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The *in air* catalytic hydroboration of ketones and aldehydes with pinacolborane by an iron(II) coordination polymer (CP) is carried out under mild and solvent-free conditions. The precatalyst is highly active towards a wide range of substrates including functionalized ketones and aldehydes in the presene of KOtBu as an activator, achieving a high turnover number (TON) of up to 9500. Excellent chemoselectivity to aldehydes over ketones was also revealed, which is in sharp contrast with the results obtained under inert atmosphere using the same catalyst system. This catalyst observed here is not only highly efficient but also recyclable for reuse for at least 5 times without losing its effectiveness.

Introduction

Metal-catalyzed hydroboration of carbonyl compounds using pinacolborane (HBpin) has attracted considerable attention in recent years, as it provides synthetically important borate ester intermediates which could be readily converted into the corresponding alcohols.¹ While many stoichiometric methods are known for the hydrogenation of carbonyls by hydride reagents, the functional group tolerance and chemoselectivity between aldehydes and ketones were often a challenge.² In the past decade, selective hydroboration of carbonyls has been intensively explored by metal catalysts, in particular those containing transition metals,³ rare earth⁴ and main group metals,⁵ although an uncatalyzed method for aldehyde hydroboration is recently reported.⁶ Among the most attractive metal-catalyzed hydroboration of carbonyl compounds, iron, as the most abundant transition metal, has only found applications for this reaction in a few reports very recently, although iron is well known for hydroboration and hydrosilylation of olefins.⁷⁻⁹ In 2017, Findlater and coworkers reported on iron-catalysed hydroboration of carbonyl compounds under N₂ atmosphere using a simple Fe(acac)₃ salt (acac = acetylacetonate, 10 mol% of catalyst loading) in the presence of an air-sensitive activator, NaHBEt₃.¹⁰ The chemoselectivity of aldehydes over ketones was also disclosed. Later on, Bai et al. developed a dimer iron(II) phosphoranimide complex for the selective hydroboration of aldehydes over ketones.¹¹ In 2018, the Baker group also revealed a dimeric Fe^{II} complex based on a N₂S₂ ligand that was suitable for the

hydroboration of aldehydes only.¹² More recently, Geetharani and coworkers reported a simple iron(II) amide complex that is also effective for the hydroboration of aldehydes and ketones, with chemoselectivity favoring the former.¹³ Accepted

Despite such advances, the current state of catalyst development for carbonyl hydroboration still suffers from nontrivial catalyst synthesis (typical metal-ligand complexes), low catalytic efficiency, limited scope of substrates and poor functional group tolerance.¹ It is also noticed that a typical hydroboration (of alkenes, alkynes and carbonyls) usually requires inert atmosphere (due to the use of air- and moisturesensitive borane reagents),^{1,3-6} and most of them involve airsensitive metal complex catalysts or activators, thus diminishing its interest for synthetic utilization in industry. In addition, the majority of metal-catalysed hydroboration reported thus far proceeded under homogeneous conditions and catalyst recycling could be very troublesome. From a viewpoint of green chemistry, practical methods for the hydroboration of carbonyl compounds are extremely limited. In 2017, Zhao's group developed a transition-metal-free method for the hydroboration of ketones, aldehydes, alkenes and alkynes, where sodium hydroxide was used to promote the reactions of a range of substrates in toluene or benzene-d6.^{5f} Later on, Hreczycho and coworkers disclosed a catalyst-free and solventfree method for the hydroboration of aldehydes under mild conditions.⁶ However, this method displayed poor effectiveness in ketone hydroboration even at elevated temperature. Therefore, a greener methodology that utilizes higherefficiency and less-expensive catalysts (ideally recyclable) and enables the reaction in air without the use of toxic organic solvents is highly desired.

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We have been in particular interested in reduction catalysis concerning unsaturated bonds by using Earth-abundant cobalt and iron catalysts14 and have reported a two-dimensional iron(II) coordination polymer (1) based on a divergent 4'-(4diphenylaminophenyl)-4,2';6',4"-terpyridine ligand (L) that catalyzed the heterogeneous hydroboration of carbonyl compounds using HBpin with KO^tBu as an activator.¹⁵ Interestingly, this catalyst system showed excellent catalytic activity towards ketone substrates, yet very poor performance for aldehyde hydroboration under inert atmosphere (Scheme 1). This is in sharp contrast with other known iron(II) hydroboration catalysts that usually favor aldehydes over ketones.¹⁵ Upon further investigation of the unique chemoselectivity of 1, we found that 1 displayed higher catalytic efficiency for hydroboration of a broad range of carbonyl compounds in air and under mild, solvent-free conditions, as well as excellent chemoselectivity towards aldehydes over ketones.

Herein, we report a green and practical approach to heterogeneous hydroboration of carbonyl compounds in air catalysed by an air-stable iron(II) coordination polymer. To our knowledge, heterogeneous carbonyl hydroboration was only rarely reported involving the use of air- and moisture-sensitive metal reagents.^{16,17}

Results and discussion

Initially, we conducted the reaction of benzaldehyde with HBpin by using catalyst 1 (0.1 mol% based on FeL₂Cl₂ unit) in the presence of KO^tBu (2 mol%) in air and found complete hydroboration in only 30 min under solvent-free conditions (Scheme 2). To compare, the same reaction proceeded very sluggishly under N₂ atmosphere affording 15% boronate ester after 16 h as reported previously.¹⁵ Further screening of reaction conditions was carried out and the results are summarized in Table 1. It was found that other base additives such as KO^tBu, KOH and K₂CO₃ were also comparable activators for Fe-catalysed hydroboration in air (entries 2-4, Table 1). The control experiments showed that the precatalyst 1 alone was inactive without added KO^tBu (entry 5), while the reaction occurred in the presence of KO^tBu with poor yield of 2 (19%, entry 6). The combination of free ligand and KO^tBu also promoted hydroboration, however, the yield was very low (entry 7). A direct comparison of the catalytic activity between polymeric framework 1 and the discrete complex Fe(tpy)Cl₂

(where tpy = 2,2';6',2''-terpyridine) further reveals the importance of a polymeric structure in **1** for effective cativity (entry 8). Solvent effect was also studied and we found that the reactions proceeded more slowly in toluene, benzene or pentane compared to that in THF, and even worse in diethyl ether giving only 20% GC yield of **2** in 30 min (entries 9-12). In contrast, we performed the reaction under the same conditions (**1**/KO'Bu in THF, rt), but under N₂, only 12% of **2** was detected in 30 min (entry 13). Finally, it was noted that the reaction was equally efficient without a solvent (entry 14) and high yield (95%) was still accomplished when decreasing the loading of precatalyst **1** to 0.01 mol%, corresponding to a high TON of 9500.



Scheme 2. The comparison of **1**-catalysed hydroboration of benzaldehyde with pinacolborane under N₂ or in air (up), and crystal structure of **1** showing the Fe^{II}N₄Cl₂-coordination environment (down, left) and a 2-D framework (down, right).

Next, we applied the green, iron-catalysed method for the hydroboration of benzaldehyde to more functionalized aldehydes as well as ketones under neat conditions in air (0.1 mol% 1 and 2 mol% KO^tBu). A range of electronically and sterically differentiated aldehydes were first explored and the results are summarized in Table 2. For these examples, the hydroborated products (2) have been analysed by GC-MS as intermediates, and the corresponding primary alcohols (3) were obtained subsequently after purification by silica gel column chromatography, due to the known silica-promoted hydrolysis of boronate esters that has been observed previously.¹⁵

	Ö			OBpin
[H +	HBpin [Fe] in air, 2	25 °C	2
Entry	Catalyst	Activator	Solvent	Yield /% ^b
1	1	KO ^t Bu	THF	99
2	1	NaO ^t Bu	THF	99
3	1	КОН	THF	97
4	1	K ₂ CO ₃	THF	98
5	1	-	THF	<5
6	-	KO ^t Bu	THF	19
7	L	KO ^t Bu	THF	25
8	Fe(tpy)Cl ₂	KO ^t Bu	THF	18

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1	KO ^t Bu	Et ₂ O	20	
1	KO ^t Bu	toluene	66	
1	KO ^t Bu	benzene	70	
1	KO ^t Bu	pentane	62	
1	KO ^t Bu	THF	12	
1	KO ^t Bu	-	99	
1	KO ^t Bu	-	95	
	1 1 1 1 1 1	1 KO'Bu 1 KO'Bu	1KOtBuEt2O1KOtButoluene1KOtBubenzene1KOtBupentane1KOtBuTHF1KOtBu-1KOtBu-	1 KO ^t Bu Et ₂ O 20 1 KO ^t Bu toluene 66 1 KO ^t Bu benzene 70 1 KO ^t Bu pentane 62 1 KO ^t Bu THF 12 1 KO ^t Bu - 99 1 KO ^t Bu - 95

^aConditions: benzaldehyde (1.0 mmol), HBpin (1.1 mmol), catalyst **1** (0.1 mol%), activator (2 mol%) and solvent (1 mL), 25°C, 30 min, in air. ^b Determined by GC-MS analysis with hexamethylbenzene as an internal standard. ^cReaction run under N₂. ^d 0.01 mol% **1** was used.

Benzyl alcohol, 3a, was isolated in 92% yield after the standard reaction in air within 30 min, while complete conversion was detected (entry 1, Table 2). Substituted benzaldehydes bearing halo, electron-donating and electron-withdrawing groups are all suitable substrates, affording the desired alcohols 3a-f in good to excellent yields (entries 2-6). While reaction with 4-methoxybenzaldehyde proceeded a little sluggishly giving boronate ester (2c) in 80% GC yield after 4 h, 4-trifluoromethylbenzaldehyde containing a strongly electron-withdrawing group was converted to the corresponding alcohol in higher yield within the same period. It is worth mentioning that all these substrates show poor to moderate reactivity with the same catalyst under N₂ atmosphere.¹⁵ Interestingly, benzaldehydes containing reducible groups such as nitro or ester functionality were selectively hydroborated at the aldehyde part under standard conditions with the corresponding alcohols (3g and 3h, entries 7 and 8) being isolated with excellent yields. 1-Pyrenecarboxaldehyde was also readily hydroborated to give the resulting adduct in high yield within a period of 4 h (entry 9). In addition, benzene-1,4dicarbaldehyde can be fully hydroborated with the use of 2.2 equiv. of HBpin, providing the desired diol in 90% yield (entry 10). Aldehydes with S- or N-heterocycle also showed equal activity as benzaldehyde, leading to isolation of the resultant alcohols (3k and 3I) in excellent yields. Trans-cinnamaldehyde containing conjugated C=C and C=O bonds was selectively hydroborated at the C=O bond in the presence of 2.2 equiv. of HBpin (entry 13). Finally, several aliphatic aldehydes were examined and all found to be active substrates for 1-catalysed hydroboration, with reactions being furnished in 30 min (entries 14-17).

Table 2. Substrate scope of iron(II)-catalysed aldehyde hydroboration in air.^a







^a Conditions: aldehydes (1.0 mmol), HBpin (1.1 mmol), catalyst **1** (0.1 mol%) and KO⁴Bu (2 mol%), rt, 30 min and in air. ^b Yields of hydroborated products (**2**) were determined by GC-MS analysis with hexamethylbenzene as an internal standard. Isolated yields of the corresponding alcohols (**3**) are shown in parenthesis. ^c Reaction run for 4 h. ^d 2.2 equiv. HBpin was used.

With success in aldehyde hydroboration, we also explored the potential of this catalyst for ketone hydroboration in air, even though it has been previously revealed that this catalyst was effective for hydroboration of a variety of ketones under N₂. A facile ketone hydroboration without protection with inert atmosphere will be more attractive with regard to green chemistry. Thus, a variety of functionalized ketones were tested and the results are presented in Table 3. Again, acetophenone and other aryl ketones with electrondonating and -withdrawing groups can be converted smoothly into the corresponding boronate esters in 1 h, with high isolated yields of secondary alcohols **5a-f** (entries 1-6, Table 3). Cyclopropyl phenyl ketone was also converted with appreciable yield as compared to the same reaction under N₂ (entry 7).¹⁵ Tetralone, 2-nathphaldehyde and 2-acetylferrocene were excellent substrates, providing the corresponding alcohols 5h-j with high yields (entries 8-10). Whereas an α , β -unsaturated ketone underwent selective 1,2-addition to give 5i with a moderate yield after 4 h when two equiv. of HBpin was used (entry 11), both heteroaryl ketone (3-acetylpyridine) and aliphatic ketones (cyclohexanone, cyclopentanone, acetone and 2heptanone) were readily hydroborated in good to high yields with HBpin in 1 h (entries 12-16). It was noted that heteroaryl ketones

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including 3- or 4-acetylpyridine were challenging substrates when the reaction was conducted under N₂ (entry 12).¹⁵ This represents an extra advantage of 'in air' hydroboration catalyzed by **1**.

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 Table 3. Substrate scope of iron(II)-catalysed ketone hydroboration in air.^a



^a Conditions: ketones or aldehydes (1.0 mmol), HBpin (1.1 mmol), catalyst **1** (0.1 mol%), KO^tBu (2 mol%), rt, 1 h and in air. ^b Yields of hydroborated products (**2**) were determined by GC-MS analysis. Isolated yields of alcohols (**3**) are shown in parenthesis. ^c Reaction run for 4 h. ^d Reaction run under N₂.

To further demonstrate the applicability of this method for reduction of more complex ketone substrates, we examined the reaction of HBpin with rotenone,¹⁸ a naturally occurring products used as a pesticide and insecticide, under Fe-catalysed

conditions (0.5 mol% of **1** was used in THF. Scheme 3) cltowas observed that hydroboration only occurred 1at9/the cketome position, displaying excellent selectivity over alkene hydroboration and possible cyclic ether ring-opening reactions that could be promoted by Lewis acid.¹⁹ Thus, compound **6** was readily isolated after boronate ester hydrolysis as the only product in good yield.



Scheme 3. Fe-catalysed selective hydroborative reduction of rotenone in air.

To ascertain whether the polymeric framework structure of 1 is the key to high catalytic activity observed here, we prepared two analogues of 1 featuring discrete structures of iron(II) complexes, and compared their catalytic performance (Scheme 4). Thus, iron(II) complexes 7 and 8 containing convergent ligands, 4'-(4-dimethylamino)phenyl-2,2';6',2"-tpy and 4'-(4diphenylamino)phenyl-2,2';6',2"-tpy, were synthesized, respectively, in good yields through a facile procedure (see ESI). 7 and 8 were then examined for the homogeneous hydroboration of benzaldehyde in air under neat conditions. It was observed that while 7 (0.1 mol%) catalysed hydroboration of benzaldehyde in 85% yield within 30 min, 8 showed higher activity that is identical to 1. This finding indicates that the ligand structure has an impact on the catalytic reactivity and the N,N-diphenylamino substituent on tpy might have played an important role in promoting the formation of active catalytic species. Furthermore, we applied discrete complex 8 as a precatalyst for the hydroboration of several functionalized aldehydes and ketones as illustrated in Scheme 4. The results show that for all examples the yields were either comparable to or slightly lower than those obtained by using 1 as a precatalyst under identical conditions, suggesting that the polymeric structure of 1 might not be determining for the excellent catalytic activity in air.

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Scheme 4. Homogeneous Fe-catalysed hydroboration of carbonyl compounds in air. Conditions: ketones or aldehydes (1.0 mmol), HBpin (1.1 mmol), 7 or 8 (0.1 mol%), KO^tBu (2 mol%), rt, 30 min (for aldehydes) or 1 h (for ketones) and in air. Yields of boronate esters were determined by using GC-MS analysis. ^a Reaction run for 4 h.

Previously, it was found that under N₂ the catalyst was inactive in the presence of an equimolar mixture of acetophenone and benzaldehyde, and the chemoselective hydroboration could not be established.¹⁵ We are further interested to explore the chemoselectivity between aldehyde and ketone when the reaction is catalyzed by 1 as a precatalyst in air (Scheme 5). Thus, when acetophenone (1 mmol) was mixed with benzaldehyde (1 mmol) and one equiv. of HBpin under standard conditions, quantitative hydroboration of aldehyde was observed with almost full recovery of the ketone. Likewise, the competing reaction between aliphatic aldehvde and ketone revealed the same selectivity for aldehyde over ketone. In addition, the intramolecular chemoselective hydroboration using 4-acetylbenzaldehyde resulted in the isolation of a primary alcohol (9) in good yield and no doubly hydroborated product was isolated, indicating excellent chemoselectivity as well. This is significant as it shows that catalysis with precatalyst 1 in air outperforms that at inert atmosphere, in terms of both its generality and chemoselectivity. Although similar chemoselectivity has been previously reported for transition metal-catalysed hydroboration of carbonyls.^{3,10-13} this example that features a heterogeneous catalysis operating in air is unique.



Furthermore, we studied the reducible functional group compatibility by conducting a simple robustness screen with iron catalyst in air. This method was first introduced by the Glorius group aiming to develop a fast and feasible method to test functional group tolerance in a catalytic reaction, before a complicated substrate containing multiple functional groups was employed.²⁰ Using the same method, we examined the Fecatalysed hydroboration of benzaldehyde in air under the standard conditions in the presence of additives bearing various reducible groups (1.0 eq.) as shown in Table 4. Products of each reaction were analysed by GC using an internal standard after 30 min. The results revealed that the hydroboration of benzaldehyde was not affected by the presence of reducible functionalities such as alkene, alkyne, nitrile, nitro, imine and pyridine (entries 1-6), while it was almost quenched by N,Ndimethylformamide (DMF, entry 7). It was noted that in all reactions, no products attributed to the additive hydroboration were detected, even in the case of DMF.



^a Determined by GC-MS analysis with hexamethylbenzene as an

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Table 4. The reducible functional group tolerance of benzaldehyde hydroboration.^a

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HBpin and activator KO^tBu would produce a reducing species. HB(O^tBu)(Pin), which is responsible for the generation of 8a critical Fe-H active species (Scheme 6).⁷ The as-formed Fe-H species allows facile carbonyl insertion to form an iron alkoxide intermediate that is reactive towards HBpin. As a result of σ-bond metathesis of HBpin, boronate ester product will be released and regenerate the active Fe-H species, closing the catalytic cycle.



Scheme 6. Plausible mechanism of Fe-CP catalysed hydroboration of carbonyl compounds in air.

Conclusions

In summary, in this work we report an unusual 'in air' hydroboration of aldehydes and ketones under solvent-free and heterogeneous conditions by a Fe^{II}-based coordination polymer as precatalyst. A wide range of functionalized aldehyde and ketone substrates have been successfully transformed to primary and secondary alcohols through a hydroboration-hydrolysis procedure. The iron(II) coordination polymer precatalyst is air-stable, recyclable and tolerant of other reducible functional groups. Excellent chemoselectivity on aldehydes over ketones was also observed. The current method represents a practical, green and operationally simple pathway to the hydroboration of carbonyl compounds utilizing the Earthabundant metal iron.

Experimental

General Considerations. The catalytic reactions were carried out under a nitrogen atmosphere using standard glove-box technique. Anhydrous grade solvents and liquid reagents used were obtained from Aldrich or Fisher Scientific and stored over 4 Å molecular sieves. FT-IR spectra were recorded on a Shimadzu 8400S instrument with solid samples under N₂ using a Golden Gate ATR accessory. ¹H NMR and ¹³C NMR spectra were obtained at room temperature on a Bruker AV 400, 500 or 600 MHz NMR spectrometer, with chemical shifts (δ) referenced to the residual solvent signal. GC-MS analysis was obtained using a Shimadzu GCMS-QP2010S gas chromatograph mass spectrometer. Inductively coupled plasma optical

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Comparing to homogeneous catalysis, reactions under heterogenous conditions with solid catalysts, such as metalorganic frameworks (MOFs) and metalated porous organic polymers, are particularly attractive due to the recyclability and reusability of catalysts,²¹ as well as improved catalytic activity in some cases.²² Although effective hydroboration of carbonyl compounds could be also promoted by homogeneous precatalyst 7 in air, the utilization of coordination polymer 1 as a precatalyst offers an opportunity for recycling and reusing the catalyst. Thus, the reusability of 1 was established using benzaldehyde as a model substrate (Fig. 1). The reaction was set up in air with standard conditions using 0.1 mol% of 1 and 2 mol% of KO^tBu for the 1st run. The reaction was then monitored by GC analysis (65% yield of 2a) after 15 min and the solid precatalyst could be readily isolated from the reaction mixture by removing the liquid followed by washing with diethyl ether for three times in a fume hood. At this end, the loss of iron from the precatalyst was analysed by Inductively coupled plasma optical emission spectrometry (ICP-OES). The iron content in the liquid sample extracted from reaction mixture of the 1st run was determined to be 7 ppm, indicating a negligible loss of Fe from 1. The precatalyst was dried in the air and then reused for the 2nd run by recharging the substrates and additional activator (2 mol%). After 15 min, 63% yield of 2a was detected by GC analysis. Following the same procedure, it was further confirmed that the precatalyst can be recycled and reused for at least 5 more cycles without losing its effectiveness (Fig. 1).





In view of the important role of the 'in air' conditions played in enabling effective hydroboration of both aldehydes and ketones, we tentatively proposed an "oxygen-participating" catalytic cycle for the iron-catalysed hydroboration (Scheme 6). Initially, the limited catalytic activity of the Fe^{II} precatalyst under N₂ is presumably oxidized to an Fe^{III} precatalyst in air, as it has been previously found by Findlater et al. that trivalent Fe(acac)₃ was effective for hydroboration of a range of aldehydes and ketones in the presence of NaHBEt₃ as activator.¹⁰ According to previous work by Thomas and coworkers, the reaction between

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emission spectrometry (ICP-OES) analyses were conducted by Robertson Microlit Laboratories in the US to determine the loss of iron for the recycling experiments. Fe(tpy)Cl₂ and Complex **1** were synthesized according to published procedure.^{15,23}

General Procedure for 1-Catalysed Hydroboration in Air. In a fume hood, precatalyst **1** (1.08 mg, 1.0 µmol, 0.1 mol% based on the $[Fe(L)_2Cl_2]$ unit) and KO'Bu (2.2 mg, 20 µmol) was loaded in a 3.8 mL glass vial equipped with a stir bar and the vial was open to air. Aldehyde or ketone (1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir in air at room temperature for indicated times shown in Tables 2 and 3. After completion of the reaction, the crude reaction mixture was first analyzed by GC-MS using a dilute CH_2Cl_2 solution, and then the product was isolated by flash column chromatography on SiO₂ using ethyl acetate/hexane (1 : 10) as an eluent. All isolated products were characterized by ¹H and ¹³C NMR spectroscopies.

Competing Experiment for Selective Hydroboration of Ketone vs. Aldehyde. In a fume hood, precatalyst 1 (1.08 mg, 1.0 μ mol, 0.1 mol% based on the [Fe(L)₂Cl₂] unit) and KO^tBu (2.2 mg, 20 μ mol) was loaded in a 3.8 mL glass vial equipped with a stir bar and the vial was open to air. Then, acetophenone (120.0 mg, 1.0 mmol), benzaldehyde (106.0 mg, 1.0 mmol) and pinacolborane (128.0 mg, 1.0 mmol) were added sequentially. The reaction mixture was allowed to stir at room temperature for 30 min. The products were analyzed by GC using hexamethylbenzene as an internal reference.

Recycling and Reusing Experiment for Hydroboration of Acetophenone. In a fume hood, precatalyst 1 (1.08 mg, 1.0 µmol, 0.1 mol% based on the [Fe(L)_2Cl_2] unit) and KO^tBu (2.2 mg, 20 $\mu mol)$ was loaded in a 3.8 mL glass vial equipped with a stir bar and the vial was open to air. Benzaldehyde (106.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were then added. The reaction mixture was allowed to stir at room temperature in air for 15 min. The reaction mixture was analyzed by using GC analysis to obtain the yield of 2a. Then the solid was centrifuged out of suspension and extracted with diethyl ether for three times. The organic extract (1 mL) was combined and analyzed by ICP-OES. The loss of iron from the precatalyst was determined to be 7 ppm. The solid precatalyst that was recovered was then dried under reduced pressure and then placed in a small vial, to which additional KO^tBu (2.1 mg, 20 µmol) was added. Then, Benzaldehyde (106.0 mg, 1.0 mmol) and pinacolborane (140.8 mg, 1.1 mmol) were added. The resultant mixture was stirred at room temperature in air for 15 min and the product was analyzed by using GC analysis again. This procedure was repeated for another 4 times and the results of in total 6 runs are summarized in Figure 1.

Conflicts of interest

There are no conflicts to declare.

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