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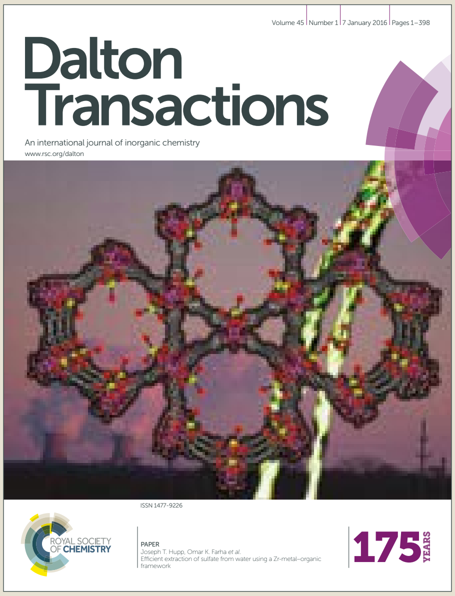

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COMMUNICATION

Iron(II) coordination polymer catalysed hydroboration of ketones

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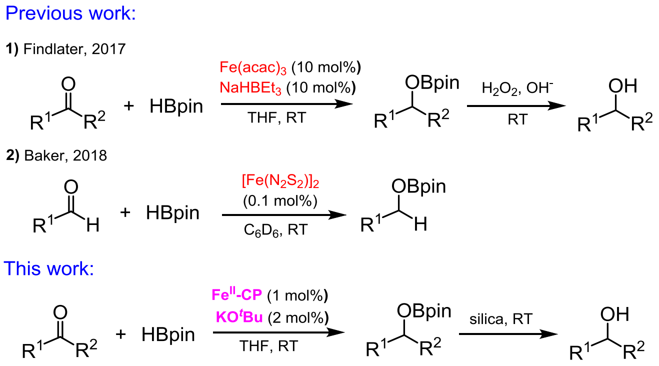
Catalytic hydroboration of ketones with pinacolborane was achieved by a 2D iron(II) coordination polymer (CP) of a divergent 4,2′;6′,4′′-terpyridine(tpy) derivative under mild conditions with high efficiency. This solid iron catalyst system is more active towards hydroboration of ketones than aldehydes, displaying different trend of reactivity from known homogeneous iron hydroboration catalysts.

Earth-abundant metal chemistry has continuingly been expanding over the past decade since a variety of Earth-abundant metals have displayed great promise in catalytic organic transformations with replacement of precious metal catalysts.[1] Notable progress has been achieved in catalytic (transfer)hydrogenation, hydrofunctionalization and dehydrogenation processes by utilizing well-defined complexes of iron, cobalt and manganese as precatalysts.[2,3] However, such catalysts developed thus far remain still limited and in most cases abundant metal catalysts are far from surrogating precious metal catalysts in terms of efficiency, selectivity and substrate tolerance.[4]

In recent years, the most abundant transition metal, iron has found valuable applications in catalytic hydrofunctionalization including hydroboration and hydrosilylation while being combined with appropriate ligand compartments.[5] Among these transformations, the hydroboration of olefins have been one focus of the research, as the resulting product, alkylboronates, can be well used in C-C bond coupling process. In contrast, hydroboration of carbonyl compounds was relatively less explored by iron-based catalysts, although a number of transition and main group metals (Ti,[6] Cu,[6] Zn,[6] Mn,[7] Co,[6] Mg,[6] Al,[6] etc.) have been exploited for this transformation. It has been well documented in the literature that hydroboration of carbonyl compounds offers an important and convenient route to converting ketones and aldehydes to the corresponding alcohols, in particular for those difficult to be reduced by traditional methods.[8] To the best of our knowledge, two examples utilizing iron complexes for the hydroboration of carbonyl compounds with pinacolborane (HBpin) have emerged very recently. In 2017, the Findlater group[9] reported on the first iron-catalysed hydroboration of carbonyl compounds at ambient temperature using simple $Fe(acac)_3$ salt (acac = acetylacetonate, 10 mol% of catalyst loading) in the presence of an activator, $NaHBEt_3$.[9] The chemoselectivity of aldehydes over ketones was disclosed. However, high catalyst loading and air-sensitive activator were required in this example. Very recently, Tom Baker and coworkers[10] revealed that a dinuclear Fe^{II} complex based on a N_2S_2 ligand was highly active towards the hydroboration of a range of aldehydes without the use of an extra activator, whereas ketones were found to be challenging substrates by this method.



Scheme 1. Fe-catalysed hydroboration of ketones and aldehydes.

In contrast to enormous examples of homogeneous catalysis for hydroboration of carbonyl compounds, the heterogeneous version, which is operationally simple, atom-economical and recyclable, remains rarely explored. Up to date, heterogeneously catalytic hydroboration of carbonyl compounds is limited to a few examples employing solid-supported single-site catalysts, for instance, the mesoporous silica-supported amidozirconium catalysts and the active Mg or Ti single-site catalysts immobilized on zirconium-based metal-organic framework (MOF) through post-synthetic modification.[11-13] Although high turnover numbers (TONs) and good recyclability were achieved, expensive MOF materials (typically

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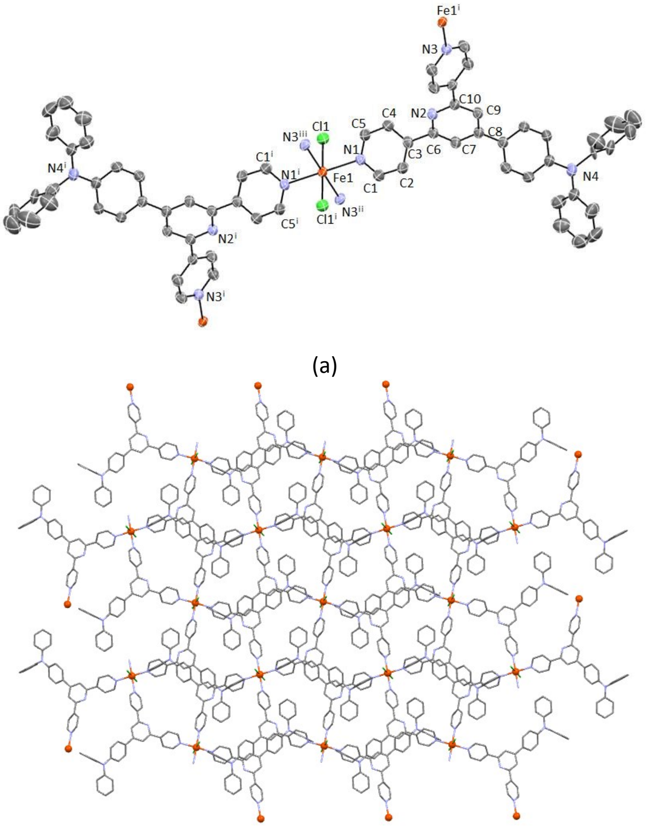
synthesized from complex organic linkers) and air- and moisture-sensitive metal reagents were required for the generation of catalytically active sites. It is quite desired to pursue more readily available heterogeneous catalysts that utilize Earth-abundant metals in the absence of air-sensitive materials for hydroboration catalysis.

To this end, we reveal herein the synthesis of a new iron(II) coordination polymer (CP) built on a modified divergent 4,2′;6′,4′′-tpy ligand, and its application in heterogeneous hydroboration of carbonyl compounds in the presence of an air-stable activator, potassium *tert*-butoxide. The unique catalytic activity of this catalyst system for ketone and aldehyde hydroboration was observed, which is in sharp contrast to the known homogeneous iron catalysts.[9,10]



(a)

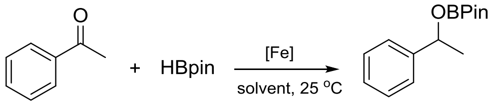
(b)

Fig. 1. (a) The ORTEP presentation of **1** plotted at 50% thermal ellipsoid probability level. Operation codes: *i* = -x, -y, -z; *ii* = -x + $^{1}/_{2}$, y + $^{1}/_{2}$, -z + $^{1}/_{2}$; *iii* = x - $^{1}/_{2}$, -y - $^{1}/_{2}$, z - $^{1}/_{2}$. (b) The representation of the extended 2D network in **1**. H Atoms are omitted for clarity.

Divergent 4,2′;6′,4′′-tpy ligands have been popular choices for the construction of low-dimensional CPs or 3-dimensional (3D) MOFs.[14] Although a variety of metals (such as Zn, Cd, Co, Mn, Ni, Cu, and Hg) have been extensively exploited,[14,15] to our knowledge, Fe^{II}-CPs of 4,2′;6′,4′′-tpy were unknown, probably due to the poor stability of the corresponding Fe(II) materials that are opt to aerobic oxidation during the coordination process. After lots of attempts using different 4′-substituted 4,2′;6′,4′′-tpy ligands and $FeCl_2$ to synthesize crystalline materials that could be structurally determined, we successfully obtained single crystal of a 2D CP of Fe^{II} (**1**) by introducing 4′-(4-diphenylaminophenyl)-4,2′;6′,4′′-tpy (**L**) as the ligand to stabilize the Fe(II) center. The synthesis of **L** was readily approached in 62% yield adopting the Kröhnke method by using 4-diphenylaminobenzaldehyde and 4-acetylpyridine as starting materials. Subsequently, carefully layering a CH_2Cl_2-MeOH solution of **L** with a solution of $FeCl_2$ in MeOH resulted in the formation of red-organge crystals of **1** after one week. **1** was collected in 86% yield and characterized by IR, elemental analysis, thermogravimetric analysis and X-ray crystallography (see Supplementary Information).

X-ray structural analysis revealed that **1** crystallized in the monoclinic space group *P*2$_1$/n.[‡] There exists one independent ligand molecule and one Fe^{II} center in the asymmetric unit (Figure 1a). Fe^{II} is hexacoordinate adopting an N_4Cl_2 coordination environment with N atoms from four distinct ligands and two Cl$^-$ anions to form an octahedral coordination geometry. The Fe-N bond lengths are in the range of 2.2528(14) and 2.2960(14) Å, while the Fe-Cl distance is 2.3963(5) Å. The aromatic rings of the tpy region are severely twisted from each other, with the torsional angles being 36.81° and 41.55°, respectively. Since each Fe^{II} center is coordinated with four ligand molecules, the resultant structure reveals a 2D coordination polymer that expands along the *bc* plane (Fig. 1b).

Table 1. Condition Screening for Iron(II)-CP Catalysed Hydroboration of Acetophenone with Pinacolborane.[a]



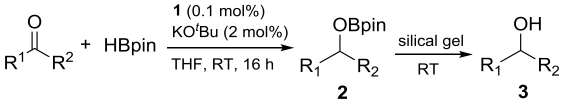
2

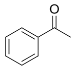
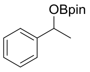
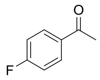
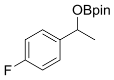
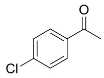
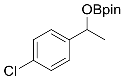
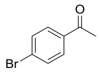
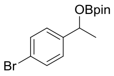
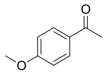
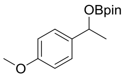
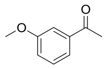
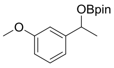
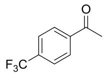
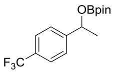
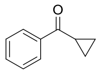
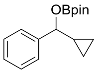
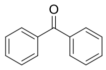
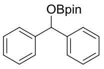
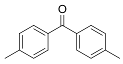
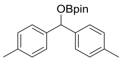
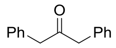
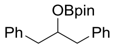
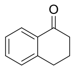
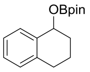
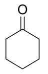
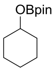
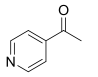
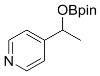
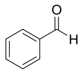
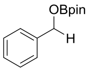
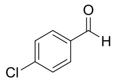
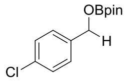
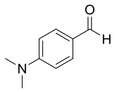
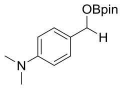
Entry	Catalyst	Activator	Solvent	Yield /%[b]
1	**1**	KO^{t}Bu	THF	98
2	**1**	KOH	THF	92
3	**1**	NaO^{t}Bu	THF	96
4	**1**	-	THF	<5
5	-	KO^{t}Bu	THF	8
6[c]	$FeCl_2$	KO^{t}Bu	THF	82
7	**L**	KO^{t}Bu	THF	15
8	Fe(tpy)Cl_2	KO^{t}Bu	THF	71
9[d]	Fe(tpy)Cl_2/TPA	KO^{t}Bu	THF	95
10	**1**	KO^{t}Bu	Et_2O	95
11	**1**	KO^{t}Bu	toluene	79
12	**1**	KO^{t}Bu	benzene	77
13	**1**	KO^{t}Bu	pentane	70
14[e]	**1**	KO^{t}Bu	THF	79
15[f]	**1**	KO^{t}Bu	THF	90

[a] Conditions: acetophenone (1.0 mmol), HBpin (1.1 mmol), catalyst **1** (0.1 mol%), activator (2 mol%) and solvent (1 mL), 25 °C, 16 h, N_2. [b] Determined by GC analysis with hexamethylbenzene as an internal standard. [c] 5 mol% $FeCl_2$ was used. [d] TPA = triphenylamine (0.1 mmol%) was added. [e] Reaction run in the air. [f] 0.01 mol% **1** was used and reaction run for 48 h.

The catalytic activity of CP **1** has been demonstrated by the catalytic hydroboration with pinacoborane (HBpin) using acetophenone as a model substrate. Table 1 summarizes the results using different conditions. We first introduced the reaction conditions from related iron and cobalt catalysts for hydroboration and used potassium *tert*-butoxide (KO^{t}Bu, 2 mol%) as an activator.[16] To our delight, when **1** (0.1 mol% based on the [Fe(**L**)$_2$Cl$_2$] unit) was utilized as a precatalysts for the hydroboration of acetophenone in THF at room temperature, 98% GC yield of the hydroborated product **2** was observed (entry 1, Table 1). Other similar base activators were found to give slightly lower yields under the same conditions (entries 2 and 3). In contrast, the blank experiments without either the activator or the iron precatalyst were unsuccessful (entries 4 and 5). Simple $FeCl_2$ or $Fe(tpy)Cl_2$ complexes catalysed the reaction with relatively lower efficiency and the combination of free ligand **L** with KO^tBu showed only poor reactivity (entries 6-8). However, the addition of triphenylamine to $Fe(tpy)Cl_2/KO^tBu$ catalyst resulted in notable improvement of yield of **2** (entry 9), indicating the redox active triarylamine unit within the structure of CP **1** plays an important role in increasing the catalytic reactivity of Fe^{II} centres. Solvent effect was further explored and the results indicated that THF is the best solvent for this reaction, whereas the reaction in diethyl ether also proceeded well (entries 10-13). It was interesting to notice that the reaction even proceeded in the air with good yield, indicating the practical applicability of this method (entry 14). Finally, a lower catalyst loading (0.01 mol% of **1**) was tested affording product **2** in 90% yield (entry 15).

Table 2. Substrate scope of iron(II)-CP catalysed hydroboration.[a]



Entry	Substrate	Product **2**	Yield (%)[b]
1			98 (95)
2			99 (94)
3			91 (90)
4			75 (70)
5			94 (88)
6			97 (95)
7			94 (91)
8			74 (70)
9			95 (94)
10			92 (90)
11			80 (76)
12			77 (71)
13			64
14			<5
15			15
16			62
17			51

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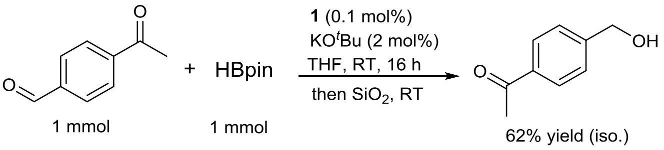
[a] Conditions: ketones or aldehydes (1.0 mmol), HBpin (1.1 mmol), catalyst **1** (0.1 mol%), KO^tBu (2 mol%) and solvent (1 mL), 25 °C, 16 h, N_2. [b] Yields of hydroborated products (**2**) were determined by GC-MS analysis. Isolated yields of alcohols (**3**) are shown in parenthesis.

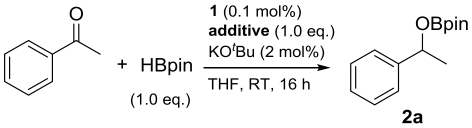
Next, we were interested to see whether the method could be applied for other substrates including functionalized ketones and aldehydes. Thus, the optimized conditions were used for **1**-catalysed hydroboration of various ketones as shown in Table 2. In all examples, the hydroborated products have been detected as intermediates which were subsequently hydrolyzed on silica gel column chromatography affording the corresponding alcohols (**3**) as final products. The silica-promoted hydrolysis of boronate esters have been reported previously.[7] It was found that differently functionalized aryl ketones were smoothly hydroborated under the standard conditions. Halogenated acetophenones are suitable substrates and well converted to the corresponding boronate esters and also isolated as alcohols in excellent to moderate yields (entries 2-4), while the trend of reactivity is related to the halogen substituents (yield drops with substituents from F to Br). Methyl phenyl ketones containing electron-donating or -withdrawing groups proceeded well, giving the reduced products in very good yield (entries 5-7). Cyclopropyl phenyl ketone was converted to the corresponding boronate ester in a reasonable yield without ring-opening, indicating that no radicals have been involved in the reaction (entry 8). In addition, high yields were also observed for diaryl ketones (entries 9 and 10). In contrast, ketone with dibenzyl groups and the aromatic and aliphatic cyclic ketone (tetralone and cyclohexanone) were converted in relatively lower yields (entries 11-13). Unfortunately, the catalyst is not tolerant of heteroatomic aryl ketone (entry 14). Finally, we examined several aldehydes as substrates under the standard conditions. It was found that benzaldehyde was a poor substrate for the hydroboration catalysed by **1**, affording the corresponding product in only 15% yield, whereas 4-chlorobenzaldehyde and 4-dimethylaminobenzaldehyde showed moderate reactivity (entries 15-17). However, when an equimolar mixture of acetophenone and benzaldehyde was tested, only a little amount of a mixture of hydroborated products was observed,[17] indicating the presence of aldehyde may deactivate the catalyst. This is in sharp contrast to the known Fe^{II} hydroboration catalysts for carbonyl compounds. For example, the Baker's catalyst, $[Fe(N_2S_2)]_2$ was effective for the hydroboration of aldehydes only, yet not active for ketones.[10] The Findlater's $Fe(acac)_3/NaHBEt_3$ system catalysed hydroboration of both ketones and aldehydes, with chemoselectivity being observed for aldehydes over ketones.[9] In addition, the chemoselectivity study for an equimolar mixture of acetophenone and benzaldehyde using $FeCl_2/KO^tBu$ as a catalyst showed the same trend, with aldehyde being hydroborated in 63% yield, while ketone was fully recovered. A further investigation on the **1**-catalysed intramolecular chemoselective hydroboration using 4-acetylbenzaldehyde as a substrate revealed, however, that the hydroboration occurred at the aldehyde only and the corresponding primary alcohol was isolated in 62% yield, with ~30% starting material being recovered (Scheme 2). The Fe^{II}-CP precatalyst here displaying unique reactivity is interesting and would deserve further investigations.[18]

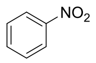
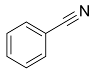
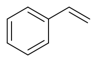
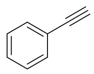
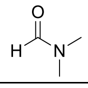


Scheme 2. Fe-catalysed hydroboration of 4-acetylbenzaldehyde.

We further conducted a robustness screen to determine whether **1**-catalysed ketone hydroboration is compatible with reducible functional groups by using the Glorius method.[19] Acetophenone was tested under the standard conditions in the presence of different additives (1.0 eq.) as summarized in Table 3. The results showed that hydroboration of the ketone was observed in good to high yields in the presence of nitro, nitrile, alkene, alkyne and amide functional groups. In all of these reactions, the additive was detected in the product mixture and have not been reduced based on GC-MS analysis. It was noted that the presence of alkene and alkyne groups did not influence the reactivity of precatalyst **1**, while nitro, nitrile and amide functional groups slightly weakened the catalytic activity of the iron catalyst.

Table 3. The functional group tolerance of ketone hydroboration.[a]



Entry	Additive	Yield of **2a** (%)[a]
1		80
2		75
3		95
4		98
5		85

[a] Determined by GC-MS analysis with hexamethylbenzene as an internal standard.

Since the hydroboration of ketones catalysed by CP **1** was carried out under heterogeneous conditions,[20] the recyclability and reusability of the solid catalyst **1** were successfully carried out for six catalytic cycles (see Supplementary Information). For example, in the recycling reaction using acetophenone as a model substrate catalyst **1** (2 mol%) was filtered out from the reaction mixture as a precipitate after the first catalytic run was completed. Additional KO^{t}Bu (2 mol%), the substrate, HBpin and the solvent were then loaded and the reaction was allowed to run for another cycle. The catalytic activity was found to remain in the same level (97% yield). This indicates the excellent recyclability of the CP pre-catalyst, in comparison with the homogeneous Fe^{II} catalysts for this reaction.[9,10]

Previously, Thomas and coworkers proposed that the activation of Fe(NNN)Cl$_2$ complexes could be approached by the formation of an *in situ* generated reducing species, HB(O^{t}Bu)(Pin) in the presence of HBPin and NaO^{t}Bu, based on NMR experiments.[16] A similar activation process could be, therefore, proposed for the current work. The HB(O^{t}Bu)(Pin) species in our case is likely to react with the Fe^{II} centres in **1** to form the active Fe-H species. This process could be also facilitated by the pendant triarylamine moiety in the ligand as it may act as a Bpin acceptor, according the data from our reactivity test (Table 1). Further catalytic cycle involving newly generated Fe-H species could be furnished through a mechanism previously proposed by Findlater.[9]

Conclusions

In this work, we have developed the first heterogeneous Fe^{II}-based coordination polymer with a divergent 4,2′;6′,4′′-tpy ligand that catalyses the hydroboration of ketones with HBpin in the presence of air-stable activator under mild conditions. The new iron catalyst system has successfully transformed a variety of ketones to the corresponding boronate esters in good to excellent yields, while showing poorer activity towards aldehydes, in contrast to the known iron hydroboration catalysts. This work demonstrates the feasible applications of readily available CPs based on Earth-abundant metals and common tpy ligands in catalytic organic transformations. Ongoing investigations are focused on the development of more active and efficient and active CP catalysts for relevant reduction processes as well as the mechanistic studies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Funding support from the Jingchu University of Technology is gratefully acknowledged. We also acknowledge the support from the PSC-CUNY awards (60328-0048, 61321-0049) and the Seed grant from the Office for Advancement of Research at John Jay College.

Notes and references

‡Crystallographic data for **1:** $C_{66}H_{48}Cl_2FeN_8$, M = 1079.87, monoclinic, space group $P2_1/n$, a = 8.9726(2), b = 17.3320(4), c = 17.2173(4) A˚, β = 91.2500(10)˚, U = 2676.88(11)A˚^{3}, Z = 2, D_c = 1.340 Mg m^{-3}, μ(Mo-Kα) = 2.3.573 mm^{-1}, T = 297(2) K. Total 38418 reflections, 4910 unique, R_{int} = 0.0394. Refinement of 4910 reflections (381 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0365 (R_1 all data = 0.0413), wR_2 = 0.1010 (wR_2 all data = 0.1061), gof = 1.032.

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20 It could not be excluded that the decomposition of the coordination polymer may result in active catalyst species in solution during the reaction without further investigation.

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Table of Contents

Catalytic hydroboration of ketones with pinacolborane was achieved by using a two-dimensional iron(II) coordination polymer based on divergent 4,2′;6′,4′′-terpyridine ligand.