

Cobalt-Catalyzed Hydroboration of Alkenes, Aldehydes, and Ketones

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Supporting Information

ABSTRACT: An operationally convenient and general method for hydroboration of alkenes, aldehydes, and ketones employing $Co(acac)_3$ as a precatalyst is reported. The hydroboration of alkenes in the presence of HBpin, PPh₃, and NaO'Bu affords good to excellent yields with high Markovnikov selectivity with up to 97:3 branched/linear selectivity. Moreover, $Co(acac)_3$ could be used effectively to hydroborate aldehydes and ketones in the absence of additives under mild reaction conditions. Inter- and intramolecular chemoselective reduction of the aldehyde group took place over the ketone functional group.



O rganic transformations catalyzed by Earth-abundant transition metals have recently garnered attention due to the increasing demand for inexpensive, efficient, atomeconomical, and environmentally benign synthetic methods. The reduction of aldehydes and ketones to generate 1° and 2° alcohols is an important reaction in the pharmaceutical industry due to the inherent value of alcohols as building blocks in the synthesis of bioactive molecules.¹ There are numerous literature examples of precious metals,² main group elements,³ rare earth metals,⁴ and alkali metals⁵ that are capable of the effective and efficient reduction of carbonyl compounds. Nevertheless, the demand for inexpensive alternatives has resulted in the development of Earth-abundant first-row transition-metal catalysis for such transformations (Ni,⁶ Co,⁷ Cu,⁸ Fe,^{9a,7b,9b-d} and Mn¹⁰).

Boronic acid derivatives are key reaction intermediates that have been used routinely to construct new bonds (C–C, C–N, C–O, C–X). For example, the Suzuki–Miyaura crosscoupling reaction utilizes boronic esters in C–C bond-forming chemistry. Organoborates also serve as excellent surrogates that can be modified into a variety of functional groups. Traditionally, organoborates are accessed via synthetic strategies such as hydroboration of alkenes or borylation of olefins or alkanes. These reactions typically favor the formation of the linear, anti-Markovnikov products and are well documented with precious-metal catalysts (Rh, Ru, Ir),¹¹ though there are examples of Earth-abundant transition metals (Fe¹² and Co¹³) that have been recently disclosed.

Selectivity for the branched Markovnikov products are generally less frequently observed. Though progress has been made, the number of reports of base metal (M = Fe,¹⁴ Co,¹⁵ Cu,¹⁶ Ni,¹⁷ and Mn¹⁸) catalyzed Markovnikov-selective alkene hydroboration remains limited. Cobalt catalysts in hydroboration of alkenes have been studied by the groups of

Chirik,^{13a} Huang,¹⁹ and Turculet.²⁰ In each system, the products favored anti-Markovnikov (linear) addition. In 2017, Thomas and co-workers reported a versatile cobalt(II) catalytic system which yields Markovnikov (branched) products while exhibiting a broad substrate scope and tolerance of diverse steric and electronic effects; it should be noted that anti-Markovnikov addition was the major product for the aliphatic substrate.²¹ Prior to the work of Thomas, only two examples of cobalt catalyzed Markovnikov addition were known (Chirik^{15a} and Hollis^{15c}); however, only 1 example of Markovnikov addition was reported. Therefore, there are still opportunities to develop catalytic systems incorporating cobalt that can generate secondary boronic esters with high yields and regioselectivity.

Our group has a long-standing interest in base metal catalysis,²² and more recently, we have focused on employing commercially available metal salts in operationally convenient transformations.^{23a,b,9b,23c,d} Herein, we report cobalt-catalyzed hydroboration of alkenes, aldehydes, and ketones by commercially available $Co(acac)_3$ (1) under mild reaction conditions (Scheme 1). This simple precatalyst delivers (1) an additive-free reduction of alkenes in the presence of an ancillary phosphine ligand and NaO^tBu at room temperature.

Initially, we chose styrene (2a) as our model substrate and ran catalytic hydroboration reactions employing HBpin in THF with Co(acac)₃ (1) for 24 h. Unsurprisingly, the reaction yielded little to no product. However, we observed full conversion of 2a in 4 h at room temperature after addition of NaHBEt₃ to 1 to generate a putative in situ "Co–H" catalytic

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Scheme 1. Select Examples of Cobalt Catalysts in Regioselective Hydroboration of Alkenes

Selected few examples of cobalt in Anti-Markovnikov selective hydroboration of alkenes:



species. The GC–MS showed a mixture of products whereby the formation of both Markovnikov and anti-Markovnikov regioisomers (73:24 b/l, 52%) was observed. It should also be noted that considerable amounts of ethylbenzene were also formed. The screening of different cobalt salts with NaHBEt₃ revealed that 1 was the most effective and efficient cobalt source (Table S1). The combination of 1/NaHBEt₃ showed good results for several substrates that were screened (Scheme S2). Appropriate control reactions determined that the combination of both 1/ NaHBEt₃ was catalyzing the reaction (Table S1). Encouraged by these results, we were motivated to develop reaction conditions that could further afford increased regioselectivity and overall yield.

The screening of various neutral ancillary ligands showed that PPh₃ (L_1) gave the best yield and regioselectivity; the ratio of branched to linear regioisomer improved to 87:13, albeit in similar yield (55%) (Scheme 2). Further optimization revealed that 1/NaHBEt₃/ L_1 in 1:1:3 ratio gave a yield of 88% with a 93:7 branched to linear ratio (Table S2). Although we were able to obtain high selectivity with good yield, we were curious about the role of NaO'Bu as an alternative additive, as it is a common and popular choice of additive in catalysis.^{7b} For

Scheme 2. Initial Screening of Alkene Hydroboration with Ligands a



 a Yield and ratio of regioisomers determined by $^1\mathrm{H}$ NMR and GC–MS.

example, it has been proposed to activate HBpin directly and subsequently serve as a hydride donor. 7b

Initial screening of the reaction with $1/\text{NaO}^{t}\text{Bu}/\text{L}_{1}$ in a 1:1:1 ratio yielded 74% of the regioisomeric products with a 94:6 branched to linear ratio. Increasing L_{1} to 2 equiv yielded 90% of the hydroborated products without any erosion in the observed regioselectivity. Control experiments showed that productive catalysis was only observed when the combination of catalyst, additive, and L_{1} was used. With these new reaction conditions in hand, we decided to pursue catalytic hydroboration of alkenes with $1/\text{NaO}^{t}\text{Bu}/L_{1}$ in 1:1:2 ratios (Scheme 3). Under these reaction conditions, a wide scope







of substrates bearing electron-donating, electron-withdrawing, halogen, and ester substituents was tolerated. Moreover, good to excellent yields with high regioselectivity were observed. The impact of steric crowding could be discerned employing the substrates 2-methylstyrene (2d) and 2,4,6-trimethylstyrene (2h). In the case of 2d, regioselectivity is degraded (4:1 Markovnikov/anti-Markovnikov), reaction time is lengthened, and yield is diminished in comparison with parent styrene (2a). Remarkably, in the case of 2h, regioselectivity was completely reversed; a linear anti-Markovnikov product was favored over the branched Markovnikov product (product ratio was determined to be 4:1 by ¹H NMR). Interestingly, when 2,6-difluorostyrene (2i) was used as the substrate, virtually no regioselectivity and a 44:56 branched to linear product ratio was observed.

When 4-phenyl-1-butene (2m) was employed as substrate, we were surprised to find that, in addition to diminished yield, borylation occurred predominantly at the 4-position. This product presumably arises from an isomerization process. In addition to the borylation at the benzylic position, the minor product was determined to be the species formed from formation of the C–B bond at the terminal position (antiMarkovnikov selectivity). Chirik and co-workers have previously investigated isomerization of 4-phenyl-1-butene in hydroboration chemistry using deuterium-labeling experiments; the rate of C–B bond formation was observed to be faster than isomerization as deuterium scrambling was not observed due to the addition of DBpin exclusively at the β position to the arene ring.^{15b} Finally, the exclusive formation of linear product was observed for the aliphatic substrate, 1-hexene (**2n**).

The ability of $Co(acac)_3$ (1) to hydroborate alkenes under mild conditions prompted us to explore the hydroboration of aldehyde and ketones. The transition-metal-catalyzed hydroboration of carbonyls is now well-established, even with the first-row metal elements;¹⁻¹⁰ in most metal-catalyzed transformations an additive of some kind is typically required. We became interested in additive-free hydroboration catalyzed by 1. We initially selected 4-methoxybenzaldehyde (4a) as the model substrate for our studies and carried out the reaction in the absence of NaO^tBu and phosphine ligand (unlike in the alkene hydroboration). We were pleased to observe that within 24 h of stirring at room temperature >95% of 4a was consumed; the reaction was monitored by ¹¹B NMR. Further optimization revealed that upon heating the reaction at 50 °C 100% conversion of 4a was observed within 4 h as determined by ¹¹B NMR and GC-MS. The control experiment in the absence of 1 showed little to no activity (Table S3), suggesting that 1 was catalyzing the reaction under mild and additive-free reaction conditions.

Examination of several different aldehyde substrates demonstrated the generality of the additive free hydroboration protocol, as in all cases, good to excellent yields of 1° alcohol (after work up) were obtained; electron-donating, electronwithdrawing, halides, and aliphatic and alicyclic substrates were all tolerated (Scheme 4, 5a-j). Moreover, introduction of sterically encumbering groups in the substrate (4e,h) did not





^aYields based on ¹H NMR using mesitylene as the internal standard.

inhibit product formation, although longer reaction times were required to achieve satisfactory conversions. The hydroboration of *trans*-cinnamaldehyde (4i) afforded the α , β -unsaturated 3-phenyl-2-propen-1-ol (5i) as the exclusive product (>99% purity).²⁴

The additive-free hydroboration method was also expanded to ketones to afford quantitative yields of reduced boronate ester products. Unsurprisingly, an examination of several different ketone substrates demonstrated the generality of the hydroboration protocol, as in most cases, yields of 2° alcohols ranged from good to excellent (Scheme 4, Sk–q). Naturally occurring molecules such as verbenone (Sp), a terpene commonly found in plants, showed limited reactivity, presumably due to the presence of steric encumbrance.

Experiments designed to test for chemoselectivity were carried out. In all cases, selectivity for aldehyde reduction over ketone under equimolar addition of substrates and HBpin was observed. The reaction mixtures of both 4-fluorobenzaldehyde and 4-fluoroacetophenone were submitted to our optimized conditions; analysis of the aliquots using ¹H NMR revealed that exclusive reduction of 4-fluorobenzaldehyde (91%) had occurred (Scheme 5a). Selective hydroboration of aldehyde

Scheme 5. Chemoselective Hydroboration Reactions^a



^aYields based on ¹H NMR using mesitylene as the internal standard. ^bYields in parentheses are after addition of second equivalent of HBpin.

over ketone was also observed in an intramolecular fashion employing, 3-acetylbenzaldehyde (6). ¹H NMR analysis of the reaction mixture showed the exclusive formation of 3-acetylbenzyl alcohol (7) (Scheme 5b) (Figure S92).

The influence of substrate electronics was also examined by means of a competition reaction employing electron-withdrawing, electron-donating, and electron-neutral substrates. The first competition reaction we carried out employed the aldehydes: benzaldehyde (4b), 4-fluorobenzaldehyde (4c), and 4-methoxybenzaldehyde (4a) (Scheme 5c). Analysis of the reaction mixture after full consumption of 1 equiv of HBpin showed approximately equal amounts of 4b and 4c were consumed, whereas 4a remained unreacted. Subsequent addition of a second equivalents of HBpin to the reaction mixture showed further conversion of both 4b and 4c with 4a present in significant unreacted quantities (Figure S93). From these data, we surmise that the aldehydes react sufficiently rapidly at the 1 h time point since similar amounts of both electron-deficient and electron-neutral substrates have been consumed. However, electron-rich substrates react at a significantly slower rate. Similarly, the competition reaction of the ketones showed analogous reactivity to that observed for the aldehydes (Scheme 5c). Analysis of the reaction mixture after addition of 1 equiv of HBpin showed that both 4fluoroacetophenone (4m) and acetophenone (4l) reacted, while 4-methylacetophenone (4k) remained largely unreacted. Addition of a second equivalent of HBpin showed further reactivity of 4l and 4m with a large amount of unreacted 4k (Figure S94).

To understand the reaction mechanism better, deuteriumlabeling experiments were performed. As expected, the formation of an exclusively proteo-boronic ester was observed when the hydroboration of styrene was performed in THF- d_8 (Scheme 6a). Similarly, when styrene- d_8 was used as the

Scheme 6. Deuterium-Labeling Experiments



substrate, proton incorporation occurred solely at the terminal methyl group (Scheme 6b). These data suggested that both H and Bpin addition during the reaction originated from the pinacolborane. A reaction with DBpin, which was synthesized according to the procedure by Chavant et al.,²⁵ showed a mixture of products. ¹H NMR revealed the formation of both the monodeuterated boronic ester and fully proteo-boronic ester in a ratio of 89:11 (Scheme 6c and Figure S103). The formation of the fully protio boronic ester warrants a further discussion, as this implies that the mechanism includes insertion of the alkene into the *in situ* generated active cobalt-hydride species and β hydride elimination during the transformation. ^{14c,21} Alternatively, the H/D exchange observed could also be due to the process of isolating the product. At this

stage, a more detailed study of the mechanism is currently ongoing in our group.

In conclusion, we have shown that commercially available $Co(acac)_3$ can be used to effect operationally convenient and regioselective hydroboration catalysis of both alkenes and carbonyls. In particular, we have developed a general method to catalyze regioselective Markovnikov hydroboration of alkenes in good to excellent yields in the presence of PPh₃ and NaO^tBu. Moreover, $Co(acac)_3$ was also employed in an additive free hydroboration of aldehydes and ketones under mild reaction conditions. Chemoselective experiments revealed that the catalytic system was selective for aldehydes over ketones.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b02775.

Experimental procedures, characterization data, and GC-MS and NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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