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Synthesis and complexes of imidazolinylidene-based CCC pincer ligands

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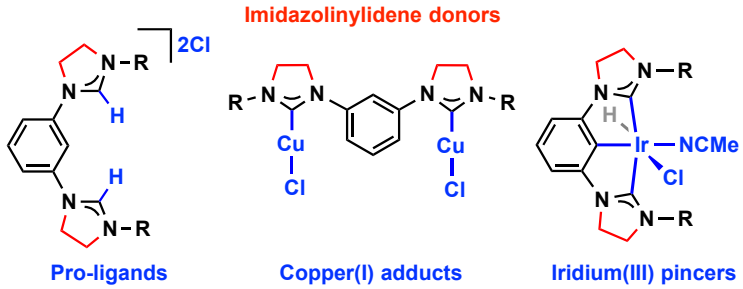
TOC graphic



Abstract

A series of imidazolinium-based CCC pro-ligands featuring *N*-Mes, Dipp, ^{i}Pr and ^{t}Bu substituents (**1**·2HCl) have been prepared. The corresponding free carbenes are readily generated through deprotonation by strong bases and, in addition to being characterised *in situ* by ^{1}H and ^{13}C NMR spectroscopy, were trapped through reaction with CuCl. Iridium pincer compounds of the *N*-Mes (**5a**) and Dipp (**5b**) substituted ligands, *viz.* [Ir(**1**)HCl(NCMe)], were obtained through reaction between the respective pro-ligand, $[Ir(COE)_2Cl]_2$, and Et_3N in acetonitrile at ca. 80^{o}C. Under similar conditions the *N*-^{i}Pr and ^{t}Bu analogues were not formed. The new iridium pincer complexes **5a** and **5b** were fully characterised in solution, by NMR spectroscopy and ESI-MS, and in the solid-state by X-ray diffraction. Under relatively forcing reaction conditions neither **5a** nor **5b**, in combination with KO^{t}Bu, show any significant catalytic activity for the transfer dehydrogenation of cyclooctane to cyclooctene using *tert*-butylethylene (ca. 2 TONs, 150^{o}C, 24 h).

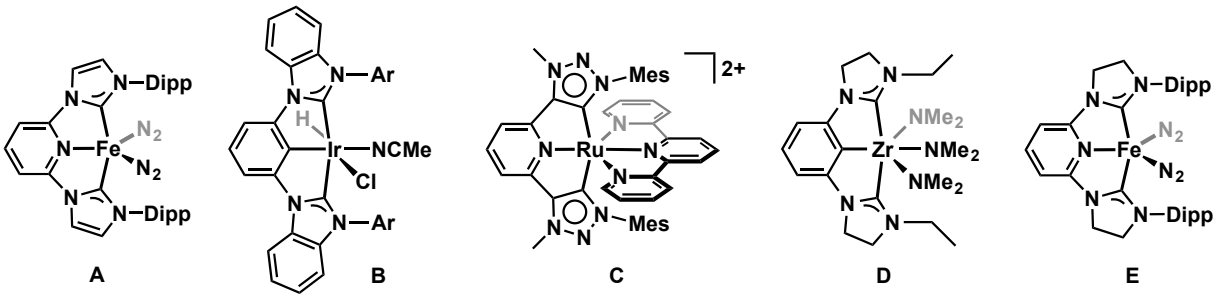
Keywords

NHC-based pincer; Imidazolinylidene ligands; NHC ligands; Iridium pincer

Introduction

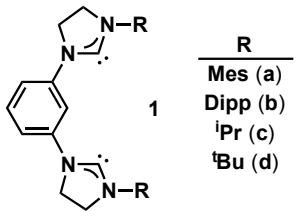
The use of N-heterocyclic carbenes (NHCs) as ancillary ligands is ubiquitous in modern organometallic chemistry and has enabled the development of new generations of homogeneous transition-metal-based catalysts.[1] The structural versatility of these privileged ligands has proven to be a major contributing factor in their widespread application and has enabled access not only a plethora of monodenate ligands, but also an extensive range of polydentate variants.[2] In particular, "pincer" architectures featuring terminal NHC donors are becoming a prominent design motif, combining the strong σ-donor characteristics of NHCs with the favorable thermal stability and reaction control possible with a mer-tridentate geometry.[3,4] For instance, first row transition metal adducts of bulky CNC ligands (e.g. **A**) are highly active catalysts for the hydrogenation of sterically hindered alkenes, while Ir(CCC) complexes of the type **B** have been shown to be effective catalysts for the thermally promoted *acceptor-less* dehydrogenation of alkanes (Chart 1).[5,6] Increasingly NHC-based pincer complexes are also becoming recognised for their useful photophysical properties: ruthenium-based **C**, for example, is notable for microsecond ^{3}MLCT excited-state lifetimes, three orders of magnitude higher than $[Ru(terpyridine)_2]^{2+}$.[7,8]

Chart 1: Selected examples of NHC-based pincer complexes



As we noted in our recent commentary, the emergence of terminal-NHC-based pincer compounds has largely involved systems bearing imidazolylidene donors, while saturated imidazolinylidene variants have curiously received little attention.[4] Such an observation is rather surprising given the successful application of mono-dentate imidazolinylidene ligands in catalysis; epitomised by their wide-spread use in olefin metathesis reactions, where they significantly out perform their unsaturated counterparts.[9] Indeed, in late 2015 when we compiled our review the only known imidazolinylidene-based example to our knowledge was zirconium adduct **D**.[10] In the intervening time, Chirik and co-workers have prepared iron-based **E** and demonstrated its ability to selectivity catalyse trituration reactions of C(sp^2)-H bonds with high efficiently, highlighting the potential versatility of such NHC-pincers.[11] As part of our work developing the organometallic chemistry of NHC-based pincer ligands, which has involved investigation of macrocyclic variants, backbone geometry, atropisomerism and transmetallation methodology,[12] in this report we describe the preparation and preliminary coordination chemistry of imidazolinylidene-based CCC pincer ligands **1** (Chart 2).

Chart 2: Target imidazolinylidene-based pincer ligands **1**.

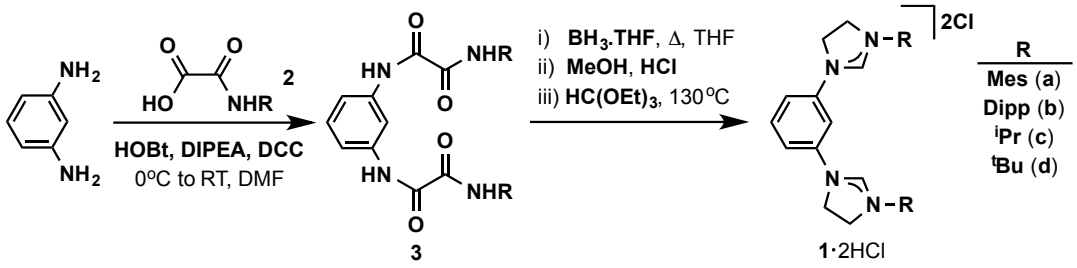


Results and discussion

Pro-ligand 1·2HCl synthesis

A variety of procedures have been reported for the preparation of imidazolinylidene ligand precursors.[13] Similar to that employed for the pro-ligand associated with **D**,[10] we chose a synthetic route involving amide coupling reactions between 1,3-diaminobenzene and aminooxoacetic acids **2** (R = Mes, **a**; Dipp, **b**; ^{i}Pr, **c**; ^{t}Bu, **d**; Scheme 1). In this way, bis-amides **3** were obtained in satisfactorily yields (52, 48, 57, and 53%, respectively) and subsequently reduced, protonated and cyclised in a three step, one pot procedure to afford the desired imidazolinium chloride pro-ligands **1**·2HCl (52, 69, 49, 52% from **2**, respectively, ca. 30% overall from 1,3-diaminobenzene). Formation of these new salts was evidenced by characteristically high frequency NCHN and NCHN resonances at δ 11.02, 11.36, 10.81, 10.53 and δ 158.5, 158.3, 155.8, 155.5 in the ^{1}H and ^{13}C{^{1}H} NMR spectra (CD_3CN) for [**1a–d**]·2HCl, respectively, and strong $[M]^{2+}Cl^{-}$ signals present in high resolution ESI-MS spectra. The central aryl proton of the pro-ligand backbones gives rise to ^{1}H signals at ca. δ 9.2 ($^{4}J_{HH}$ coupling of ca. 2 Hz), with the associated ^{13}C signals at ca. δ 109; both are useful spectroscopic indicators for subsequent investigation of the coordination chemistry of **1**·2HCl.

Scheme 1: Preparation of pro-ligands **1**·2HCl

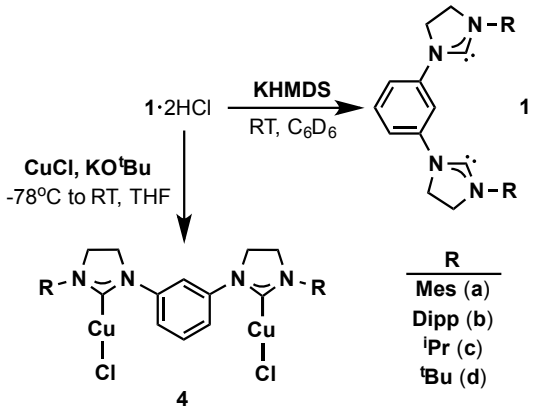


Characterisation and copper complexes of 1

Free carbenes **1** are readily generated by deprotonation of **1**·2HCl with strong bases. In particular, the formation of these reactive adducts was followed *in situ* by NMR spectroscopy for the reaction between **1**·2HCl and KHMDS in C_6D_6 at room temperature (Scheme 2). In each case the C_{2v} symmetry of the pro-ligand was retained and the deprotonation was confirmed by the disappearance of the high frequency NCHN resonances in the ^{1}H NMR spectra and appearance of very high frequency carbenic resonances at δ 240.3, 241.9, 234.3 and 237.4 for **1a–d**, respectively; ca. 80 ppm downfield from the corresponding signals of the pro-ligands. These ^{13}C chemical shift values are fully consistent with resonances reported for mono-dentate imidazolinylidene ligands, which are characteristically ca. 25 ppm higher than their imidazolylidene

congeners.[14] The closest well-defined NHC-based pincer analogues to our knowledge are unsaturated CNC analogues 2,6-(3-arylimidazol-2-ylidene)pyridine (aryl = Mes, Dipp) that exhibit carbenic resonances at δ 220, C_6D_6.[15] The central aryl proton ^{1}H and associated ^{13}C signals of **1** are located at ca. δ 8.3 and ca. δ 106, respectively.

Scheme 2: Generation of free NHC **1** and preparation of copper(I) complexes **4**



The *N*-aryl and *N*-^{i}Pr substituted pincer ligands **1a–c**, generated in C_6D_6 as described above, decompose slowly on standing in solution with approximate half lives of 1, 9 and 3 h, respectively. No significant change was observed in the ^{1}H NMR spectrum of **1d** after 24 h, inferring significantly greater solution stability. Such differences in stability cannot be rationalised by steric arguments alone; electronics as marked out from the ^{13}C NMR data, appear to play a significant role also, i.e. stability: aryl < alkyl.

Alongside *in situ* generation, formation of the free NHC ligands **1** was also probed through formation of copper adducts, prepared via low temperature deprotonation using KO^{t}Bu in the presence of a slight excess of cuprous chloride (ca. 3 eqv / **1**). In this way, dinucelar Cu(I) adducts of **1a** (64% yield), **1c** (65% yield) and **1d** (45% yield) were isolated (Scheme 2). Although formation of a copper adduct of the Dipp variant **1b** was evident from ^{1}H NMR and ESI-MS data, under a range of similar conditions an intractable mixture including **4b** as a minor component resulted. Formation of **4a**, **4c** and **4d** was readily evidenced by the disappearance of the high frequency NCHN resonances of the pro-ligand in the ^{1}H NMR spectra, appearance of high frequency carbenic resonances at ca. δ 200 (CD_2Cl_2), and strong $[M–Cl]^+$ signals in high resolution ESI-MS spectra. The central aryl proton ^{1}H and associated ^{13}C signals of **4a**, **4c** and **4d** are located at ca. δ 8.3 and ca. δ 111, respectively. A closely related dinuclear copper chloride adduct of unsaturated NHC-based pincer ligand 2,6-(3-butyllimidazol-2-ylidene)benzene (**F**) has been reported and is characterised by a carbene resonance at δ 176.6 (CD_2Cl_2), ca. 25 ppm lower than those of isolated **4** – a difference expected based on the nature of the NHC donors (*vide supra*). The NMR data for the central aryl CH moiety of the pincer backbone of **F** and isolated **4** show good agreement (δ_{1H} 8.17, δ_{13C} 119.6 for **F**).[16]

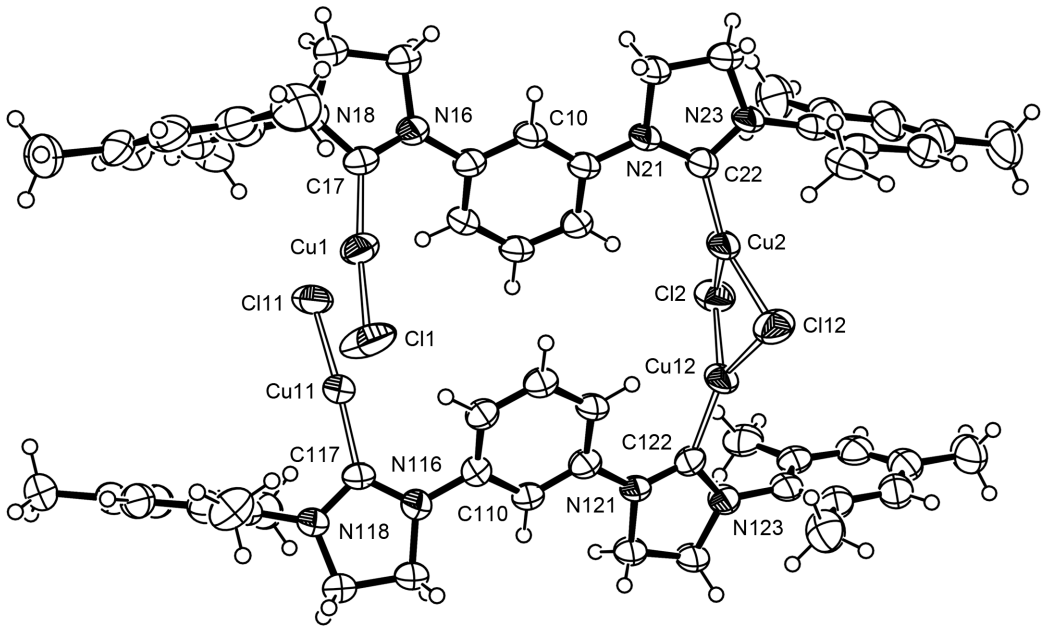


Figure 1: Solid-state structure of **4a**. Thermal ellipsoids drawn at the 50% probability level; solvent molecules omitted for clarity. Selected bond lengths (Å) and angles (º): Cu1···Cu11, 3.789(2); Cu1-Cl1, 2.116(3), Cu1···Cl11, 3.483(4); Cu1-C17, 1.908(8); Cu11···Cl1, 3.635(4); Cu11-Cl11, 2.103(3); Cu11-C117, 1.895(7); Cu2···Cu12, 2.8715(16); Cu2-Cl2, 2.274(3); Cu2-Cl12, 2.331(3); Cu2-C22, 1.891(8); Cu12-Cl2, 2.339(3); Cu12-Cl12, 2.270(3); Cu12-C122, 1.903(8); Cnt(C10)···Cnt(C110), 5.140(12); C17-Cu1-Cl1, 168.7(3); C17-Cu1···Cl11, 89.1(3); C117-Cu11···Cl1, 90.8(3); C117-Cu11-Cl11, 171.4(3); C22-Cu2-Cl2, 136.6(3); C22-Cu2-Cl12, 125.6(3); C122-Cu12-Cl2, 125.5(3); C122-Cu12-Cl12, 136.8(3); Cu1-Cl1···Cu11, 77.48(11); Cu1···Cl11-Cu11, 81.39(10); Cu2-Cl2-Cu12, 76.98(9); Cu2-Cl12-Cu12, 77.21(10).

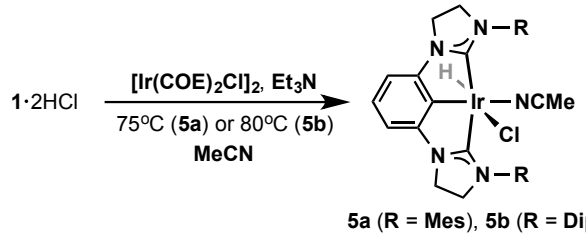
The structure of **4a** was further interrogated using single crystal X-ray diffraction. The resulting structure is depicted in Figure 1, and illustrates the formation of a chloro-bridged assembly of two molecules of **4a** mediated through one of the coordinated CuCl units. The bridging interaction is evidenced by Cu-Cl distances of 2.274(3)/2.270(3) Å and 2.331(3)/2.339(3) Å, with the longer distances associated with more acute C_{NCN}-Cu-Cl bond angles (ca. 126 vs 137º), and adoption of a weak cuprophilic interaction of 2.8715(16) Å.[17] The non-bridging NHC-CuCl moieties display more regular geometries, with shorter Cu-Cl distances of 2.116(3)/2.103(3) Å and distorted, but near linear C_{NCN}-Cu-Cl bond angles (ca. 170º). Complex **F** is notable for adoption of a similar μ^2-Cl interaction in the solid-state, but instead results in the formation of a coordination polymer – an outcome that would be encumbered in the case of **4a** by the significantly more bulky *N*-substituent (Mes vs. ^{n}Bu).[16]

Iridium complexes of 1

Motivated by the previous reports of **B** as catalysts for alkane dehydrogenation reactions, we turned our attention to the preparation of analogous iridium hydride complexes through metalation of **1**, *viz.* [Ir(**1**)HCl(NCMe)] **5**.[6] Based on the reported procedures for **B**, iridium complexes of the *N*-aryl substituted pro-ligands, **5a** and **5b**, were obtained as analytically pure materials from reaction between $[Ir(COE)_2Cl]_2$, **1a**/**1b**, and Et_3N in acetonitrile at elevated temperature, but in low isolated yields of 13 and 11%, respectively (Scheme 3).[18] Under these conditions analysis, by ^{1}H NMR spectroscopy, of similar reactions

carried out with **1c** and **1d**, however, showed no meaningful evidence for formation of the desired hydride containing products.

Scheme 3: Preparation of iridium(III) complexes **5a** and **5b**



5a (**R = Mes**), **5b** (**R = Dipp**)

Isolated **5a**/**5b** were fully characterised in solution using ^{1}H and ^{13}C NMR spectroscopy (CD_2Cl_2), and ESI-MS ($[M–Cl]^+$ fragment ions observed). These new complexes display distinctive low frequency proton signals at δ -24.15/-23.69 attributed to the hydride ligands and the ^{1}H NMR spectra are notable for C_s symmetry and the absence of both the NCHN and NCCHCN resonances of the respective pro-ligands. Coordination of the pincer is affirmed by ^{13}C signals at ca. δ 200 and ca. δ 140 for the carbene and aryl donors, respectively, while intact coordination of acetonitrile is evidenced by a sharp 3H signals at δ 1.24/1.10 in the ^{1}H NMR spectra and pair of sharp resonances at ca. δ 115 and ca. δ 3 in the ^{13}C{^{1}H} NMR spectra of **5a**/**5b**. For comparison, the carbene and aryl resonances of **B** (R = Mes) are reported at δ 186.6 and δ 145.2, respectively (CD_2Cl_2).[6]

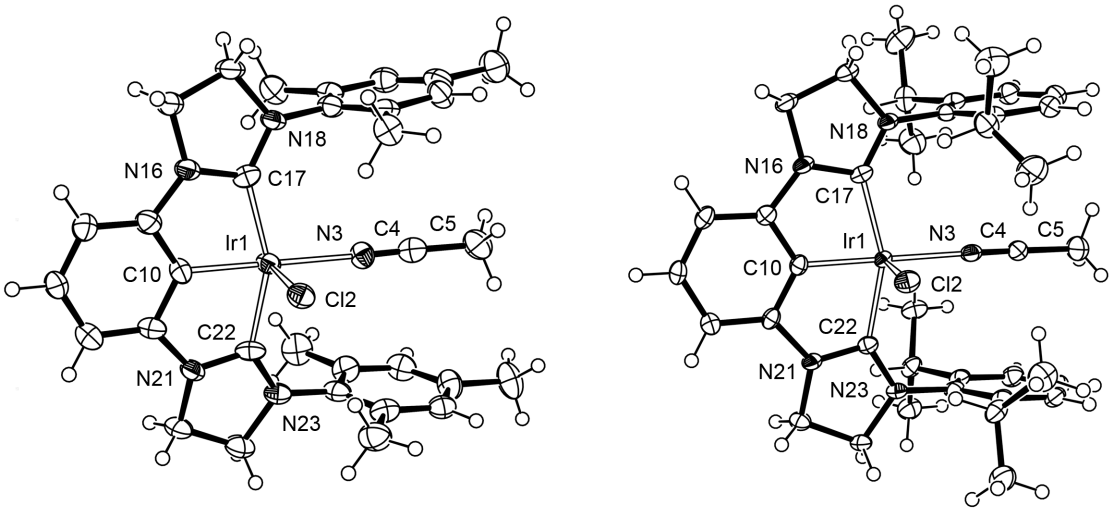
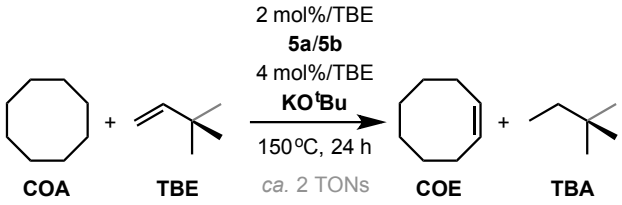


Figure 2: Solid-state structures of **5a** (left) and **5b** (right). Thermal ellipsoids for selected drawn at the 50% probability level; hydride ligands were not located reliably, solvent molecules omitted for clarity. Selected bond lengths (Å) and angles (º): **5a**: Ir1-Cl2, 2.525(2); Ir1-N3, 2.117(7); Ir1-C10, 1.968(7); Ir1-C17, 2.040(7); Ir1-C22, 2.055(8); C10-Ir1-Cl2, 90.9(2); C10-Ir1-N3, 177.1(3); C17-Ir1-C22, 155.5(3); **5b**: Ir1-Cl2, 2.4971(8); Ir1-N3, 2.092(3); Ir1-C10, 1.959(3); Ir1-C17, 2.040(3); Ir1-C22, 2.048(3); C10-Ir1-Cl2, 91.99(10); C10-Ir1-N3, 177.68(11); C17-Ir1-C22, 156.08(14);

The solid-state structures of the new Ir(CCC) complexes were interrogated using single crystal X-ray diffraction and fully corroborate the structural formulations inferred from NMR spectroscopy and ESI-MS,

although in both cases the hydride ligands were not definitively located from the Fourier difference map (Figure 2). In comparison to **B** (R = Mes), **5a** and **5b** are characterised by marginally longer Ir-C_{NCN} bond lengths (2.040(7), 2.055(8) Å, **5a**; 2.040(3), 2.048(3) Å, **5b**; 2.008(4), 2.014(4) Å, **B** (R = Mes)), but otherwise very similar metrics about the metal centre: for instance the Ir-C_{Ar} bond lengths (1.968(7) Å, **5a**; 1.959(3) Å, **5b**; 1.958(3) Å, **B** (R = Mes)) and C_{NCN}-Ir-C_{NCN} angles (155.5(3)º, **5a**; 156.08(14)º, **5b**; 156.0(2)º, **B** (R = Mes)). Solid-state structures of related, cationic, Ir(CCC) complexes have also been reported recently.[19]

Scheme 4: Transfer dehydrogenation of cyclooctane mediated by **5a**/**5b**



As part of our on-going interest in alkane dehydrogenation reactions, **5a** and **5b** were evaluated as catalysts for the *transfer* dehydrogenation of cyclooctene using tert-butylethylene, in combination with KO^{t}Bu to generate the necessary, putative 14 VE Ir(I) species (Scheme 4). Under relatively forcing reaction conditions (150ºC, 24 h), however, only ca. 2 total turnovers were achieved: far inferior catalytic activity compared to related and highly active Ir(PCP) systems (TONs approaching up to 6000 in some cases),[20] but similar to that reported for other imidazolylidene/benzimidazolylidene-based Ir(CCC) systems (TONs < 20).[6,21]

Summary

With a view to expanding the structural diversity of NHC-based pincer compounds, a series of imidazolinium-based CCC pro-ligands featuring *N*-Mes, Dipp, ^{i}Pr and ^{t}Bu substituents (**1**·2HCl) have been prepared. The corresponding free carbenes are readily generated through deprotonation by strong bases and, in addition to being characterised *in situ* by ^{1}H and ^{13}C NMR spectroscopy, were trapped through reaction with CuCl. Iridium pincer compounds of the *N*-Mes (**5a**) and Dipp (**5b**) substituted ligands, *viz.* [Ir(**1**)HCl(NCMe)], were obtained through reaction between the respective pro-ligand, $[Ir(COE)_2Cl]_2$, and Et_3N in acetonitrile at ca. 80^{o}C. Under similar conditions the *N*-^{i}Pr and ^{t}Bu analogues were not formed. Although isolated in low yield (ca. 10 – 13%), **5a** and **5b** were fully characterised in solution, by NMR spectroscopy and ESI-MS, and in the solid-state by X-ray diffraction. Under relatively forcing reaction conditions neither **5a** nor **5b**, in combination with KO^{t}Bu, show any significant catalytic activity for the transfer dehydrogenation of cyclooctane to cyclooctene using *tert*-butylethylene (ca. 2 TONs, 150^{o}C, 24 h).

Experimental

General considerations

All manipulations were performed under an atmosphere of argon, using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150ºC overnight and flamed under vacuum prior to use. Anhydrous DMF, THF, MeCN, pentane (<0.005% H_2O) were purchased from ACROS or Aldrich and freeze-pump-thaw degassed three times before being placed under argon. CD_2Cl_2 was dried over CaH_2, vacuum distilled, and freeze-pump-thaw degassed three times before being placed under argon. Cyclooctane, mesitylene, tert-butylethylene, and C_6D_6 were dried over Na, vacuum distilled, and freeze-pump-thaw degassed three times before being placed under argon. Triethylamine and *N*,*N*-diisopropylethylamine were dried over dried over 3 Å molecular sieves and freeze-pump-thaw degassed three times before being placed under argon. Aminooxoacetic acids **3** were prepared by hydrolysis of the corresponding ethyl esters (NaOH in THF), which were in turn prepared by reaction between ethyl chlorooxoacetate, triethylamine and the respective aniline/amine (THF) – as previously described for **3a**.[22] $[Ir(COE)_2Cl]_2$ was synthesised using a literature protocol.[23] All other solvents and reagents are commercial products and were used as received. NMR spectra were recorded on Bruker AV spectrometers at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS analyses were recorded on Bruker Maxis Impact instrument. Gas chromatography was carried out using an Agilent 7820A GC fitted with a 7693A Auto-injector. Microanalyses were performed by Stephen Boyer at London Metropolitan University.

Preparation of bis-amides 3

General procedure:

To a ice cold solution of 1,3-diaminobenzene (ca. 5 mmol), aminooxoacetic acid **2** (2 equivalents), 1-hydroxybenzotriazole (2.1 equivalents), and N,N-diisopropylethylamine (2 equivalents) in dry DMF (60 mL) was added 1,3-dicyclohexylcarbodiimide (1 M in CH_2Cl_2, 2.3 equivalents) under an atmosphere of dinitrogen. The reaction was stirred at 0ºC for 2 h and then warmed to room temperature overnight. During this time a white precipitate formed and was subsequently separated by filtration. The filtrate was concentrated to minimum volume yielding a yellow oily solid, which was washed with a mixture of ethanol/dichloromethane 95/5 to afford **3** as white solids.

3a: Prepared using the general procedure. Yield: 1.23 g (52%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.44 (s, 2H, amide), 8.84 (s, 2H, amide), 8.41 (t, $^4J_{HH}$ = 2.0, 1H, Ar{NCCHCN}), 7.32 – 7.48 (m, 3H, Ar), 6.94 (s, 4H, Mes), 2.30 (s, 6H, Mes), 2.22 (s, 12H, Mes). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ 158.2 (amide), 157.8 (amide), 137.9 (C), 137.3 (C), 134.9 (Mes), 130.1 (Ar), 129.7 (C), 129.3 (Mes), 116.7 (Ar), 111.2 (Ar{NCCHCN}), 21.1 (Mes), 18.5 (Mes). **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 509.2163 *m*/*z* $[M+Na]^+$ (calcd 509.2159).

3b: Prepared using the general procedure. Yield: 1.09 g (48%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.43 (s, 2H, amide), 8.86 (s, 2H, amide), 8.50 (t, $^4J_{HH}$ = 2.0, 1H, Ar{NCCHCN}), 7.39 – 7.43 (m, 3H, Ar), 7.37 (t, $^3J_{HH}$ = 7.7, 2H, Dipp), 7.23 (d, $^3J_{HH}$ = 7.7, 4H, Dipp), 3.04 (hept, $^3J_{HH}$ = 6.8, 4H, Dipp), 1.22 (d, $^3J_{HH}$ = 6.8, 24H, Dipp). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ 159.4 (amide), 157.8 (amide), 146.0 (Dipp), 137.3 (CN), 130.2 (Ar), 129.6 (CN), 129.2 (Dipp), 123.9 (Dipp), 116.7 (Ar), 111.2 (Ar{NC<u>C</u>HCN}), 29.1 (Dipp), 23.8 (Dipp). **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 593.3096 *m/z* $[M+Na]^+$ (calcd 593.3098).

3c: Prepared using the general procedure. Yield: 1.45 g (57%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.31 (s, 2H, amide), 8.13 (br, 2H, amide), 7.60 (br, 1H, Ar{NCCHCN}), 7.31 – 7.45 (m, 3H, Ar), 4.11 (br, 2H, ^{i}Pr), 1.26 (br, 12H, ^{i}Pr). **^{1}H NMR** (DMSO-d_6, 400 MHz): δ 10.57 (s, 2H, amide), 8.74 (d, $^3J_{HH}$ = 8.5, 2H, amide), 8.24 (t, $^4J_{HH}$ = 2.0, 1H, Ar{NCCHCN}), 7.51 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.0, 2H, Ar), 7.31 (t, $^3J_{HH}$ = 8.2, 1H, Ar), 3.98 (octet, $^3J_{HH}$ = 7, 2H, ^{i}Pr), 1.16 (d, $^3J_{HH}$ = 6.6, 12H, ^{i}Pr). Compound is poorly soluble in $CDCl_3$ or DMSO-d_6, encumbering acquisition of ^{13}C NMR data. **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 357.1533 *m/z* $[M+Na]^+$ (calcd 357.1533).

3d: Prepared using the general procedure. Yield: 1.35 g (53%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.34 (s, 2H, amide), 8.15 (t, $^4J_{HH}$ = 2.0, 1H, Ar{NCCHCN}), 7.45 (s, 2H, amide), 7.33 – 7.39 (m, 3H, Ar), 1.44 (s, 18H, ^{t}Bu). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ 158.9 (s, amide), 158.4 (s, amide), 137.4 (CN), 130.0 (Ar), 116.3 (Ar), 111.0 (Ar{NC<u>C</u>HCN}), 51.9 (^{t}Bu), 28.4 (^{t}Bu). **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 385.1845 *m/z* $[M+Na]^+$ (calcd 385.1846).

Preparation of pro-ligands 1·2HCl

General procedure:

To a solution of bis-amide **3** (ca. 2 mmol) in dry THF (30 mL) was added BH_3·THF (1M in THF) (16 equivalents) and the resulting solution heated at refluxed overnight under a stream of dry dinitrogen. After cooling to room temperature, methanol was added cautiously until all bubbling ceased. Conc. HCl (ca. 2.0 mL) was then added, and the solvent removed under reduced pressure. The resulting solid was dissolved in methanol, and the solvent removed in vacuo. This process was repeated twice more, to remove $B(OMe)_3$, and the resulting white solid dried thoroughly under high vacuum (< 1 x 10^{-2} mbar). To the crude dihydrochloride diamine was added triethylorthoformate (ca. 15 mL) and the resulting suspension heated to 130ºC for 6 h. After cooling to room temperature excess diethyl ether was added to the suspension and **1**·2HCl obtained as pale yellow solids on filtration, washing with 2 or three times with a minimum volume of acetone.

1a·2HCl: Prepared using the general procedure. Yield: 0.56 g (52%). **^{1}H NMR** (CD_3CN, 500 MHz): δ 11.02 (s, 2H, NCHN), 9.24 (t, $^4J_{HH}$ = 2.3, 1H, Ar{NCCHCN}), 7.64 (t, $^3J_{HH}$ = 8.3, 1H, Ar), 7.24 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.3, 2H, Ar), 7.05 (s, 4H, Mes), 4.59 – 4.67 (m, 4H, CH_2), 4.29 – 4.36 (m, 4H, CH_2), 2.36 (s, 12H, Mes), 2.31 (s, 6H,

Mes). **$^{13}C\{^1H\}$ NMR** (CD_3CN, 126 MHz): δ 158.5 (s, NCHN), 141.6 (Mes), 138.7 (Ar{CN}), 136.4 (Mes), 132.3 (Ar), 131.9 (Mes{CN}), 130.7 (Mes), 116.1 (Ar), 109.4 (Ar{NC$\underline{C}$HCN}), 52.3 (CH_2), 49.6 (CH_2), 21.1 (Mes), 18.1 (Mes). **ESI-MS** (180°C, 4.0 kV) positive ion: 487.2634 *m/z* $[M]^{2+}Cl^-$ (calcd 487.2623).

1b·2HCl: Prepared using the general procedure. Yield: 0.65 g (69%). **^1H NMR** (CD_3CN, 500 MHz): δ 11.36 (s, 2H, NCHN), 9.21 (t, $^4J_{HH}$ = 2.3, 1H, Ar{NCCHCN}), 7.67 (t, $^3J_{HH}$ = 8.3, 1H, Ar), 7.51 (t, $^3J_{HH}$ = 7.8, 2H, Dipp), 7.35 (d, $^3J_{HH}$ = 7.8, 4H, Dipp), 7.24 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.2, 2H, Ar), 4.61 – 4.68 (m, 4H, CH_2), 4.26 – 4.32 (m, 4H, CH_2), 3.04 (hept, $^3J_{HH}$ = 6.9, 4H, Dipp), 1.27 (d, $^3J_{HH}$ = 6.9, 12H, Dipp), 1.22 (d, ^3J = 6.8, 12H, Dipp).**$^{13}C\{^1H\}$ NMR** (CD_3CN, 126 MHz): δ 158.3 (NCHN), 147.3 (Dipp), 138.6 (Ar{CN}), 132.5 (Ar), 132.3 (Dipp), 131.2 (Dipp{CN}), 125.9 (Dipp), 116.2 (Ar), 109.3 (Ar{NC$\underline{C}$HCN}), 54.9 (CH_2), 49.5 (CH_2), 29.3 (Dipp), 25.3 (Dipp), 23.9 (Dipp). **ESI-MS** (180°C, 4.0 kV) positive ion: 571.3554 *m/z* $[M]^{2+}Cl^-$ (calcd 571.3562).

1c·2HCl: Prepared using the general procedure. Yield: 0.49 g (49%). **^1H NMR** (CD_3CN, 500 MHz): δ 10.81 (s, 2H, NCHN), 8.86 (t, $^4J_{HH}$ = 2.2, 1H, Ar{NCCHCN}), 7.52 (t, $^3J_{HH}$ = 8.2, 1H, Ar), 7.04 (dd, $^3J_{HH}$ = 8.2, $^4J_{HH}$ = 2.2, 2H, Ar), 4.30 – 4.37 (m, 4H, CH_2), 4.03 – 4.17 (m, 6H, CH_2 + ^{i}Pr), 1.47 (d, $^3J_{HH}$ = 6.7, 12H, ^{i}Pr). **$^{13}C\{^1H\}$ NMR** (CD_3CN, 126 MHz): δ 155.8 (NCHN), 139.1 (Ar{CN}), 132.2 (Ar), 114.6 (Ar), 107.8 (Ar{NC$\underline{C}$HCN}), 52.8 (^{i}Pr), 48.5 (s, CH_2), 47.6 (CH_2), 21.1 (^{i}Pr). **ESI-MS** (180°C, 4.0 kV) positive ion: 335.1999 *m/z* $[M]^{2+}Cl^-$ (calcd 335.1997).

1d·2HCl: Prepared using the general procedure. Yield: 0.56 g (52%). **^1H NMR** (CD_3CN, 500 MHz): δ 10.53 (s, 2H, NCHN), 9.19 (t, $^4J_{HH}$ = 2.2, 1H, Ar{NCCHCN}), 7.52 (t, $^3J_{HH}$ = 8.3, 1H, Ar), 7.02 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.2, 2H, Ar), 4.28 – 4.37 (m, 4H, CH_2), 4.09 – 4.17 (m, 4H, CH_2), 1.57 (s, 18H, ^{t}Bu). **$^{13}C\{^1H\}$ NMR** (CD_3CN, 126 MHz): δ 155.5 (NCHN), 139.1 (Ar{CN}), 132.0 (Ar), 114.9 (Ar), 108.8 (Ar{NC$\underline{C}$HCN}), 59.5 (^{t}Bu), 48.8 (CH_2), 47.0 (CH_2), 28.7 (^{t}Bu). **ESI-MS** (180°C, 4.0 kV) positive ion: 363.2310 *m/z* $[M]^{2+}Cl^-$ (calcd 363.2310).

In situ generation of free carbenes 1

General procedure:

To a J. Young's valve NMR tube charged with **1**·2HCl (15 mg) and $K[N(SiMe_3)_2]$ (2.1 equivalents) was added C_6D_6 (0.8 mL). The resulting free carbenes were generated quantitatively and characterised in *situ*.

1a: Limited solution stability, $t_{1/2}$ ~ 1 h. **^1H NMR** (C_6D_6, 500 MHz): δ 8.39 (br, 1H, Ar{NCCHCN}), 7.30 – 7.43 (m, 3H, Ar), 6.81 (s, 4H, Mes), 3.31 – 3.37 (m, 4H, CH_2), 3.07 – 3.14 (m, 4H, CH_2), 2.17 (s, 12H, Mes), 2.14 (s, 6H, Mes). **$^{13}C\{^1H\}$ NMR** (C_6D_6, 126 MHz, selected data only): δ 240.3 (NCN), 106.0 (Ar{NC$\underline{C}$HCN}), 51.3 (CH_2), 47.0 (CH_2).

1b: Limited solution stability, $t_{1/2}$ ~ 9 h. **^1H NMR** (C_6D_6, 500 MHz): δ 8.36 (t, $^4J_{HH}$ = 2.1, 1H, Ar{NCCHCN}),

7.24 (dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 2.1, 2H, Ar), 7.21 – 7.31 (m, 3H, Ar + Dipp), 7.2 (obscured, 4H, Dipp), 3.34 – 3.43 (m, 4H, CH_2), 3.25 – 3.34 (m, 4H, CH_2), 3.12 (hept, $^3J_{HH}$ = 6.7, 4H, Dipp), 1.30 (d, $^3J_{HH}$ = 6.9, 12H, Dipp), 1.19 (d, ^3J = 7.0, 12H, Dipp). **^{13}C{^{1}H} NMR** (C_6D_6, 126 MHz, selected data only): δ 241.9 (NCN), 105.8 (Ar{NCCHCN}), 54.2 (CH_2), 46.9 (CH_2).

1c: Limited solution stability, $t_{1/2}$ ~ 3 h. **^{1}H NMR** (C_6D_6, 500 MHz): δ 8.25 (t, $^4J_{HH}$ = 2.2, 1H, Ar{NCCHCN}), 7.33 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 7.06 (br d, $^3J_{HH}$ = 8, 2H, Ar), 4.06 (hept, $^3J_{HH}$ = 6.8, 2H, ^{i}Pr), 3.14 – 3.21 (m, 4H, CH_2), 2.73 – 2.80 (m, 4H, CH_2), 1.11 (d, $^3J_{HH}$ = 6.8, 12H, ^{i}Pr). **^{13}C{^{1}H} NMR** (C_6D_6, 126 MHz, selected data only): δ 234.3 (NCN), 105.5 (Ar{NCCHCN}), 46.6 (CH_2), 44.9 (CH_2).

1d: No change to spectra after 24 h. **^{1}H NMR** (C_6D_6, 500 MHz): δ 8.24 (br, 1H, Ar{NCCHCN}), 7.46 (d, $^3J_{HH}$ = 7.9, 2H, Ar), 7.31 (t, $^3J_{HH}$ = 7.9, 1H, Ar), 3.21 – 3.28 (m, 4H, CH_2), 2.87 – 2.95 (m, 4H, CH_2), 1.33 (s, 18H, ^{t}Bu). **^{13}C{^{1}H} NMR** (C_6D_6, 126 MHz): δ 237.4 (NCN), 146.6 (Ar{CN}), 129.3 (Ar), 110.4 (Ar), 104.7 (Ar{NCCHCN}), 54.9 (^{t}Bu), 47.0 (CH_2), 44.9 (CH_2), 29.9 (^{t}Bu).

Preparation of copper complexes 4

General procedure:

To a suspension of **1**·2HCl (ca. 0.3 mmol) and CuCl (3 equivalents) in dry THF (5 mL) cooled to -78ºC was added a solution of KOtBu (2.5 equivalents) in THF (2mL). The mixture reaction was stirred for 10 min at this temperature and then warmed to room temperature and stirred for a further and 4 h. The solution was filtered and then concentrated to ca. 3 mL and an excess of pentane added to precipitate the crude product, which was washed with a minimal amount of either THF (**1a**) or MeCN (**1c**, **1d**).

4a: Prepared using the general procedure. Yield: 0.16 g (64%). **^{1}H NMR** (CD_2Cl_2, 500 MHz): 8.45 (t, $^4J_{HH}$ = 2.1, 1H, Ar{NCCHCN}), 7.46 – 7.56 (m, 3H, Ar), 7.02 (s, 4H, Mes), 4.36 – 4.42 (m, 4H, CH_2), 3.95 – 4.01 (m, 4H, CH_2), 2.34 (s, 6H, Mes), 2.30 (s, 12H, Mes). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 200.0 (CuC), 142.5 (Ar{CN}), 139.6 (Mes), 136.1 (Mes{CN}), 135.9 (Mes), 130.8 (Ar), 130.2 (Mes), 116.0 (Ar), 110.7 (Ar{NCCHCN}), 51.7 (CH_2), 50.2 (CH_2), 21.4 (Mes), 18.5 (Mes). **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 613.1043 *m/z* $[M–Cl]^+$ (calcd 613.1037).

4c: Prepared using the general procedure. Yield: 0.86 g (65%). **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 8.18 (t, $^4J_{HH}$ = 2.1, 1H, Ar{NCCHCN}), 7.34 – 7.42 (m, ^{3}H, Ar), 4.61 (hept, $^3J_{HH}$ = 6.8, 2H, ^{i}Pr), 4.12 – 4.18 (m, 4H, CH_2), 3.71 – 3.77 (m, 4H, CH_2), 1.36 (d, $^3J_{HH}$ = 6.8, 12H, ^{i}Pr). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 196.7 (CuC), 142.9 (Ar{CN}), 130.6 (Ar), 115.2 (Ar), 110.3 (Ar{NCCHCN}), 54.2 (^{i}Pr), 49.4 (s, CH_2), 44.3 (CH_2), 21.5 (^{i}Pr). **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 461.0410 *m/z* $[M–Cl]^+$ (cald 461.0413).

4d: Prepared using the general procedure. Yield: 0.90 g (45%). **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 8.39 (t, $^4J_{HH}$ = 2.2, 1H, Ar{NCCHCN}), 7.39 (app t, *J* = 8, 1H, Ar), 7.32 (app dd, *J* = 8, *J* = 2, 2H, Ar), 4.07 – 4.14 (m, 4H, CH_2), 3.83 – 3.89 (m, 4H, CH_2), 1.65 (s, 18H, ^{t}Bu). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 197.7 (CuC), 143.5 (Ar{CN}), 130.3 (Ar), 116.4 (Ar), 112.5 (Ar{NCCHCN}), 56.7 (^{t}Bu), 49.4 (CH_2), 47.4 (CH_2), 30.9 (^{t}Bu). **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 489.0715 *m/z* $[M–Cl]^+$ (cald 489.0615).

Preparation of iridium complex 5a

A flame-dried Schlenk flask was charged with **1a**·2HCl (0.200 g, 0.38 mmol) and $[Ir(COE)_2Cl]_2$ (0.171 g, 0.19 mmol) and then suspended in dry MeCN (15 mL) and Et_3N (1.6 mL, 11.4 mmol) added. The reaction mixture was heated at 75ºC for 15 h and then the solvent removed *in vacuo*. The crude material was dissolved in CH_2Cl_2 and the filtrate washed twice with water, dried over $MgSO_4$, and then reduced to dryness. The resulting material was washed with a minimum volume of MeOH to afford the product as a light yellow solid. Yield 0.036 g (13%).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.88 (br, 2H, Mes), 6.85 (t, $^3J_{HH}$ = 7.7, 1H, Ar), 6.84 (br, 2H, Mes), 6.38 (d, $^3J_{HH}$ =7.7 Hz, 2H, Ar), 3.99 – 4.26 (m, 8H CH_2), 2.44 (s, 6H, Mes), 2.21 (s, 6H, Mes), 2.18 (s, 6H, Mes), -24.15 (s, 1H, IrH). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 200.1 (NCN), 148.1(Ar{CN}), 139.0 (Mes), 138.5 (Ar{IrC}), 137.8 (Mes), 137.1 (Mes{CN}), 129.3 (Mes), 128.7 (Mes), 121.3 (Ar), 115.2 (MeCN), 102.0 (Ar), 52.9 (CH_2) 44.9 (CH_2), 21.2 (Mes), 18.9 (Mes), 18.3 (Mes), 2.8 (MeCN). **Anal.** Calcd for $C_{32}H_{37}ClIrN_5$ (719.350 g·mol^{-1}): C, 53.43; H, 5.18; N, 9.74. Found: C, 53.19; H, 5.38; N, 9.63. **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 684.2683 *m/z* $[M–Cl]^+$ (calcd 684.2674).

Preparation of iridium complex 5b

A flame-dried Schlenk flask was charged with **1b**·2HCl (0.200 g, 0.33 mmol) and $[Ir(COE)_2Cl]_2$ (0.147 g, 0.16 mmol) and then suspended in dry MeCN (15 mL) and Et_3N (1.4 mL, 9.87 mmol) added. The reaction mixture was heated at 80ºC for 15 h and then the solvent removed *in vacuo*. The crude material was dissolved in CH_2Cl_2 and the filtrate washed twice with water, dried over $MgSO_4$, and then reduced to dryness. The resulting material was washed with a minimum volume of MeOH to afford the product as a light yellow solid. Yield 0.029 g (11%).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.22 (app. t, *J* = 8, 2H, Dipp), 7.17 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.8, 2H, Dipp), 7.10 (dd, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.8, 2H, Dipp), 6.86 (t, $^3J_{HH}$ = 7.7, 1H, Ar), 6.40 (d, $^3J_{HH}$ = 7.7, 2H, Ar), 4.15 – 4.31 (m, 4H, CH_2), 3.97 – 4.13 (m, 4H, CH_2), 3.55 (hept, $^3J_{HH}$ = 6.7, 2H, Dipp), 3.07 (hept, $^3J_{HH}$ = 6.7, 2H, Dipp), 1.25 (d, $^3J_{HH}$ = 6.7, 6H, Dipp), 1.18 (d, $^3J_{HH}$ = 6.7, 6H, Dipp), 1.15 (d, $^3J_{HH}$ = 6.7, 6H, Dipp), 1.10 (d, $^3J_{HH}$ = 6.7, 6H, Dipp), 1.09 (s, 3H, MeCN), -23.69 (s, 1H, IrH). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 126 MHz): δ 200.4 (NCN), 149.7 (Dipp), 148.6 (Dipp), 147.8 (Ar{CN}), 139.6 (Ar{IrC}), 136.7 (Dipp{CN}), 129.1 (Dipp), 124.1 (Dipp), 124.0 (Dipp), 121.3 (Ar), 115.8

(MeCN), 102.1 (Ar), 56.1 (CH_2) 44.9 (CH_2), 28.6 (Dipp), 28.4 (Dipp), 26.5 (Dipp), 25.5 (Dipp), 24.39 (Dipp), 24.37 (Dipp), 2.3 (MeCN). **Anal.** Calcd for $C_{38}H_{49}ClIrN_5$ (803.512 g·mol^{-1}): C, 56.80; H, 6.15; N, 8.72. Found: C, 56.69; H, 6.08; N, 8.82. **ESI-MS** (180^{o}C, 4.0 kV) positive ion: 768.3613 *m/z* $[M–Cl]^+$ (calc. 768.3614).

Transfer dehydrogenation reactions mediated by 5

To a J. Young's reaction flask charged with **5** (4 µmol) and KO^{t}Bu (8 µmol) was added 1 mL of a stock solution of cyclooctane/*tert*-butylethylene/mesitylene (0.0622 mol : 1.68 mmol : 0.86 mmol). The flask was sealed and the solution heated at 150ºC for 24 h. The mixture was cooled to room temperature and a 50 µL aliquot taken, diluted with pentane up to 1 mL, and then analysed by Gas chromatography. Reactions were carried out in duplicate.

Crystallography

Full details about the collection, solution and refinement are documented in the CIF, which have been deposited with the Cambridge Crystallographic Data Centre under CCDC 1487626 (**4a**), 1487627 (**5a**), and 1487628 (**5b**). 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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