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Novel quasi-scorpionate ligand structures based on a bis-N-heterocyclic carbene chelate core: synthesis, complexation and catalysis

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Novel *quasi*-scorpionate ligand structures based on a bis-N-heterocyclic carbene chelate core: synthesis, complexation and catalysis

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Abstract

A series of novel *quasi*-scorpionate CNC donor ligands, MeC(2-C₅H₄N){CH₂(imidazole-R) (R = methyl, n-butyl, n-propenyl), in which a chelating bis(NHC) core is supplemented by a hemi-labile pyridyl donor, have been prepared. The coordination chemistry of these ligands has been investigated with silver, palladium, rhodium, and iridium. The single crystal X-ray structures of [Rh(NC₂^{Me})(COD)]Cl **8a** and [Ir(NC₂^{Pr})(COD)]Br **9b** have been determined. The catalytic potential of the rhodium and iridium complexes has been assessed in the transfer hydrogenation of ketones; the iridium complexes, which show superior performance, form very effective and stable catalysts.

Introduction

The rational design of functional, yet robust molecular complexes relies heavily on the availability of kinetically inert chelating ligands. Metal complexes thus prepared have found widespread application in many diverse areas, from catalysis to biomedical imaging. Consequently, the continued search for new functional complexes must also incorporate the design of novel, readily adaptable supporting ligand environments. Scorpionate ligands are one such group that have an important role in this field.¹⁻³ Scorpionate ligands possessing two amide donors, and a third (and possibly a fourth) pyridine or amine donor (Scheme 1),⁴⁻⁸ have been shown to support metal complexes which exhibit a range of unusual reactivity, often allowing catalytic intermediates to be

isolated and studied to an unprecedented level of detail.⁹ Peris and coworkers have prepared an interesting tripodal bis(imidazolyliene) with a phenoxy moiety providing the third donor (Scheme 1).^{10(a)} Such a ligand is extremely strongly bound, and for octahedral metals provides three *cis*-arranged coordination sites available for further chemistry. In a second paper Peris and coworkers have also reported a bis-carbene ligand containing a pyridine donor on the backbone.^{10(b)} However, the rigid structure of this ligand would probably preclude it from coordinating in a tridentate fashion. Other tridentate NHC based ligands with labile donors, have also been reported, for example see Hahn and Oro *et al.*^{10(c),11}

Scheme 1: Selected amido- and NHC- based scorpionate ligands

N-Heterocyclic carbenes (NHCs) are now well established as powerful co-ordinating ligands that provide a very effective base on which to build new polydentate ligands. Very many publications describing NHC ligands and their application in catalysis have appeared in the past twenty years; a number of excellent reviews have now appeared outlining the synthesis, and chemistry of these ligands and their multidentate derivatives.¹¹ The field is extremely vibrant and novel developments in NHC ligand design appear regularly.^{12, 13}

As part of our ongoing investigation into novel functionalised N-heterocyclic carbene ligands as supporting environments for metal complexes and their application in catalysis, we herein report the synthesis and coordination chemistry of chelating bis(NHC) ligands, possessing a pyridyl-donor, with silver, palladium, rhodium, and iridium. Catalytic transfer hydrogenation reactions employing the rhodium and iridium complexes are reported. The pyridyl ring is seen as an interesting structural feature of this ligand, in square-planar complexes the hemi-labile pyridyl donor is well placed to coordinate to the metal centre to stabilise a catalyst resting state, whilst easily decoordinating to allow a reaction to proceed when a lower coordination number is required.

Results and Discussion

Ligand synthesis

The ligands $\text{MeC}(2\text{-C}_5\text{H}_4\text{N})\{\text{CH}_2(\text{imidazole-R})$ ($\text{R} = \text{methyl, n-butyl, n-propenyl}$) were prepared according to the procedure depicted in Scheme 2. The di-hydroxy species, **2**, was synthesised by the hydroxymethylation of 2-ethylpyridine with aqueous formaldehyde, following the method of Gade;⁴ this gave a mixture of the monohydroxymethylation product **1** and the dihydroxymethylation product **2**. The yield of **2** was increased by reacting **1** with further equivalents of formaldehyde under identical conditions. Treatment of a solution of **2** with methanesulfonyl chloride gave the product, **3**, as a red oil in nearly quantitative yield (93%); further reaction of **3** with dry lithium bromide yielded **4** as pale yellow oil (56% yield). The bis-imidazolium salts were synthesised by reaction of **4** with selected N-substituted imidazoles to give the imidazolium salts $[\text{H}_2\text{NC}_2^{\text{R}}]\text{Br}_2$ ($\text{R} = \text{Me, Bu, Pr}$) **5a-c**, shown in Scheme 2 (75-80% yields).

Scheme 2: Synthesis of the bis-imidazolium ligand precursors

Synthesis of metal complexes

Silver complexes of the new ligands were prepared by dissolving the bis-imidazolium salts in CH_2Cl_2 (DCM) to which Ag_2O was added (Scheme 3). The resulting suspension was stirred at room temperature overnight, yielding a grey precipitate and red solution. After filtration and washing, the silver complexes **6a – c** were obtained as white powders (in 65-80% yield), which rapidly discoloured on standing (the structure depicted in Scheme 3 is based on the molecular formulae obtained from high resolution MS data).

Scheme 3: Synthesis of the Ag-bis-NHC complexes 6a-c

A common function of Ag-NHC complexes is to act as a ligand transfer agent. To demonstrate the feasibility of such an approach for the current ligands a square-planar bis-NHC-Pd complex was prepared by treating the Pd precursor $[\text{PdCl}_2(\text{NCCH}_3)_2]$ with a solution of the Ag complex as shown in (Eq 2, Scheme 4); complex **7** was obtained in good yield as a stable yellow compound. Rh and Ir complexes were readily prepared from the bis-imidazolium salt, $\text{KN}(\text{SiMe}_3)_2$ and the appropriate metal precursor complex, according to Eq 3, Scheme 4.

***Scheme 4:** Synthesis of transition metal complexes of the bis-imidazole ligands*

Structural characterisation

The structure of complexes $[\text{Rh}(\text{NC}_2^{\text{Me}})(\text{COD})]\text{Cl}$ **8a** and $[\text{Ir}(\text{NC}_2^{\text{Pr}})(\text{COD})]\text{Br}$ **9b** were confirmed by crystallographic analyses. The molecular structures of the two complexes are depicted in Figures 1 and 2 respectively, with selected bond lengths and angles provided in Table 1. The precision in the bond lengths and angles is somewhat low. Nevertheless, the two structures confirm the overall connectivity of the ligands, and indicate the coordination mode *via* the two NHC moieties. In these cases it can be seen that the pyridyl arm remains pendant, presumably owing to the preference for a square planar coordination geometry in these d^8 complexes. However, it can be clearly seen that the pyridyl donor lies in a position which makes coordination likely, should the metal require further coordinative saturation, for example, in octahedral complexes, or should coordination be required to stabilise a catalyst resting state. The principal bond lengths and angles (i.e. those associated with the central coordination sphere) are comparable to those reported in the Cambridge Structural Database: Rh- C_{NHC} = 1.901–2.224, mean 2.038 for 161 examples); Rh- C_{COD} = 1.998 – 2.397, mean 2.160 for 1098 examples; Ir- C_{NHC} = 1.907 – 2.115, mean 2.040 for 111 examples; Ir- C_{COD} = 1.984 – 2.363, mean 2.165 for 509 examples.¹⁴ Complex **9b** crystallises with two independent molecules in the asymmetric unit; the two show no significant differences, the corresponding metric parameters are provided in parentheses in Table 1. Complex **8a** crystallises with a chloride anion, whereas **9b** crystallises with a bromide. Since both complexes were

prepared using an analogous route, and both halide ions were present (chloride being derived from the metal precursor and bromide being derived from the imidazolium salt), we ascribe this phenomenon to subtle differences in crystal packing. However, neither structure indicates any evidence of interaction between the anion and the cationic complex, and we therefore deem this difference to be of little consequence in relation to the coordination motif of the ligand or the catalytic ability of the complexes.

Figure 1: Molecular structure of $[Rh(NC_2^{Me})(COD)]Cl$ (**8a**). H atoms and anion omitted for clarity, thermal ellipsoids are drawn at 25% probability

Figure 2: Molecular structure of $[Ir(NC_2^{Bu})(COD)]Br$ (**9b**). H atoms, the second crystallographically independent molecule, and anion omitted for clarity, thermal ellipsoids are drawn at 25% probability

Table 1 here

Catalytic studies

To explore the effectiveness of these new ligands as ligands in catalysis, preliminary catalytic investigations were undertaken into the transfer hydrogenation of ketones. Initial results were very promising and good catalytic activity, and catalyst stability was observed.

The performances of Iridium(I) and Rhodium(I) complexes, **8** and **9**, $[M(NC_2^R)(COD)]^+X^-$, were tested using a variety of substrates. The complexes catalyse the hydrogen transfer from i PrOH with potassium *tert*-butoxide as the base, according to Eq. 4. As previously observed,¹⁵ the Ir(I)-NHC complexes show higher catalytic activity than their rhodium analogues. With 1 mol% catalyst loading, each of the Ir complexes gave 100% conversion in 60 min or less for all substrates tested, hence lower concentrations of catalyst (0.3 and 0.01 mol%) were also investigated, and results for the lower loadings are reported in Table 2. $[Rh(NC_2^{Me})(COD)]Cl$ **8a**, (0.3 mol%; the only Rh

complex tested) required over 16 hr to yield 100% conversion of 4-bromoacetophenone into the corresponding alcohol (entry 19, Table 2). Although all iridium complexes gave rise to very effective catalysts, complexes with ligands bearing the longer chain, propenyl and n-butyl groups show better performance than the methyl bearing catalyst system.

Equation 4 here

Table 2. here

Plots of conversion *versus* time for Ir(I)-NHC complex **9c**, with different substrates were investigated using a concentration of 0.3 mol% catalyst and the results are shown in Figs 4 and 5. Reactions were monitored by taking aliquots from the reaction mixture at set intervals and the % conversion determined. Complete conversion of 4-bromoacetophenone to the alcohol is achieved after approximately 30 min (Fig 4).

Figure 3: Plot of conversion versus time for *p*-bromoacetophenone (1 mmol) catalysed by **9c (0.3 mol%)**

Figure 4: Plot of conversion versus time for *p*-methylacetophenone (1 mmol) catalysed by **9c (0.3 mol%)**

To test the stability of the catalyst system, catalyst **9c** was tested under normal operating conditions, however, after 30 min (and ~100 % conversion) an additional 1 mmol of *p*-bromoacetophenone was added and the reaction monitored, and then after 100 min a third aliquot of substrate was added (Results are shown Fig 5). A similar procedure was also followed using *p*-methylacetophenone as substrate. Importantly, results indicate that there is little diminution in catalyst performance with time, despite the reduced catalyst concentration and increasing product concentration.

Figure 5: Lifetime studies for catalyst **9c (0.3 mol%) with *p*-bromocetophenone as substrate**

The catalytic performance of the chelating NHC-Ir complexes, although not optimised in terms of ligand substituents or reaction conditions, generally compare quite favourably with previously reported systems for transfer hydrogenation.¹⁵⁻²⁰ The catalyst systems showed good stability and activity for the range of substrate tested.

Conclusions

A new series of bis(carbene)pyridine ligands have been shown to provide valuable supporting environments for a range of late transition metals. The complexes have been applied as catalysts in transfer hydrogenation, they exhibit good activity and excellent catalyst stability. It is clear that there is potential for these ligands to find applications with many other metals and catalytic processes other than those described here; the CNC coordination motif is expected to facilitate the development of novel organometallic complexes for both fundamental studies as well as in catalytic applications. Further studies are currently underway, to determine the efficacy of the pyridyl coordination with a variety of transition metals, and also in the development of new donor-functionalised ligand structures based on a related bis-NHC core.

Experimental

All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. Complexes $[\text{Rh}(\text{COD})\text{Cl}]_2$, $[\text{Ir}(\text{COD})\text{Cl}]_2$ were synthesised according to literature methods.²¹ NHC salts and the Rh and Ir complexes were prepared as previously reported.^{13(l)} Solvents of analytical grade were freshly distilled from sodium/benzophenone (thf, hexane) or from calcium hydride (CH_2Cl_2) or dried using a Braun SPS-800 system (hexane, CH_2Cl_2) or a Vacuum Atmospheres recirculating SPS system (thf). Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately prior to use, following standard literature methods. Air-sensitive compounds were stored and weighed in a glovebox. All reagents (1,3-dibromopropane, 1,4-diiodobutane, 2-aminopyridine, o-anisidine, 2,6-dimethylaniline, 2,6-diisopropylaniline, triethylorthoformate, sodium tetrafluoroborate, and potassium bis(trimethylsilyl)amide) were obtained from commercial suppliers and used as received. ^1H and ^{13}C NMR spectra were obtained on Bruker Advance AMX 400, 500 or Jeol Eclipse 300 spectrometers.

Chemical shifts (δ) were expressed in ppm downfield from tetramethylsilane using the residual protio solvent (^1H) or solvent (^{13}C) as an internal standard (CDCl_3 , ^1H 7.26 ppm and ^{13}C 77.0 ppm; benzene- d_6 ^1H 7.15 ppm and ^{13}C 128.0 ppm). Coupling constants J are expressed in Hertz. HRMS were obtained on a Waters LCT Premier XE instrument and are reported as m/z (relative intensity). Infrared spectra were recorded using a JASCO FT/IR-660 Plus spectrometer and analysed in solution (dichloromethane).

Synthesis of 2-(1,3-dihydroxy-2-methylpropan-2-yl)pyridine, **2**

Compound **2** was synthesised following the method of Gade *et al*⁴ using a mixture of 2-ethylpyridine (37.5 mL, 35.2 g, 0.327 mol) and an aqueous solution of formaldehyde (37%, 115.5 mL, 1.60 mol). As described by Gade, the total yield of **2** was increased to 48% by reaction of **1** with a further 4 equivalents of formaldehyde under the same reaction conditions. ^1H NMR (400.1 MHz, CDCl_3 , 293 K) δ 1.16 (s, CCH_3 , 3 H), 3.74 (d, $J=11.1$ Hz, CCH_3CH_2 , 2 H), 3.94 (d, $J=11.1$ Hz, CHCH_3CH_2 , 2 H), 7.14 (d, $J=7.6$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1 H), 7.27 (m, $\text{C}_5\text{H}_4\text{N}$, 1 H), 7.66 (m, $\text{C}_5\text{H}_4\text{N}$, 1 H), 8.43 (d, $\text{C}_5\text{H}_4\text{N}$, 1 H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 293 K) δ 19.7, 45.7, 69.3, 121.5, 121.7, 137.0, 147.8, 165.1 ppm.

Synthesis of 2-(1,3-dibromo-2-methylpropan-2-yl)pyridine, **4**

This compound was synthesised in a two-step process.

Part (a): Synthesis of 2-[bis-1,3-methylsulfonate-2-methylpropan-2-yl]pyridine, **3**

A solution of **2** (16.7 g, 0.1 mol) and triethylamine (62.6 mL, 0.45 mol) in dichloromethane (200 mL) was cooled to -2°C , and a solution of methanesulfonyl chloride (19.3 mL, 0.25 mol) in dichloromethane (50 mL) added dropwise, taking care that the temperature did not exceed $+2^\circ\text{C}$. The resulting suspension was warmed to room temperature and stirred for one hour. The reaction product was washed successively with hydrochloric acid (1 M, 1×50 mL), water (1×50 mL), sodium carbonate solution (1×50 mL), brine (1×50 mL) and finally again with water (1×50 mL). After drying over Na_2SO_4 and evaporating the solvent, the residue was dried in vacuo to yield **3** as a red oil which was used without further purification (29.3 g, 93%). ^1H NMR (400.1 MHz, CDCl_3 , 293 K): δ 1.50 (s, CCH_3 , 3H), 2.96 (s, $\text{CH}_2\text{SO}_2\text{CH}_3$, 6H), 4.63–4.52 (dd, AB, $J = 8.8$ Hz,

CCH₃CH₂, 4H), 7.21 (d, *J* = 7.9 Hz, C₅H₄N, 1H), 7.27 (d, *J* = 7.9 Hz, C₅H₄N, 1H), 7.70 (t, *J* = 8.0 Hz, C₅H₄N, 1H), 8.49 (d, *J* = 8.0 Hz, C₅H₄N, 1H) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 293 K) δ 19.1, 36.7, 36.8, 45.1, 72.7, 119.1, 137.5, 158.4, 163.3 ppm.

Part (b): Synthesis of 4

Compound **3** (31.6 g, 0.1 mol) was dissolved in anhydrous dimethyl sulfoxide (150 mL) and heated to 70 °C. Vigorously dried (vacuo, 100 °C, 3 d) lithium bromide (21.75 g, 0.25 mol) was then added in one portion, and the solution stirred for two days at 70 °C. After cooling to room temperature, water (200 mL) was added, and the mixture stirred for 30 min. The milky solution was extracted with diethyl ether (7×70 mL), and the combined ether extracts washed with water (3×50 mL) to remove residual dimethyl sulfoxide. The organic phase was separated, dried with Na₂SO₄, and the solvent evaporated to give an oily, crude product. Column chromatography (SiO₂, 0.060–0.200 mm, pore diameter ca. 6 nm) using a combination of ethyl acetate and hexane (3:1) as eluent yielded compound **4** as a light yellow oil (16.4 g, 56 %). ¹H NMR (400.1 MHz, CDCl₃, 293 K): δ 1.63 (s, CCH₃, 3H), 4.00–3.86 (dd, AB, *J* = 10.0 Hz, CCH₃CH₂, 4H), 7.18 (d, *J* = 7.9 Hz, C₅H₄N, 1H), 7.23 (d, *J* = 7.9 Hz, C₅H₄N, 1H), 7.66 (t, *J* = 7.9 Hz, C₅H₄N, 1H), 8.54 (d, *J* = 8.0 Hz, C₅H₄N, 1H) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 293 K): δ 23.1, 42.1, 46.0, 118.3, 118.4, 137.1, 160.0, 164.1 ppm. HR-MS (ES), *m/z* = 291.9345 [M+H]⁺ (calc. for C₉H₁₂Br₂N: 291.9336).

Synthesis of 2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine bromide, **5a**

2-(1,3-dibromo-2-methylpropan-2-yl)pyridine (2.93 g, 10 mmol) and 1-methylimidazole (1.97 g, 24 mmol) were stirred at 100 °C overnight. The resulting hygroscopic brown solid was washed with diethyl ether and dried under vacuum to give the pure salt **5a** (3.65 g, 80%). ¹H NMR (400.1 MHz, D₂O, 293 K): δ 1.43(s, CCH₃, 3H), 3.82 (s, NCH₃, 6H), 4.61–4.86 (dd, AB, *J* = 11.2 Hz, CCH₃CH₂, 4H), 7.25 (s, NCHCHN, 2H), 7.65 (s, NCHCHN, 2H), 7.21 (m, C₅H₄N, 1H), 7.38 (m, C₅H₄N, 1H), 7.85 (m, C₅H₄N, 1H), 8.7 (t, *J* = 3.2 Hz, C₅H₄N, 1H), 9.06 (s, NCHN, 2H) ppm. ¹³C{¹H} NMR (100.6 MHz, D₂O, 293 K): 17.8, 35.8, 46.6, 56.2, 122.7, 123.4, 124.3, 138.6, 139.0, 148.9, 149.8, 156.9 ppm. HR-MS (ES), *m/z* = 376.1127 [M+Br]⁺ (calc. for C₁₇H₂₃BrN₅: 376.1137).

Synthesis of 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5b**

This compound was prepared in an analogous manner to **5a**; using 1-butylimidazole (2.98 g, 24 mmol). The resulting hygroscopic white solid was washed with diethyl ether and dried under vacuum to give the salt **5b** (4 g, 75%). ^1H NMR (400.1 MHz, DMSO- d_6 , 293 K): δ 0.84 (t, $J=7.6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 6H), 1.09 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 1.42 (s, CCH_3 , 3H), 1.66 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 4.11 (t, $J=7.2$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 4.65–4.85 (dd, AB, $J=13.6$ Hz, CCH_3CH_2 , 4H), 7.37 (s, NCHCHN , 2H), 7.4 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.6 (s, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.74 (s, NCHCHN , 2H), 7.85 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.7 (d, $J=1.2$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.97 (s, NCHN , 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, DMSO- d_6 , 293 K): δ 13.8, 19.4, 23.9, 31.1, 38.9, 51.48, 55.8, 113.7, 121.4, 123.0, 123.4, 136.0, 148.1, 159.7, 160.2 ppm.

Synthesis of 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5c**

This compound was prepared in an analogous manner to **5a**; from 1-propenylimidazole (2.6 g, 24 mmol). The resulting hygroscopic brown solid was washed with diethyl ether and dried under vacuum to give the salt **5c** (3.97 g, 78 %). ^1H NMR (400.1 MHz, DMSO- d_6 , 293 K): δ 1.43 (s, CCH_3 , 3H), 4.82 (d, $J=6.8$ Hz, $\text{NCH}_2\text{CHCH}_2$, 4H), 4.63–4.89 (dd, AB, $J=13.6$ Hz, CCH_3CH_2 , 4H), 5.32 (d, $J=0.8$ Hz, $\text{NCH}_2\text{CHCH}_2$, 4H), 5.97 (m, $\text{NCH}_2\text{CHCH}_2$, 2H), 6.9 (s, NCHCHN , 2H), 7.34 (s, NCHCHN , 2H), 7.38 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.68 (s, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.82 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.7 (t, $J=1.2$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H), 9.03 (s, NCHN , 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, DMSO- d_6 , 293 K): δ 20.6, 39.5, 46.6, 51.3, 56.0, 120.3, 122.8, 123.7, 124.2, 132.2, 137.6, 149.3, 149.8, 158.5 ppm.

Synthesis of Ag(I)-NHC Complexes

Synthesis of 2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine Silver(I) bromide, **6a**

2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine bromide, **5a**, (0.45 g, 1 mmol) was dissolved in dried DCM (20 mL) and Ag_2O (0.271, 1 mmol) added. The

resulting suspension was stirred at room temperature for overnight, yielding a gray precipitate and red solution. The supernatant was separated and stripped in vacuo and the red solid washed with ether and hexane. The resultant white powder was dried in vacuo but rapidly discoloured, giving **6a** (0.37 g, 75 %) a red creamy powder that showed no further signs of decomposition at room temperature. ^1H NMR (400.1 MHz, D_2O , 293 K): δ 1.55 (s, CCH_3 , 3H), 3.76 (s, NCH_3 , 6H), 4.73-4.93 (dd, AB, $J = 13.6$ Hz, CCH_3CH_2 , 4H), 6.8 (s, NCHCHN , 2H), 7.3 (d, $J = 3.2$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.42 (s, NCHCHN , 2H), 7.43 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.80 (t, $J = 2.4$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.75 (d, $J = 1.6$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, D_2O , 293 K), 19.7, 34.8, 46.7, 54.9, 58.4, 64.9, 122.5, 122.6, 122.8, 137.5, 149.5, 160.0, 181.7 ppm. ES-MS: $m/z = 484$ (20%) $[\text{M}+\text{H}]^+$, 402 (100%) $[\text{M}-\text{Br}]^+$.

Synthesis of 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine

Silver(I) bromide, **6b**.

This compound was prepared an analogous manner to **6a**; from 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5b** (0.54 g, 1 mmol) and Ag_2O (0.27 g, 1 mmol). The resultant solid was dried in vacuo giving **6b** (0.37 g, 66 %) as a grey creamy powder. ^1H NMR (400.1 MHz, $\text{DMSO}-d_6$, 293 K): δ 0.74 (t, $J=6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 6H), 1.09 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 1.43 (s, CCH_3 , 3H), 1.55 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 3.90 (t, $J=4.8$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 4.55-4.76 (dd, AB, $J=13.6$ Hz, CCH_3CH_2 , 4H), 6.95 (s, NCHCHN , 2H), 7.2 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.4 (s, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.45 (s, NCHCHN , 2H), 7.65 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.5 (d, $J=1.2$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, $\text{DMSO}-d_6$, 293 K): δ 14.3, 17.6, 18.5, 31.5, 54.6, 57.5, 63.5, 120.8, 121.3, 121.9, 122.5, 136.4, 148.5, 158.8, 179.4 ppm.

Synthesis of 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine

Silver(I) bromide, **6c**

This compound was prepared an analogous manner to **6a**; from 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5c**, (0.51 g, 1 mmol) and Ag_2O (0.27 g, 1 mmol). The resultant solid was dried in vacuo, giving **6c** (0.4 g, 77 %) as a grey creamy powder, which rapidly discoloured on standing. ^1H NMR (400.1

1
2
3 MHz, CDCl₃, 293 K): δ 1.40 (s, CCH₃, 3H), 4.6 (d, $J=2$ Hz, NCH₂CHCH₂, 4H), 4.65-
4
4.75 (dd, AB, $J=13.2$ Hz, CCH₃CH₂, 4H), 5.08 (d, $J=4$ Hz, NCH₂CHCH₂, 4H), 5.7 (m,
5
6 NCH₂CHCH₂, 2H), 6.26 (s, NCHCHN, 2H), 6.64 (s, NCHCHN, 2H), 6.95 (d, $J=3.2$ Hz,
7
8 C₅H₄N, 1H), 7.32 (m, C₅H₄N, 1H), 7.5 (t, $J=0.8$ Hz, C₅H₄N, 1H), 8.6 (d, $J=1.6$ Hz,
9
10 C₅H₄N, 1H) ppm. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 293 K): δ 15.2, 47.4, 59.2, 65.8,
11
12 120.4, 121.7, 122.5, 122.9, 132.6, 132.9, 137.5, 150.1, 160.1, 183.6 ppm.
13
14

15
16 **Synthesis of 2-(2-methyl-1,3-bis(3-propenylimidazolidin-1-yl)propan-2-yl)pyridine**
17 **acetonitrile Palladium(II) Chloride, 7**

18
19 2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine Silver(I) bromide **6c**
20 (0.24 g, 0.05 mmol) was dissolved in 20 mL DCM, and PdCl₂(CH₃CN)₂ (129.7 mg, 0.05
21
22 mmol) was added to the solution of **6c**. The mixture was stirred in the dark at room
23
24 temperature overnight. The solution was filtered to remove AgBr. All volatiles were
25
26 removed under vacuum. The yellow solid was washed with ether (2x10 mL) and dried
27
28 under vacuum. Yield: 75%, 180 mg. ¹H NMR (500.1 MHz, DMSO-d₆, 293 K): δ 1.15 (s,
29
30 CCH₃, 3H), 4.22 (d, $J=14.5$ Hz, NCH₂CHCH₂, 4H), 5.12-5.26 (m, CCH₃CH₂, 4H), 5.57
31
32 (d, $J=14.5$ Hz, NCH₂CHCH₂, 4H), 6.15 (m, NCH₂CHCH₂, 2H), 7.21 (s, NCHCHN, 2H),
33
34 7.47 (s, NCHCHN, 2H), 7.4 (m, C₅H₄N, 1H), 7.77 (d, $J=8$ Hz, C₅H₄N, 1H), 8.01 (t, $J=6$
35
36 Hz, C₅H₄N, 1H), 8.79 (d, $J=3.5$ Hz, C₅H₄N, 1H) ppm. ¹³C{¹H} NMR (125.7 MHz,
37
38 DMSO-d₆, 293 K): δ 16.4, 44.5, 51.9, 59.6, 117.4, 118.1, 118.6, 120.0, 125.4, 134.1,
39
40 137.6, 148.9, 160.4, 163.1 ppm. C_{NHC} not observed.. HR-MS (ES), m/z = 486.0851 [M-
41
42 Cl]⁺, (calc. for C₂₁H₂₅³⁵ClN₅¹⁰⁴Pd: 486.0839).
43
44

45
46 **Synthesis of 2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine**
47 **Rhodium(I) cyclooctadiene chloride, 8a**

48
49 2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine bromide, **5a**, (0.457
50
51 g, 1 mmol) and KN(SiMe₃)₂ (0.4 g, 1 mmol) were placed into a Schlenk tube followed by
52
53 the addition of THF (10 mL). The solution was stirred for 2 hours and subsequently
54
55 filtered into another Schlenk tube containing 10 mL of a THF solution of [Rh(COD)Cl]₂
56
57 (0.24 g, 0.5 mmol). An immediate colour change was observed from light yellow to dark
58
59 orange and after 5 minutes yellow solid precipitated out. After the reaction mixture was
60

stirred at room temperature for 2 h, the volatiles were removed in vacuo. The yellow solid obtained was washed with cold hexane (2x10 mL) and dried under vacuum. Yield: 65 %, 164 mg. The structure of complex characterised by X-ray diffraction. ^1H NMR (500.1 MHz, CDCl_3 , 293 K): δ 1.2 (s, CCH_3 , 3H), 2.1-2.6 (m, CHCH_2 , 8H), 3.99 (s, NCH_3 , 6H), 4.01 (d, J = 15 Hz, CHCH_2 , 2H), 4.5 (dd, AB, J = 13.2 Hz, CCH_3CH_2 , 4H), 5.62 (d, J = 24.5 Hz, CHCH_2 , 2H), 6.99 (s, NCHCHN , 2H), 7.02 (s, NCHCHN , 2H), 7.27 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.64 (d, J = 8 Hz, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.78 (t, J = 6 Hz, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.58 (d, J = 1 Hz, $\text{C}_5\text{H}_4\text{N}$, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 293 K): δ 14.2, 17.23, 27.0, 29.7, 30.1, 37.1, 45.1, 54.5, 62.6, 64.8, 87.6, 89.2, 118.9, 121.5, 123.7, 127.6, 136.6, 148.1, 162.2, 182.0 (d, J = 52.5 Hz) ppm. HR-MS (ES): m/z = 506.1813 $[\text{M}]^+$, (calc. for $\text{C}_{25}\text{H}_{33}\text{N}_5\text{Rh}$: 506.1791).

Synthesis of 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine

Rhodium(I) cyclooctadiene Chloride, **8b**

Complex **8b** was prepared from 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5b**, (0.54 g, 1 mmol), $\text{KN}(\text{SiMe}_3)_2$ (0.4 g, 1 mmol) and $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.24 g, 0.5 mmol) according to the method described for **8a**. A yellow solid was obtained in 75 % yield, 221 mg. ^1H NMR (500.1 MHz, CDCl_3 , 293 K): δ 0.95 (t, J = 6.2 Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 6H), 1.10 (s, CCH_3 , 3H), 1.40-2.3 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H and CHCH_2 , 8H), 3.77 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 3.97 (s, CCH_3CH_2 , 4H), 4.04 (d, J = 11.5 Hz, CHCH_2 , 2H), 5.30 (d, J = 14 Hz, CHCH_2 , 2H), 6.95 (s, NCHCHN , 2H), 7.15 (s, NCHCHN , 2H), 7.26 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.70 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.75 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.50 (d, J = 4.8 Hz, $\text{C}_5\text{H}_4\text{N}$, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 293 K): δ 13.8, 18.8, 26.6, 30.0, 31.7, 44.7, 49.3, 59.5, 64.4, 66.5, 86.8, 88.9, 118.4, 121.7, 123.4, 127.2, 136.4, 147.8, 161.6, 180.9 (d, J = 62.5 Hz) ppm. HR-MS (ES), m/z = 590.2734 $[\text{M}]^+$ (calc. for $\text{C}_{31}\text{H}_{45}\text{N}_5\text{Rh}$: 590.2730).

Synthesis of 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine

Rhodium(I) cyclooctadiene Chloride, **8c**

Complex **8c** was prepared from 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5c**, (0.51 g, 1 mmol), $\text{KN}(\text{SiMe}_3)_2$ (0.4 g, 1 mmol) and

[Rh(COD)Cl]₂ (0.24 g, 0.5 mmol) according to the method for **8a**. A yellow solid was obtained in 55 % yield, 163 mg. ¹H NMR (500.1 MHz, CDCl₃, 293 K): δ 1.34 (s, CCH₃, 6H), 1.63-2.3 (m, CHCH₂, 8H), 4.2-4.6 (m, CCH₃CH₂, 4H, NCH₂CHCH₂, 4H and CHCH₂, 2H), 5.65 (d, *J*=14.2 Hz, NCH₂CHCH₂, 4H), 5.85 (m, CHCH₂, 2H), 6.90-7.45 (m, NCHCHN, 2H, C₅H₄N, 1H, NCHCHN, 2H), 7.86 (m, C₅H₄N, 2H), 8.59 (d, *J*=3.2 Hz, C₅H₄N, 1H) ppm. ¹³C{¹H} NMR (125.7 MHz, DMSO-d₆, 293 K): δ 13.2, 16.6, 23.6, 26.0, 28.5, 44.3, 59.2, 66.0, 87.4, 88.9, 119.4, 122.8, 123.5, 125.8, 126.7, 135.9, 147.0, 161.0, 183.1 (d, *J*= 75 Hz) ppm. HR-MS (ES), *m/z* = 558.2103 [M]⁺ (calc. for C₂₉H₃₇N₅Rh: 558.2104).

Synthesis of 2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine Iridium(I) cyclooctadiene Chloride, **9a**

2-(2-methyl-1,3-bis(3-methylimidazolidin-1-yl)propan-2-yl)pyridine bromide, **5a**, (0.457 g, 1 mmol) and KN(SiMe₃)₂ (0.4 g, 1 mmol) were placed into a Schlenk tube followed by the addition of THF (10 mL). The solution was stirred for 2 hours and subsequently filtered into another Schlenk tube containing a 10 mL THF solution of [Ir(COD)Cl]₂ (335 mg, 0.5 mmol). An immediate color change was observed from light orange to dark orange and after half an hour orange solid formed. The reaction mixture was stirred at room temperature for 2 h, and the volatiles were removed in vacuo. The yellow solid obtained was washed with cold hexane (2x10 mL) and dried under vacuum. Yield: 60 %, 178 mg. The complex was characterised by X-ray diffraction. ¹H NMR (500.1 MHz, CDCl₃, 293 K): δ 1.17 (s, CCH₃, 3H), 1.9-2.4 (m, CHCH₂, 8H), 3.36 (s, NCH₃, 6H), 3.95 (d, *J*= 4.5 Hz, CHCH₂, 2H), 4.1 (s, CCH₃CH₂, 4H), 5.4 (d, *J*= 14.5 Hz, CHCH₂, 2H), 7.02 (s, NCHCHN, 2H), 7.07 (s, NCHCHN, 2H), 7.27 (m, C₅H₄N, 1H), 7.61 (d, *J*= 8 Hz, C₅H₄N, 1H), 7.77 (t, *J*= 7.5 Hz, C₅H₄N, 1H), 8.58 (d, *J*= 1 Hz, C₅H₄N, 1H) ppm. ¹³C{¹H} NMR (125.7 MHz, CDCl₃, 293 K): δ 17.1, 24.6, 27.0, 30.3, 36.9, 45.7, 59.6, 67.0, 74.9, 76.6, 118.9, 121.2, 121.6, 123.4, 127.7, 136.7, 148.1, 162.2, 177.8 ppm. HR-MS (ES), *m/z* = 594.2350 [M]⁺ (calc. for C₂₅H₃₃N₅Ir: 594.2342).

Synthesis of 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine

Iridium(I) cyclooctadiene bromide, **9b**

Complex **9b** was prepared from 2-(1,3-bis(3-butylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5b**, (0.54 g, 1 mmol), $\text{KN}(\text{SiMe}_3)_2$ (0.4 g, 1 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.33 g, 0.5 mmol) according to the method of **9a**. Orange solid was obtained in 60 % yield, 200 mg. The complex was characterised by X-ray diffraction. ^1H NMR (400.1 MHz, CDCl_3 , 293 K): δ 0.99 (t, $J=6$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 6H), 1.15 (s, CCH_3 , 3H), 1.45-2.4 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 8H and CHCH_2 , 8H), 3.87 (m, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, 4H), 4.05 (s, CCH_3CH_2 , 4H), 4.1 (d, $J=12$ Hz, CHCH_2 , 2H), 5.36 (d, $J=14$ Hz, CHCH_2 , 2H), 7.0 (s, NCHCHN , 2H), 7.22 (s, NCHCHN , 2H), 7.27 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.78 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.8 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 8.55 (d, $J=4.4$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 293 K): δ 14.1, 18.7, 20.6, 30.1, 31.6, 31.8, 33.5, 47.1, 50.7, 61.0, 75.6, 77.7, 120.0, 120.9, 123.0, 125.7, 138.2, 149.3, 163.6, 178.2 ppm. HR-MS (ES), $m/z = 680.3282$ $[\text{M}]^+$ (calc. for $\text{C}_{31}\text{H}_{45}\text{N}_5\text{Ir}$: 680.3304).

Synthesis of 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine

Iridium(I) cyclooctadiene chloride, **9c**

Complex **9c** was prepared from 2-(1,3-bis(3-propenylimidazolidin-1-yl)-2-methylpropan-2-yl)pyridine bromide, **5c**, (0.51 g, 1 mmol), $\text{KN}(\text{SiMe}_3)_2$ (0.4 g, 1 mmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.33 g, 0.5 mmol) according to the general method for **9a**. Orange solid was obtained in 55 % yield, 180 mg. ^1H NMR (500.1 MHz, CDCl_3 , 293 K): δ 1.32 (s, CCH_3 , 6H), 1.63-2.3 (m, CHCH_2 , 8H), 4.0-4.22 (m, CCH_3CH_2 , 4H and $\text{NCH}_2\text{CHCH}_2$, 4H), 4.26 (d, $J=14.4$ Hz, $\text{NCH}_2\text{CHCH}_2$, 2H), 5.34 (d, $J=14.4$ Hz, $\text{NCH}_2\text{CHCH}_2$, 2H), 5.57 (m, CHCH_2 , 2H), 6.94 (d, $J=8$ Hz, CHCH_2 , 2H), 7.0 (s, NCHCHN , 2H), 7.27 (m, $\text{C}_5\text{H}_4\text{N}$, 1H), 7.44 (s, NCHCHN , 2H), 7.82 (m, $\text{C}_5\text{H}_4\text{N}$, 2H), 8.52 (d, $J=3.2$ Hz, $\text{C}_5\text{H}_4\text{N}$, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ (125.7 MHz, DMSO-d_6): δ 11.6, 17.4, 27.0, 30.2, 45.9, 59.9, 75.6, 75.7, 77.2, 118.8, 119.8, 121.6, 123.6, 125.7, 137.0, 147.7, 162.0, 179.4 ppm. HR-MS (ES), $m/z = 648.2676$ $[\text{M}]^+$ (calc. for $\text{C}_{31}\text{H}_{45}\text{N}_5\text{Ir}$: 648.2678).

Catalytic Transfer Hydrogenation

The Ir/Rh catalyst precursor (1, 0.3, 0.01 mol%) was dissolved in a solution of K^tBuO (10 mmol) in 2-propanol (5 mL) and substrate (1 mmol) in a Schlenk tube. The solution was heated to 80 °C for 30 minutes, the final conversion determined by ¹H NMR.

Reaction progress was monitored by ¹H NMR and GC-MS: aliquots (0.1 ml) were taken every 3 or 5 minutes for the first hour, and finally another two samples were taken after 2 hours. The samples were filtered through a short pad of silica, and the silica was washed with DCM (2 × 2 ml), and the sample subsequently analysed. Yields and substrate identities were determined by GC-MS analysis of reaction mixtures using an Agilent Technologies 6890N GC system with Agilent Technologies 5973 inert MS detector with MSD. Column: Agilent 190915-433 capillary, 0.25mm x 30 m x 0.25 µm. Initial temperature 50 °C, held for 4 minutes, ramp 5 °C/minute next 100 °C, ramp 10 °C/minute next 240 °C hold for 15 minutes. The temperature of the injector and detector were held at 240 °C. The retention times for analytes (minutes), e.g. 4-bromoacetophenone 18.3 and 1-(4-bromophenyl)ethanol 18.7.

Crystallographic studies

Crystal data and details of the structure determinations are listed in Table 3. Intensity data were collected at low temperature with an Enraf-Nonius Kappa CCD diffractometer. Data were corrected for air and detector absorption, Lorentz and polarisation effects, absorption by the crystal was treated with a semiempirical multi-scan method. The structures were solved by direct methods and refined by full-matrix least squares methods based on F^2 against all unique reflections (**8a**). Owing to unsatisfactory refinement, the structure of **9b** was refined against all data with $I > -5\sigma(I)$. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and were refined with the riding model.

Table 3 here

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Table 1: Selected bond lengths (Å) and angles (°) for **8a** and **9b**. Values in parentheses are for the crystallographically independent molecule.

	8a	9b
M(1) – C(1)	2.163(12)	2.168(9) [2.189(10)]
M(1) – C(2)	2.036(11)	2.185(9) [2.186(9)]
M(1) – C(5)	2.170(12)	2.182(9) [2.177(10)]
M(1) – C(6)	2.240(13)	2.185(9) [2.178(9)]
M(1) – C(17)	1.998(12)	2.033(9) [2.027(9)]
M(1) – C(21)	1.916(12)	2.059(9) [2.047(9)]
N(2) – C(17) – N(3)	106.7(9)	104.2(8) [104.9(7)]
N(4) – C(21) – N(5)	109.6(9)	104.7(7) [104.7(7)]
C(17) – M(1) – C(21)	85.1(4)	87.1(3) [84.7(3)]

Table 2. Results of Hydrogen Transfer Reactions

Entry	Catalyst	Substrate (1 mmol)	Catalyst Concentration (mol%)	Time (min)	Conversion %
1	9c	<i>p</i> -bromoacetophenone	0.3	30	100
2	9c	“	0.01	30	60
3	9b	“	0.3	30	100
4	9b	“	0.01	30	55
5	9a	“	0.3	30	100
6	9a	“	0.01	30	45
7	9c	<i>p</i> -methylacetophenone	0.3	60	100
8	9c	“	0.01	60	50
9	9b	“	0.3	60	100
10	9b	“	0.01	60	46
11	9a	“	0.3	60	80
12	9a	“	0.01	60	30
13	9c	cyclohexanone	0.3	30	100
14	9c	“	0.01	30	100
15	9b	“	0.3	30	100
16	9b	“	0.01	30	100
17	9a	“	0.3	30	100
18	9a	“	0.01	30	90
19	8a	<i>p</i> -bromoacetophenone	0.3	16 hours	100

Catalyst (0.3 mol%, 0.01 mol%), (substrate 1 mmol), ⁱPrOH (5 mL), KOBu^t (10 mol %), 80 °C, 0.5-1 h. Products were determined by NMR spectroscopy and yields are based on the corresponding aryl ketone or cyclo ketone.

Table 3 Details of the crystal structure determinations for **8a** and **9b**

	8a	9b
Empirical formula	C ₂₅ H ₃₃ ClN ₅ Rh	C ₃₁ H ₄₅ BrIrN ₅
<i>M_r</i>	541.93	759.86
<i>T</i> /K	150	150
<i>λ</i> /Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /a	P-1
<i>a</i> /Å	14.885(3)	14.109(3)
<i>b</i> /Å	13.167(3)	15.263(3)
<i>c</i> /Å	13.902(3)	16.214(3)
<i>α</i> /°	90	117.13(3)
<i>β</i> /°	115.41(3)	90.52(3)
<i>γ</i> /°	90	95.31(3)
<i>V</i> /Å ³	2461.1(11)	3088.9(14)
<i>Z</i>	4	4
<i>D_c</i> /mg m ⁻³	1.462	1.634
<i>μ</i> (MoKα)/mm ⁻¹	0.825	5.644
<i>F</i> ₀₀₀	1120	1512
Crystal dimensions/mm	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.05
<i>θ</i> range/°	8 – 21	4 – 26
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	-13 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 12 0 ≤ <i>l</i> ≤ 14	-17 ≤ <i>h</i> ≤ 17 -19 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 20
Reflections measured	3401	17730
Unique reflections [<i>R_{int}</i>]	2026 [0.054]	12416 [0.058]
Max, min trans.	0.96, 0.92	0.75, 0.57
Data/restraints/parameters	2024 / 0 / 289	12379 / 42 / 685
GOF on <i>F</i> ²	1.1528	0.9728
R indices [<i>F</i> > 4σ(<i>F</i>)] R(<i>F</i>), wR(<i>F</i> ²)	0.074, 0.134	0.062, 0.133
R indices (all data) R(<i>F</i>), wR(<i>F</i> ²)	0.093, 0.141	0.089, 0.146
Largest residual peak/e Å ⁻³	0.74, -0.84	2.31, -2.10

Scheme 1: Selected amido- and NHC- based scorpionate ligands

Scheme 2: Synthesis of the bis-imidazolium ligand precursors

Scheme 3: Synthesis of the Ag-bis-NHC complexes **6a-c**

Scheme 4: Synthesis of transition metal complexes of the bis-imidazole ligands

Figure 1: Molecular structure of $[\text{Rh}(\text{NC}_2^{\text{Me}})(\text{COD})]\text{Cl}$ (**8a**). H atoms and anion omitted for clarity, thermal ellipsoids are drawn at 25% probability

Figure 2: Molecular structure of $[\text{Ir}(\text{NC}_2^{\text{Bu}})(\text{COD})]\text{Br}$ (**9b**). H atoms, the second crystallographically independent molecule, and anion omitted for clarity, thermal ellipsoids are drawn at 25% probability

Figure 3: Plot of conversion versus time for *p*-bromoacetophenone (1 mmol) catalysed by **9c** (0.3 mol%)

Figure 4: Plot of conversion versus time for *p*-methylacetophenone (1 mmol) catalysed by **9c** (0.3 mol%)

Figure 5. Lifetime studies for catalyst **9c** (0.3 mol%) with *p*-bromocetophenone as substrate