Acceptorless dehydrogenative oxidation of secondary alcohols catalysed by Cp\*IrIII-NHC complexes

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**Abstract:** A series of new iridium(III) complexes with carbene ligands comprising different benzyl wingtip groups have been prepared and fully characterized by NMR, high resolution mass spectroscopy, elemental analysis, and X-ray diffraction. All these complexes are found to be active for the acceptorless dehydrogenation of alcohol substrates to the corresponding carbonyl compounds in 2,2,2-trifluoroethanol, with the most active one bearing electron-rich carbene ligand. Using this catalyst, a wide range of secondary alcohols were dehydrogenated to ketones highly efficiently and chemoselectively, affording up to 1660 TON. Mechanistic study suggests that the dehydrogenation is turnover-limited by the step of dihydrogen formation.

Introduction

N-Heterocyclic carbenes (NHCs) have emerged as a versatile class of ligands in organometallic chemistry and catalysis. NHCs often form stable complexes with transition metals irrespective of their oxidation states[1] Additionally, their tunable characters allow for the easy control of the electronic and steric properties at the metal centre. Recently, NHC-bearing transition metal complexes have found applications in the acceptorless dehydrogenative β-alkylation,[2] amidation,[3] N-formylation[4] and imine formation.[5] However, concerning the acceptorless dehydrogenative oxidation of alcohols to afford carbonyl compounds, there are only a few reported examples of NHC-based complexes, which have been reported to catalyse this transformation.[6] In these reports, the acceptorless dehydrogenation (AD) reactions are typically carried out under refluxing conditions in high-boiling solvents such as toluene, and full conversion of the alcohol to the corresponding carbonyl compound requires high catalytic loadings (2-5 mol%), furnishing turnover numbers (TONs) only up to 50.

Oxidation of alcohols to carbonyl compounds is one of the most fundamental reactions in organic synthesis, both in academic laboratories and industrial processes, to access chemicals, fuels and pharmaceuticals. The removal of hydrogen from a hydrogen-rich organic molecule is often a thermodynamically unfavourable process. Thus, conventional dehydrogenation reactions are typically carried out by using stoichiometric or excess amount of metal-based oxidants. Environmentally acceptable oxidants, such as molecular oxygen,[7] hydrogen peroxide,[8] or less desirably acetone,[9] have been used in catalytic oxidation reactions. However, from an atom efficiency and environment viewpoint, the oxidant-free AD is more desirable, where the hydrogen is released as a gas.[10]

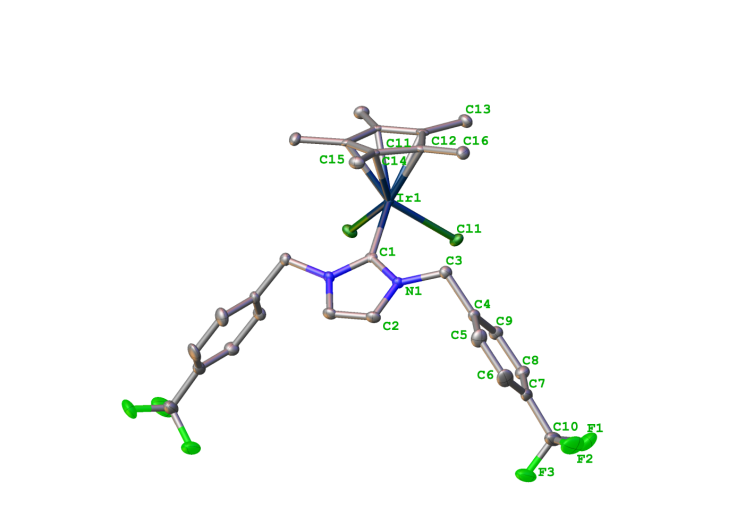
Herein, we report the synthesis and characterization of a range of Cp\*IrIII–NHC complexes with different benzyl substituents and azole skeleton. These complexes are found to be active catalysts for the AD of secondary benzylic and aliphatic alcohols to ketones in refluxing 2,2,2-trifluoroethanol (TFE; bp 78 °C), achieving TONs up to 1660. To the best of our knowledge, this is one of the highest TONs obtained for the AD of secondary alcohols to the corresponding ketones by using an NHC-containing catalyst as well as the first example of Cp\*IrIII–NHC catalysts for these transformations. It is noted, however, that transition metal complexes bearing C–N, NCN and PCP pincer ligands have been reported to be efficient catalysts for the AD of secondary and primary alcohols.[11-15]

Results and Discussion

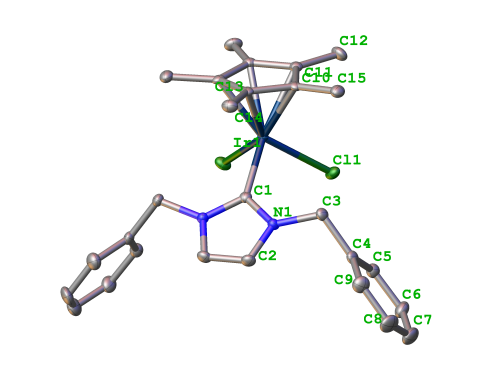
Scheme 1 outlines the route used for the synthesis of [Cp\*Ir(NHC)Cl2] complexes (**2a-f**). The new Cp\*IrIII–NHC complexes (**2a-f**) were prepared by a two-step process involving transmetalation[16] from the in-situ formed Ag–NHC derivatives, in high yields as air and moisture stable yellow solids (Scheme 1). The characterization of Cp\*IrIII–NHC complexes was made by means of NMR, high resolution mass spectroscopy, and elemental analysis. These complexes exhibit 13C chemical shifts at δ = 156.5, 157.5, 158.7, 186.5, 172.0 and 161.9 ppm, respectively, for the characteristic Ir–Ccarbene carbon and are comparable to those of other reported Cp\*IrIII–NHC complexes with an azole skeleton.[9c-e,17] Meanwhile, the characteristic downfield signals for the NCHN+ proton of azolium salts (**1a-f**) disappeared in the 1H NMR spectrum. Finally, the molecular structure of all complexes was determined by single crystal X-ray diffraction analysis, which confirmed the coordination of a single NHC to the iridium centre (Figures 1-6). Single crystals were obtained by diffusion of pentane into concentrated chloroform solution of complexes. Figures 1−6 show the molecular diagrams of the iridium complexes with the atom-numbering scheme and the selected bond lengths (Å) and angles (°). All the complexes exhibit piano-stool type geometry. The Ir–Ccarbene distances (2.065(5)-2.023(6) Å) are in the expected range (Figures 1-6),[9c-e,17] and it appears that the Ir–Ccarbene distance is slightly longer with more electron-rich NHC ligands.



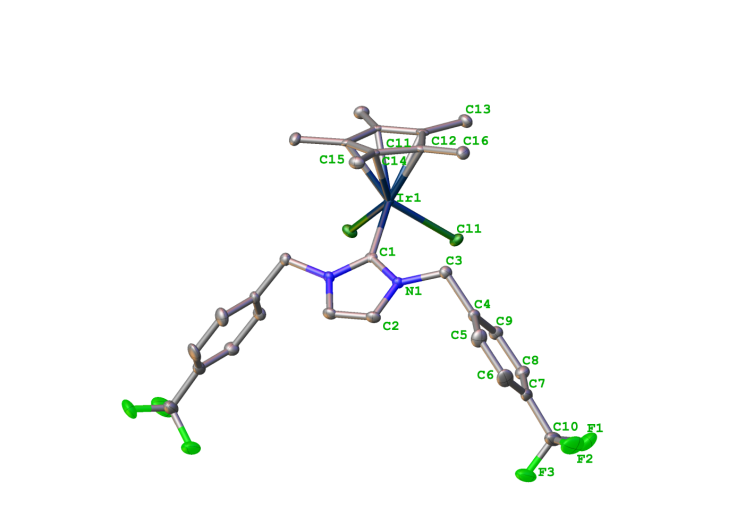
**Scheme 1.** Synthesis of Cp\*IrIII–NHC (**2a-f**) used in this study.



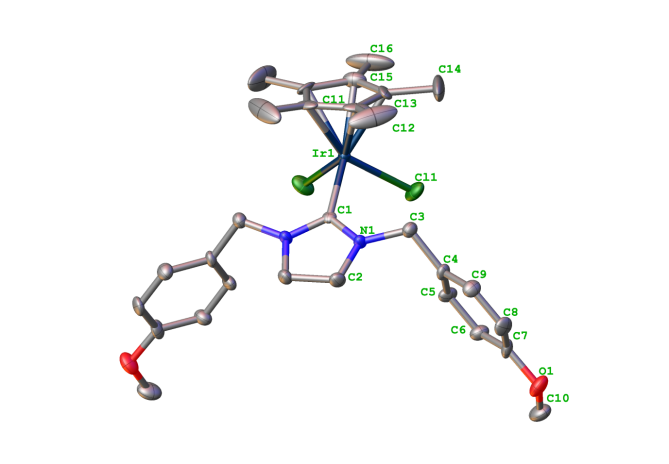
**Figure 1.** Molecular structure of **2a** with hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.059(5), Ir(1)–Cl(1) 2.4399(10), C(1)–N(1) 1.374(4), C(2)–N(1) 1.392(4); C(1)–Ir(1)–Cl(1) 91.38(11), C(1)–N(1)–C(2) 111.2(3).



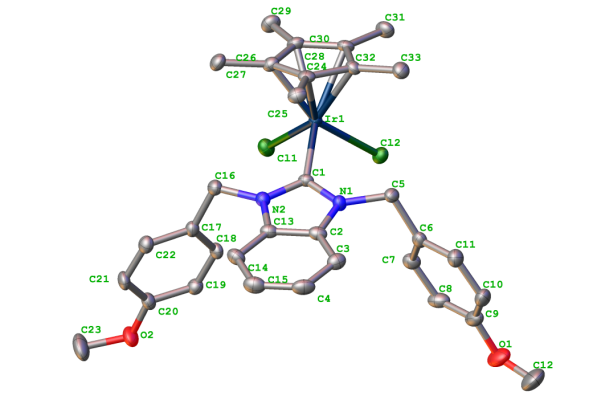
**Figure 2.** Molecular structure of **2b** with hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.055(6), Ir(1)–Cl(1) 2.4300(9), C(1)–N(1) 1.367(6), C(2)–N(1) 1.395(6); C(1)–Ir(1)–Cl(1) 92.09(11), C(1)–N(1)–C(2) 111.6(4).



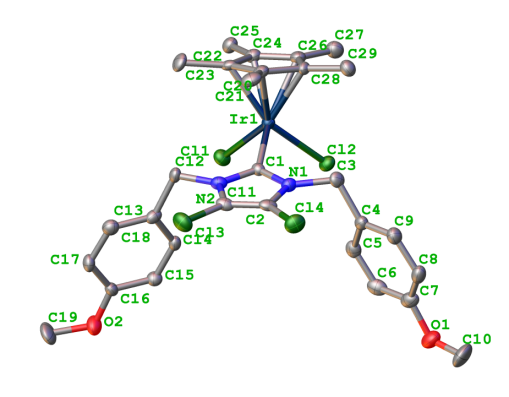
**Figure 3.** Molecular structure of **2c** with hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.051(4), Ir(1)–Cl(1) 2.4383(7), C(1)–N(1) 1.364(3), C(2)–N(1) 1.385(3); C(1)–Ir(1)–Cl(1) 91.36(8), C(1)–N(1)–C(2) 111.5(2).



**Figure 4.** Molecular structure of **2d** with hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.065(6), Ir(1)–Cl(1) 2.4182(12), C(1)–N(1) 1.345(5), C(2)–N(1) 1.468(6); C(1)–Ir(1)–Cl(1) 92.93(12), C(1)–N(1)–C(2) 113.6(4).



**Figure 5.** Molecular structure of **2e** with hydrogen atoms and chloroform solvent removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.029(3), Ir(1)–Cl(2) 2.4054(9), C(1)–N(1) 1.373(4), C(2)–N(1) 1.397(5); C(1)–Ir(1)–Cl(2) 93.23(10), C(1)–N(1)–C(2) 110.8(3).



**Figure 6.** Molecular structure of **2f** with hydrogen atoms and chloroform solvent removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.023(6), Ir(1)–Cl(2) 2.3909(16), C(1)–N(1) 1.378(7), C(2)–N(1) 1.381(8); C(1)–Ir(1)–Cl(2) 93.21(17), C(1)–N(1)–C(2) 110.5(5).

We started the investigation choosing 1-phenylethanol (**3a**) as the model substrate and TFE as the solvent for AD reactions catalysed by **2a**. In cyclometalated Cp\*IrIII catalysed AD of heterocycles, TFE has been shown to be most effective, possibly promoting the dissociation of the chloride from the complex, and hence the coordination of substrate to the metal centre, as well as protonation of intermediate hydride to facilitate dihydrogen formation.[18] The AD of **3a** under various conditions was first examined (Table 1). When a solution of **3a** in TFE was refluxed for 2 h in the presence of **2a** (1.0 mol%), we observed the formation of acetophenone (**4a**) but unexpectedly also a fluorinated ether (**5**), with the ratio of **3a**:**4a**:**5** being 66:20:14 (entry 1). Addition of 5.0 mol% NaBF4 or NH4BF4 increased the ratio of the undesired **5** (entries 2-3). This could result from the formation of acidic HF, which would be expected to catalyse the etherisation of **3a** by TFE.[19] Hence, the reaction was examined by introducing different bases (5.0 mol%) to suppress the etherisation (entries 4-8). Indeed, **5** was not detected when a base was introduced, and delightedly, in the presence of NaOAc, the conversions to **4a** increased to 82%. Complete conversion to **4a** was achieved in the presence of 0.1 mol% **2a** and NaOAc (5.0 mol%) in 20 h (entry 9). However, further decreasing of catalyst loading to 0.05 mol% resulted in a lower conversion (77%) in 20 h (entry 10). The amount of NaOAc was also found to affect the rate of AD (entries 11-13), with the highest conversion to the ketone obtained in the presence of 2.5 mol% NaOAc (83%, TON = 1660, entry 12). Using this lowered amount of base, full conversion was also obtained with 0.1 mol% catalyst loading (entry 14).

Other iridium complexes with different NHC ligands (**2b-e**) were subsequently evaluated under same reaction conditions and complex **2a** with the 1,3-bis(4-methoxylbenzyl)-imidazol-2-ylidene ligand provided the highest conversion (entries 15-19). It is clear that both the electronic effect of the wing type (*p*-OMe, *p*-H and *p*-CF3) and the type of NHC skeleton are important for the AD reaction. Comparing the conversions obtained with the sterically-similar **2a**, **2b** and **2c** indicates that the more electron-rich the iridium centre is, the higher the catalytic activity. In contrast, only 3% conversion was obtained with [IrCl2Cp\*]2 under the same conditions, showing the importance of the NHC ligand in the AD (entry 20). The blank experiment was carried out without catalyst, and no product formation is observed (entry 21). Worth noting is that when carried out in a closed system, the AD only afforded 62% of **4a** (entry 22), indicating that the AD is reversible and is facilitated by the release of H2. In addition, we detected H2 gas evolved during dehydrogenation of **3a** by gas chromatography analysis.[20] However, performing the reaction in open air also resulted in a lower conversion (87%) (entry 23). This could be due to the intermediate iridium hydride being unstable toward O2.[21] The use of TFE is critical for the reaction to proceed, as very little or no reaction was observed with other solvents tested (entries 24 and 25). This is reminiscent of the observations made with iridicycles in the AD of N-heterocycles, and suggests that the formation of H2 may be turnover limiting, which is facilitated by the acidic TFE.[18]

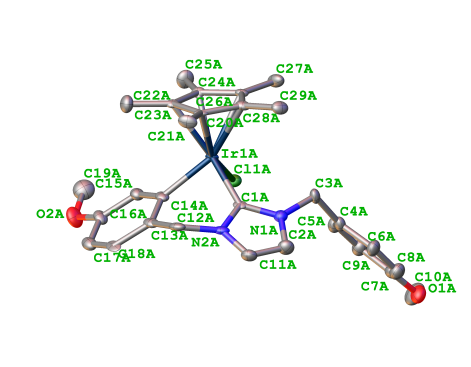
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| **Table 1.** Cp\*IrIII–NHC catalysed AD of 1-phenylethanol in TFE.[a] | | | | | |
| Entry | Cat. (mol% Ir) | Solvent | Additive (%) | Time (h) | **3a**:**4a**:**5** ratio (%)[b] |
| 1 | **2a** (1.0) | TFE | — | 2 | 66:**20**:14 |
| 2 | **2a** (1.0) | TFE | NaBF4 (5.0) | 2 | 10:**10**:80 |
| 3 | **2a** (1.0) | TFE | NH4BF4 (5.0) | 2 | —:**13**:87 |
| 4 | **2a** (1.0) | TFE | NaHCO3 (5.0) | 2 | 59:**41**:— |
| 5 | **2a** (1.0) | TFE | Na2CO3 (5.0) | 2 | 56:**44**:— |
| 6 | **2a** (1.0) | TFE | NaOAc (5.0) | 2 | 18:**82**:— |
| 7 | **2a** (1.0) | TFE | KOAc (5.0) | 2 | 31:**69**:— |
| 8 | **2a** (1.0) | TFE | AgOAc (5.0) | 2 | 40:**60**:— |
| 9 | **2a** (0.1) | TFE | NaOAc (5.0) | 20 | —:**100**:— |
| 10 | **2a** (0.05) | TFE | NaOAc (5.0) | 20 | 23:**77**:— |
| 11 | **2a** (0.05) | TFE | NaOAc (10) | 20 | 55:**45**:— |
| 12 | **2a** (0.05) | TFE | NaOAc (2.5) | 20 | 17:**83**:— |
| 13 | **2a** (0.05) | TFE | NaOAc (1.0) | 20 | 29:**71**:— |
| 14 | **2a** (0.1) | TFE | NaOAc (2.5) | 20 | —:**100**:— |
| 15 | **2b** (0.1) | TFE | NaOAc (2.5) | 20 | 21:**79**:— |
| 16 | **2c** (0.1) | TFE | NaOAc (2.5) | 20 | 69:**31**:— |
| 17 | **2d** (0.1) | TFE | NaOAc (2.5) | 20 | 7:**93**:— |
| 18 | **2e** (0.1) | TFE | NaOAc (2.5) | 20 | 85:**15**:— |
| 19 | **2f** (0.1) | TFE | NaOAc (2.5) | 20 | 54:**46**:— |
| 20 | [IrCl2Cp\*]2 (0.1) | TFE | NaOAc (2.5) | 20 | 97:**3**:— |
| 21 | — | TFE | NaOAc (2.5) | 20 | 100:—:— |
| 22[c] | **2a** (0.1) | TFE | NaOAc (2.5) | 20 | 38:**62**:— |
| 23[d] | **2a** (0.1) | TFE | NaOAc (2.5) | 20 | 13:**87**:— |
| 24 | **2a** (0.1) | Toluene | NaOAc (2.5) | 20 | 98:**2**:— |
| 25 | **2a** (0.1) | EtOH | NaOAc (2.5) | 20 | 100:—:— |
| [a] Reaction conditions: Alcohol (1 mmol), **2** ( 0.05 - 1.0 mol%), additive (1 - 10 mol%), TFE (1 mL), under a flow of N2, under reflux. [b] 1H NMR conversion. [c] Closed system. [d] Open to air. | | | | | |

The ability of Cp\*IrIII–NHC complexes to undergo intramolecular aromatic C–H activation had been reported by Peris and co-workers.[22] They reported that, in most cases, the orthometalation occurs under very mild conditions. In order to investigate the possible effect of orthometalation on the AD reaction, we studied the reaction of complex **2a** with 5 eq. NaOAc in dichloromethane (Scheme 2). It was found that the Cp\*IrIII–NHC complex **2a** was converted to a new complex **2a'**, which could be isolated in 90% yield. Comparison of the 1H NMR spectra of **2a** and **2a'** suggests that complex **2a'** could arise from intramolecular aromatic C–H activation. The protons of the CH2 of benzyl groups display signals at 6.03 (d, *J* = 14.4 Hz, 2H) and 5.10 (d, *J* = 14.4 Hz, 2H) ppm for **2a** and at 5.95 (d, *J* = 14.0 Hz, 1H), 4.99 (d, *J* = 14.0 Hz, 1H), 4.83 (d, *J* = 14.0 Hz, 1H) and 4.62 (d, *J* = 14.0 Hz, 1H) ppm for **2a'**, which are consistent with the results of orthometalation reported in the previous works.[17b,22] The 13C NMR spectrum of compound **2a'** also supports that orthometalation have occurred, showing the additional Ir–CAr signal at 146.1 ppm.[17b,22] Furthermore, crystals of complex **2a'** suitable for X-ray diffraction were obtained by diffusion of pentane into a concentrated chloroform solution, confirming the proposed structure. Figure 7 shows the molecular diagram of **2a'** and the most representative distances and angles. As can be seen, the orthometalation of the phenyl ring of the imidazol-2-ylidene ligand has occurred, thus leading to a chelating coordination of the ligand. The Ir–Ccarbene and Ir–Cphenyl distances are 2.05 and 2.04 Å, respectively, and lie in the expected range.[17b,22]

Complex **2a'** was evaluated as catalyst for the AD reaction of **3a**. The reaction condition used in this experiment was the same as that described in Table 1, entry 14. 80% conversion to **4a** was achieved in the presence of 0.1 mol% **2a'** and NaOAc (2.5 mol%) in 20 h. The results show that catalyst **2a** is more active than its orthometalated complex **2a'** (*cf* Table 1, entry 14), suggest that orthometalation does not play, if any, a significant role in the AD.



**Scheme 2.** Synthesis of orthometalated Cp\*IrIII–NHC complex (**2a'**).



**Figure 7.** Molecular structure of **2a'** with hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1A) 2.050(13), Ir(1)–C(14) 2.040(13), Ir(1)–Cl(1A) 2.428(5); C(1A)–Ir(1)–C(14A) 85.1(5), C(1A)–Ir(1)–Cl(1A) 92.5(4), C(14A)–Ir(1)–Cl(1A) 88.0(4).

To explore the scope of the present catalytic AD system, reactions of a wide range of secondary alcohols were conducted under the optimised conditions (Table 2). Various 1-arylethanols (**3a-e**) bearing electron-donating or –withdrawing substitutions at the para-position of the phenyl ring were effectively converted into the corresponding ketones (**4a-e**) in high yields by using 0.1 mol% of **2a** as catalyst (entries 1-5). Only the *para*-CF3 substituted 1-arylethanol (**3e**) gave a lower conversion and isolated yield (entry 5). Sterically more hindered 1-arylalcohols (**3f-n**) proceeded well to the corresponding ketones, affording 83-98% isolated yields (**4f-n**) (entries 6-14). In addition to the aromatic substrates, aliphatic secondary alcohols (**3o-s**) were also dehydrogenated to give aliphatic ketones (**4o-s**) (entries 15-19). However, some of these substrates require a higher catalyst loading, probably due to subtle steric effects, e.g. entries 6-8, 15, 17 and 18.

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| **Table 2.** Acceptorless dehydrogenation of various secondary alcohols catalyzed by **2a**.[a] | | | | | | |
|  | | | | | | |
| Entry | Product | | S/C | Conv. (%)[b] | Yield (%)[c] | |
| 1 |  | **4a** | 1000 | 100 | 96 | |
| 2 |  | **4b** | 1000 | 100 | 97 | |
| 3 |  | **4c** | 1000 | 100 | 94 | |
| 4 |  | **4d** | 1000 | 98 | 91 | |
| 5 |  | **4e** | 1000 | 84 | 81 | |
| 6 |  | **4f** | 500 | 96 | 93 | |
| 7 |  | **4g** | 500 | 93 | 88 | |
| 8 |  | **4h** | 500 | 100 | 97 | |
| 9 |  | **4i** | 1000 | 100 | 98 | |
| 10 |  | **4j** | 1000 | 86 | 83 | |
| 11 |  | **4k** | 1000 | 100 | 97 | |
| 12 |  | **4l** | 1000 | 100 | 95 | |
| 13 |  | **4m** | 1000 | 100 | 97 | |
| 14 |  | **4n** | 1000 | 92 | 87 | |
| 15 |  | **4o** | 500 | 88 | 85 | |
| 16 |  | **4p** | 1000 | 96[d] | 95[e] | |
| 17 |  | **4q** | 200 | 83[d] | 82[e] | |
| 18 |  | **4r** | 1000 | 96[d] | 96[e] | |
| 19 |  | **4s** | 200 | 95[d] | 92[e] | |
| [a] Reaction conditions: Alcohol (1 mmol), **2a** ( 0.1-0.5 mol%), NaOAc (2.5 mol%), TFE (1 mL), under a flow of N2, under reflux, 20 h. [b] 1H NMR conversion. [c] Isolated yield. [d] GC conversion.[e] GC yield, decane or nonane as internal standard. | | | | | |

Next, we examined the dehydrogenation of primary alcohols. However, the AD of benzyl alcohol (**6**) (1.0 mmol) in the presence of 1.0 mol% of **2a** did not proceed well, with only 18% conversion to benzaldehyde (**7**) observed, based on the NMR analysis (Eq. 1). Considering that the AD reactions may be reversible and aldehydes are easier to reduce than ketones, the low conversion to **7** could be a result of the product being reduced under the AD conditions. In fact, AD can be seen as a transfer hydrogenation reaction where the removed hydrogen is not captured by a sacrificial acceptor but released from the reaction.[10f] To show the possibility of **2a** catalysing the reverse reaction of primary alcohol dehydrogenation, we examined its activity toward the hydrogenation of benzaldehyde. We found that **2a** (0.1 mol%) indeed catalysed quantitative hydrogenation of benzaldehyde (**7**) (1.0 mmol) to benzyl alcohol (**6**) under 1 atm H2 pressure (balloon) in TFE at 40 °C after 4 h (Eq. 1). Further evidence on the AD of **6** being reversible is found in the reduction of **7** when **3a** was dehydrogenated (Eq. 2). Thus, when a mixture of **3a** (1.0 mmol) and **7** (1.0 mmol) was subjected to the AD **2a** (0.25 mmol%, relative to alcohol), **3a** was fully converted into **4a**, while **7** was reduced to **6** in 96% conversion, “borrowing” the hydrogen from **3a** (Eq. 2).[23] These results also show that **2a** is an active catalyst for both hydrogenation and transfer hydrogenation reactions, and indicate that the low efficiency in the AD of **6** is due to the easier reduction of the product.

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The reversibility of primary alcohols can be exploited for chemoselective AD reactions. An example is shown in the AD of **3a** (1.0 mmol) and **6** (1.0 mmol) with catalyst **2a** (2.5×10-3 mmol), which resulted in full conversion of **3a** to **4a** but only 3% conversion of **6** to **7** after 20 h (Eq. 3), demonstrating the excellent selectivity of the catalysts for secondary benzylic alcohols over primary ones.

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Furthermore, we investigated the AD of diols, which can potentially release two equivalents of H2 to form stable lactones.[11c,12b,15c,24] Thus, in the presence of 1.0 mol% complex **2a** and 5.0 mol% NaOAc, 1,2-dibenzenedimethanol (**8a**) and 1,5-pentanediol (**8b**) were converted into the corresponding lactones phthalide (**9a**) and δ-valerolactone (**9b**) in 95 and 92% isolated yield, respectively (Eq. 4). These results show that it is possible to dehydrogenate molecules bearing primary alcohol units if there is a functional group to intercept the newly formed aldehyde.

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To gain insights into the rate-limiting step of the present Cp\*IrIII–NHC catalysed AD reaction kinetic isotope effect (KIE) was studied. Figure 8 shows the conversion-time profiles obtained with 1-phenylethanol and the 1-deuterated analogue. Clearly, deuteration has little effect on the kinetics of the AD, suggesting that C-H cleavage is not involved in the rate-limiting step of the present AD reaction. Revealing that the AD rates do not vary with time (at <50% conversion) the linearity of the profiles is also supportive of this view, i.e. the alcohol does not appear in the rate-limiting step.



**Figure 8.** AD reactions aimed for KIE study. Deuterated or non-deuterated 1-phenyl ethanol (1 mmol), **2a** (0.1 mol%), NaOAc (2.5 mol%), TFE (1 mL), under a flow of N2, under reflux.

To gain further insight into the reaction mechanism, the AD of 1-phenylethanol with **2a** (20 mol%) in TFE-d3 was monitored by VT NMR (Figure 9). No product formation observed after 30 min at room temperature. In contrast, a new peak rapidly appeared in the hydridic region of the 1H NMR spectrum ( ̶ 17.4 ppm) upon warming the reaction mixture to 50 °C along with formation of acetophenone, suggesting that the catalytically active species is related to this iridium hydride. The hydride remained unaltered during the VT experiment along with increasing conversion of 1-phenylethanol to acetophenone. These observations indicate that the AD is rate-limited by the step of dihydrogen formation. Rate-limiting hydrogen formation has been noted in the iridicycle-catalysed AD reactions, which was considered to be facilitated by TFE through protonation of the intermediate hydride.[18,25]

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**Figure 9.** 1H NMR hydride region of in situ AD reaction carried out in sealed NMR tube: A solution of 1-phenylethanol (0.5 mmol), **2a** (20 mol%) and NaOAc (2.5 mol%) mixed in TFE-d3 at RT and 1H NMR spectra recorded after 30 min. The appearance of a new peak at -17.4 ppm was observed after increasing the temperature to 50 °C.

We also attempted to look into if there was a structure-activity relationship in the AD reaction. Non-competitive dehydrogenation of a series of para-substituted secondary benzyl alcohols was thus carried out. Using the initial rate for each AD reaction, a Hammett plot of log(*kX*/*kH*) (*krel*) against the substituent constant σp could be constructed. As can be seen from Figure 10, there is a fairly good correlation between log(*kX*/*kH*) and the σp parameters, with a negative slope (*ρ* = ̶ 1.03, R2= 0.99). Since the substrate is not involved in the turnover limiting step, this negative correlation may be indicative of a pre-equilibrium involving the necessary substitution of the coordinated chloride anion of **2a** by the alcohol, with the substitution favoured by more nucleophilic alcohols.



**Figure 10.** Hammett plots for catalyst **2a** obtained from non-competitive experiments for the AD of para-substituted 1-phenylethanol. Alcohol (1 mmol), **2a** (0.1 mol%), NaOAc (2.5 mol%), TFE (1 mL), under a flow of N2, under reflux.

On the basis of the observations above, a possible mechanism for the AD reaction is suggested. As outlined in Scheme 3, the AD starts with displacement of the chloride of **2a**, which affords an iridium-alkoxide species. This is followed by *β*-hydrogen elimination to give rise to an iridium-hydride intermediate, protonation of which completes the catalytic cycle. The turnover rate is determined by the step of protonation, with the hydride being the catalyst resting state. All the steps appear reversible. An electron-rich alcohol and the introduction of a catalytic base would both be expected to shift the equilibrium of the substitution reaction towards the right side, leading to a higher concentration of the iridium-alkoxide species and hence a faster AD rate.



**Scheme 3.** Suggested mechanism for the **2a** catalysed AD of secondary alcohols.

Conclusions

In summary, a series of Cp\*IrIII–NHC complexes were prepared as catalyst precursors for AD of secondary alcohols to the corresponding carbonyl compounds by using TFE as solvent. Variation in the NHC ligand framework allowed trends to be established. Electron donating methoxy group on the *para* position of N-bound benzyl group and imidazole as a NHC skeleton induce higher activity in this transformation. Using the most active catalyst **2a**, a variety of secondary alcohols were converted to aldehydes and ketones accompanied by the release of hydrogen gas. Mechanistic observations point to the AD reaction being rate-limited by the step of H2 formation. To the best of our knowledge, the TON achieved is the highest in the acceptorless dehydrogenative oxidation of secondary alcohols with metal-NHC catalysts. Additionally, the catalyst shows excellent selectivity for oxidation of secondary benzylic alcohols over primary ones.

Experimental Section

**General.** Experiments involving air or moisture sensitive reagents were performed under an atmosphere of purified N2 using standard Schlenck techniques. Unless otherwise specified, all reagents were obtained commercially and used without further purification. NMR spectra were recorded on a Brucker 400 MHz NMR spectrometer and reported in units of parts per million (ppm) relative to tetramethyl silane (δ 0 ppm) or CDCl3 (for 1H and δ 77.0 ppm for 13C NMR). Melting points were measured on an X-5 Melting Point Apparatus (Beijing Tech Instrument) without correction. Elemental analysis was carried out at the Microanalysis Centre of University of Liverpool. Mass spectra were obtained at the Analytical Services of the Chemistry Department, University of Liverpool and EPSRC National Mass Spectrometry Service Centre, College of Medicine, Swansea University. Gas chromatography (GC) analysis was performed on an Agilent 6890N gas chromatograph with a HP-5 Agilent 19091J-413 column.

**Synthesis of Cp\*IrIII–NHC complexes.** Under an argon atmosphere, a mixture of azolium salt (**1a-f**) (0.5 mmol) and Ag2O (116 mg, 0.5 mmol) was suspended in degassed and dry dichloromethane (5 mL) and stirred at ambient temperature for 1 h shielded from light. [IrCp\*Cl2]2 (198 mg, 0.25 mmol) was then added to the suspension and the reaction mixture was stirred at ambient temperature for an additional 4 h. The resulting suspension was filtered over Celite®. The remaining solid was washed with dichloromethane (2×5 mL) and the solvent of the filtrate was evaporated. The residue was purified via column chromatography on silica gel with dichloromethane:ethyl acetate (9:1) as eluent, affording a yellow powder.

**2a.** Yield: 91%, 322 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.33 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 6.87 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 6.62 (s, 2H, NC*H*=C*H*N), 6.03 (d, *J* = 14.4 Hz, 2H, NC*H*2), 5.10 (d, *J* = 14.4 Hz, 2H, NC*H*2), 3.80 (s, 6H, OC*H*3), 1.65 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 159.4 (Ar-*C*), 156.5 (Ir-*C*), 130.1 (Ar-*C*), 128.6 (Ar-*C*), 121.5 (N*C*H=*C*HN), 114.1 (Ar-*C*), 89.0 (*C*5(CH3)5), 54.1 (O*C*H3), 54.1 (N*C*H2), 9.3 (C5(*C*H3)5). Anal. Calc. for C29H35Cl2IrN2O2 (%): C, 49.29; H, 4.99: N, 3.96. Found: C, 49.36; H, 4.90: N, 4.01. HRMS (ESI+): calcd. *m/z* for C29H35ClIrN2O2 [*M*-Cl]+: 671.2004; found: 671.2005.

**2b.** Yield: 87%, 281 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.36-7.32 (m,10H, Ar-*H*), 6.67 (s, 2H, NC*H*=C*H*N), 6.01 (d, *J* = 14.8 Hz, 2H, NC*H*2), 5.34 (d, *J* = 14.8 Hz, 2H, NC*H*2), 1.63 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 157.5 (Ir-*C*), 136.8 (Ar-*C*), 128.8 (Ar-*C*), 128.4 (Ar-*C*), 128.0 (Ar-*C*), 121.9 (N*C*H=*C*HN), 89.1 (*C*5(CH3)5), 54.7 (N*C*H2), 9.3 (C5(*C*H3)5). Anal. Calc. for C27H31Cl2IrN2 (%): C, 50.15; H, 4.83: N, 4.33. Found: C, 49.99; H, 4.87: N, 4.31. HRMS (ESI+): calcd. *m/z* for C27H30IrN2 [*M*-H-2Cl]+: 575.2034; found: 575.2034.

**2c.** Yield: 86%, 335 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.62 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 7.55 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 6.68 (s, 2H, NC*H*=C*H*N), 6.30 (d, *J* = 14.8 Hz, 2H, NC*H*2), 5.22 (d, *J* = 14.8 Hz, 2H, NC*H*2), 1.64 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 158.7 (Ir-*C*), 140.5 (Ar-*C*), 130.5 (q, *J*C-F = 33.0 Hz ), 128.9 (Ar-*C*), 125.7 (q, *J*C-F = 4.0 Hz ), 124.7 (q, *J*C-F = 270.0 Hz ), 122.2 (N*C*H=*C*HN), 89.3 (*C*5(CH3)5), 54.2 (N*C*H2), 9.3 (C5(*C*H3)5). 19F NMR (376 MHz, CDCl3) δ (ppm): -62.6. Anal. Calc. for C29H29Cl2F6IrN2 (%): C, 44.50; H, 3.73: N, 3.58. Found: C, 44.43; H, 3.75: N, 3.55. HRMS (ESI+): calcd. *m/z* for C29H29ClF6IrN2 [*M*-Cl]+: 747.1545; found: 747.1535.

**2d.** Yield: 90%, 318 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.41 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 6.85 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 5.61 (d, *J* = 14.0 Hz, 2H, NC*H*2), 4.38 (d, *J* = 14.0 Hz, 2H, NC*H*2), 3.79 (s, 6H, OC*H*3), 3.43 (t, *J* = 9.6 Hz, 2H, NC*H*2CH2N), 3.28 (t, *J* = 9.6 Hz, 2H, NCH2C*H*2N), 1.66 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 186.5 (Ir-*C*), 159.1 (Ar-*C*), 129.8 (Ar-*C*), 128.6 (Ar-*C*), 113.8 (Ar-*C*), 89.4 (*C*5(CH3)5), 55.3 (O*C*H3), 55.1 (N*C*H2), 48.6 (N*C*H2*C*H2N), 9.3 (C5(*C*H3)5). Anal. Calc. for C29H37Cl2IrN2O2 (%): C, 49.15; H, 5.26: N, 3.95. Found: C, 49.13; H, 5.31: N, 3.99. HRMS (ESI+): calcd. *m/z* for C29H37ClIrN2O2 [*M*-Cl]+: 673.2166; found: 673.2158.

**2e.** Yield: 81%, 305 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.07 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 6.99 (t, *J* = 6.0 Hz, 2H, Ar-*H*), 6.92 (dd, *J* = 6.0 and 3.2 Hz, 2H, Ar-*H*), 6.85 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 6.18 (d, *J* = 16.4 Hz, 2H, NC*H*2), 5.90 (d, *J* = 16.4 Hz, 2H, NC*H*2), 3.79 (s, 6H, OC*H*3), 1.55 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 172.0 (Ir-*C*), 158.8 (Ar-*C*), 135.3 (Ar-*C*), 128.8 (Ar-*C*), 127.6 (Ar-*C*), 122.9 (Ar-*C*), 114.1 (Ar-*C*), 112.5 (Ar-*C*), 90.0 (*C*5(CH3)5), 55.3 (O*C*H3), 53.0 (N*C*H2), 9.2 (C5(*C*H3)5). Anal. Calc. for C33H37Cl2IrN2O2 (%): C, 52.37; H, 4.93: N, 3.70. Found: C, 52.29; H, 4.88: N, 3.72. HRMS (ESI+): calcd. *m/z* for C33H35ClIrN2O2 [*M*-2H-Cl]+: 719.2009; found: 719.2005.

**2f.** Yield: 75%, 283 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 6.95 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 6.91 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 6.32 (d, *J* = 16.8 Hz, 2H, NC*H*2), 5.43 (d, *J* = 16.8 Hz, 2H, NC*H*2), 3.83 (s, 6H, OC*H*3), 1.43 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 161.9 (Ir-*C*), 158.9 (Ar-*C*), 128.8 (Ar-*C*), 126.5 (Ar-*C*), 118.9 (Ar-*C*), 114.2 (Ar-*C*), 89.8 (*C*5(CH3)5), 55.3 (O*C*H3), 53.7 (N*C*H2), 9.1 (C5(*C*H3)5). Anal. Calc. for C29H33Cl4IrN2O2 (%): C, 44.91; H, 4.29: N, 3.61. Found: C, 44.98; H, 4.32: N, 3.57. HRMS (ESI+): calcd. *m/z* for C29H35Cl2IrN3O2 [*M*-2H-2Cl+NH4]+: 720.1725; found: 720.1716.

**Synthesis of 2a'.** A mixture of 2a (141 mg, 0.2 mmol) and NaOAc (82 mg, 1.0 mmol) was suspended in dichloromethane (5 mL) and stirred at ambient temperature for 12 h, and then the solvent was evaporated. The residue was purified via column chromatography affording a yellow powder. Yield: 90%, 120 mg. 1H NMR (400 MHz, CDCl3) δ (ppm): 7.36 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.27 (d, *J* = 2.8 Hz, 1H, Ar-*H*), 6.87-6.82 (m, 4H, Ar-*H* and NC*H*=C*H*N), 6.59 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 6.40 (dd, *J* = 8.0 and 2.4 Hz, 1H, Ar-*H*), 5.95 (d, *J* = 14.0 Hz, 1H, NC*H*2), 4.99 (d, *J* = 14.0 Hz, 1H, NC*H*2), 4.83 (d, *J* = 14.0 Hz, 1H, NC*H*2), 4.62 (d, *J* = 14.0 Hz, 1H, NC*H*2), 3.80 (s, 3H, OC*H*3), 3.78 (s, 3H, OC*H*3), 1.69 (s, 15H, C5(C*H*3)5). 13C NMR (100 MHz, CDCl3) δ (ppm): 159.4 (Ar-*C*), 158.3 (Ar-*C*), 156.7 (Ir-*Ccarbene*), 146.1 (Ir-*CAr*), 131.7 (Ar-*C*), 130.6 (Ar-*C*), 128.6 (Ar-*C*), 125.9 (Ar-*C*), 124.6 (Ar-*C*), 120.2 (N*C*H=CHN), 120.2 (NCH=*C*HN), 114.0 (Ar-*C*), 108.0 (Ar-*C*), 90.3 (*C*5(CH3)5), 56.7 (O*C*H3), 55.3 (N*C*H2), 55.2 (O*C*H3), 52.8 (N*C*H2), 9.6 (C5(*C*H3)5). Anal. Calc. for C29H34ClIrN2O2 (%): C, 51.97; H, 5.11: N, 4.18. Found: C, 52.04; H, 5.07: N, 4.21. HRMS (ESI+): calcd. *m/z* for C29H33ClIrN2O2 [*M*-H]+: 669.1847; found: 669.1827.

**General procedure for the acceptorless dehydrogenative oxidation of 1-phenylethanol.** 1-Phenylethanol (1.0 mmol), additive (1.0-10 mol%) and catalyst (0.05-1.0 mol%) were dissolved in TFE (1 mL) in a carousel reaction tube. The tube was then degassed and reaction mixture was refluxed under N2 for 2-20 h. It was then cooled to room temperature and the solvent evaporated under reduced pressure. Conversions were determined by 1H NMR spectroscopy.

**X-ray crystallography:** Crystallographic data and refinement are provided in Table S1-S7 in the Supporting Information. CCDC 1424271, 1470605-1470610 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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**Keywords:** Acceptorless dehydrogenation • N-heterocyclic carbene • iridium • alcohol oxidation

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