View Article Online
View Journal

Dalton Transactions

An international journal of inorganic chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: D. Borah, B. Saha, B. Sarma and P. Das, *Dalton Trans.*, 2020, DOI: 10.1039/D0DT02341H.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

Cyclometalated Ir(III)-NHC complex as recyclable catalyst for acceptorless dehydrogenation of alcohols to carboxylic acids

Dhrubajit Borah,[a,b] Biswajit Saha,[c,d] Bipul Sarma,[e] Pankaj Das*[a]
[a] Department of Chemistry, Dibrugarh University, Dibrugarh, Assam, India, 786004.
[b] Department of Chemistry, N. N. Saikia College, Titabar, Assam, India, 785630.
[c] Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006 Assam, India
[d] Academy of Scientific and Innovative Research (AcSIR), CSIR-NEIST Campus, Jorhat 785006, India
[e] Department of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam, India, 784028.
*Corresponding author E-mail address: pankajdas@dibru.ac.in.

Abstract

In this work, we have synthesized two new [C,C] cyclometalated Ir(III)-NHC complexes, [IrCp*(C∧C:NHC)Br](**1a,b**), [Cp* = pentamethylcyclopentadienyl; NHC = (2–flurobenzyl)–1–(4–methoxyphenyl)–1H–imidazoline–2–ylidene (**a**); (2–flurobenzyl)–1–(4–formylphenyl)–1H–imidazoline–2–ylidene) (**b**)] via intramolecular C-H bond activation. The molecular structure of the complex **1a** was determined by X–ray single crystal analysis. The catalytic potentials of the complexes were explored for acceptorless dehydrogenation of alcohols to carboxylic acids with concomitant hydrogen gas evolution. Under similar experimental conditions, the complex **1a** was found to be slightly more efficient than the complex **1b**. Using 0.1 mol% of complex **1a**, good-to-excellent yields of carboxylic acids/carboxylates have been obtained for a wide range of alcohols, both aliphatic and aromatic including those involved heterocycles, in a short reaction time with a low loading of catalyst. Remarkably, our method can produce benzoic acid from benzyl alcohol in gram scale with a catalyst–to–substrate ratio as low as 1:5000 and exhibiting a TON of 4550. Furthermore, the catalyst could be recycled at least three times without losing its activity. A mechanism has been proposed based on controlled experiments and in *situ* NMR study.

Keywords: Cyclometalated complex; intramolecular C-H bond activation; N-heterocyclic carbene; iridium(III); acceptorless dehydrogenation; recyclable catalyst

Introduction

Oxidant–free catalytic oxidation of alcohols to carbonyl compounds with concomitant hydrogen gas evolution, so–called acceptorless dehydrogenation reaction, has recently been emerged as a highly attractive process in organic synthesis.[1] This approach of hydrogen

generation from an organic substrate is not only an atom economical and environmentally benign method to access carbonyl compounds but also has the potential to be exploited in "Hydrogen economy" as liquid hydrogen storage material.[1b,2] Though alcohols can be easily dehydrogenated to corresponding aldehydes or ketones with the help of various noble metal catalyst,[3]direct conversion of alcohols to carboxylic acids/carboxylates via dehydrogenative transformation without using any oxidant has got relatively less attention.The reaction was first reported by Milstein's group in 2013 using a pincer–based ruthenium–PNN catalyst.[4] Since then, several Ru-based systems have been reported that contained tridentate PNP[5], CNP[6] or NNN[3g,m,7] type pincer–ligands or N, N[8]- / NHC[9]- based non–pincer ligands. Although remarkable advancements have been seen in terms of product yields or substrate–scope improvements, in most cases, the catalytic systems suffer from crucial disadvantages like excessive metal loadings (up to 5 mol%),[8,9c] low turnover numbers (TON),[8,9c] prolonged reaction times (40h),[9d] non–recyclable nature, *etc*. Nevertheless, recent works by the groups of Madsen (1 mol%, 6h),[10] Szymczak (0.2 mol%, 18h),[11] Li[12](1–0.002 mol%; 24h) and others[13] showed some improvements over catalyst loading or TON, however, in almost all the cases, catalytic systems used non–innocent phosphines, either as a principal ligand system[6] or as a supporting ligand along with other phosphine–free systems like NHC,[10,12] bipyridine,[13,14] *etc*. It is noteworthy to mention that from economical and environmental perspectives, phosphines are no longer considered as the most desired ligand system in organometallic chemistry because of their inherent toxicity, air, and moisture sensitive property, handling inconvenience, and synthetic inaccessibility,[15] *etc*. Thus, it is extremely important to design novel recyclable phosphine–free catalytic systems that could exhibit superior activity for acceptorless dehydrogenation of alcohols to acids with a low loading of catalyst.

In the past few years, N–heterocyclic carbenes (NHCs) has emerged as a highly sustainable alternative to traditional phosphine ligands in organometallic catalysis.[16,17c] Like phosphines, the stereo–electronic environment of NHC ligands can be easily tuned by changing the pendant groups attached to the imidazole moiety.[17] One unique advantage of using NHCs as ligands is that due to their strong σ–donors and poor π–acceptors properties, they often facilitate intramolecular C–H bond activation leading to highly stable cyclometalated complex.[18] Recently, cyclometalated NHC–based Ir^{III} systems have received enormous attentions because of their applications in diverse fields that include organometallic

catalysis,[19] catalysts for water oxidation,[20] as chemosensors materials,[17c] as photophysical devices in organic light-emitting diodes,[21] as anticancer agents,[22] *etc*.

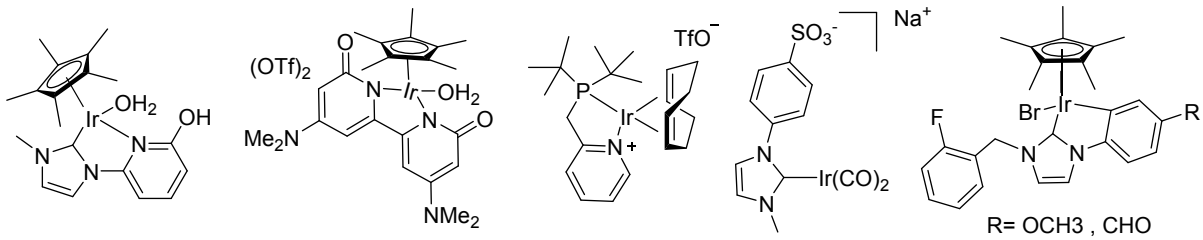


Fig. 1 Example of iridium comlexes employed in acceptorless dehydrogenation of alcohols to acids.

In 2012, for the first time, Fukuzumi's group has reported catalytic evolution of hydrogen from aliphatic alcohols to afford aldehyde or ketone using a [C, C] cyclometalated Ir (III) catalyst.[23] Since then, several cyclometalated Ir(III) systems were reported that served as effective catalysts for various types of dehydrogenative reactions to afford aldehydes and ketones[14], amines or imines, and dehydrogenation of formic acid[2a,19e,24]. However, to the best of our knowledge, [C, C] cyclometalated Ir(III)–NHC systems has not been explored so far for direct conversion of alcohols to carboxylic acids. Thus, intending to develop robust phosphine–free catalytic system for acceptorless dehydrogenations of alcohols to carboxylic acids, herein, we have synthesized two new cyclometalated Ir^{III}–NHC complexes and explored their potentials as catalysts. It may be worth to mention that until now only a handful of iridium−based systems are reported for direct dehydrogenations of alcohols to carboxylic acids including conversion of glycerol to lactic acid.[9c,9d,25] Among them, a dicationic Ir(III) complex[9c]containing a functional NHC ligand reported by Fujita [Fig. 1] is the most significant as it can produce carboxylic acids from alcohols using water as a solvent under a base-free environment, however the protocols showed efficiency only with benzyl alcohols with a relatively high catalyst loading (2-5 mol%). The catalyst loading as well as the substrate scope were significantly improved using a monocationic Ir(I) system[9d] by Williams [Fig. 1] in the presence of stoichiometric quantity of KOH. Although, this method provides aliphatic and benzylic carboxylates in high yield with a catalyst loading as low as 0.2 mol%, however the use of phosphine-based ligand was its principal limitation.Hence,

from the practical viewpoint, our system is advantageous as we could produce carboxylic acids from alcohols using a recyclable phosphine-free system with a low loading of catalyst (0.1 mol%) for a wide range of substrates. Interestingly, this is the first example of a [C, C] cyclometalated Ir^{III}–NHC system explored for this transformation.

Results and Discussion

Synthesis of cyclometalated iridium complexes

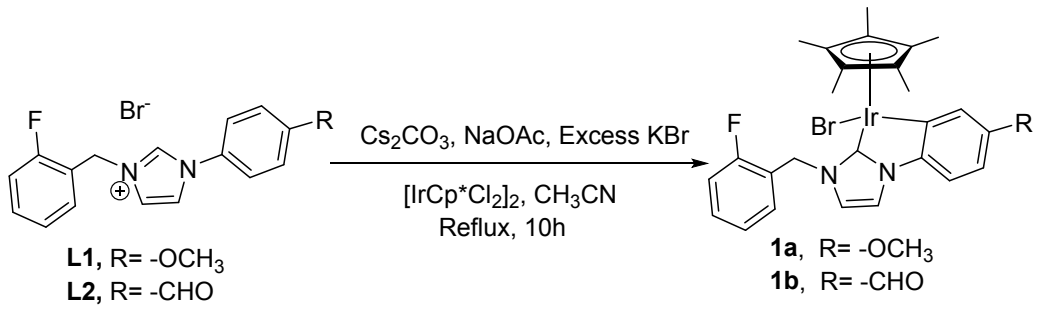
The ligand precursor $\mathbf{L_1}$ was recently reported by us.[26] The same procedure was adopted for synthesizing $\mathbf{L_2}$ by reacting 1–(4–formylphenyl)–1H–imidazole with 10 equivalent of 2–fluoro benzyl bromide in CH_3CN for 48 h. The formation of $\mathbf{L_2}$ was confirmed by ESI–MS spectrum which showed a base peak at *m/z* =281.106 corresponds to $[M–Br]^+$ ion. The characteristics imidazolium proton (NCHN) resonance in the ^1H NMR spectrum was observed at 10.25 ppm. In the ^{13}C NMR spectrum, a signal appeared at 139.04 ppm attributed to NCN carbon.[27] The complexes (**1a** and **1b**) were synthesized by *in situ* deprotonation of imidazolium salts ($\mathbf{L_1}$ and $\mathbf{L_2}$) in CH_3CN by treating a mixture of Cs_2CO_3, NaOAc and $[Cp^*IrCl_2]_2$ in presence of excess potassium bromide (Scheme 1).[19g] The formation of the complexes **1a** and **1b** was confirmed by ESI–HRMS spectra which rendered base peaks at *m/z* 609.186 and 607.258 respectively corresponds to $[M–Br]^+$ ions. Successful coordination of the NHC ligands to the iridium centers was confirmed by the disappearances of the NCHN protons in the ^1H NMR spectroscopy. The signal corresponds to the methyl groups of the Cp^* ligands appeared at around 1.84 ppm. The ^{13}C resonances of the $Ir–C_{NHC}$ carbons of the complexes **1a** and **1b** appeared at 164.01 and 167.57 ppm respectively and the values are in good agreement with reported Ir–NHC complexes.[28] The resonances due to orthometalated carbon ($Ir–C_{Ph}$) appeared at 142.79 and 141.83 ppm for the complexes **1a** and **1b** respectively.

Crystal Structure analysis

Suitable single crystals of the complex **1a** were grown for X-ray studies by layering a saturated dichloromethane solution with hexane. Unfortunately, after repeated attempts, good quality single crystals could not be generated for the complex **1b.**The ORTEP of the complex **1a** is displayed in Fig. **2** which confirms the expected connectivity pattern. Crystallographic parameters are documented in Table S1 in the Supporting Information. The iridium center of

View Article Online
DOI: 10.1039/D0DT02341H

the complex **1a** adopts typical piano stool geometry where three "legs" of the piano stool are comprised of N–heterocyclic carbene carbon, carbon from adjacent phenyl ring and a bromide. Residual Cp* ligand is connected to the metal center in η^5 fashion. The bond distance of Ir–C_{NHC} is 2.04 (1) Å falls within the expected range.[28] The Ir–C_{Ph} (2.08(1) Å) bond length is found to be slightly longer compared to the Ir–C_{NHC} bond length. The cyclometalated five–member ring Ir(1)–C(28)–N(1)–C(4)–C(29) of the complex **1a** is almost planar and the dihedral angle between the two planes of C(29)–Ir(1)–C(28) and C(28)–N(1)–C(4)–C(29) is found to be 1.61°.The planarity of the cyclometalated ring is further confirmed by observing the fact that the sum of the inner angles of the five–member ring is approximately 540°.



Scheme 1 Synthesis of Cyclometalated NHC– Ir^{III} Complexes **1a** and **1b**

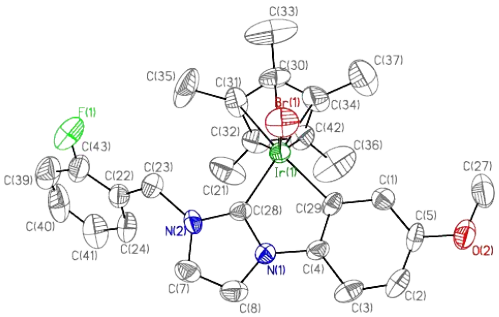


Fig. 2 ORTEP plot of the complex **1a** (50% probability thermal ellipsoid). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir_1– Br_1 2.527(2), Ir_1–C_{28} 2.04(1), Ir_1–C_{29} 2.08(1), C(28)–N1 1.38(1), C(4)–N(1) 1.44(2), C(4)–C(29) 1.37(2), Br_1–Ir_1–C_{28} 88.6(3), Br_1–Ir_1–C_{29} 91.0(3), C_{28}–Ir_1–C_{29} 76.9(4), N_1–C_{28}–N_2 104.3(9).

Catalytic studies

Optimization of reaction variables

To investigate the efficacies of the Ir(III) complexes **1a** and **1b** as catalysts for acceptorless dehydrogenation of alcohols to acids, benzyl alcohol was chosen as a test substrate. A model reaction was carried out with benzyl alcohol (1mmol) using complex **1a** (1mol %) as a

catalyst, in presence of KOH (1.1mmol) as a base in refluxing toluene with a reaction time of 24 h. To our delight, benzyl alcohol was effectively converted to potassium benzoate in 100% yield, accompanied by the evolution of hydrogen gas as a byproduct (Table 1, entry 1). Almost quantitative formation of benzoic acid was achieved by treating the benzoate salt with hydrochloric acid. However, the yield drops to 82% when the same reaction was carried out using complex **1b** as catalyst (entry 16).The higher catalytic performance of the complex **1a** compared to **1b** could be attributed to more electron donating ability of the ligand **a** over **b**.[9c] Moreover, the presence of a formyl group at the para position in one of the phenyl groups attached to N- atom in the complex **1b** is expected to make the complex relatively unstable under our catalytic condition. To check the stability of the complex **1b**, a reaction was carried out with complex **1b** under our standard conditions in absence of benzyl alcohol for 24h and the reaction mixture was analyzed by HR-MS spectrometry which showed an intense peak at 607.17 corresponding to the fragment $[M\text{-}Br]^+$ with the isotopic pattern in a perfect match with the original compound **1b** (ESI, Fig S 25)**.** This observation clearly suggests that ligand site of the complex remains intact during the course of reaction. Although, initially, the model reaction with the complex **1a** was continued for 24 h, a time–dependent conversion study reveals that the reaction gets completed within 4 h (entry 3, time profile conversion graph, ESI Fig S24). Moreover, the decrease in catalyst loadings from 1 mol% to 0.1 mol% does not have any impact on the yield (95 %, entries 3 and 5). It is noteworthy to highlight that under comparable conditions, William's catalyst (Fig.1) required a double amount of catalyst (0.2 mol%) along with 10 fold increase in reaction time (40 h) to achieve similar conversion, suggesting the superiority of our system over the reported one. A temperature optimization study with the complex **1a** reveals that a refluxing condition is indispensable for the smooth performance of the catalyst. An attempt to decrease the reaction temperature from 110^0C to 80^0C significantly slow down the process and only 65% yield was obtained (entry 6). Further decrease in temperature from 80^0C to 50^0C resulted in a complete cessation of the reaction and no desired carboxylic acid was obtained (entry 7). Lower conversion of benzyl alcohol was also observed when the base was replaced from KOH to NaOH (entry 8) and the reaction completely terminated in presence of weak bases such as K_2CO_3 and Cs_2CO_3 (entries 9 & 10). Not only that, the amount of base has also had some impact in our catalytic system as decreasing the quantity of KOH from 1.1 mmol to 0.75 mmol resulted in a sharp drop in activity (entry 15). It may be pertinent to mention here that there are literature precedents available where bases can also promote a transfer dehydrogenation reaction with alcohol.[29]

However, in our system, such a possibility would be extremely remote as we have not used any acceptor and it is very unlikely that toluene would serve as a hydrogen acceptor.[30]

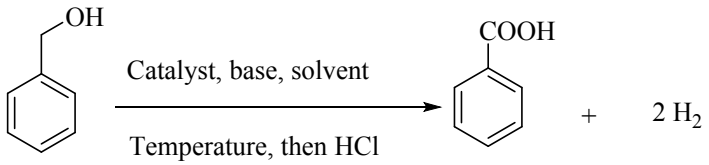
After the initial optimizations of bases, temperatures, and catalyst loadings, the influence of various solvents on acceptorless dehydrogenation of alcohols has been studied. The reaction also proceeded well in a nonpolar solvent like xylene and afforded 80% yield (entry 11) while polar solvents like water, THF, isopropanol are not effective and delivered much lower yields (entries 12−14). Therefore, the optimization condition of the dehydrogenation reaction is found to be 0.1% of **1a**, 1.1 equivalent of KOH, toluene and 110^0C (bath temperature, 120˚C). Noteworthy to mention that under similar experimental conditions, the parent complex $[Ir(Cp^*)Cl_2]_2$ gave only 35% benzoic acid (entry 19) indicating the predominant role played by the cyclometalated NHC ligand in the complex **1a** or **1b**.

Reaction scopes

With this optimized condition, we have attempted to extend the scope of our catalytic system for a broad range of primary alcohols. Both benzyl (Table 2, Entries 1−13) and aliphatic alcohols (without branched chains) (entries 16 and 17) can be easily converted to their corresponding carboxylate salts in high yields. Under optimal conditions, the sterically hindered 2- methylbutanol was found to be inactive for the reaction (entry 18). In general, aliphatic alcohols required a longer reaction time than benzyl alcohols (entries 16 and 17). Benzyl alcohols bearing electron−donating or withdrawing groups at the meta or para positions furnished corresponding benzoic acids (entries 2−8) in high yields, however a nitro group at para position provided only moderate yield (46%, entry 9) accompanied with 4-nitrobenzaldehyde as a side product (ESI, Fig. S44-45). In fact, the incompetency of nitro−substituted compounds in alcohol dehydrogenation reactions has also been noticed earlier.[9d] Orthosubstituted alcohols such as 2-methylbenzyl alcohol and 2-chlorobenzyl alcohol were also amenable for acceptorless dehydrogenation reactions to give corresponding acids in high yields (Entries 10 & 11). In contrast, alcohol bearing coordinating functional groups at ortho positions such as 2-amino and 2-methoxybenzyl alcohols gave the expected products in moderate yields i.e.54 and 36 % respectively. (entries 12 & 13). In addition; our catalyst can convert highly challenging alcohols that contain aromatic heterocycles like furan and pyridine to their corresponding acids in high yields (entries 14 and 15). It needs to mention that all the carboxylic acids presented in Table 2 were precipitated as potassium salts in refluxing toluene during the reaction and hence were easily isolated by filtration. Potassium carboxylates have been transformed into corresponding acids by treatment of

aqueous HCl and the products were isolated by extraction with ethyl acetate and subsequent removal of solvents under vacuum. This gave pure products for analysis and did not require further purification. The filtrate contains the catalyst which is further used for fresh catalytic cycles.

Table 1. Optimization of reaction variables for acceptorless dehydrogenation of benzyl alcohol[a]



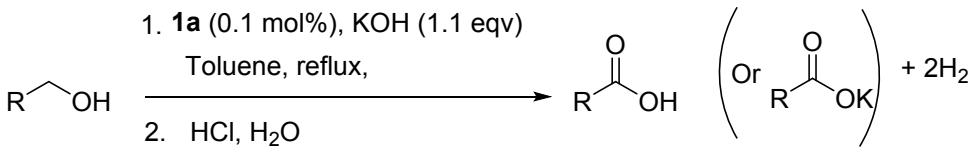
Entry	Catalyst (mol%)	Solvent	Base	Temperature (°C)	Time (h)	Isolated yield (%)
1	**1a** (1)	Toluene	KOH	110	24	95(100)*
2	**1a** (1)	Toluene	KOH	110	2	80 (83)*
3	**1a** (1)	Toluene	KOH	110	4	94(100)*
4	**1a** (0.5)	Toluene	KOH	110	4	95
5	**1a** (0.1)	Toluene	KOH	110	4	95
6	**1a** (0.1)	Toluene	KOH	80	4	65
7	**1a** (0.1)	Toluene	KOH	50	4	00
8	**1a** (0.1)	Toluene	NaOH	110	4	75
9	**1a** (0.1)	Toluene	K_2CO_3	110	4	Traced
10	**1a** (0.1)	Toluene	Cs_2CO_3	110	4	Traced
11	**1a** (0.1)	Xylene	KOH	110	4	80
12	**1a** (0.1)	Isopropranol	KOH	82	4	20
13	**1a** (0.1)	THF	KOH	66	4	10
14	**1a** (0.1)	Water	KOH	110	4	32
15	**1a**(0.1)	Toluene	KOH	110	4	67[b]
16	**1b** (1)	Toluene	KOH	110	24	82
17	**1b** (0.1)	Toluene	KOH	110	24	81
18	**1b** (0.1)	Toluene	KOH	110	4	70
19	$[IrCp*Cl_2]_2$ (0.1)	Toluene	KOH	110	4	35(42)*
20	--	Toluene	KOH	110	4	00

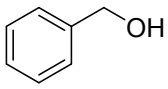
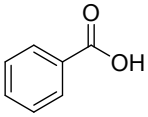
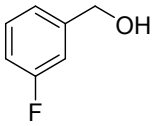
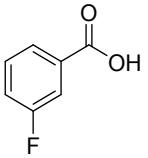
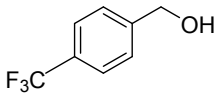
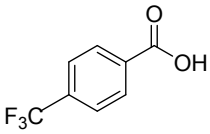
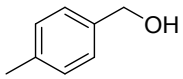
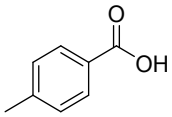
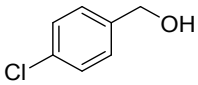
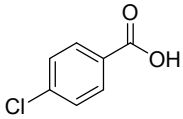
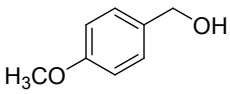
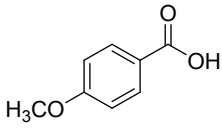
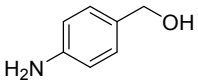
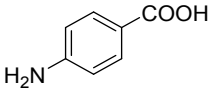
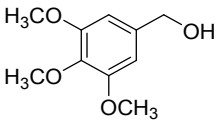
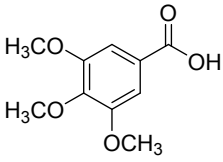
[a]Reaction Conditions: alcohol (1mmol), catalyst (1–0.1 mol %), base (1.1mmol), solvents (10 mL) in the N_2 atmosphere.* Values within parenthesis indicate conversion of benzyl alcohol to potassium benzoate determined by ^1H NMR spectroscopy.[b] KOH (0.75 mmol)

1

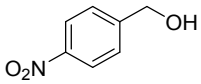
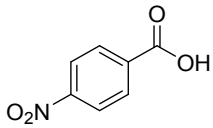
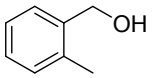
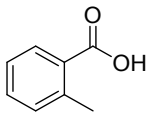
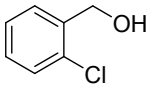
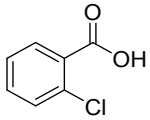
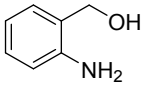
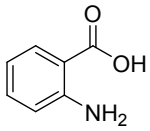
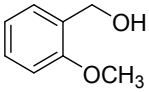
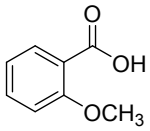
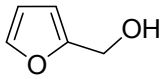
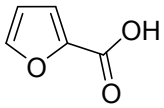
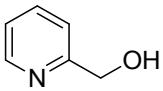
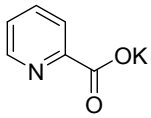
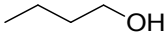
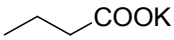
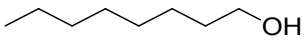
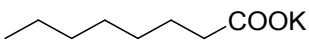
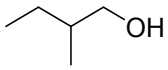
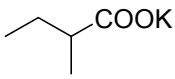
2

Table 2. Acceptorless Dehydrogenation of Alcohols to Acids[a] using complex **1a** as a catalyst



Entry	Substrate	Product	Isolated yield (%)
1			**94**
2			**80**
3			**76**
4			**87**
5			**85**
6			**81**
7			**67**
8			**72**

View Article Online
DOI: 10.1039/D0DT02341H

9			**46**
10			**84**
11			**83**
12			**54**
13			**36**
14			**80**
15			**71**
16			**82**
17			**75**
18			**00**

[a]Reaction Conditions: alcohol (2 mmol), KOH (2.2 mmol),**1a** (0.1 mol%), toluene (10 mL), reflux, 4–15 h, (entries 1-6, 8, 10, 11, 13 ; 4h, entries 7, 9, 12, 14, 18; 10h, entries 16-17, 15h.) then aq HCl.

The catalyst can be reused at least three times without a discernible decrease in the product yield (94%, 92% and 92%, ESI Fig S65). It is interesting to note that the acceptorless dehydrogenation reaction with our catalyst can be scaled up easily. Benzyl alcohol could be smoothly converted to benzoic acid in 91% yield in a gram scale experiment with a substrate to catalyst ratio of 5000:1 and a TON of 4550 has been achieved.

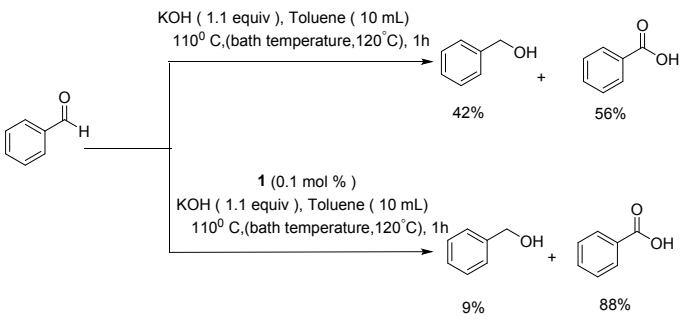
Reaction mechanism

A series of controlled experiments were carried out to gain mechanistic insights of reaction. At first, a mercury poisoning test was conducted by reacting benzyl alcohol (2 mmol) with KOH (2.2 mmol) in presence of catalyst **1a** (0.1 mol%) and Hg(10 mmol) at 110°C. After 4h of reaction, 80% yield of benzoic acid was obtained which suggests metallic Hg has virtually no impact on our catalytic system demonstrating that the reaction proceeds with molecular intermediate.

Then, to garner evidence on the evolution of hydrogen gas during dehydrogenation of alcohols to acids, we have designed a hydrogenation experiment using styrene as a substrate in presence of Pd/C catalyst without using any external hydrogen source. The reaction was carried out in a closed vessel using benzyl alcohol (1 mmol), KOH (1.1 mmol), complex **1a** (0.1 mol %), styrene (1mmol), toluene and Pd/C (5 mol %). After 4h of refluxing, it has been observed by ^{1}H NMR that 89% of styrene was converted to ethylbenzene. Based on this outcome, we conclude that hydrogen gas was generated during the transformation of benzyl alcohol to potassium benzoate. To measure the amount of hydrogen evolved, the reaction vessel was connected with a gas burette filled with water. It has been observed that when 0.5 mmol of benzyl alcohol was allowed to react, a total gas volume of 23.5 mL (approx. 0.96 mmol) was obtained which is consistent with the release of 2 equivalents of hydrogen.[10,12]

As we know that the catalytic dehydrogenation of alcohols to corresponding acids can proceed via an aldehyde or ester intermediate and therefore, to distinguish between these two pathways, we have conducted two experiments. Firstly, benzyl alcohol was reacted with KOH in presence of catalyst **1a** at 110°C (bath temperature 120°C) without using any solvent and after 4h of reactions, benzaldehyde was observed as the only product by GC and no corresponding ester was formed.[9a] Similarly, when the same reaction was carried out using toluene as solvent at 50°C, only benzaldehyde without any ester formation was observed indicating that ester is the less likely intermediate and the reaction might proceed through a Cannizzaro pathway.[9d] To examine this, two parallel experiments were conducted with or without the catalyst **1a** taking benzaldehyde as a substrate under similar experimental condition for a reaction time of 1h (Scheme 2). The reaction in presence of the catalyst **1a** produces 88% benzoic acid, while in absence of catalyst produces only 56%.These results suggest that both the Cannizzaro and catalytic dehydrogenation processes are taking place in the case of benzylic alcohol derivatives

View Article Online
DOI: 10.1039/D0DT02341H



Scheme 2 Cannizzaro and dehydrogenation reactions of benzaldehyde.

Further, to assess whether the F atom present in the wingtip of the imidazole moiety of the complex **1a** has any role in the catalytic pathway, we synthesized an analogous complex without F atom by the reaction of 3-benzyl-1-(4-methoxyphenyl)-1H-imidazolium bromide(See ESI Fig S19-S23) with $[Ir(Cp^*)Cl_2]$ following a similar experimental procedure as reported for **1a** or **1b** and performed the dehydrogenation reaction of benzyl alcohols by using **1c** (0.1 mol%) as a catalyst. Under optimal conditions, the performance of the catalyst **1c** is more or less comparable with the catalyst 1a (85% vs 94%) which suggests that F atom attached with wingtip of imidazole moiety in the complex **1a** may not play a significant role in catalytic activity of the complex **1a** in the dehydrogenation reaction.

Moreover, it may be worthy to note that, there are instances where Cp^* ligand dissociated from a metal center during catalytic conditions.[31] However, to investigate this, we have recorded LC-MS of the complex **1a** isolated from a post catalytic reaction mixture, and we observed a strong peak at m/z 609.42 which is very close to the $[M-Br]^+$ peak of the original complex **1a**. These results, along with almost no loss in activity on recycling the catalyst suggest, although not conclusively, that the complexes remains intact during our catalytic conditions and Cp^* may not get dissociated.

To get more rationality about the mechanism, we have examined the catalytic dehydrogenation process of benzyl alcohol through an *in situ* ^1H NMR. A mixture of benzyl alcohol (1mmol), KOH (1.1 mol), and the complex **1a** (0.01mmol) was dissolved in 0.8 mL of deuterated toluene in an NMR tube and the headspace of the tube was tightly closed with Teflon cap. The NMR tube was placed in a preheated oil bath at 50°C for 10 minutes and then the ^1H NMR spectrum was recorded. Indeed, a highly shielded peak was observed at −17.5 ppm which indicated the presence of an iridium hydride species (ESI, Fig S22).Moreover, we have performed a similar experiment taking complex **1a** in deuterated toluene (0.8 mL) in presence of KOH base at 120°C for 20 minutes(under standard catalytic conditions). The ^1H NMR spectrum of the reaction displayed the characteristic Ir-H peak at -

17.5 along with the signals for Cp^* and NHC ligands(ESI, Fig S23). These experiments suggest, although not conclusively, Ir-H is likely intermediate of the reaction.

Thus, based on control studies and literature precedents of metal-catalyzed acceptors dehydrogenation of alcohols,[9c,10,12,13] a plausible mechanism of the reaction is proposed (ESI, Scheme 1)

Conclusions

In summary, we have synthesized and characterized two new cyclometalated Cp*Ir(III)-NHC complexes and explored their potentials as catalysts for acceptorless dehydrogenation of alcohols to carboxylic acids. By using one of the complexes (**1a),** a wide range of alcohols could be efficiently converted to corresponding acids in high yields accompanied by the evolution of hydrogen gas. It is interesting to note that the catalyst **1a** could be easily recycled at least three times without compromising with its activity. Besides, complex **1a** is compatible to carry out large scale synthesis of benzoic acid from benzyl alcohol. Interestingly, this is the first example of a [C, C] cyclometalated Ir^{III}–NHC system exploited for acceptorless dehydrogenation of alcohols to carboxylic acids.

Acknowledgements

We gratefully acknowledge the financial support from the Department of Science and Technology, New Delhi (Grant no: CRG/2018/001669) and UGC, New Delhi for SAP-DRS grant to the Department of Chemistry, Dibrugarh University (DU). DB is thankful to UGC, NERO for providing teacher's fellowship under UGC FDP programme. Authors are grateful to Mr. Bibekananda Gogoi, JRF, DST project for experimental assistance respectively.

Supporting information

The supporting information is available free of charge on the RSC publication website. ^1H, ^{13}C NMR, ^{19}F, mass spectra of the ligands and complexes, crystallographic data of the complex **1a**; ^1H and ^{13}-NMR spectra of all the catalytic reaction product.

Experimental Section

General Information: All reactions were carried out under a nitrogen atmosphere using the schlenk technique. All solvents were purified through the standard purification method. All the reagents and deuterated solvents, $CDCl_3$, $(CD_3)_2SO$, CD_3OD, and D_2O were purchased

from commercial suppliers and used as received. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on the Bruker AVANCE III HD−500 MHz spectrometer. HRMS was measured on Shimadzu LCMS−IT−TOF mass spectrometer. The ligand 3-(2-flurobenzyl)-1-(4-methoxyphenyl)-1H-imidazolium bromide (**L_1**) was prepared as per the previously reported procedure.[26]

Synthesis of *3-(2-flurobenzyl)-1-(4-formylphenyl)-1H-imidazolium bromide* (L_2)

Ligand L_2 was prepared by following the same procedure of L_1 where (4−formylphenyl)−1H−imidazole (172 mg, 1mmol) and 2−fluorobenzyl bromide (1.89g, 10 mmol) were employed. The ligand L2 was isolated as white powder. Yield: 250 mg (69%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.25 (s, 1H, NCHN), 10.12 (s, 1H, CHO), 8.51 (s, 1H, Ar), 8.20 (d, J = 8.7 Hz, 2H, Ar), 8.11 – 8.07 (m, 3H, Ar), 7.64 (t, J = 7.7 Hz, 1H, CH = CH, imidazole), 7.51 (q, J = 7.4 Hz, 1H, Ar), 7.37 – 7.28 (m, 2H,Ar), 5.65 (s, 2H, benzyl CH_2). ^{13}C NMR (126 MHz, DMSO) δ 192.55 (s), 161.63 (d,$^{1}J_{C,F}$ = 248.22 Hz), 139.04 (s), 136.79 (d, $^{3}J_{C,F}$ = 13.1 Hz), 131.89 (d, $^{3}J_{C,F}$ = 8.2 Hz), 131.51 (s), 125.41 (d, $^{4}J_{C,F}$= 3.4 Hz), 124.04 (s), 122.86 (s), 121.88 (s), 121.59 (d, $^{2}J_{C,F}$ = 14.4 Hz), 116.23 (s), 116.07 (s), 47.13 (s).HRMS: $[M-Br]^+$ = 281.106, calculated: 281.11.

Synthesis of *3-benzyl-1-(4-methoxyphenyl)-1H-imidazolium bromide* (L_3)

Ligand **L_3** was prepared by following the same procedure of **L_1** where (4−methoxyphenyl)−1H−imidazole (174 mg, 1mmol) and benzyl bromide (1.71g, 10 mmol) were employed. The ligand L3 was isolated as white powder. Yield : 254 mg (73.5%).

^{1}H NMR (500 MHz, CD_3OD) δ 9.63 (s, 1H), 8.02 (s, 1H), 7.81 (s, 1H), 7.66 (dd, J = 9.1, 2.7 Hz, 2H), 7.50 (dt, J = 23.2, 8.3 Hz, 5H), 7.17 (d, J = 8.5 Hz, 2H), 5.55 (s, 2H), 3.90 (s, 3H).^{13}C NMR (126 MHz, CD_3OD) δ 160.96, 134.89, 133.56, 128.99, 128.29, 127.77, 124.77 , 123.53 , 122.71, 122.14 , 114.91 , 52.99 . LC-MS : [M-Br]$^+$ = 265.24, calculated : 265.13.

Synthesis of complex 1a

A mixture of $[IrCp^*Cl_2]_2$ (84mg, 0.105 mmol), ligand precursor L_1(76 mg, 0.21mmol), Cs_2CO_3 (202mg, 0.62mmol), NaOAc (172 mg, 2.092mmol) and excess KBr were taken in 100 mL schlenk flask and the mixture was refluxed for 10 h in dry CH_3CN under nitrogen atmosphere. After it cooled to room temperature, the mixture was filtered through celite and washed using CH_3CN three times. The solvent was removed under reduced pressure. The crude product was purified through column chromatography (SiO_2, CH_2Cl_2/ methanol (9: 1). The complex was isolated as brown solid. Yield: 110 mg (76%). ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.55 (t, *J* = 7.9 Hz, 1H, CH=CH,imidazole), 7.41 – 7.27 (m, 3H,Ar), 7.15-7.10 (m, 2H,Ar), 7.06 (d, *J* = 10.1 Hz, 1H, CH = CH, imidazole), 6.84 (d, *J* = 13.3 Hz, 1H, Ar), 6.51 (dd, *J* = 13.3, 7.5 Hz, 1H, Ar), 5.52 (s, 2H, benzyl CH_2), 3.86 (s, 3H, $-OCH_3$), 1.84 (s, 15H, Cp*).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.04 (s), 161.39 (d, $^1J_{C,F}$=246.96 Hz), 156.83 (s), 142.68 (s), 140.22 (s), 131.64 (d, $^3J_{C,F}$ = 3.2 Hz), 130.09 (d, $^3J_{C,F}$ = 8.2 Hz), 124.97 (d, $^4J_{C,F}$ = 3.4 Hz), 123.29 – 122.85 (m), 122.40 (s), 121.90 (s), 119.14 (s), 115.16 (d, $^2J_{C,F}$ = 20.9Hz), 110.56 (d, $^2J_{C,F}$ = 16.2 Hz), 106.82 (s), 106.61 (s), 91.08 (s), 55.28 (s), 9.76 (s).MS (ESI; CH_3CN), *m/z*, $[M-Br]^+$ =609.186 (Found), 609.19 (Calculated).

Synthesis of complex 1b

Complex **1b** was synthesized by following same procedure of **1a** where $[IrCp^*Cl_2]_2$ (84 mg, 0.105 mmol), ligand precursor $\mathbf{L_2}$ (76 mg, 0.21 mmol), Cs_2CO_3 (202 mg, 0.62 mmol), NaOAc (172 mg, 2.092 mmol) and excess KBr were employed. Complex **1b** was isolated as brown solid. Yield: 104 mg (72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H, CHO), 8.22 (s, 1H, Ar), 7.53 – 7.49 (m, 1H, Ar), 7.45 (dd, *J* = 8.0, 1.7 Hz, 1H,Ar), 7.32 (d, *J* = 2.3 Hz, 1H, Ar), 7.11 – 7.04 (m, 3H, Ar), 6.84 (d, *J* = 2.2 Hz, 1H, CH = CH, imidazole), 6.72 (s, 1H, CH = CH, imidazole), 5.49 (s, 2H,CH_2, benzyl), 1.80 (s, 15H, Cp*).^{13}C NMR (126 MHz, $CDCl_3$) δ 192.48 (s), 167.57 (s), 161.45 (d, $^1J_{C,F}$= 246.96 Hz), 151.53 (s), 141.83 (s), 139.08 (s), 136.43 (s), 133.62 (s), 131.79 (d, $^3J_{C,F}$= 2.9 Hz), 130.40 (d, $^3J_{C,F}$ = 8.2 Hz), 120.41 (s), 115.99 – 115.65 (m), 115.47 (d,$^2J_{C,F}$ = 41.2 Hz), 115.14 (s), 110.57 (s), 91.78 (s), 47.03 (s), 9.73 (s). *m/z*, $[M-Br]^+$ =607.258 (Found), 607.17 (Calculated)

Synthesis of complex 1c

Complex **1c** was synthesized by following same procedure of **1a** where $[IrCp^*Cl_2]_2$ (84 mg, 0.105 mmol), ligand precursor $\mathbf{L_3}$ (72 mg, 0.21 mmol), Cs_2CO_3 (202 mg, 0.62 mmol), NaOAc (172 mg, 2.092 mmol) and excess KBr were employed. Complex **1c** was isolated as brown solid. Yield: 97 mg (69%) (^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.8 Hz, 2H, Ar), 7.41 – 7.35 (m, 4H, Ar), 7.27 (d, *J* = 2.1 Hz, 1H, CH=CH,imidazole), 7.08 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H,CH=CH, imidazole), 6.53 (dd, *J* = 8.4, 2.7 Hz, 1H,Ar), 5.65 (d, *J* = 14.4 Hz, 1H, benzyl CH), 5.27 (d, *J* = 14.4 Hz, 1H, benzyl CH), 3.88 (s, 3H,OCH_3), 1.85 (s, 15H, Cp*).^{13}C NMR (126 MHz, $CDCl_3$) δ 163.88, 156.84, 142.69, 140.26, 135.98, 128.85, 128.62, 128.18, 122.46, 119.26, 114.89, 110.44, 106.66, 91.04, 55.30, 9.79 . *m/z*,[M-Br]$^+$ = 591.20 (Found), 591.20 (calculated)

View Article Online
DOI: 10.1039/D0DT02341H

Single crystal X-ray diffraction

Diffraction quality single crystals of the complex **1a** (CCDC No :1973746) were grown by slow diffusion of hexane into a saturated dichloromethane solution. Single crystal X-ray diffractions were collected on a Bruker SMART APEX-II CCD diffractometer using Mo Kα (λ =0.71073 Å) radiation.[32] Bruker SAINT software has been employed for reducing the data and SADABS for correcting the intensities of absorption.[33] All co–crystal structures were solved and refined using SHELXL with anisotropic displacement parameters for non-H atoms. In all crystal structures, H-atoms are located experimentally, whereas C–H atoms were fixed geometrically using the HFIX command in SHELX–T.[34] Not, any missed symmetry observed in the final check of the CIF file using PLATON.[35,36]

General Procedure for Alcohol Dehydrogenation A mixture of alcohol (2 mmol), KOH (2.2 mmol), and iridium complex **1a** was taken in a 100 mL two neck round–bottomed flask and allowed to dissolve in dry toluene (10 mL). The mixture was refluxed (bath temperature 120°C) for the required time under nitrogen. The reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure, affording the crude potassium carboxylate.

Isolation Method A. Dichloromethane (10 mL) was added to potassium carboxylate and allowed to stir for 10 min to dissolve the catalyst and the solvent was decanted. Thereafter, the solid residue was washed with ethyl acetate several times and filtered. The resulting solid mass was dissolved in deionized water (40 mL) and the solution was acidified with 1M HCl and extracted with ethyl acetate. The organic phase was separated and dried over (Na_2SO_4). Finally, the ethyl acetate was removed under vacuum, affording pure carboxylic acid.

Isolation Method B. Dichloromethane (10 mL) was added to potassium carboxylate and allowed to stir for 10 min to dissolve the catalyst and the solvent was decanted, followed by washed with ethyl acetate thrice (3X15 mL) and filtered. The solid mass was dissolved in methanol (40 mL) and filtered. The solution was removed to dryness, under vacuum, affording pure potassium carboxylate.

Benzoic acid (1). White solid, Yield: 0.23g (94 %).^{1}H NMR (500 MHz, DMSO−d_6) δ 12.94 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H).^{13}C NMR (126 MHz, DMSO−d_6) δ 167.7, 133.2, 131.1, 129.6, 128.9

3–Fluorobenzoic acid (2). White solid, Yield: 0.224 g (80 %).^{1}H NMR (500 MHz, DMSO−d_6) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 12.1 Hz, 1H), 7.54−7.59 (m,1H), 7.46−7.50 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 166.66 , 163.39 (s), 161.45 (s), 133.67 (d, *J* = 7.1 Hz), 131.29 (d, *J* = 8.0 Hz), 125.89 (d, *J* = 2.7 Hz), 120.45 (s), 120.34 (d, *J* = 21.2 Hz), 116.15 (d, *J* = 16.6 Hz).

4–(Trifluoromethyl) benzoic Acid (**3**). White solid, Yield: 0.289g (76%). ^{1}H NMR (500 MHz, DMSO−d_6) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 166.68, 135.04, 133.08 (s), 132.83, 130.57, 126.06 (q, *J* = 3.6 Hz), 125.35.

4− Methylbenzoic acid (**4**). White solid, Yield: 0.237 g, (87%). ^{1}H NMR (500 MHz, DMSO) δ12.76 (br, 1H), 7.85(d, *J*= 10Hz, 2H), 7.31(d, J= 5Hz, 2H), 2.37(s, 3H), ^{13}C NMR (126 MHz, DMSO) δ 167.62, 143.39, 129.67, 129.47, 128.34, 21.46.

4− Chlorobenzoic acid (5). White solid, Yield: 0.267 g (85%).^{1}H NMR (500 MHz, DMSO−d_6) δ 13.24 (s, 1H), 7.95(d, *J* = 10 Hz, 2H), 7.57(d, *J* = 5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO−d_6) δ 166.7, 138.09, 131.48, 129.96, 129.08 .

4− Methoxybenzoic acid (**6**). White solid, Yield: 0.247 g (81%). ^{1}H NMR (500 MHz, DMSO−d_6) δ12.66 (br, 1H), 7.91 (d, *J* = 10Hz, 2H), 7.03(d, *J* = 10Hz , 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, DMSO−d_6), δ 167.36, 163.17, 131.69, 123.28, 114.15, 55.77

4– Amino benzoic acid (**7**). White solid, Yield: 0.184 g (67%). ^{1}H NMR (500 MHz, DMSO−d_6) δ 11.98 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 2H), 6.55 (d,*J* = 8.3 Hz, 2H), 5.86 (s, 2H). ^{13}C NMR (126 MHz, DMSO−d_6), 167.86, 153.48,131.56,117.27, 112.91

3,4,5–trimethoxybenzoic Acid (**8**). White solid, Yield: 0.153g (72%) ^{1}H NMR (500 MHz, DMSO) δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO−d_6),δ 171.76, 152.98, 142.98, 124.11, 107.41, 60.98, 56.26.

4– Nitrobenzoic acid (**9**). White solid, Yield: 0.154 g (46%). ^{1}H NMR (500 MHz, DMSO) δ 8.28 (d, *J* = 6.7 Hz, 2H), 8.13 (d, *J* = 7.0 Hz, 2H). ^{13}CNMR (126 MHz, DMSO−d6) δ 166.36, 150.30, 136.52, 131.19, 123.77.

4– Nitrobenzaldehyde **(9a)**.Pale yellow solid, Yield: 0.030 g (10%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.42 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H). ^{13}CNMR (126 MHz, $CDCl_3$−d1) δ 190.15, 151, 140.13, 130.3, 124.21.

2−Methylbenzoic Acid (**10**). White solid, Yield: 0.229 g (84%). ^{1}H NMR (500 MHz, DMSO−d_6) δ 12.84 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 10.5 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, DMSO−d_6) δ 169.02, 139.33, 132.06, 131.84, 130.76, 130.51, 126.17, 21.58.

2−Chlorobenzoic acid (11). White solid, Yield: 0.26 g (83%). ^{1}H NMR (500 MHz, DMSO−d_6) δ 13.33 (s, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 – 7.39 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.3, 131.9, 131.8, 131.1, 130.9, 127.6

2− Aminobenzoic acid (**12**). White solid, Yield: 0.148 g (54%). ^{1}H NMR (500 MHz, DMSO−d_6) δ 8.51 (br, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.50 (t, *J* = 8.0 Hz, 1H).^{13}C NMR (126 MHz, DMSO−d_6) δ 169.93, 151.84, 134.07, 131.50, 116.66, 114.91, 109.93.

2- Methoxybenzoic acid **(13).** White solid, Yield : 0.110 g, (36%), ^{1}H NMR (500 MHz, DMSO) δ 12.60 (s, 1H), 7.65 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H). ^{13}C (126 MHz, DMSO-d_6) δ 167.60, 158.40, 133.36, 130.98, 121.60, 120.34, 112.71, 55.84.

2-Furancarboxylic acid (**14**). White solid, Yield: 0.179 g (80%). ^{1}H NMR (500 MHz, DMSO−d_6) δ 7.92 – 7.91 (m, 1H), 7.22 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.65 (dd, *J* = 3.5, 1.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO−d6) δ 159.66, 147.39, 145.21, 118.07, 112.44.

Potassium Pyridine–2–carboxylate (**15**). This compound was isolated by method B as a white powder. Yield: 0. 229 g (71%). ^{1}H NMR (500 MHz, CD_3OD) δ 8.58 (d, *J* = 4.5 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.86 (t, *J* = 8.5 Hz, 1H), 7.45 – 7.40 (m, 1H). ^{13}C NMR (126 MHz, CD_3OD) δ 171.61, 154.98, 147.97, 136.66, 124.40, 123.43.

Potassium Butyrate (**16**). This compound was isolated by method B as a white powder Yield: 0.207g (82%). ^{1}H NMR (500 MHz, D_2O) δ 2.08 (t, *J* = 8.7 Hz, 2H), 1.49 (m, 2H), 0.82 (t, *J* = 8.7 Hz, 3H). ^{13}C NMR (126 MHz, D_2O) δ 184.12, 39.57, 19.30, 13.24

Potassium Octanoate (**17**). This compound was isolated by method B as a white powder. Yield: 0.137 g (75%). ^{1}H NMR (500 MHz, D_2O) δ 2.06 (t, *J* = 7.5 Hz, 2H), 1.49 – 1.37 (m, 2H), 1.17 (m, 8H), 0.75 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, D2O) δ 184.22, 37.51, 30.85, 28.55, 28.10, 25.31, 21.84, 13.24.

Procedure for the large scale synthesis of benzoic acid

A mixture of benzyl alcohol (1.08 g, 10 mmol), KOH (617.1 mg, 11mmol), and iridium complex **1a** (1.38 mg, 0.002 mmol) was taken in a 100 mL two neck round−bottomed flasks and allowed to dissolve in dry toluene (20 mL). The mixture was refluxed (bath temperature 120°C) for 72h under nitrogen. The solvent was removed under reduced pressure, affording the crude potassium carboxylate. Dichloromethane (10 x 3 mL) was added to potassium carboxylate and allowed to stir for 10 min to dissolve the catalyst and the solvent was decanted. Thereafter, the solid residue was washed with ethyl acetate several times and

View Article Online
DOI: 10.1039/D0DT02341H

filtered. The resulting solid mass was dissolved in deionized water (60 mL) and the solution was acidified with 1M HCl and extracted with ethyl acetate. The organic phase was separated and dried over (Na_2SO_4). Finally, the ethyl acetate was removed under vacuum, affording pure carboxylic acid as a white solid (1.12 g, 91%)

Volumetric Estimation of Evolved Hydrogen. A 100 mL schlenk flask was flame dried and purged with nitrogen. Thereafter, the flask was charged with alcohol (0.5 mmol), **1a** (0.1 mol%), and potassium hydroxide (0.11 mmol) in 10 mL of toluene. The reaction mixture was placed in a preheated oil bath (bath temperature 120°C). The sidearm of the schlenk flask was connected to a gas burette and headspace was closed tightly with glass stopcock. The reaction was allowed to continue until the evolution of gas ceased. To get consistent readings, the experiment was repeated three times and the number of moles of hydrogen was calculated by applying ideal gas law. Vapour pressure of water at 293 K = 17.5424 Torr, Atmospheric pressure = 761.3126 Torr, R = 62.3635 L Torr K^{-1} mol^{-1}, Volume of water displaced 23.5 mL. $n(H_2) = [(P_{atm} - P_{water})V]/RT = 0.00096$ mol, expected value 0.001 mol.

Hg Poisoning Experiment:

A mixture of benzyl alcohol (2 mmol), KOH (2.2 mmol), and iridium complex **1a**, (0.1 mol%) Hg (10mmol) was taken in a 100 mL two neck round–bottomed flask and allowed to dissolve in dry toluene (10 mL). The mixture was refluxed (bath temperature 120°C) for 4h under nitrogen. After completion of the required time, the solvent was removed under reduced pressure, affording the crude potassium carboxylate. Corresponding benzoic acid was found in 80 % (0.195 g) in yield by following the isolation procedure A.

Control experiments and reusability

Verification of ester formation in the dehydrogenation of alcohols

a) Benzyl alcohol (3 mL) and KOH (1.1 mmol) were taken in a 100 mL two neck round–bottomed flask and placed in a preheated oil bath (bath temperature 120°C).The mixture was stirred for 4 h under an N_2 atmosphere. The reaction mixture was allowed to cool to room temperature and the reaction mixture was analyzed by GC. However, the formation of ester was not observed, only a small amount of benzaldehyde was detected.

b) Benzyl alcohol (1 mmol) and KOH (1.1 mmol) were dissolved in toluene (10 mL) in a 100 mL two neck round–bottomed flask and placed in a preheated oil bath (bath temperature 120°C).The mixture was stirred for 4h under an N_2 atmosphere. The reaction mixture was allowed to cool to room temperature and the reaction mixture was analyzed by GC. However, the formation of ester was not observed, only a small amount of benzaldehyde was detected.

View Article Online
DOI: 10.1039/D0DT02341H

The reaction of benzaldehyde with KOH.

Benzaldehyde (1 mmol) and KOH (1.1 mmol) were dissolved in toluene (10 mL) in a 100 mL two neck round–bottomed flask and placed in a preheated oil bath (bath temperature 120°C).The mixture was refluxed for 1 h under an N_2 atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was removed under vacuum. Thereafter, the solid residue was washed with ethyl acetate several times and filtered. The resulting solid mass was dissolved in deionized water (30 mL) and the solution was acidified with 1M HCl and extracted with ethyl acetate. The organic phase was separated and dried over (Na_2SO_4). Finally, the ethyl acetate was removed under vacuum, affording pure carboxylic acid as a white solid (68 mg, 56%). Residual ethyl acetate solution (washing part) was collected in a round bottom flask and the solvent was removed under vacuum to recover benzyl alcohol.

The reaction of benzaldehyde with KOH in the presence of catalyst 1a

Benzaldehyde (1mmol), **1a** (0.1 mol%), and KOH (1.1 mmol) were dissolved in toluene (10 mL) in a 100 mL two neck round–bottomed flask and placed in a preheated oil bath (bath temperature 120°C).The mixture was refluxed for 1 h under an N_2 atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was removed under vacuum. Dichloromethane (10 x 3 mL) was added to a mixture of potassium carboxylate and benzyl alcohol and allowed to stir for 10 min to dissolve the catalyst and the solvent was decanted. Thereafter, the solid residue was washed with ethyl acetate several times and filtered. The resulting solid mass was dissolved in deionized water (30mL) and the solution was acidified with 1M HCl and extracted with ethyl acetate. The organic phase was separated and dried over (Na_2SO_4). Finally, the ethyl acetate was removed under vacuum, affording pure carboxylic acid as a white solid (107mg, 88%). Residual ethyl acetate and dichloromethane solution were collected in a round bottom flask and the solvent was removed under vacuum. To the collected mixture small amount of dichloromethane was added and to this solution, diethyl ether was added in stirring conditions to get precipitate of the catalyst. The solution is filtered and the filtrate part is removed under vacuum to recover benzyl alcohol (9%).

Reusability Experiment:

Benzyl alcohol (2 mmol), 1a (0.1 mol%), and KOH (1.1 mmol) were dissolved in toluene (10 mL) in a 100 mL two neck round-bottomed flask and placed in a preheated oil bath (bath temperature 120°). The mixture was refluxed for 4h under an N_2 atmosphere. The reaction mixture was allowed to cool to room temperature and the mixture was filtered. To the filtrate,

benzyl alcohols (2 mmol), KOH (1.1mmol) are added and again the reaction was carried out for 4h. The process was repeated three times.

Hydrogenation

Complex **1a** (0.005mmol), KOH(1.1mmol), styrene (1 mmol), Pd/C (5 mol %) and benzyl alcohol (1 mmol) were dissolved in toluene (10 mL) in a 100 ml Schlenk tube. The solution was allowed to reflux for 4h under an N_2 atmosphere at 120°C. The mixture was cooled to room temperature and the solution was filtered to remove potassium carboxylate. The solvent was removed under vacuum and the mixture was dissolved in ethyl acetate and filtered. Ethyl acetate was removed in vacuum and the sample was submitted for ^{1}H NMR analysis.

[1] (a) J. Jeong, T. Shimbayashi and K.-I. Fujita, *Catalysts*., 2019, **9**, 846. (b) R. H. Crabtree, *Chem. Rev.*, 2017, **117**, 9228. (c) C. Gunanathan and D. Milstein, *Science*., 2013, **341**, 122.

[2] (a) G. Gonzalez Miera, E. Martínez-Castro and B. Martínez-Castro, *Organometallics,* 2018, **37**, 636−644. (b) E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H.-J. Drexler, W. Baumann, H. Junge and M. Beller, *Angew. Chem.,Int. Ed.*, 2013, **52**, 14162−14166. (c) K. Fujita, R. Kawahara, T. Aikawa and R. Yamaguchi, *Angew. Chem.,Int. Ed.*, 2015, **54**, 9057−9060. (c) A. Züttel, A. Borgschulte, L. Schlapbach, in Hydrogen as a future energy carrier; Eds.; Wiley–VCH: Weinheim, Germany, **2008**; DOI: 10.1002/9783527622894. (d) M. Nielsen, E Alberico, W. Baumann, H–J. Drexler, H. Junge, S. Gladiali, M. Beller, *Nature*, 2013, **495**, 85–89. (e) R. Rodríguez–Lugo, M. Trincado, M. Vogt, F. Tewes, G. Santiso–Quinones and H. Grützmacher, *Nat Chem*., 2013, **5**, 342–347. (e) M. Trincado, D. Banerjee and J. Grützmacher, *Energy Environ. Sci*., 2014, **7**, 2464−2503. (f) T. C. Johnson, D. J. Morris and M. Wills, *Chem. Soc. Rev.,* 2010, **39**, 81-88. (g) L. Schlapbach, A. Zuttel, *Nature,* 2001, **414**, 353−358.

[3] (a) I. Dutta, A. Sarbajna, P. Pandey, S. M. W. Rahaman, K. Singh and J. K. Bera, *Organometallics,* 2016, **35**, 1505−1513. (b) K. Toyomura and K. Fujita, *Chem. Lett*., 2017, **46**, 808−810.(c) Z. Wang, B. Pan, Q. Liu, E. Yue, G. A. Solan, Y. Ma and W. H. Sun, *Catal. Sci.Technol*., 2017, **7**, 1654−1661. (d) Q. Wang, H. Chai and Z.

View Article Online
DOI: 10.1039/D0DT02341H

Yu, *Organometallics,* 2017, **36**, 3638−3644. (e) D. Sengupta, R. Bhattacharjee, R. Pramanick, S. P. Rath, N. S. Chowdhury, A. Datta and S. Goswami, *Inorg. Chem.*, 2016, **55**, 9602−9610. (f) H. Song, B. Kang and S. H. Hong, *ACS Catal.,* 2014, **4**, 2889−2895. (g) R. G. Alabau, M. A. Esteruelas, A. Martínez, M. Oliván and E. Oñate, *Organometallics,* 2018**, 37** (16), 2732−2740. (h) R. Pretorius, J. Olguín and M. Albrecht, *Inorg. Chem.,* 2017, **56**, 12410−12420. (i) A. Prades, E. Peris and M. Albrecht, *Organometallics,* 2011, **30**, 1162−1167. (j) M. Nielsen, A. Kammer, D. Cozzula , H. Junge, S. Gladiali and M. Beller, *Angew. Chem. Int. Ed*., 2011, **50**, 9593−9597. (k) J. Zhang, E. Balaraman, G. Leitus and D. Milstein , *Organometallics,* 2011, **30**, 5716−5724. (l) K.-N. T. Tseng, J. W. Kampf and N. K. Szymczak,. *Organometallics,* 2013, **32**, 2046−2049. (m) Q. Wang, H. Chai and Z.Yu, *Organometallics,* 2017, **36**, 3638−3644. (n) Z. Wang, B. Pan, Q. Liu, E. Yue, G. A. Solan, Y. Ma and W.H. Sun, *Catal. Sci. Technol*., 2017, **7**, 1654−1661.

[4] E. Balaraman, E. Khaskin, G. Leitus and D. Milstein, *Nature Chem.*, 2013, **5**, 122–125.

[5] (a)J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg and D. Milstein, *Organometallics,* 2004, **23**, 4026−4033. (b) P. Sponholz, D. Mellmann, C. Cordes, P. G. Alsabeh, B. Li, Y. Li, M. Nielsen, H. Junge, P. Dixneuf, and M. Beller, *ChemSusChem.*, 2014, **7**, 2419–2422. (c) J–H. Choi, L. E. Heim, M. Ahrens and M. H. G. Prechtl, *Dalton Trans.,* 2014, **43**, 17248–17254. (d) L. Zhang, D. H. Nguyen, G. Raffa, X. Trivelli, F. Capet, S. Desset, S. Paul, F. Dumeignil and R. M. Gauvin, *ChemSusChem.,* 2016, **9**, 1413–1423.

[6] X. He, Y. Li, H. Fu, X. Zheng, H. Chen, R. Li and X. Yu, *Organometallics,* 2019, **38**, 1750-1760.

[7] (a) K.-N. T. Tseng, J. W. Kampf and N. K. Szymczak, *ACS Catal*., 2015, **5**, 5468−5485. (b) Z. Dai, Q. Luo, X. Meng, R. Li, J. Zhang and T. Peng, *J. Organomet. Chem.,* 2017, **830**, 11–18.

[8] (a) A. Sarbajna, I. Dutta, P. Daw, S. Dinda, W. S. M. Rahaman, A. Sarkar, J. K. Bera, *ACS Catal*., 2017, **7**, 4, 2786–2790. (b) M. K. Awasthi and S. K. Singh, *Inorg.Chem.,* 2019, **58**, 21, 14912-14923.

View Article Online
DOI: 10.1039/D0DT02341H

[9] (a) D. Gong, B. Hu and D. Chen, *Dalton Trans*., 2019, **48**, 8826. (b) J. Malineni, H.Keul and M. A Möller, *Dalton Trans.*, 2015, **44**, 17409−17414. (c) K. Fujita, R. Tamura, Y. Tanaka, M. Yoshida, M. Onoda, R. Yamaguchi, *ACS Catal*., 2017, **7**, 7226−7230.(d) V. Cherepakhin, T. J. Williams, *ACS Catal.,* 2018, **8**, 3754–3763.

[10] C. Santilli, I. S. Makarov, P. Fristrup and R. Madsen, *J. Org. Chem.,* 2016, **81**, 9931−9938.

[11] E. W. Dahl, T. Louis-Goff and N. K. Szymczak, *Chem.Commun*., 2017, **53**, 2287–2289.

[12] H-M. Liu, L. Jian, C. Li, C.C. Zhang, H.Y. Zheng, X. Li. H.Chen and R. Xiang, *J. Org. Chem.,* 2019, **84**, 9151−9160.

[13]M. Kuwahara, M. Nishioka, M. Yoshida and K.-i.A Fujita, *Chem Cat Chem,* 2018, **10**, 3636–3640.

[14] G. Zeng, S. Sakaki, K.-I. Fujita, H. Sano and R. Yamaguchi, *ACS Catal*., 2014, **4**, 1010−1020.

[15] S. Diez-Gonzalez and S. P. Nolan, *Top. Organomet. Chem*., ed. F. Glorius, Springer-Verlag, Berlin, Heidelberg, 2007, vol. **21**, pp 47.

[16] M. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature.,* 2014, **510,** 485–496.

[17] (a) K. R. Balinge and P. R. Bhagat, *Comptes Rendus Chimie*., 2017, **20**, 773. (b) A. Ortiz, P. G. Sal, J. C. Flores and E. de. Jesus, *Organometallics,* 2018, **37**, 3598. (c) E. Peris, *Chem. Rev.,*2018**,** ***118***(19), 9988-10031. (d) H. V. Huynh, *Chem. Rev.,* 2018, **118**, 19, 9457-9492.

[18] (a) R.Corbera´n, M. Sanau´and E. Peris, *Organometallics,* 2006, **25**, 4002-4008. (b) R.Corbera´n, M. Sanau´and E. Peris, *J. Am. Chem. Soc.*, 2006, **128**, 12, 3974-3979.

[19] Selected examples, (a) L. S. Sharninghausen, Jesu´s. Campos, M. G. Manas, R. H. Crabtree, *Nat Commun,* 2014, **5**, 5084. (b) D. Gülcemal, S. Gülcemal, C. M. Robertson, J. Xiao, *Organometallics,* 2015, **34**, 4394−4400. (c) A. Azua, M. Finn, H. Yi, A. B. Dantas, A. Voutchkova−Kostal, *ACS Sustainable Chem. Eng.,* 2017, **5**, 3963−3972. (d) M. Iglesias, L. A. A. Oro, *Chem. Soc. Rev.,* 2018, **47**, 2772. (e) M. Huang, Y. Li, J.Liu, X. Lan, Y. Liu, C. Zhaoa, Z. Ke, *Green Chem.,* 2019, **21**, 219. (f) L. G. Pezük, B. Şen, F. E. Hahn and H.

View Article Online
DOI: 10.1039/D0DT02341H

Türkmen, *Organometallics*, 2019, **38**, 2, 593-601. (g) M. Böhmer, F. K ampert, T. T. Y. Tan, G. Guisado-Barrios, E. Peris, F. E. Hahn, *Organometallics,* 2018, **37**, 21, 4092-4099. (h) D. Ventura-Espinosa, S. Sabater, A. Carretero-Cerdán, M. Baya, J. A. Mata, *ACS Catal.,* 2018, **8**, 2558−2566.

[20] Selected examples, (a) N. D. McDaniel, H. Müller-Bunz, S. Bernhard and M. Albrecht, *Angew. Chem., Int. Ed.,* 2010, **49**, 9765–9768. (b) D. G. H. Hetterscheid and J. N. H. Reek, ***Chem. Commun.,*** 2011, **47**, 2712–2714. (c)A.Volpe,A.Sartorel,C.Tubaro ,L.Meneghini, M. D. Valentin and C. Graiff ,*Eur.J.Inorg.Chem*.,2014,**568**,665–675. (d) J. A. Woods, R. Lalrempuia, A.Petronilho, N. D. McDaniel, H. MüllerBunz, M. Albrecht and S. Bernhard, ***Energy Environ. Sci.***, 2014, **7**, 2316-2328. (e) T. P. Brewster, J. D.Blakemore, N. D. Schley, C.D. Incarvito, N. Hazari, G. W. Brudvig, R. H. Crabtree, *Organometallics,* 2011, **30**, 965–973.

[21] Selected examples (a) P. H. Lanoe, J.Chan, A. Groue, G. Gontard, A. Jutand, M. N. Rager, N. Armaroli, F. Monti, A. Barbieri and H.Amouri, *Dalton Trans.,* 2018, **47**, 3440−3451.(b) S. Lam, K.Tong , C. Yang , W.Kwong , X. Guan, M. Li, V. K. Lo, S.L. Chan, D. L. Phillips, C.Lok and C. Che, *Chem. Sci.,* 2019, **10**, 293-309. (c) B. Liu, S. Monro, M. A. Jabed , C. G. Cameron, K. L. Colón, W. Xu , S. Kilina, S. A. McFarland and W. Sun, *Photochem. Photobiol. Sci*., 2019, **18**, 2381-2396. (d) M. Quan, B. D.Stringer, M. A. Haghighatbin, J. Agugiaro, G. J. Barbante, D. J. D. Wilson, C. F. Hogan and P. J. Barnard. *Dalton Trans.***,** 2019, **48**, 653-663. (e) B. Liu, M. A. Jabeb, J. Guo, W. Xu, S. L. Brown, A. Ugrinov, E. K. Hobbie, S. Kilina, A.Qin and W. Sun, *Inorg. Chem.,* 2019, **58**, 21, 14377-14388.

[22] Selected Examples (a) L. Mercs and M.Albrecht, ***Chem. Soc. Rev.,*** 2010, **39**, 1903-1912.

(b) J. Kralj, A. Bolje, D. S.Polančec, I. Steiner, T. Gržan, A.Tupek, N. Stojanović, S. Hohloch, D. Urankar, M. Osmak, B. Sarkar, A. Brozovic and J. Košmrlj, *Organometallics,* 2019, **38**, 21, 4082-4092.

(c) T. Nishioka, T.Shibata and I. Kinoshita, *Organometallics,* 2007, **26**, 1126-1128 (d) W. Zhao, V.Ferro and M. V. Baker, *Coord. Chem. Rev.,* 2017, **339**, 1–16. (e) C. Wang, J. Liu, Z. Tian, M. Tian, L.Tian, W. Zhao, Z. Liu, ***Dalton Trans.,*** 2017**, 46,** 6870-6883.

View Article Online
DOI: 10.1039/D0DT02341H

[23] Y. Maenaka, T. Suenobu, S. Fukuzumi, *J. Am. Chem. Soc.,* 2012, **134**, 22, 9417-9427.

[24] Selected Examples (a) J.Wu, D. Talwar, S. Johnston and M. Yan, *Angew. Chem., Int. Ed.,* 2013, **52**, 6983–6987. (b) D. Zhang, X. Chen, H. Liu, X-R. Huang, ***New J. Chem.,*** 2014, **38**, 3862-3873. (c) Z. Mazloomi, R.Pretorius, O. Pamies, M. Albrecht and M. Dieguez, *Inorg. Chem.,* 2017, **56**, 18, 11282-11298. (e) X. Chen, Y. Li, L. Chen, Z. Zhu, B.Li, Y.Huang and Z. Min, *J. Org. Chem.,* 2019, **84**, 6, 3559-3565. (f) M. Valencia, H. Mü er-Bunz, R. A. Gossage and M. Albrecht, *Chem. Commun*., 2016, **52**, 3344−334.

[25] (a) M. Finn, J.A. Ridenour, J. Heltez, C. Cahil, A. V-Kostal, *Organometallics*, 2018, 37, 9, 1400-1409.(b) L. S. Sharnighausen, B. Q. Marcado, R. H. Crabtree, N. Hazari, N. *Chem. Commun*. 2015, 17(1), 193-198. (c) Z. Lu, I. Demianets, R. Hamze, N. J. Terrile, T.J. Williams, *ACS Catal*. 2016, 6(3), 2014-2017. (d) Z. M. Sun, Q.Y. Liu, J. B. Chen, C. Y. Huang, T. Tu, , *ACS Catal*.2015, 5, 6573l.

[26] D. Borah, B. Saha, B. Sarma and P. Das, *J. Chem Sc*., 2020, **51**, 132.

[27] M. C. Jahnke, M. Hussain, F. Hupka, T. Pape, S. Ali, F. E. Hahn, and K. J. Cavell, *Tetrahedron,* 2009, **65** 909.

[28] (a) A. Majumder, R. Naskar, P. Roy, R. Maity, *Eur. J. Inorg. Chem.,* 2019, **13**, 1810–1815.

(b) S. Semwal, I. Mukkatt, R. Thenarukandiyil and J.Choudhury, *Chem. Eur. J.,* 2017, **23**, 13051−13057.

[29] J. P. Majoral, A. M. Caminade and M. Taillefer, *ChemCatChem,* 2009, **1**, 504 – 509.

[30] Y. Tang, R. I. L. Meador, C.T. Malinchak, E.F. Harrison, K. A. McCaskey, M. C. Hempel and T.W. Funk, *J. Org. Chem.,* 2020, **85**, 4, 1823-1834.

[31] J.Campos, U.Hintermair, T.P.Brewster, M.K Takase and R.H.Crabtree, *ACS Catal*., 2014, **4**, 973-985.

[32] SAINT Plus (v 6.14) Bruker AXS Inc., Madison, WI, **2008.**

[33] Bruker AXS Inc., Madison, WI, **2008.**

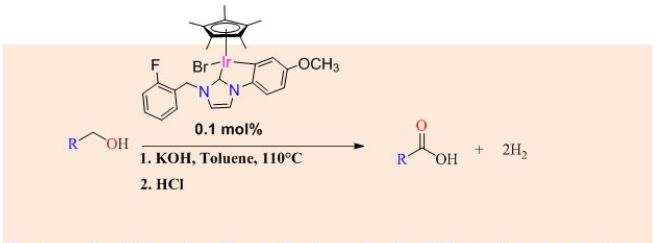
[34]G. M. Sheldrick, SHELXS and SHELXL97 Programs for structure refinement and solution, Göttingen, Germany. **1997.**

[35]A. L. Spek. PLATON, A Multipurpose Crystallographic Tool Utrecht University, Utrecht, Netherland. **2002.**

[36] A. L. Spek, Single-crystal structure validation with the program *PLATON J. Appl. Cryst.* 2003,**36,** 7.

View Article Online
DOI: 10.1039/D0DT02341H

View Article Online
DOI: 10.1039/D0DT02341H



First example of delineating efficacy of cyclometalated Ir NHC complexes in acceptorless dehydrogenation of alcohols to acids with a low loading of catalyst (0.1 mol%) in a short reaction time(4h). Notably, one of the complexes can be reused for the three times without decreasing its catalytic efficencies and can be utilised for large scale synthesis of benzoic acids.

254x190mm (96 x 96 DPI)