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# Ambient-Pressure and Base-Free Aldehyde Hydrogenation Catalyst Supported by a Bifunctional Abnormal NHC Ligand

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#### Supporting Information

ABSTRACT: Catalytic aldehyde hydrogenation is an essential and routinely used chemical synthesis process in both academia and industry. However, there is a serious scarcity of efficient homogeneous catalysts for this process to work under highly demanding atmospheric-pressure, base-free, and aqueous conditions. Addressing this problem, herein, we report an iridium-based catalyst for facile atmospheric-pressure and base-free hydrogenation of various aromatic, heteroaromatic, and aliphatic aldehydes. The catalyst also displays excellent chemoselectivity toward aldehyde over other carbonyl functionalities and unsaturated motifs. Moreover, the catalyst is found to work in  $H_2O$  (and in  $H_2O$ -ethanol) medium at ambient temperature. All of the above attributes have been possible to incorporate into this unique catalyst via employing



a hybrid bifunctional ligand, which plays a crucial role in facilitating the cleavage of  $H_2$  as well as effectively delivering hydride to the substrate without any help of base or pressure.

# INTRODUCTION

Aldehyde-to-alcohol is a fundamental organic transformation utilized on a regular basis not only in academic laboratories but also in industry for the synthesis of various fine and bulk chemicals.<sup>1</sup> To realize such a transformation, environmentally unfriendly traditional reduction with NaBH<sub>4</sub>, boranes, LiAlH- $(OR)_3$ , or Bu<sub>3</sub>SnH is still employed, leading to a large amount of undesirable waste.<sup>2</sup> This problem necessitated development of a catalytic aldehyde hydrogenation (CAH) protocol using H<sub>2</sub> gas as a clean and green reagent.<sup>3</sup> Accordingly, there has been a gradual evolution of many highly efficient homogeneous hydrogenation catalysts, pioneered by Milstein, Kirchner, Beller, Kempe, and others,<sup>4</sup> to fulfill some of the practical requirements such as using ambient temperature, earthabundant metals, etc. These individual successes were achieved using high-pressure H<sub>2</sub> gas and an inorganic/organic base. Whereas the use of pressurized H<sub>2</sub> gas needs specialized experimental setup to take care of safety issues, the presence of base may mediate aldol-type side reactions from aldehyde or may limit the functional group tolerance.<sup>5</sup> Thus, developing suitable catalysts that work both at atmospheric pressure of H<sub>2</sub> as well as under base-free conditions is highly desirable (Figure 1a). The use of base could be avoided for some of the recently developed catalysts by Kirchner,<sup>6a</sup> Grainger,<sup>6b</sup> van Leeuwen,<sup>64</sup> Zhang,<sup>6d</sup> and others<sup>7</sup> via exploring new ligands and various metals. Similarly, high pressure was avoided with Crabtree's catalyst using 50 mol % of base as an essential additive.<sup>8</sup> To the best of our knowledge, only two catalysts were reported

independently by Hanson<sup>9a</sup> and Do,<sup>9b</sup> which hydrogenate aldehydes under 1 atm H<sub>2</sub> pressure and base-free conditions with some limitations, such as using tetrahydrofuran (THF) solvent, 4 atm pressure, and longer reaction time (64 h at 60 °C) for aliphatic aldehydes, and no demonstration of chemoselectivity (Figure 1b). In contrast to atmosphericpressure and base-free aldehyde hydrogenation with H<sub>2</sub>, the transfer hydrogenation of aldehyde with a non-H<sub>2</sub> hydrogen source is well-developed, and many elegant mild catalysts were reported.<sup>10</sup> At this juncture, considering the existing status of the relatively economic<sup>10f</sup> CAH protocol, we paid attention to develop a unique ligand which would serve two crucial functions to facilitate the key steps of the catalytic cycle for the hydrogenation reaction. For facile H-H bond cleavage at mild pressure and temperature without any external base, we relied on an Ir-anionic benzimidazolato motif having a free basic imino nitrogen in the ring (exo nitrogen site) to capture the proton  $(H^+)$  generated from  $H_2$ . In our previous work, we found that this exo basic imino nitrogen is susceptible toward protonation.<sup>11</sup> In parallel, for efficient hydride transfer, we also configured the ligand with the powerful  $\sigma$ -donor capacity of an abnormal NHC (aNHC) moiety based on the imidazol-5ylidene motif.<sup>12</sup> Based on these considerations, the hybrid bifunctional ligand, as depicted in Figure 1c, was designed to utilize the corresponding Cp\*Ir-based complex [Ir]-Cl for

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# Organometallics

(a) aldehyde hydrogenation: demanding conditions H<sub>2</sub> (g), conditions O ambient temperature OH₂O or aq. org. solvent Catalyst ● base-free • cheap/abundant catalysts RCH<sub>2</sub>OH RCHO • atm. pressure of H<sub>2</sub> Solvent-free (b) current state-of-the-art and limitations high pressure+base: many<sup>[4]</sup> • high pressure+base-free: relatively few<sup>[6,7]</sup> atmospheric pressure + base-free: rare<sup>[9]</sup> |<sup>†</sup> [BAr<sup>F</sup>₄]<sup>−</sup> OH<sub>2</sub> 1 atm H<sub>2</sub> OH 1-4 atm H<sub>2</sub> Cy<sub>2</sub>F base-free base-free Do (2014) Hanson (2012) ĊH<sub>2</sub>SiMe<sub>2</sub> (c) this work 1 atm H<sub>2</sub> (balloon) + base-free -abnormal NHC (aNHC) anionic amido ligand--strona  $\sigma$ -donoi -stronaer σ-donor C -free basic imino N -enhances hydricity of Ir-H and H<sup>-</sup>delivery to (H)C=O

Figure 1. Current status of aldehyde hydrogenation catalysts toward developing an atmospheric-pressure and base-free version (a,b) and the present approach (c).

facile, atmospheric-pressure and base-free hydrogenation of various routinely used aromatic, heteroaromatic, and aliphatic aldehydes. Furthermore, the catalyst was found to work in a much desirable chemoselective fashion, in  $H_2O$  as well as in aqueous ethanol solvent and also at ambient temperature.

#### RESULTS AND DISCUSSION

The hybrid benzimidazolato *a*NHC-bound Cp\*Ir complex, [Ir]-Cl, was synthesized as shown in Figure 2a. The coordination modes of the ligand in [Ir]-Cl were characterized by <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and electronspray ionization mass spectrometry (ESIMS) and confirmed unambiguously by single-crystal X-ray diffraction studies



Figure 2. Synthesis (a), structure (b), and activity (c) of the catalyst [Ir]-Cl.

(Figure 2b and Supporting Information, SI). Initially, catalytic hydrogenation reaction of benzaldehyde was screened with 0.5 mol % loading of [Ir]-Cl under base-free and hydrogen balloon conditions (H<sub>2</sub> pressure of about 1 bar) in ethanol as solvent at 35 °C (Figure 2c). Delightedly, just after 3 h of reaction time, 98% yield of benzyl alcohol was recorded by gas chromatographic (GC) analysis. Interestingly, the yield was found to be 85% when the reaction was analyzed after 2 h. Other organic solvents such as acetonitrile (CH<sub>3</sub>CN) or dichloromethane  $(CH_2Cl_2)$  resulted in <5% yield of product. On the other hand, in water  $(H_2O)$ , nearly quantitative yield (99%) of benzyl alcohol was obtained after 2 h under identical conditions. An ambient temperature of 27  $\pm$  1 °C was also found to be perfectly suitable for furnishing 99% product yield in H<sub>2</sub>O in just 2 h. Decreasing the reaction time to 1 h led to a decrease in yield to 85%. It is noteworthy that many aromatic aldehydes are not soluble in water. To address this issue, the efficacy of [Ir]-Cl was tested in H<sub>2</sub>O-EtOH (2:1, v/v) mixed solvent under identical conditions. The screening results with benzaldehyde were found to be almost the same in this mixed aqueous ethanol solvent, as well, furnishing 99% yield of benzyl alcohol after 2 h at 27  $\pm$  1 °C. Notably, conversion of benzaldehyde to benzyl alcohol did not take place in the absence of hydrogen gas, thus ruling out the possibility of hydride transfer from EtOH (or  $H_2O$ ) in this catalysis.

With the above-developed highly practical, simple, and mild reaction conditions in hand, the activity of this promising catalyst, [Ir]-Cl, was explored toward hydrogenation of several aromatic, heteroaromatic, and aliphatic aldehydes in H<sub>2</sub>O or  $H_2O$ -EtOH (2:1, v/v) mixed solvent, as shown in Table 1. A similarly high activity was observed with a variety of aromatic aldehydes containing electron-donating (-Me, -OMe) as well as electron-withdrawing (-F, -Cl, -Br) substituents, affording the corresponding benzyl alcohols in 85-99% yield without any side products. Moreover, substituents such as -OH, -NO2, and -CN on the arene backbone could also lead to high yield (93-97%) of the benzyl alcohol products without any adverse interference to or inhibition of the catalytic activity. Intramolecular chemoselectivity was examined with aromatic substrates containing both aldehyde and other carbonyl functionalities like ketone, ester, amide, etc. For these substrates, only the aldehyde group was selectively hydrogenated to alcohol without compromising the yield of the desired alcohols (85-98%). For many catalysts, selectivity between aldehyde and ketone becomes an issue because of similar energies of hydrogenation of aldehydes  $(-\Delta H^{\circ}_{298} =$ 16–20 kcal/mol) and ketones  $(-\Delta H^{\circ}_{298} = 14 \text{ kcal/mol})^{13}$ although steric factors favor the aldehyde kinetically. Moreover, complete intermolecular chemoselectivity toward hydrogenation of aldehyde over other unsaturated organic substrates, such as alkene, alkyne, ketone, and enone, was also achieved with this catalyst in competitive reactions using an equimolar mixture of benzaldehyde and the respective cosubstrates. While heteroaromatic aldehydes were tested, interestingly, no decomposition and/or unselective reaction was observed for the hydrogenation of 2-furaldehyde and 2-thiophenecarboxaldehyde, and high yields of the respective alcohols (94 and 93%, respectively) were obtained. The efficacy of [Ir]-Cl was checked for aliphatic aldehydes also. Gratifyingly, hexanal and heptanal were hydrogenated easily under similar balloon pressure conditions to their alcohol products in 95 and 92% yields, respectively, after 3 h reaction time. Finally, a reaction





was conducted with 5 mmol of benzaldehyde, which furnished an isolated yield of 95% after 4 h.

After establishing the merits of the present catalyst in CAH process, we next sought to gain insights into the mechanistic issues related to the catalytic cycle. At first, a stoichiometric reaction containing [Ir]-Cl (0.002 mmol) and benzaldehyde (0.002 mmol) in a Wilmad low-pressure/vacuum (LPV) NMR tube with occasional charging of H<sub>2</sub> gas from an external balloon source was followed by <sup>1</sup>H NMR spectroscopy in CD<sub>3</sub>OD at ambient temperature (see SI). A hydride signal at -14.6 ppm was observed just after 10 min, along with the signals due to benzyl alcohol (a broad singlet at 4.60 ppm for PhCH<sub>2</sub>OH and a broad triplet at 4.58 ppm for PhCH<sub>2</sub>OD), which was generated in a small amount. After another 10 min, upon the disappearance of the hydride signal, the mixture was again charged with H<sub>2</sub> gas, and the reaction was followed at 10 min intervals. A gradual decrease of the benzaldehyde signals at 10.0 ppm (a singlet) with concomitant increase of the benzyl alcohol signals was observed. No other intermediate was observed in this experiment. To investigate this stoichiometric reaction further, a similar experiment was monitored by variable-temperature <sup>1</sup>H NMR (VT <sup>1</sup>H NMR) spectroscopy from 263 to 313 K in  $CD_3OD$  (Figure 3). Upon increasing the temperature, a gradual decrease of hydride and benzaldehyde peaks along with increase of benzyl alcohol peak was recorded (Figure 3a-c). Interestingly, the intensity of the methyl peaks of the catalyst backbone remained unchanged throughout the experiment (Figure 3d), suggesting the integrity of the catalyst. In the above VT <sup>1</sup>H NMR experiment, the signal due to H<sub>2</sub> gas





Figure 3. VT (263–313 K)  $^{1}$ H NMR spectroscopic monitoring of a stoichiometric reaction of [Ir]-Cl (0.002 mmol) and PhCHO (0.002 mmol) in the presence of H<sub>2</sub> in CD<sub>3</sub>OD: monitoring of PhCHO peak (a); PhCH2OH, PhCH2OD, and H2 peaks (b); Ir-H peak (c); and ligand N-Me and C-Me peaks (d).

at 4.57 ppm was also observed along with the Ir-H peak at -14.6 ppm at the lower temperatures, whereas both peaks disappeared at higher temperatures, suggesting a plausible reversibility of the H<sub>2</sub> cleavage step. To probe this, a similar VT <sup>1</sup>H NMR experiment, but without introducing benzaldehyde into the NMR tube, was monitored from 233 to 313 K in CD<sub>3</sub>OD (Figure 4). Indeed, the appearance of the sharp Ir–H peak along with a broad H<sub>2</sub> peak at lower temperature regime and slow, gradual disappearance of the same with increasing temperature (Figure 4a,b) supported such a hypothesis of reversible cleavage of H<sub>2</sub> by the catalyst, generating a fast equilibrium of the type (Ir-solvento +  $H_2$ )  $\leftrightarrow$  Ir-H species. The broadening effect of the ligand backbone protons (along with Cp\* protons) with increasing temperature was also observed as expected for a fast equilibrium between two Ir species (Figure 4c-e). The plausible N-H peak could not be traced probably due to hydrogen bonding and/or H/D exchange with the solvent  $(CD_3OD)$ . In this regard, previously, Xiao also demonstrated that the N-H peak present within the ligand backbone of similar Ir complexes could not be observed in <sup>1</sup>H NMR spectra because of hydrogen bonding.<sup>14</sup> Attempts to isolate and crystallize the Ir-H species from a reaction of [Ir]-Cl and  $H_2(g)$  under an atmosphere of  $H_2$  were unsuccessful, even at low temperature.

Next, for the present CAH reaction by [Ir]-Cl, initial rate kinetics was carried out to determine the order of each component, and the results suggested a rate law of rate =  $k_{obs}$ [cat][H<sub>2</sub>][aldehyde]. A plausible catalytic cycle was depicted in Figure 5. The initial dissociation of the chloride ligand from [Ir]-Cl followed by reversible cleavage of H<sub>2</sub> was already supported by the VT <sup>1</sup>H NMR experiments. Inhibition of rate by added chloride was also observed (see SI, Figure S8). The actual mechanism of H<sub>2</sub> cleavage needs further extensive

#### **Organometallics**



**Figure 4.** VT (233 K–313 K) <sup>1</sup>H NMR spectroscopic monitoring of a stoichiometric reaction of [**Ir**]-**Cl** (0.002 mmol) and H<sub>2</sub> in CD<sub>3</sub>OD: monitoring of Ir–<u>H</u> peak (a); <u>H</u><sub>2</sub> peak (b); Cp\*-<u>M</u>e peak (c); ligand N-<u>M</u>e and C-<u>M</u>e peaks (d); and ligand aromatic backbone peaks (e).



Figure 5. Plausible mechanistic steps.



Figure 6. KDIE rate plots (a) and Hammett plot (b).

investigation and is the subject of a future study. The firstorder rate dependence on an aldehyde suggested involvement of a bimolecular reaction between the Ir-H species and the aldehyde, which was not coordinated directly to the metal center in its primary coordination sphere (required zero-order dependency and inner-sphere hydride transfer<sup>15</sup>), indicating the possibility of an outer-sphere hydride transfer pathway. To check the nature of hydride and proton transfer to aldehyde to form alcohol, rates of the catalytic hydrogenation of benzaldehyde with 0.5 mol % of [Ir]-Cl were evaluated in water at 27  $\pm$  1 °C under the following four reaction conditions: (i) H<sub>2</sub> balloon, H<sub>2</sub>O solvent; (ii) H<sub>2</sub> balloon, D<sub>2</sub>O solvent; (iii) D<sub>2</sub> balloon, H<sub>2</sub>O solvent; and (iv) D<sub>2</sub> balloon,  $D_2O$  solvent (Figure 6a). The plausible H/D exchange between the acidic NH proton on the catalyst and the solvent (as suggested earlier from <sup>1</sup>H NMR experiments) allowed us to compare the relative reactivity of NH and ND. On the other hand, as discussed previously, <sup>1</sup>H NMR studies suggested no H/D exchange between Ir-H and solvent D under the present reaction conditions (neutral medium) (see SI), although acidcatalyzed Ir-H/D<sub>2</sub>O exchange was reported previously.<sup>16</sup> With this information in hand, the above four experiments afforded the following deuterium kinetic isotope effect (DKIE) values: (i)  $k_{(Ir-H)(N-H)}/k_{(Ir-D)(N-H)} = 2.05 \pm 0.03$ ; (ii)  $k_{(Ir-H)(N-H)}/k_{(Ir-H)(N-D)} = 1.04 \pm 0.05$ ; and (iii)  $k_{(Ir-H)(N-H)}/k_{(Ir-D)(N-D)} = 2.07 \pm 0.05$ . These values of DKIEs suggested the involvement of only Ir-H hydride transfer to the aldehyde C=O group in the rate-determining step. A Hammett plot of relative reactivities of para-substituted benzaldehydes to unsubstituted benzaldehyde resulted in a small reaction constant ( $\rho$ ) value of +1.47 (Figure 6b), indicating development of only small negative charge on the carbonyl carbon of benzaldehyde in the transition state, in line with the outer-sphere hydride delivery mechanism.<sup>17</sup> This is in contrast to the relatively large  $\rho$  value of +4.7 observed for NaBH<sub>4</sub> reduction of benzaldehyde, implying a more anionic nature of the transition state.<sup>18</sup> Of course, more experiments will be required to scrutinize our proposal and to consider other alternatives, especially for the hydride and proton transfer steps. For example, a solvent (H<sub>2</sub>O/EtOH)-assisted NH proton transfer step via hydrogen bonding could not be ruled out at this stage. Nevertheless, we believe that the abnormal Ir-bound imidazol-5-ylidene-based strong  $\sigma$ -donor NHC ligand must have favored the hydride transfer significantly by making the Ir-H species more hydridic. Previously, it was shown that strong electron-donating ligands enhance hydricity of metal hydrides.<sup>19</sup> Additionally, Peris's work on CO<sub>2</sub> hydrogenation also suggested that an Irabnormal NHC catalyst performed better than its Ir-normal NHC counterpart, presumably due to the higher electron  $\frac{1}{12c}$ donor character of the former.<sup>1</sup>

# CONCLUSION

In summary, a highly efficient, chemoselective, aldehyde hydrogenation catalyst was developed for general applicability under atmospheric-pressure, base-free, ambient temperature and aqueous conditions. A variety of substituted aromatic aldehydes as well as heteroaromatic and aliphatic aldehydes were tested successfully with this practical catalyst. This may compliment the existing mild transfer hydrogenation protocol of aldehyde. Applicability toward complex organic molecules and in-depth mechanistic study are ongoing.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00729.

Experimental details and spectra (PDF)

# Accession Codes

CCDC 1854352 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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