**Variable coordination of amine functionalised *N*-heterocyclic carbene ligands to Ru, Rh and Ir: C-H and N-H activation and catalytic transfer hydrogenation**

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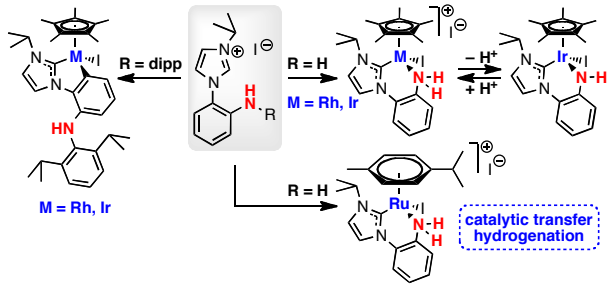
**Graphical Contents Entry**




Reactions of amine functionalised imidazolium salts with half-sandwich Ru(II), Rh(III) and Ir(III) halides are reported, including the first primary amine- or amido-NHC complexes of Rh and Ir.

**Abstract**

Chelating amine and amido complexes of late transition metals are highly valuable bifunctional catalysts in organic synthesis, but complexes of bidentate amine-NHC and amido-NHC ligands are scarce. Hence, we report the reactions of a secondary-amine functionalised imidazolium salt **2a** and a primary-amine functionalised imidazolium salt **2b** with [(*p*-cymene)$RuCl_2]_2$ and $[Cp^*MCl_2]_2$ (M = Rh, Ir). Treating **2a** with $[Cp^*MCl_2]_2$ and NaOAc gave the cyclometallated compounds Cp*M(C,C)I (M = Rh, **3**; M = Ir, **4**), resulting from aromatic C-H activation. In contrast, treating **2b** with [(*p*-cymene)$RuCl_2]_2$, $Ag_2O$ and KI gave the amine-NHC complex [(*p*-cymene)Ru(C,$NH_2$)I]I (**5**). The reaction of **2b** with $[Cp^*MCl_2]_2$ (M = Rh, Ir), NaO$^t$Bu and KI gave the amine-NHC complex [Cp*Rh($NH_2$)I]I (**6**) or the amido-NHC complex Cp*Ir(C,NH)I (**7**); both protonation states of the Ir complex could be accessed: treating **7** with trifluoroacetic acid gave the amine-NHC complex

[Cp*Ir(C,$NH_2$)I][$CF_3CO_2$] (**8**). These are the first primary amine- and amido-NHC complexes of Rh and Ir. Solid-state structures of the complexes **3** - **8** have been determined by single crystal X-ray diffraction. Complexes **5**, **6** and **7** are pre-catalysts for the catalytic transfer hydrogenation of acetophenone to 1-phenylethanol, with ruthenium complex **5** demonstrating especially high reactivity.

## Introduction

Late transition metal amine and amido complexes are important compounds that have found valuable applications in bifunctional catalysis.[1–3] In organic synthesis, chelating amine and amido complexes have come to prominence in reactions such as hydrogenation under $H_2$,[4] transfer hydrogenation,[5,6] and isomerisation of allylic alcohols.[7]

Of these reactions, the asymmetric transfer hydrogenation between alcohols and carbonyl compounds, catalysed by half-sandwich complexes of Ru, Ir or Rh with a chiral diamine ligand such as *N*-tosyl-1,2-diphenylethylenediamine, has been the most fully investigated. Elucidation of the mechanism has revealed that deprotonation of the primary amine group gives a metal amido complex that catalyses the transfer of an acidic and a basic hydrogen from *i*-PrOH to the carbonyl substrate.[8] The second donor of the chelating amine ligand is crucial, as it increases the resistance to undesirable M-N bond cleavage.[9]

In addition to the commonly employed sulfonamide donor, other chelating groups such as aryl,[10] phosphine[11–13] and thiol/thioether[14] have also been used to tether the reactive nitrogen to the metal in transfer hydrogenation. However, despite the recent dominance of *N*-heterocyclic carbene ligands in catalysis, there are very few examples of NHC donor groups tethering a nucleophilic amido ligand to an electrophilic metal in bifunctional catalysis, a consequence of the scarcity of efficient routes to these catalysts. The coordination of secondary amine- and amido-functionalised NHC ligands to Rh(I) has been described, but these complexes showed poor activity for the hydrogenation of cyclohexene and no activity was observed for the transfer hydrogenation of ketones and imines.[15] More closely related to this work, Morris has recently reported the coordination of a primary benzylamine functionalised NHC ligand to (*p*-cymene)Ru(II) and Cp*Ru(II): reaction of a benzonitrile functionalised imidazolium salt with nickel(II) chloride and *in situ* reduction of the nitrile group with $NaBH_4$ gave a nickel complex [Ni(C,$NH_2$)][$PF_6$]$_2$. Subsequent

transmetallation of the amine-NHC ligand from nickel to ruthenium gave the complexes **A** and **B (**Fig. 1), which were shown to catalyse transfer hydrogenation and hydrogenation under $H_2$.[16–18]

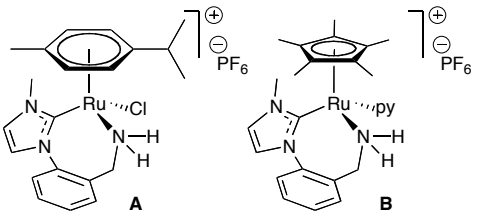
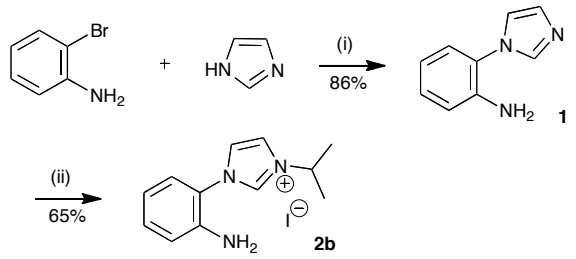



**Fig. 1** Ruthenium (C,$NH_2$) complexes reported by Morris.[16–18]

Previously, we have reported tridentate amido-bis(NHC) (CNC) complexes of palladium and platinum and a bidentate amido-NHC (C,N-dipp) complex of palladium.[19] These complexes were prepared from secondary amine functionalised imidazolium salts, which were obtained using an efficient cross-coupling/alkylation strategy. Herein, we report that the same efficient strategy can be used for the synthesis of primary amine functionalised imidazolium salts. Subsequently, we describe methods for the coordination of both primary- and secondary-amine functionalised NHC ligands to half-sandwich complexes of Ru(II), Ir(III) and Rh(III) and our observations of C-H and N-H activation. In doing so, we disclose the first primary amine- and amido-functionalised NHC complexes of rhodium and iridium. In addition, we evaluate the catalytic activity of these complexes for the transfer hydrogenation of acetophenone.

## Results and Discussion

The imidazolium pro-ligand **2a**, functionalised with a secondary amine, has been previously reported by our group.[19] The same strategy was also used to prepare the primary amine functionalised imidazolium salt **2b**, but with two modifications in the Ullman-type coupling of 2-bromoaniline with imidazole: changing the solvent from DMF to acetonitrile and changing the catalyst from CuI to $Cu_2O$ enabled a more facile isolation of intermediate **1** (Scheme 1).




[a]Reaction conditions:
(i) $Cu_2O$ (5 mol%), 8-hydroxyquinoline (20 mol%), $Cs_2CO_3$, MeCN, 100 °C
(ii) *i*-PrI, MeCN, 90 °C

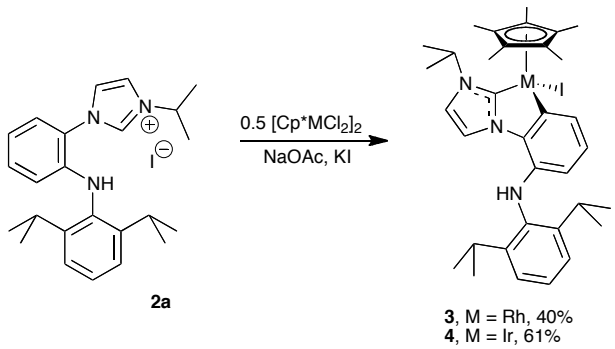
**Scheme 1** Synthesis of primary amine functionalised imidazolium salt **2b**.[a]

To prepare half-sandwich complexes of Ru and Ir containing NHC ligands, several bases have been employed for the deprotonation of an appropriate imidazolium salt: most prominently silver(I) oxide,[20–27] sodium acetate[22,23,28,29] and sodium/potassium *t*-butoxide,[30,31] but also sodium hydride,[32] cesium carbonate[33] and *n*-butyl lithium.[34] We chose to investigate the reactions of pro-ligands **2a** and **2b** with $Ag_2O$, NaOAc and NaO$^t$Bu in the presence of the metal half-sandwich dimers [(*p*-cymene)$RuCl_2]_2$, [Cp*$RhCl_2]_2$ and [Cp*$IrCl_2]_2$.

## Synthesis and structure of rhodium and iridium (C,C) complexes

Reacting the secondary amine functionalised imidazolium salt **2a** with [(*p*-cymene)$RuCl_2]_2$ and either $Ag_2O$, NaOAc or NaO$^t$Bu in dichloromethane at 33 °C gave an intractable mixture of products. In contrast, performing the reaction of **2a** with [Cp*$RhCl_2]_2$ and NaOAc for 5 days at room temperature gave a 40% yield of a single product: the cyclometallated compound Cp*Rh(C,C)I (**3**), resulting from the activation of an aromatic C-H bond, Scheme 2. With $Ag_2O$ as the base there was no reaction, whereas NaO$^t$Bu gave a lower conversion to **3**, as judged by $^1$H NMR spectroscopy. The identity of **3** is clear from its spectroscopic data and was confirmed by X-ray crystallography, *vide infra*. The observation of a nOe between the amine NH resonance at 4.78 ppm and the signals for the protons on the NHC ring confirmed that the amine group was not bound to the metal; it was clear, therefore, that the amine remained protonated and was not bound to the metal in a bidentate (C,NR) or (C,NHR) complex. Further evidence that **3** contained a cyclometallated (C,C) ligand was provided by the presence of only three signals for the aromatic ring linking the NHC to the amine nitrogen. The $^{13}C\{^1H\}$ NMR spectrum recorded for **3** also verifies the cyclometallated structure, with a doublet at 158.3 ppm ($J_{Rh\text{-}C}$ = 40 Hz)

for the aryl carbon and another at 163.6 ppm ($J_{Rh-C}$ = 63 Hz) for the NHC carbon bonded to rhodium.




**Scheme 2** Cyclometallation of secondary amine functionalised NHC ligands on Rh and Ir.

The same cyclometallation reaction was also observed with iridium: stirring pro-ligand **2a** with $[Cp^*IrCl_2]_2$ and NaOAc overnight at room temperature, followed by stirring with KI for 3 h, gave the cyclometallated complex Cp*Ir(C,C)I (**4**) in 61% yield. As has been observed in other studies, it was clear that the cyclometallation reaction proceeded much faster and more efficiently for Ir than Rh.[35,36] Using NaO$^t$Bu as the base in place of NaOAc gave an intractable mixture of products, with no evidence for the formation of **4**. However, unlike with Rh the reaction did proceed with $Ag_2O$ as the base, but the reaction was much slower. The $^1$H NMR spectrum for **4** is almost identical to that recorded for the Rh analogue **3**, with only small differences in the chemical shifts for the signals in each spectrum. Hence, the $NH_2$ singlet at 4.85 ppm showed a nOe with the two protons on the NHC ring and there are only three signals for the aromatic ring linking the NHC to the amine nitrogen. In the $^{13}C\{^1H\}$ NMR spectrum for **4**, the signal for the carbene was found at 163.6 ppm.

In complexes **3** and **4**, C-H activation is preferred over coordination of the amine to the metal. Indeed, no reaction occurred upon treating the dimers $[Cp^*MCl_2]_2$ (M = Rh and Ir) with pro-ligand **2a** in the absence of base, and there was no evidence of amine coordination to cleave the chloride bridged dimers, even at elevated temperatures. Computational and experimental studies of the mechanism of cyclometallation at Cp*Ir(III) have suggested that acetate acts as an intramolecular base in an ambiphilic reaction.[37,38] Cyclometallation of NHC ligands coordinated to Cp*Ir has been observed previously, involving activation of both aromatic C-H[22,23,28,39] and C($sp^3$)–H bonds.[21,40] These complexes have also found applications in catalysis: Albrecht and Crabtree have independently

reported Cp*Ir(C,C) complexes that are pre-catalysts for water oxidation,[39,41] and Peris has demonstrated diboration of alkenes and catalytic H/D exchange.[23,28]

The solid-state structures of **3** and **4** were determined by X-ray crystallography, the structures are shown in Fig. 2 and selected bond lengths and angles are presented in Table 1. The racemic complexes **3** and **4** contain stereogenic metal centres and both crystallise in the centrosymmetric, monoclinic space group $P2_1/c$ with both enantiomers in the unit cell. Moreover, **3** and **4** have very similar structures and almost identical unit cell dimensions. The complexes adopt a piano stool geometry, with ligand bite angles (*ca.* 78°) that are consistent with those previously reported for 5-membered rings resulting from the cyclometallation of an NHC ligand on Cp*Ir.[21,39,40] In **4**, the Ir–NHC bond length (1.978(8) Å) and Ir–aryl bond length (2.048(7) Å) are also consistent with related Cp*Ir(C,C)X complexes.[22,23,28,39] In **3**, the Rh–NHC (1.993(6) Å) and Rh–aryl (2.048(6) Å) bond lengths are almost identical to those in **4**, reflecting the almost identical ionic radii of Rh(III) and Ir(III).[42] In both complexes there is a tilt in the Cp* ring relative to the metal centre, which reflects the relative *trans* influence of the other three ligands. Hence, in each complex the two M-C(Cp*) bonds opposite the iodide ligand are the shortest (2.161(6) to 2.198(7) Å), whilst the three M-C(Cp*) bonds opposite to the NHC and aryl ligands are longest (2.231(6) to 2.280(7) Å). There is a twist of *ca.* 11.5° between the mean plane of NHC ring and the mean plane of the aryl ring in both **3** and **4**, most likely as a consequence of the *ortho*-amine substituent.

**Fig. 2** Solid-state structures of (a) Cp*Rh(C,C)I (**3**) and (b) Cp*Ir(C,C)I (**4**) (ellipsoids drawn at 50% probability). Hydrogen atoms except N-H have been omitted for clarity.

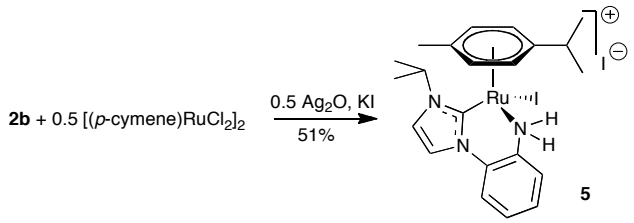
**Table 1** Selected bond lengths (Å) and angles (°) for **3** and **4**

| | Cp*Rh(C,C)I (**3**) | Cp*Ir(C,C)I (**4**) |
|---|---|---|
| M-C(1) (NHC) | 1.993(6) | 1.978(8) |
| M-C(5) (aryl) | 2.048(6) | 2.048(7) |
| M-I(1) | 2.6756(9) | 2.6693(8) |
| M-C(Cp*) | 2.161(6)<br>2.188(6) | 2.169(7)<br>2.198(7) |

| | | |
|---|---|---|
| | 2.231(6) | 2.253(8) |
| | 2.271(6) | 2.264(7) |
| | 2.276(5) | 2.280(7) |
| C(1)-M(1)-C(5) | 78.2(2) | 78.1(3) |

## Synthesis and structure of ruthenium, rhodium and iridium (C,$NH_2$) and (C,NH) complexes

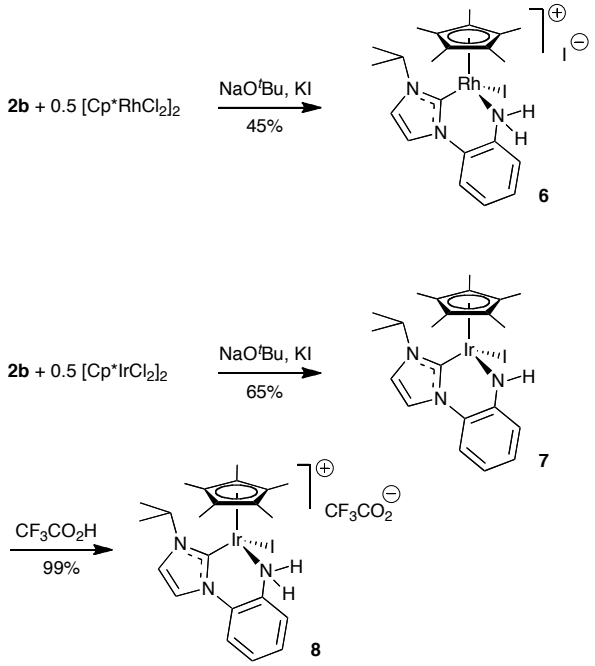
On the basis that the bulky 2,6-di*iso*propylphenyl substituent may prevent the amine nitrogen binding to the metal in a half-sandwich complex, we next investigated the reactions of the primary amine functionalised imidazolium salt **2b** with [(arene)$MCl_2]_2$ and base. Whereas we were unable to isolate an identifiable product from the reaction of imidazolium salt **2a** with [(*p*-cymene)$RuCl_2$] and $Ag_2O$, the same reaction with **2b** gave the amine-NHC complex [(*p*-cymene)Ru(C,$NH_2$)I]I (**5**) in 51% yield after column chromatography, Scheme 3. The salt **5** was clearly identified from its $^1$H NMR spectrum: four doublets for the aromatic *p*-cymene protons are consistent with the coordination of a bidentate (C,$NH_2$) ligand and a monodentate (iodide) ligand. Further evidence for the coordination of the amine to ruthenium was obtained from the two NH doublets at 4.17 and 8.52 ppm ($^2J_{HH}$ = 10.8 Hz). In the $^{13}C\{^1H\}$ NMR spectrum recorded for **5**, the carbene resonance is found at 175.9 ppm, very similar to the carbene resonance reported for the related complex **A** (175.1 ppm).[16] The solid-state structure of **5** was confirmed by single crystal X-ray diffraction, *vide infra*. Using either NaOAc or NaO$^t$Bu in place of silver(I) oxide also gave **5**, but in each case the conversion was lower than that with $Ag_2O$, as judged from the $^1$H NMR spectrum of the crude product.




**Scheme 3** Synthesis of the ruthenium amine-NHC complex **5**.

As for ruthenium, the reaction of imidazolium salt **2b** and $[Cp^*RhCl_2]_2$ also gave the amine-NHC complex, this time [$Cp^*$Rh(C,$NH_2$)I]I (**6**), in 45% yield after column chromatography (Scheme 4). For $Cp^*$Rh, sodium *tert*-butoxide proved to be the optimum base, using $Ag_2O$

or NaOAc gave byproducts that could not be separated from **6**. Coordination of the amine to the metal was again apparent from the two NH signals (4.76 and 7.32 ppm) present in the $^{1}$H NMR spectrum recorded for **6**. In the $^{13}C\{^{1}H\}$ NMR spectrum for **6**, the carbene signal is a doublet ($J_{RhC}$ = 54 Hz) at 169.5 ppm.




**Scheme 4** Synthesis of the Rh and Ir (C,$NH_2$) and (C,NH) complexes **6** to **8**.

Whereas the reaction of **2b** with $[Cp^*RhCl_2]_2$ and NaO$^t$Bu gave the amine-NHC salt **6**, in the analogous reaction with $[Cp^*IrCl_2]_2$ the amine was also deprotonated to give the neutral amido-NHC complex Cp*Ir(C,NH)I (**7**) in 65% yield, Scheme 4; the different outcome for Ir is consistent with a mechanism involving deprotonation of the amine group upon coordination to the metal: since Ir(III) has a greater charge density than Rh(III) the amine will be more acidic when coordinated to Ir(III) than when coordinated to Rh(III).[43] Reactions with either $Ag_2O$ or NaOAc as the base instead gave a complex mixture of products, and we were unable to isolate a pure compound on a preparative scale. As expected for a (C,NH) coordination complex, the $^{1}$H NMR spectrum for **7** contains four signals for the aromatic ring linking the NHC ring to the amido nitrogen and an NH singlet resonance that integrates to 1H. In the $^{13}C\{^{1}H\}$ NMR spectrum recorded for **7**, the carbene resonance appears at 154.6 ppm. The solid-state structure of **7** was determined by X-ray crystallography, *vide infra*.

Considering the base employed in the reactions of imidazolium salts with Ru(II), Rh(III) and Ir(III) halides, we found sodium acetate to be the optimum choice for the preparation of

the Rh and Ir cyclometallated-NHC complexes **3** and **4**, whilst sodium *tert*-butoxide was the optimum choice for preparing the Rh and Ir amine- and amido-NHC complexes **6** and **7**. For the preparation of the Ru amine-NHC complex **5**, silver oxide was the optimum base. Importantly, our investigations do not suggest that the outcome of the reactions were necessarily dictated by the nature of the base: as described above, for most of the reactions an alternative base gave the same major product but in lower yield.

With a view to applications in bifunctional catalysis, we were keen to access both protonation states of a nitrogen donor atom for the same metal-ligand scaffold. We were pleased to find that treating the iridium amido-NHC complex **7** with one equivalent of trifluoroacetic acid gave quantitative conversion to the amine-NHC salt [Cp*Ir(C,$NH_2$)I][$CF_3CO_2$] (**8**), Scheme 4. The identity of **8** was evident from its $^1$H NMR spectrum, which contained the familiar pair of NH doublets at 5.87 and 6.78 ppm. In the $^{13}C\{^1H\}$ NMR spectrum recorded for **8**, the carbene resonance was evident at 156.4 ppm. The solid-state structure of **8** was also determined by X-ray crystallography, *vide infra*.

**Fig. 3** Solid-state structure of one of the unique molecules of [(*p*-cymene)Ru(C,$NH_2$)I]I (**5**) (ellipsoids drawn at 50% probability). Hydrogen atoms except N-H have been omitted for clarity. There is intermolecular hydrogen-bonding between the anion and cation. There is intermolecular hydrogen-bonding d(H··I2) = 2.730 Å.

**Fig. 4** Solid-state structures of **(a)** one of the unique molecules of [Cp*Rh(C,$NH_2$)I]I (**6**), **(b)** Cp*Ir(C,NH)I (**7**), **(c)** [Cp*Ir(C,$NH_2$)I][$CF_3CO_2$] (**8**) (ellipsoids drawn at 50% probability). Hydrogen atoms except N-H have been omitted for clarity. There is intermolecular hydrogen-bonding for **6** d(H··I2A) = 2.680 Å and **8** d(H··O2) = 1.989 Å.

**Table 2** Selected bond lengths (Å) and angles (°) for **5**, **6**, **7** and **8**

| | [(*p*-cymene)Ru(C,$NH_2$)I]I (**5**) | | [Cp*Rh(C,$NH_2$)I]I (**6**) | | Cp*Ir(C,NH)I (**7**) | [Cp*Ir(C,$NH_2$)I][$CF_3CO_2$] (**8**) |
|---|---|---|---|---|---|---|
| | molecule 1 | molecule 2 | molecule 1 | molecule 2 | | |
| M-C(1) | 2.054(11) | 2.082(13) | 2.041(12) | 2.060(11) | 1.978(9) | 2.026(9) |
| M-N(1) | 2.154(8) | 2.114(9) | 2.121(9) | 2.118(10) | 2.101(7) | 2.153(7) |
| M-I(1) | 2.7116(16) | 2.7177(17) | 2.6985(16) | 2.7034(16) | 2.6843(11) | 2.7082(9) |
| M-C(arene) | 2.163(12) | 2.175(13) | 2.143(12) | 2.136(13) | 2.129(8) | 2.172(10) |
| | - 2.275(11) | - 2.342(19) | - 2.231(13) | - 2.227(12) | - 2.228(9) | - 2.256(9) |
| C(1)-M(1)-N(1) | 80.4(4) | 79.9(4) | 80.4(5) | 80.7(4) | 81.1(3) | 80.0(3) |

The solid-state structures of the amine- and amido-NHC complexes **5** to **8** were confirmed by single crystal X-ray diffraction (Figs. 3 and 4, selected bond lengths and angles in Table 2). The complexes adopt the expected piano stool geometry, with a stereogenic metal centre; they crystallise in centrosymmetric space groups (*P*-1 for **5** to **7**; $P2_1/n$ for **8**) with both enantiomers in the unit cell. The ligand bite angles in the six-membered chelate rings in **5** to **8** are only slightly larger than those in the five-membered cyclometallated chelate rings of **3** and **4** (79.9(4) to 81.1(3)° for **5** to **8**, *cf.* 78.2(2) and 78.1(3)° for **3** and **4**). However, the angle between the mean plane of the NHC ring and the mean plane of the aryl ring is much larger in **5** to **8** than it is in **3** and **4** (36.3 and 31.4° in **5**, 32.6 and 32.8° in **6**, 36.8° in **7**, 34.5° in **8**, compared with *ca.* 11.5° in **3** and **4**).

In each of the amine-NHC complexes **5**, **6** and **8**, there is intermolecular hydrogen bonding between one of the amine N-H protons and the non-coordinated anion (iodide for **5** and **6**, trifluoroacetate for **8**). The M–N bond lengths vary only by *ca.* 0.05 Å for the series of complexes **5** to **8** (2.101(7) Å for the amido complex **7** and 2.114(9) to 2.154(8) Å for the amine complexes **5**, **6** and **8**). The M–C(NHC) bond lengths in **5** to **8** are also very similar, lying within *ca.* 0.1 Å of each other (1.978(9) to 2.082(13) Å). Looking more closely at ruthenium complex **5**, the Ru–C distance (2.054(11) Å) and Ru–N distance (2.154(8) Å) are similar to those reported for the related complex **A** (d(Ru–C) = 2.092(5); d(Ru–N) = 2.146(4) Å).[16] In contrast, the ligand bite angle is much smaller in the 6-membered chelate ring of **5** (*ca.* 80°) than in the 7-membered chelate ring of **A** (91.98(17)°).[16]

**Catalytic transfer hydrogenation**

The Ru and Rh amine-NHC complexes **5** and **6** and the Ir amido-NHC complex **7** were investigated for their ability to act as pre-catalysts for the transfer hydrogenation of acetophenone to 1-phenylethanol. The reactions were performed in *iso*-propanol in the presence of sodium *tert*-butoxide, with a catalyst/base/substrate ratio of 1:8:200, Table 3.

**Table 3** Catalytic transfer hydrogenation of acetophenone to 1-phenylethanol[a]

| | | | | | Conversion /% (determined by GC) | | | |
|---|---|---|---|---|---|---|---|---|
| Entry | Cat. | Base | Additive | Temp. /°C | 0.5 h | 1 h | 24 h | 72 h |
| 1 | **5** | NaO$^t$Bu | – | 80 | 91 | 95 | – | – |
| 2 | **5** | NaO$^t$Bu | $AgPF_6$ | 80 | 93 | 93 | – | – |
| 3 | **5** | NaO$^t$Bu | – | 20 | 0 | 0 | 0 | 0 |
| 4 | **6** | NaO$^t$Bu | – | 80 | – | 7 | 86 | 99 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | **6** | NaO$^t$Bu | $AgPF_6$ | 80 | – | 3 | 75 | 96 |
| 6 | **7** | NaO$^t$Bu | – | 80 | – | 7 | 78 | 96 |
| 7 | **7** | NaO$^t$Bu | $AgPF_6$ | 80 | – | 9 | 46 | 68 |
| 8 | **7** | – | – | 80 | – | 0 | 11 | 24 |
| 9 | **7** | – | $AgPF_6$ | 80 | – | 0 | 2 | 3 |

[a] All reactions were performed in *i*-PrOH, with a cat./base/substrate ratio of 1:8:200

The ruthenium complex **5** demonstrated excellent catalytic activity, with a conversion >90% after only 0.5 h at 80 °C (Table 3, entry 1). Lowering the temperature to 20 °C, however, gave no detectable conversion, even after 72 h (entry 3). The rhodium amine-NHC complex **5** also gave high conversion (>95%), but only after 72 h (entry 4); adding $AgPF_6$ to eliminate the iodide anion did not aid the reaction (entry 5). The iridium amido-NHC complex **7** showed a similar catalytic activity to the rhodium amine-NHC complex **6** (entry 6), but including the $AgPF_6$ additive had a detrimental effect on the rate of the reaction (entry 7). For an otherwise similar inner coordination sphere, the higher reactivity of (arene)Ru compared with Cp*Rh and Cp*Ir pre-catalysts has been observed previously in transfer hydrogenation reactions.[44]

Noyori and co-workers showed that the ruthenium amido complex [(*p*-cymene)Ru(TsNCHPhCHPhNH)] catalyses the transfer hydrogenation of acetophenone in the absence of base.[8] Hence, we also attempted the reaction involving iridium amido complex **7** in the absence of base: the reaction did proceed, but the conversion over the same time period was significantly reduced (entry 8). When $AgPF_6$ was added to the reaction, with the aim of forming the 16-electron complex [Cp*Ir(C,NH)][$PF_6$] *in situ*, the conversion was even lower (entry 9). This poor activity for **7** in the absence of base suggests that the reaction may not proceed by the outer-sphere bifunctional mechanism.[8] Indeed for pre-catalyst **A**, an alternative inner-sphere mechanism has been proposed for the $H_2$-hydrogenation of ketones, in which the H–H bond is cleaved by a metal-alkoxide.[18]

## Conclusions

We have investigated the coordination of bidentate amine functionalised *N*-heterocyclic carbene ligands to (*p*-cymene)Ru(II) and Cp*M(III) (M = Rh,Ir) scaffolds. Reacting the secondary-amine functionalised imidazolium salt **2a** with [Cp*$MCl_2$]$_2$ and NaOAc gave the

cyclometallated NHC complexes Cp*M(C,C)I (M = Rh, **3**; M = Ir, **4**), *via* activation of an aromatic C-H bond. In these complexes, the bulky 2,6-di*iso*propylphenyl substituent appears to prevent the amine nitrogen from coordinating to the metal. Unlike for **2a**, reactions of the primary-amine functionalised imidazolium salt **2b** gave nitrogen-bound products. Hence, the reaction of **2b** with [(*p*-cymene)$RuCl_2]_2$, $Ag_2O$ and KI gave the amine-NHC complex: [(*p*-cymene)$Ru(C,NH_2)I$]I (**5**). For the reaction of **2b** with $[Cp^*MCl_2]_2$ (M = Rh or Ir) and $NaO^tBu$, the outcome depended upon the nature of the metal: for rhodium the product was the amine-NHC complex [$Cp^*Rh(C,NH_2)I$]I (**6**), whereas for iridium the product was the amido-NHC complex Cp*Ir(C,NH)I (**7**). Hence we have described an efficient route to ($C,NH_2$) and (C,NH) complexes, involving only 3 steps from commercial materials. Protonation of the amido donor in **7** with trifluoroacetic acid gave the amine-NHC complex [$Cp^*Ir(C,NH_2)I$][$CF_3CO_2$] (**8**). These are the first primary amine- or primary amido-NHC complexes of Rh and Ir. There are very few reports of the application of functionalised NHC ligands in bifunctional catalysis; hence, complexes **5**, **6** and **7** were tested for the catalytic transfer hydrogenation of acetophenone to 1-phenylethanol at 80 °C. The Rh and Ir pre-catalysts **6** and **7** showed high conversion (>95%) but over a relatively long time period of 72 h. In contrast, the Ru pre-catalyst **5** was significantly more active, giving >90% conversion after only 0.5 h.

## Experimental

All manipulations were performed under dry, oxygen free nitrogen using standard Schlenk techniques unless otherwise stated. THF was dried over and distilled from sodium-benzophenone prior to use, $CH_2Cl_2$ was distilled from $CaH_2$ and *i*-PrOH was distilled from Mg turnings. *N*-(2-(3-*iso*-propyl-1*H*-imidazolium)phenyl)-2,6-di*iso*propylaniline iodide (**2a**)[19] and $[Cp^*MCl_2]_2$ (M = Rh, Ir)[45] were prepared as reported in the literature. All other reagents were obtained from Sigma-Aldrich, Johnson Matthey or Alfa Aesar and used as supplied. NMR spectra were recorded on a Bruker DPX300, DRX400 or AV500 spectrometer; chemical shifts have been referenced to the residual protonated solvent peak and *J* values are given in Hz. For some compounds, assignments for $^1H$ and $^{13}C\{^1H\}$ NMR spectra were aided by $^1H$-$^1H$ COSY, $^1H$-$^1H$ NOESY and $^1H$-$^{13}C$ HMQC 2D NMR experiments. ESI mass spectra were recorded on a micromass Quattra LC spectrometer in MeCN/MeOH with a cone voltage of +25 V; FAB mass spectra were obtained on a Kratos concept

spectrometer using NBA as the matrix. Elemental analyses were performed at London Metropolitan University.

**2-(1*H*-imidazol-1-yl)phenylamine (1)**

2-bromoaniline (1.000 g, 5.952 mmol), imidazole (0.607 g, 8.92 mmol), $Cu_2O$ (0.043 g, 0.30 mmol), $Cs_2CO_3$ (3.881 g, 11.90 mmol) and 8-hydroxyquinoline (0.173 g, 1.19 mmol) were suspended in MeCN (10 mL) in a pre-dried sealable tube under an atmosphere of air. The tube was sealed and heated at 100 °C with stirring for 3 days. The volatiles were then removed *in vacuo* and the product extracted into $CH_2Cl_2$ (70 mL). The solution was washed with $H_2O$ (3 x 150 mL) and brine (100 mL), dried ($MgSO_4$) and the solvent removed *in vacuo* to give **1** (0.791 g, 86%) as a brown solid m.p. 103-104 °C (lit. 103-106 °C).[46]

**2-(3-*iso*-propyl-1*H*-imidazolium)phenylamine iodide (2b)**

In a sealable tube under an atmosphere of air, *i*-propyl iodide (0.77 mL, 7.6 mmol) was added to a suspension of **1** (1.07 g, 6.93 mmol) in MeCN (10 mL). The tube was sealed and heated at 90 °C for 3 days. The mixture was then allowed to cool to room temperature and the volatiles removed *in vacuo*. Recrystallisation from hot MeOH / $Et_2O$ three times gave analytically pure **2b** (1.480 g, 65%) as pale green crystals m.p. 190-191 °C.$^1$H NMR (400 MHz, $d_4$-MeOH) δ 1.66 (6H, d, $J$ = 6.7, CHC$H_3$),4.79 (1H, sept, $J$ = 6.7, C$H$CH$_3$), 6.79 (1H, t, $J$ = 7.7, ArH), 6.97 (1H, d, $J$ = 8.2, ArH), 7.25 (1H, d, $J$ = 7.7, ArH), 7.30 (1H, t, $J$ = 8.2, ArH), 7.71 (1H, s, NCHC$H$N), 7.92 (1H, s, NCHC$H$N), 9.27 (1H, s, $N_2$CH); $^{13}$C{$^1$H} NMR (100 MHz, $d_4$-MeOH) δ 23.0 (CH$C$H$_3$), 55.0 ($C$HCH$_3$), 118.4, 118.6 (ArCH), 121.9 (ArC), 122.4, 25.4 (NCH$C$HN), 128.1, 132.7 (ArCH), 137.2 ($N_2$CH), 144.8 (ArC); *m/z* (ESI) 202 (100%, [M-I]$^+$); Anal. Calcd. for $C_{12}H_{16}IN_3$: C, 43.78; H, 4.90; N, 12.77. Found C, 43.69; H, 4.82; N, 12.60%.

**Cp*Rh(C,C)I (3)**

A suspension of $[Cp^*RhCl_2]_2$ (0.100 g, 0.178 mmol) and NaOAc (0.052 g, 0.63 mmol) in $CH_2Cl_2$ (5 mL) were stirred at room temperature for 10 min. Imidazolium salt **2a** (0.158 g, 0.324 mmol) was then added and the mixture stirred for 5 days. The mixture was then filtered through celite and evaporated to dryness. Purification by flash column chromatography ($CH_2Cl_2$) gave **3** (0.091 g, 40%) as a yellow-orange solid m.p. 230 °C (dec.), $R_f$ = 0.60 ($CH_2Cl_2$). Crystals suitable for structure determination by X-ray diffraction

were obtained from $CH_2Cl_2$/hexane. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, d, *J* = 6.9, CHC*H*$_3$), 1.10 (3H, d, *J* = 6.8, CHC*H*$_3$), 1.16 (3H, d, *J* = 6.8, CHC*H*$_3$), 1.17 (3H, d, *J* = 6.9, CHC*H*$_3$), 1.56 (3H, d, *J* = 6.9, NCHC*H*$_3$), 1.67 (3H, d, *J* = 6.9, NCHC*H*$_3$), 1.82 (15H, s, η$^5$-$C_5$*Me*$_5$), 3.04 (1H, sept, *J* = 6.9, C*H*CH$_3$), 3.13 (1H, sept, *J* = 6.8, C*H*CH$_3$), 4.78 (1H, s, NH), 4.88 (1H, sept, *J* = 6.9, NC*H*CH$_3$), 6.07 (1H, d, *J* = 7.8, ArH), 6.73 (1H, t, *J* = 7.7, ArH), 7.04 (1H, d, *J* = 2.1, NC*H*CHN), 7.18 (3H, m, ArH), 7.35 (1H, d, *J* = 7.4, ArH), 8.40 (1H, d, *J* = 2.2, NC*H*CHN); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 10.5 (η$^5$-$C_5$*Me*$_5$), 22.7, 23.3, 23.8, 24.3, 24.8, 24.9 (CH*C*H$_3$), 27.9, 28.1 (2,6-$C_6H_3$-(*C*H(CH$_3$)$_2$)$_2$), 52.1 (N*C*H(CH$_3$)$_2$), 98.0 (d, $J_{Rh-C}$ = 6, η$^5$-*C*$_5$Me$_5$), 115.2 (ArCH), 115.6 (NHC-CH), 119.3 (NHC-CH), 123.8, 123.9, 124.5, 124.9, 133.1, 134.1, 136.5 (ArCH), 138.2, 142.7, 144.1, (ArC), 158.3 (d, $J_{Rh-C}$ = 40, ArC–Rh), 163.6 (d, $J_{Rh-C}$ = 63, $N_2$C–Rh); *m/z* (ESI) 726 (80%, [M+H]$^+$), 598 (100%, [M-I]$^+$); Anal. Calcd. for $C_{34}H_{45}IN_3Rh$: C, 56.28; H, 6.25; N, 5.79. Found C, 56.39; H, 6.19; N, 5.88.

**Cp*Ir(C,C)I (4)**

A suspension of $[Cp^*IrCl_2]_2$ (0.040 g, 0.050 mmol) and NaOAc (0.016 g, 0.20 mmol) in $CH_2Cl_2$ (3 mL) were stirred at room temperature for 10 min. Imidazolium salt **2a** (0.048 g, 0.10 mmol) was then added and the mixture stirred for a further 15 h. After this time, a saturated solution of aq. KI (3 mL) was added, and the mixture stirred vigorously for 3 h. The organic layer was separated, dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography ($CH_2Cl_2$) gave **4** (0.050 g, 61%) as a yellow-orange solid m.p. 218-220 °C, $R_f$ = 0.67 ($CH_2Cl_2$). Crystals suitable for structure determination by X-ray diffraction were obtained from an $Et_2O$/pentane solution of **4** at 3 °C. $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 0.96 (3H, d, *J* = 6.9, CHC*H*$_3$), 1.13 (3H, d, *J* = 6.9, CHC*H*$_3$), 1.15 (3H, d, *J* = 6.9, CHC*H*$_3$), 1.17 (3H, d, *J* = 6.9, CHC*H*$_3$), 1.53 (3H, d, *J* = 6.9, NCHC*H*$_3$), 1.66 (3H, d, *J* = 6.9, NCHC*H*$_3$), 1.86 (15H, s, η$^5$-$C_5$*Me*$_5$), 3.04 (1H, sept, *J* = 6.9, C*H*CH$_3$), 3.18 (1H, sept, *J* = 6.9, C*H*CH$_3$), 4.85 (2H, m, NC*H*CH$_3$ + NH), 6.00 (1H, d, *J* = 7.9, ArH), 6.68 (1H, t, *J* = 7.7, ArH), 7.08 (1H, d, *J* = 2.2, NC*H*CHN), 7.23 – 7.15 (3H, m, 2,6-$^i$PrC$_6$*H*$_3$), 7.27 (1H, d, *J* = 7.5, ArH), 8.39 (1H, d, *J* = 2.2, NC*H*CHN); $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$) δ 10.3 (η$^5$-$C_5$*Me*$_5$), 22.9, 23.3, 23.8, 24.5, 24.9, 25.1(CH*C*H$_3$), 28.3, 28.4 (2,6-$C_6H_3$-(*C*H(CH$_3$)$_2$)$_2$), 52.3 (N*C*H(CH$_3$)$_2$), 92.1 (η$^5$-*C*$_5$Me$_5$), 115.0 (ArCH), 115.3 (NHC-CH), 119.4 (NHC-CH), 124.1, 124.2, 125.0, 125.3, 132.6, 134.3 (ArCH), 137.8, 138.9, 142.3, 143.5, 144.4 (ArC), 163.6 ($N_2$C–Ir); *m/z* (ESI) 727 (20%, [M-I+MeCN]$^+$), 686 (15%, [M-I]$^+$), 362 (100%, [(C,C)+2H]$^+$); Anal. Calcd. for $C_{34}H_{45}IIrN_3$: C, 50.11; H, 5.57; N, 5.16. Found C, 50.20; H, 5.48; N, 5.08%.

**[(*p*-cymene)Ru(C,$NH_2$)I]I (5)**

A suspension of [(*p*-cymene)$RuCl_2]_2$ (0.090 g, 0.15 mmol), imidazolium salt **2b** (0.099 g, 0.30 mmol) and $Ag_2O$ (0.036 g, 0.16 mmol) in $CH_2Cl_2$ (20 ml) was stirred for 32 h at 33 °C in the dark. The solvent was removed *in vacuo*, and then the crude mixture was dissolved in acetone (20 mL). KI (0.498 g, 3.00 mmol) was added to the solution, which was then heated at reflux for 1 h. The solvent was removed *in vacuo* and the crude solid redissolved in $CH_2Cl_2$ (20 mL) filtered through Celite, and then concentrated under vacuum. Purification by flash column chromatography (gradient of $CH_2Cl_2$ to 50% acetone/$CH_2Cl_2$) gave **5** (0.105 g, 51%) as a dark green/blue solid m.p. 200 °C (dec.). Crystals suitable for structure determination by X-ray diffraction were obtained by diffusion of $Et_2O$ into a saturated $CHCl_3$ solution of **5**. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 0.90 (3H, d, *J* = 6.9, *p*-cymene CHC*H*$_3$), 0.92 (3H, d, *J* = 6.9, *p*-cymene CHC*H*$_3$), 1.56 (3H, d, *J* = 6.7, NCHC*H*$_3$), 1.58 (3H, d, *J* = 6.7, NCHC*H*$_3$), 2.06 (3H, s, *p*-cymene $CH_3$), 2.10 (1H, sept, *J* = 6.9, *p*-cymene C*H*$CH_3$), 4.17 (1H, d, $^2J_{HH}$ = 10.8, NH), 4.99 (1H, sept, *J* = 6.7, NC*H*$CH_3$), 5.21 (2H, m, *p*-cymene ArH), 5.76 (1H, d, *J* = 6.2, *p*-cymene ArH), 6.22 (1H, d, *J* = 6.2, *p*-cymene ArH), 7.31-7.38 (3H, m, ArH), 7.39 (1H, d, *J* = 2.3, NCHC*H*N), 7.71 (1H, d, *J* = 2.3, NCHC*H*N), 8.52 (1H, d, $^2J_{HH}$ = 10.8, NH), 8.63 (1H, d, *J* = 7.7 ArH); $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$) δ 20.2 (*p*-cymene $CH_3$), 21.0, 23.9 (*p*-cymene CH*C*$H_3$), 24.0, 24.8 (NCH*C*$H_3$), 31.9 (*p*-cymene *C*$HCH_3$), 55.4 (N*C*$HCH_3$), 83.0, 83.2, 84.1, 89.5 (*p*-cymene ArCH), 103.0, 110.6 (*p*-cymene ArC), 121.08, 121.13, 121.9, 122.9, 127.7, 128.8 (ArCH), 133.0, 136.3 (ArC), 175.9 ($N_2$C-Ru); *m/z* (ESI) 564 (100 %, $[M\text{-}I]^+$, 202 (100 % $[(C,NH_2)+H]^+$); Anal. Calcd. for $C_{22}H_{29}I_2N_3Ru$: C, 38.27; H, 4.23; N, 6.09. Found C, 38.07; H, 4.02; N, 5.91%.

**[Cp*Rh(C,$NH_2$)I]I (6)**

A suspension of [Cp*$RhCl_2]_2$ (0.020 g, 0.032 mmol), NaO$^t$Bu (0.012 g, 0.13 mmol), imidazolium salt **2b** (0.021 g, 0.064 mmol) and KI (0.054 g, 0.32 mmol) in $CH_2Cl_2$ (5 mL) was stirred at room temperature for 4 days. The mixture was then filtered through celite and evaporated to dryness. The crude residue was re-dissolved in acetone (3 mL) and stirred vigorously for 2 h with a saturated solution of aq. KI (3 mL). The organic layer was separated, dried ($MgSO_4$) and the volatiles removed *in vacuo*. Purification by flash column chromatography (10% acetone/$CH_2Cl_2$) gave **6** (0.020 g, 45%) as a dark red solid m.p. 95 °C, $R_f$ = 0.6 (10% acetone/$CH_2Cl_2$). Crystals suitable for structure determination by X-ray

diffraction were obtained from $CH_2Cl_2$/hexane. $^1$H NMR (400 MHz, $CDCl_3$) δ 1.53 (3H, d, *J* = 6.7, CHC*H*$_3$), 1.59 (3H, d, *J* = 6.7, CHC*H*$_3$), 1.62 (15H, s, η$^5$-$C_5Me_5$), 4.69 (1H, sept, *J* = 6.7, C*H*CH$_3$), 4.76 (1H, br, NH), 7.32 (3H, m, ArH, NH), 7.54 (2H, m, ArH, NC*H*CHN), 7.97 (1H, d, *J* = 2.2, NCHC*H*N), 8.31 (1H, dd, *J* = 7.0, 1.2, ArH); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 10.3 (η$^5$-$C_5$*Me*$_5$), 23.8, 25.8 (CH*C*H$_3$), 54.5 (*C*H(CH$_3$)$_2$), 98.1 (d, $J_{Rh-C}$ = 6, η$^5$-*C*$_5$Me$_5$), 121.5 (N*C*HCHN), 122.2 (ArCH), 122.3 (N*C*HCHN), 123.0, 127.2, 128.0 (ArCH), 132.5, 134.7 (ArC), 169.5 (d, $J_{Rh-C}$ = 54, $N_2C$–Rh); *m/z* (FAB) 566 (100%, [M-I]$^+$); Anal. Calcd. for $C_{22}H_{30}N_3I_2Rh$: C, 38.12; H, 4.36; N, 6.06. Found C, 38.05; H, 4.26; N, 5.87%.

**Cp*Ir(C,NH)I (7)**

[Cp*IrCl$_2$]$_2$ (0.040 g, 0.050 mmol), imidazolium salt **2b** (0.033 g, 0.10 mmol) and NaO$^t$Bu (0.019 g, 0.20 mmol) were suspended in THF (5 mL) and stirred for 15 h at room temperature. After this time, the solvent was removed *in vacuo* and the solid redissolved in $CH_2Cl_2$ (10 mL) and filtered through Celite. The volatiles were then removed *in vacuo* to give a crude solid that was extracted with boiling $Et_2O$ (5 x 15 mL). The $Et_2O$ washings were combined, hot filtered through Celite and the filter pad washed with hot $Et_2O$ (2 x 5 mL). Removal of the solvent *in vacuo* gave **7** (0.043 g, 65%) as a red-orange solid m.p. 160 °C (dec.). Crystals suitable for structure determination by X-ray diffraction were obtained from an $Et_2O$/pentane solution of **7** at 3 °C. $^1$H NMR (500 MHz, $CDCl_3$) δ 1.59 (6H, d, *J* = 6.8, CHC*H*$_3$), 1.62 (15H, s, η$^5$-$C_5$*Me*$_5$), 2.39-2.59 (0.8H, br s, NH), 5.02 (1H, sept, *J* = 6.8, C*H*CH$_3$), 6.38 (1H, t, *J* = 7.6, ArH), 6.67 (1H, d, *J* = 7.6, ArH), 6.85 (1H, t, *J* = 7.6, ArH), 7.02-7.05 (2H, m, ArH + NCHC*H*N), 7.46 (1H, d, *J* = 2.2, NCHC*H*N); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 9.6 (η$^5$-$C_5$*Me*$_5$), 23.2 – 26.4 (br, CH*C*H$_3$), 53.5 (*C*HCH$_3$), 88.8 (η$^5$-*C*$_5$Me$_5$), 114.4 (ArCH), 118.2, 118.3, 119.2, 119.7 (ArCH / NCH*C*HN), 126.4 (ArCH), 128.2, 151.4 (ArC), 154.6 ($N_2$C-Ir); *m/z* (ESI) 656 (100%, [M+H]$^+$), 528 (10%, [M-I]$^+$); Anal. Calcd. for $C_{22}H_{29}IIrN_3$: C, 40.37; H, 4.47; N, 6.42. Found C, 40.48; H, 4.52; N, 6.31%.

**[Cp*Ir(C,NH$_2$)I][CF$_3$CO$_2$] (8)**

Trifluoroacetic acid (6 µL, 0.009 g, 0.08 mmol) was added to a stirred solution of **7** (0.050 g, 0.076 mmol) in $CH_2Cl_2$ (10 mL) at room temperature, resulting in an immediate colour change from dark orange to yellow. After stirring for 1 h, the solvent was removed *in vacuo* to give **8** (0.058 g, 99%) as a yellow solid m.p. 100 °C (dec.). Crystals suitable for structure determination by X-ray diffraction were obtained by diffusion of pentane into a saturated $CHCl_3$ solution of **8**. $^1$H NMR (500 MHz, $CDCl_3$) δ 1.57 (15H, s, η$^5$-$C_5$*Me*$_5$), 1.60 (6H, d, *J* =

6.8, CHC*H*$_3$), 4.78 (1H, sept, *J* = 6.8, C*H*CH$_3$), 5.87 (1H, d, *J* = 11.9, NH), 6.78 (1H, d, *J* = 11.9, NH), 7.30 (1H, d, *J* = 2.2, NCHC*H*N), 7.33 (1H, t, *J* = 7.7, ArH), 7.38 (1H, t, *J* = 7.7, ArH), 7.45 (1H, d, *J* = 7.7, ArH), 7.48 (1H, d, *J* = 7.7, ArH), 7.67 (1H, d, *J* = 2.2, NCHC*H*N); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 9.4 (η$^5$-C$_5$*Me*$_5$), 23.5, 26.0 (CH*C*H$_3$), 54.3 (*C*HCH$_3$), 91.1 (η$^5$-*C*$_5$Me$_5$), 115.5 (q, *J* = 287.4, $CF_3$), 120.5, 120.6 (NCH*C*HN), 121.6, 121.9, 128.0, 128.2 (ArCH), 132.9, 135.3 (ArC), 156.4 ($N_2$C-Ir), 160.1 (q, *J* = 39.9, $CF_3CO_2$); *m/z* (ESI) 656 (100%, [M-$CF_3CO_2$]$^+$), 528 (20%, [M-HI-$CF_3CO_2$]$^+$); Anal. Calcd. for: $C_{24}H_{30}F_3IIrN_3O_2$: C, 37.50; H, 3.93; N, 5.47. Found C, 37.58; H, 3.87; N, 5.38%.

**X-ray Crystallographic Studies**

All single crystal diffraction data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å ) on a Bruker APEX 2000 CCD diffractometer at 150 K. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structures were solved by Patterson methods and structures refined by least-squares full-matrix refinement against $F^2$ employing SHELXTL version 6.10.[47] Hydrogen atoms were included in calculated positions (d(C-H) = 0.95 to 0.99 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 $U_{eq}$(C) for methyl H atoms and 1.2 $U_{eq}$(C) for all other C atoms. All non-H atoms were refined with anisotropic displacement parameters. For complexes **5**, **6** and **8**, disordered solvent was removed using the SQUEEZE option of PLATON.[48]

**Crystal data for 3.** $C_{34}H_{45}IN_3Rh$, $M_W$ = 725.54, monoclinic, space group P2(1)/c, *a* = 13.277(5), *b* = 8.466(3), *c* = 28.869(11) Å, α = 90, β = 95.710(8), ɣ = 90°, *V* = 3229(2) Å$^3$, *Z* = 4, $\rho_{calcd}$ = 1.493 Mg/m3, μ = 1.511 mm$^{-1}$, F(000) = 1472, crystal size 0.16 x 0.12 x 0.08 mm$^3$, 24670 reflections collected, 6361 unique [R(int) = 0.1738] (completeness to theta = 26.00° = 99.9%). Empirical absorption correction made, $T_{max}$ and $T_{min}$ 0.831 and 0.521 respectively. GOF = 0.922, final R indices [I>2σI] $R_1$ = 0.0599, $wR_2$ = 0.1103, R indices (all data) $R_1$ = 0.0907, $wR_2$ = 0.1242. Largest diff. peak and hole 2.034 and -1.294 eÅ$^{-3}$.

**Crystal data for 4.** $C_{34}H_{45}IIrN_3$, $M_W$ = 814.83, monoclinic, space group P2(1)/c, *a* = 13.219(4), *b* = 8.444(3), *c* = 29.021(9) Å, α = 90, β = 95.654(5), γ = 90°, *V* = 3223.7(16) Å$^3$, *Z* = 4, $\rho_{calcd}$ = 1.679 Mgm$^{-3}$, μ = 5.126 mm$^{-1}$, F(000) = 1600, crystal size 0.23 x 0.19 x 0.13 mm$^3$, 24406 reflections collected, 6341 unique [R(int) = 0.0652] (completeness to theta = 26.00° 99.9%). Empirical absorption correction made, $T_{max}$ and $T_{min}$ 0.831 and 0.587 respectively. GOF = 1.049, final R indices [I>2σI] $R_1$ = 0.0487, $wR_2$ = 0.1305, R

indices (all data) $R_1$ = 0.0615, $wR_2$ = 0.1370. Largest diff. peak and hole 2.542 and –2.850 eÅ$^{-3}$.

**Crystal data for 5.(0.5CHCl$_3$).(Et$_2$O).** $C_{26.50}H_{39.50}Cl_{1.50}I_2N_3ORu$, $M_W$ = 824.16, triclinic, space group P-1, $a$ = 11.772(6), $b$ = 14.552(7), c = 16.056(8) Å, $\alpha$ = 77.716(9), $\beta$ = 88.809(9), $\gamma$ = 85.046(10)°, $V$ = 2678(2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.044 Mg/m$^3$, $\mu$ = 3.068 mm$^{-1}$, F(000) = 1612, crystal size 0.15 x 0.10 x 0.04 mm$^3$, 21113 reflections collected, 10398 unique [R(int) = 0.1013] (completeness to theta = 26.00° 98.7%). Empirical absorption correction made, $T_{max}$ and $T_{min}$ 0.831 and 0.574 respectively. GOF = 0.869, final R indices [I>2σI] $R_1$ = 0.0684, $wR_2$ = 0.1444, R indices (all data) $R_1$ = 0.1308, $wR_2$ = 0.1635. Largest diff. peak and hole 1.183 and -1.139 eÅ$^{-3}$.

**Crystal data for 6.(5CH$_2$Cl$_2$).** $C_{27.50}H_{41}Cl_{11}I_2N_3Rh$, $M_W$ = 1160.29, triclinic, space group P-1, $a$ = 9.430(3), $b$ = 11.745(4), $c$ = 29.671(10) Å, $\alpha$ = 89.104(8), $\beta$ = 86.111(8), $\gamma$ = 75.463(7)°, $V$ = 3173.7(19) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.428 Mg/m$^3$, $\mu$ = 3.442 mm$^{-1}$, F(000) = 2260, crystal size 0.23 x 0.13 x 0.08 mm$^3$, 25014 reflections collected, 12332 unique [R(int) = 0.1037] (completeness to theta = 26.00° 98.7%). Empirical absorption correction made, $T_{max}$ and $T_{min}$ 0.831 and 0.535 respectively. GOF = 0.937, final R indices [I>2σI] $R_1$ = 0.0840, $wR_2$ = 0.2165, R indices (all data) $R_1$ = 0.1193, $wR_2$ = 0.2301. Largest diff. peak and hole 2.920 and -1.356 e.Å$^{-3}$.

**Crystal data for 7.** $C_{22}H_{29}IIrN_3$, $M_W$ = 654.58, triclinic, space group P-1, $a$ = 9.218(3), $b$ = 10.812(3), $c$ = 11.389(4) Å, $\alpha$ = 75.863(5), $\beta$ = 78.648(5), $\gamma$ = 86.600(5)°, $V$ = 1079.1(6) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 2.015 Mg/m$^3$, $\mu$ = 7.628 mm$^{-1}$, F(000) = 624, crystal size 0.13 x 0.11 x 0.05 mm$^3$, 8383 reflections collected, 4177 unique [R(int) = 0.0537] (completeness to theta = 26.00° 98.5%). Empirical absorption correction made, $T_{max}$ and $T_{min}$ 0.862 and 0.586 respectively. GOF = 1.012, final R indices [I>2σI] $R_1$ = 0.0471, $wR_2$ = 0.0963, R indices (all data) $R_1$ = 0.0612, $wR_2$ = 0.1008. Largest diff. peak and hole 2.294 and -1.647 e.Å$^{-3}$.

**Crystal data for 8.(5C$_5$H$_{12}$).** $C_{49}H_{90}F_3IIrN_3O_2$, $M_W$ = 1129.34, monoclinic, space group P2(1)/n, $a$ = 16.957(3), $b$ = 10.360(2), c = 21.186(4) Å, $\alpha$ = 90, $\beta$ = 110.741(4), $\gamma$ = 90°, $V$ = 3480.6(12) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 2.155 Mg/m$^3$, $\mu$ = 4.795 mm$^{-1}$, F(000) = 2312, crystal size 0.15 x 0.13 x 0.03 mm$^3$, 26753 reflections collected, 6829 unique [R(int) = 0.1501] (completeness to theta = 26.00° 100.0 % ). Empirical absorption correction made, $T_{max}$ and $T_{min}$ 0.862 and 0.539 respectively. GOF = 0.795, final R indices [I>2σI] $R_1$ = 0.0541,

$wR_2$ = 0.1052, R indices (all data) $R_1$ = 0.0949, $wR_2$ = 0.1136. Largest diff. peak and hole 0.991 and -1.925 e.Å$^{-3}$.

**Catalytic transfer hydrogenation**

**General procedure.** In a Schlenk flask under an atmosphere of nitrogen, a solution of acetophenone (0.200 g, 1.70 mmol) in *iso*-propanol (6 mL) was preheated to 80 °C with stirring. The appropriate pre-catalyst (**5**, **6** or **7**, 0.0085 mmol), sodium *tert*-butoxide (6 mg, 0.062 mmol) and $AgPF_6$ (0.003 g, 0.01 mmol) were then added as appropriate. Periodically, aliquots were removed from the reaction mixture by syringe. The aliquots were immediately quenched by dilution with EtOAc and then analysed by gas chromatography using a Perkin-Elmer Clarus 500 chromatograph equipped with a Perkin-Elmer Elite 5 column (PE5 30 m x 0.25 mm). Helium was used as a mobile phase with a flow rate of 1 mL/min and a split rate of 50 mL/min. The injector temperature was 250 °C, the oven temperature was 130 °C and the FID temperature was 280 °C. Retention times ($t_R$/min) were: acetophenone, 3.54; (*R*/*S*)-1-phenylethanol, 3.45. All reported conversions are an average of two reactions.

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**Electronic supplementary information (ESI) available**

$^1$H and $^{13}$C{$^1$H} NMR spectra for all new compounds; X-ray crystallographic data (CIF) for compounds **3** to **8**.

## Figures

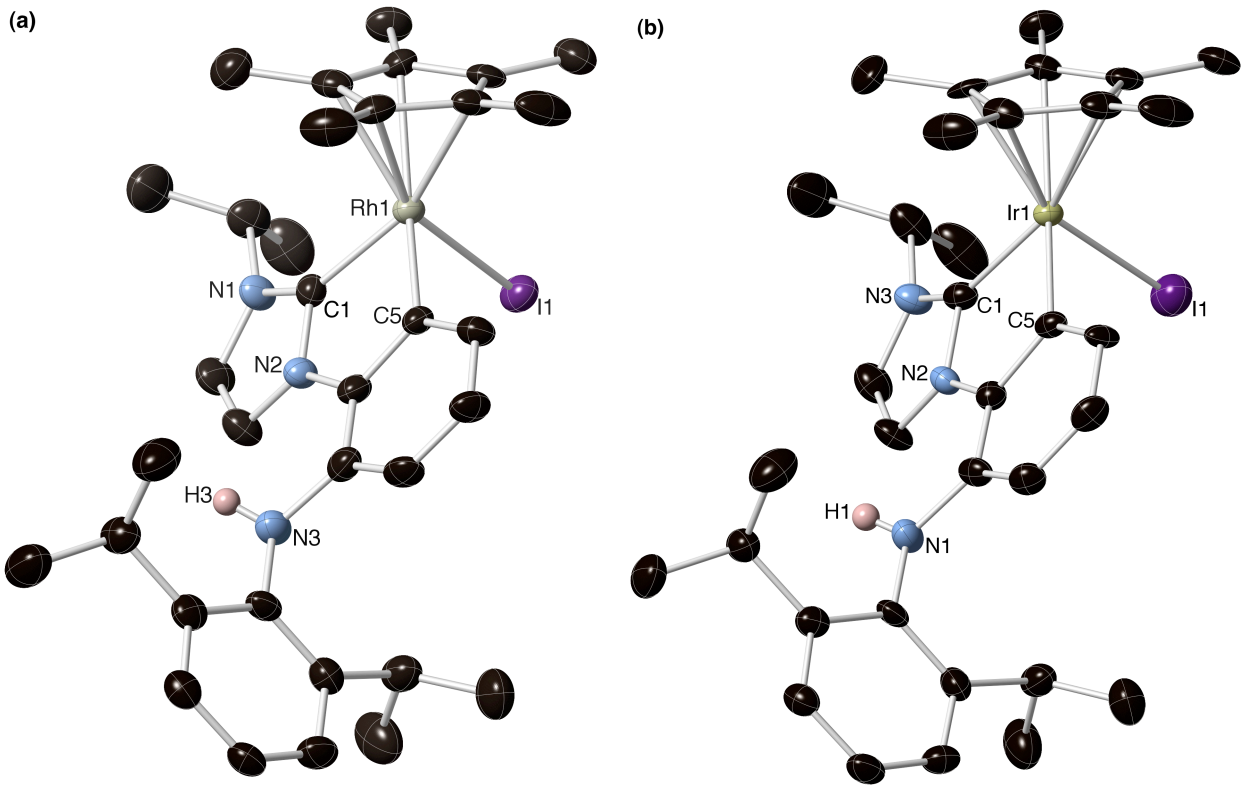


**Fig. 2** Solid-state structures of (a) Cp*Rh(C,C)I (**3**) and (b) Cp*Ir(C,C)I (**4**) (ellipsoids drawn at 50% probability). Hydrogen atoms except N-H have been omitted for clarity.

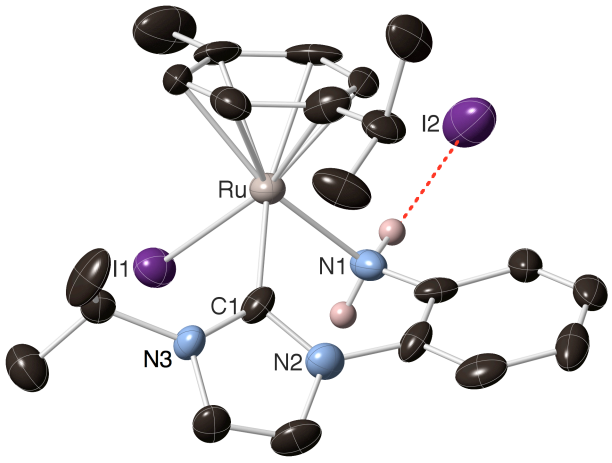


**Fig. 3** Solid-state structure of one of the unique molecules of [(*p*-cymene)Ru(C,$NH_2$)I]I (**5**) (ellipsoids drawn at 50% probability). Hydrogen atoms except N-H have been omitted for clarity. There is intermolecular hydrogen-bonding d(H..I2) = 2.730 Å.

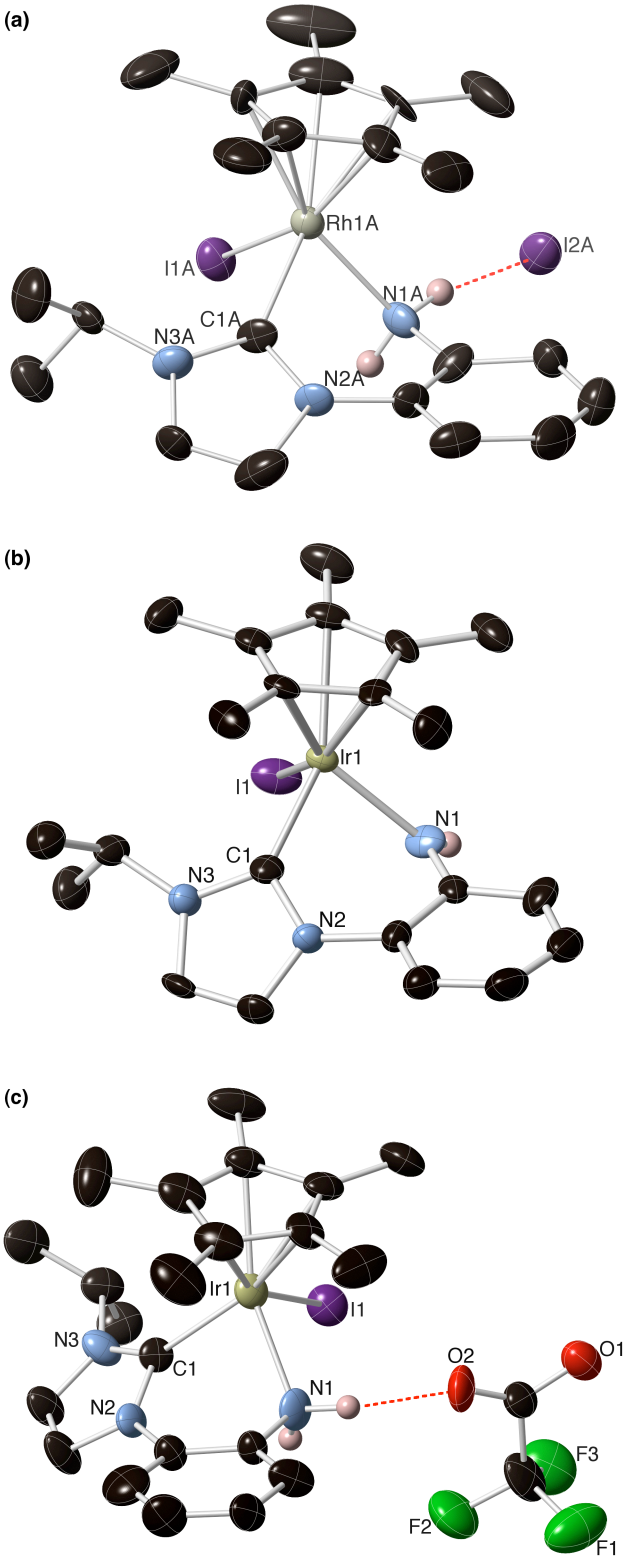


**Fig. 4** Solid-state structures of **(a)** one of the unique molecules of [Cp*Rh(C,$NH_2$)I]I (**6**), **(b)** Cp*Ir(C,NH)I (**7**), **(c)** [Cp*Ir(C,$NH_2$)I][$CF_3CO_2$] (**8**) (ellipsoids drawn at 50% probability). Hydrogen atoms except N-H have been omitted for clarity. There is intermolecular hydrogen-bonding for **6** d(H..I2A) = 2.680 Å and **8** d(H..O2) = 1.989 Å.

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