), while the use of an activator led to a double hydroboration product (**3b**).

This unique selectivity provides a number of interesting opportunities that may find application in the synthesis of highly complex precursors of advanced materials. The applicability of this approach was demonstrated in two model functionalization reactions of the monohydroborated product involving an intact allylic group (Scheme 5). To the best of our knowledge, this is the first example of a catalytic hydroboration that distinguishes the vinyl group of silanes from other alkenyl groups and allows selective functionalization without further isomerization or reduction of the obtained molecule.

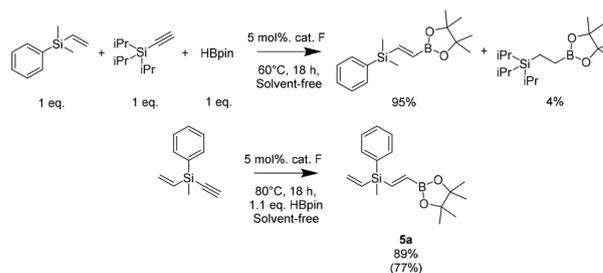
Finally, we conducted tests to check the selectivity of our system in the competitive hydroboration reaction of vinylsilane in the presence of triisopropylsilylacetylene (Scheme 6). The results showed almost full conversion of acetylene (95%) while



Scheme 4 Comparison of the selectivity of the two developed hydroboration methods.



Scheme 5 Functionalization of the monohydroborated product using hydrosilylation and *O*-silylation⁵² reactions.

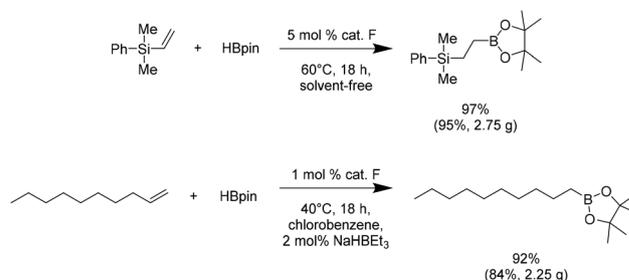


Scheme 6 Inter- and intramolecular competition hydroboration experiment.

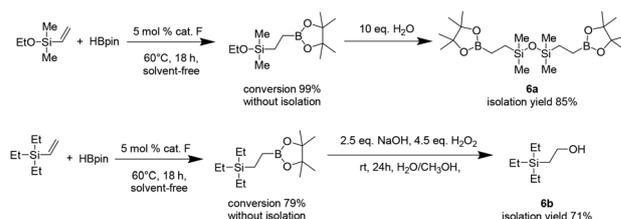
vinylsilane gave only a trace amount of the product (4%). This prompted us to modify the bifunctional (methylphenyl(vinyl)silyl)acetylene molecule, which allowed selective functionalization of the acetylene group. This is in accordance with our previous reports in which we demonstrated the possibility of the hydroboration of silylacetylenes on the described catalyst.⁴⁶

To prove the synthetic potential of the developed method, we tested its scalability by performing two gram-scale reactions for both the solvent-free hydroboration of vinylsilanes and the reaction with an activator. In both cases, we observed quantitative conversion which resulted in excellent isolation yields (Scheme 7).

Bifunctional organometallic compounds having moieties with different reactivities are interesting building blocks in synthetic chemistry. Therefore, we decided to demonstrate the possibilities offered by the developed method by performing two one-pot functionalizations (Scheme 8). In the first synthetic pathway, we modified the hydroboration product through a hydrolysis and condensation reaction of the organo-



Scheme 7 Gram-scale hydroboration reactions.



Scheme 8 One-pot functionalization of hydroboration products.

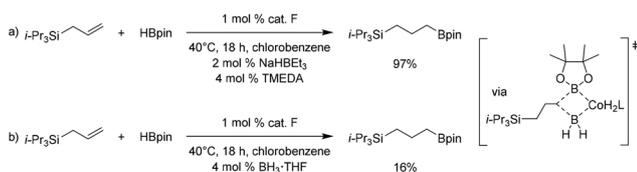


silicon moiety, while in the second, we introduced a new functional group through the transformation of the organoboron moiety. The high compatibility of the developed method with commonly used reactions allows omitting the necessity to isolate the hydroboration products perfectly fits into the tenets of modern chemistry and increases its application potential.

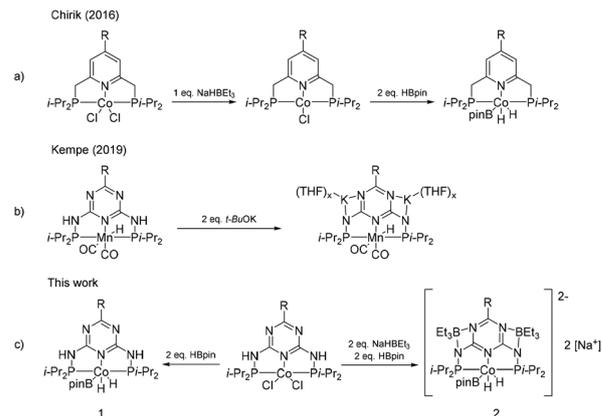
To confirm the reaction mechanism, we conducted a series of studies. First, if sodium triethylboron hydride is utilized as an activator, there is a possibility of BH_3 generation, which can act as a hidden catalyst.^{53–56} Our experiment under standard conditions using the addition of tetramethylethylenediamine as a complexing agent for potentially forming borane showed no effect of TMEDA on substrate conversion (Scheme 9a). In the case of using $\text{BH}_3\cdot\text{THF}$ instead of NaHBET_3 , we observed only partial conversion of the substrate (Scheme 9b). Therefore, we cannot fully exclude a mechanism based on the decomposition of HBpin to BH_3 , which then undergoes addition to the double bond with simultaneous transborylation with LCoH_2Bpin , but it is certainly a minor phenomenon.

To rule out the possibility of a heterogeneous mechanism driven by catalytically active cobalt nanoparticles, which may have been formed due to the reduction of the complex with sodium triethylboron hydride, we conducted the hydroboration reaction under the developed conditions by introducing a drop of mercury into the reaction vessel (refer to the ESI for details[†]). GC-MS analysis of the experiment confirmed complete substrate conversion, thereby ruling out the occurrence of a heterogeneous mechanism in the reaction.

Therefore, we conducted NMR tests in an attempt to detect the active form of the catalyst. Since our precatalysts are paramagnets, the NMR tests performed clearly indicate that there is a change in the oxidation state of cobalt during activation. In earlier studies, Chirik *et al.* investigated the activation of pinacolborane complexes with NaHBET_3 , in which cobalt is reduced from its second oxidation state to the first oxidation state, followed by an oxidative addition by HBpin to the third oxidation state (Scheme 10a).⁵⁷ However, in the case of our precatalysts, such an activation mechanism for both the reactions with pinacolborane and with the addition of NaHBET_3 leads to the same active form of the complex, thus not explaining the differences in the activity that we observed. Moreover, in the structure of the ligand from the Chirik group, the acidic NH protons were not present. Thus, for our precatalysts, the addition of NaHBET_3 is probably responsible for the deprotonation of the NH groups of the complex, in a manner analogous to that proposed in the studies of the Kempe group



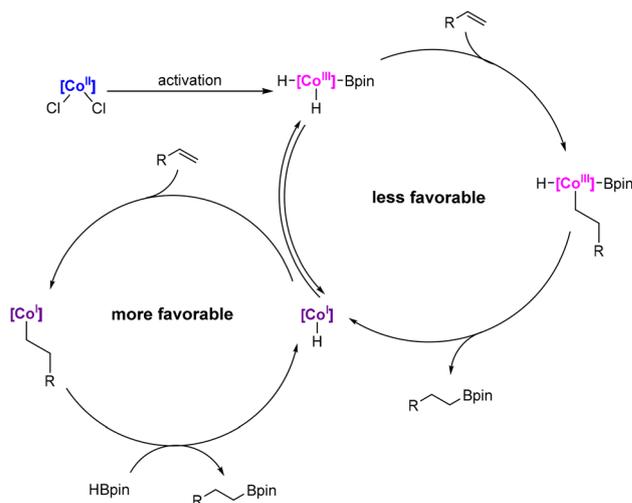
Scheme 9 Experiments verifying the potential formation of borane as a hidden reaction catalyst.



Scheme 10 Mechanisms of the activation of pincer complexes.^{57,58}

(Scheme 10b), in which they postulate that the anionic nature of the catalyst affects its high activity.⁵⁸ In our study, we did not observe a difference in the catalytic activity depending on the activator used or its counterion (see the ESI, Table S8[†]), therefore we believe that the deprotonated form of the complex is fully responsible for its high catalytic activity in the olefin hydroboration reaction. The ^{11}B NMR spectrum acquired for structure 2 (Scheme 10c) indicates the presence of several diverse boron nuclei (see the ESI[†]), probably originating from BET_3 adducts with the anionic form of the complex, which is in agreement with the literature reports by the Pawluć group.⁵⁹ In the case of the non-anionic form, its lower catalytic activity is probably compensated by the β -silicon effect, stabilizing the alkyl complex and remarkably accelerating the reaction rate.^{60–62}

Based on this and our previous studies on pincer cobalt complexes, as well as literature reports,^{44–46,57,63–67} we postulate that in the reaction mixture, as a result of activation with pinacolborane or sodium triethylboron hydride, the two



Scheme 11 Proposed catalytic cycle.



forms of the cobalt complex (Co(i) and Co(III)) coexist in equilibrium. Either of them can catalyze the process; however, based on recent reports,⁶⁶ we assume that the main catalytically active form is Co(i) (LCo-H). First, the alkene undergoes 1,2-insertion into a Co-H bond, which is followed by transmetalation with the pinacolborane moiety, resulting in the regeneration of the active form (Scheme 11). In the case of the hydroboration of vinylsilanes using pinacolborane alone as an activator, we assume that the active form of the complex is LCo-H being in equilibrium with structure **1** (Scheme 9c and see the ESI†), while for activation with the addition of NaHBET₃, we are unable to conclusively determine the active form of the complex; however, we postulate analogous structures with a deprotonated ligand (Scheme 9c and see the ESI†).

Conclusions

In conclusion, we have developed new highly efficient catalytic methods for anti-Markovnikov hydroboration of terminal alkenes using a cheap catalyst based on Earth-abundant cobalt and proceeding under mild conditions. The proposed protocols allow the functionalization of a wide range of alkene derivatives (silanes, amines, ethers, natural products) showing high chemo- and regioselectivity, with the obtained compounds being interesting synthons for the synthesis of fine chemicals, pharmaceuticals, and polymers. We also demonstrated the possibility of selective functionalization of the vinyl group in alkenyl(vinyl)silanes or of the alkynyl group in alkynyl(vinyl)silanes based on the developed solvent and activator-free method. Moreover, we proved the high scalability and compatibility of the described methodology with other procedures allowing further one-pot modification of the obtained products highlighting the high applicability character of the developed protocol.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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