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N-Heterocyclic Carbenes

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Westfälische Wilhelms-Universität, Münster, Germany

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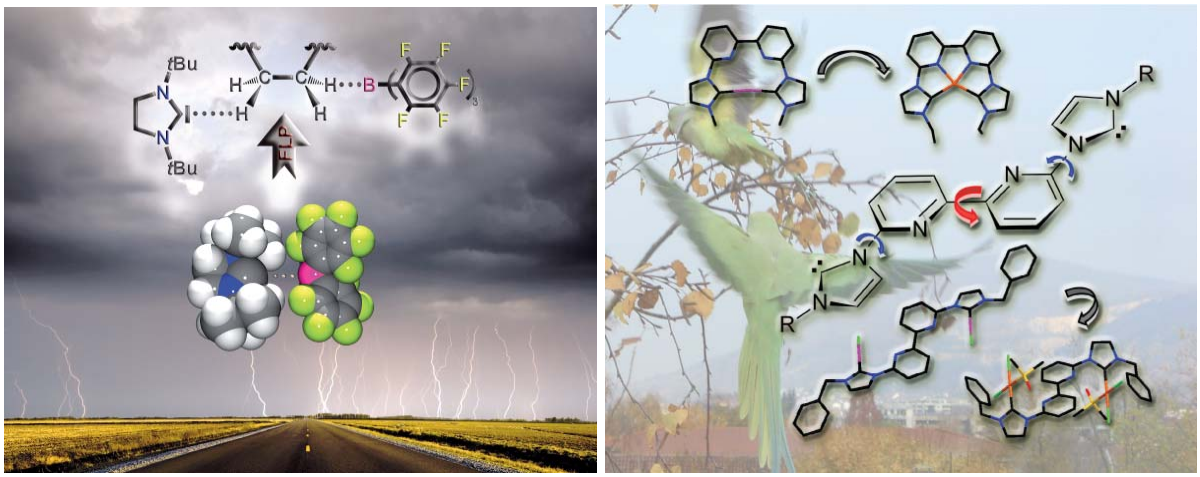

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Synthesis of rhodium(I) and iridium(I) complexes of chiral *N*-heterocyclic carbenes and their application to asymmetric transfer hydrogenation†

Gavin Dyson, Jean-Cédric Frison, Adrian C. Whitwood and Richard E. Douthwaite*

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Rhodium and iridium complexes of chiral NHC–phenolimine and NHC–amine ligands have been prepared and studied for asymmetric transfer hydrogenation. X-ray and NMR spectroscopy show that for NHC–phenolimine complexes abstraction of chloride results in a change in ligand coordination from NHC only to chelating NHC–imine. Complexes of NHC–amines are inactive for transfer hydrogenation, whereas complexes of NHC–phenolimines are active at room temperature for a range of aryl containing ketones. Enantioselectivity is very sensitive to the NHC *N*-substituent resulting in a switch in the predominant enantiomer.

Introduction

The chemistry of *N*-heterocyclic carbenes (NHCs) has developed significantly over recent years encompassing their synthesis, reactivity, coordination chemistry and application.[1–7] Arguably, the most significant stimulus for continued interest is the catalytic application to organo- and metal-mediated catalysis and there is now ample evidence demonstrating that NHC systems can lead to new reactivity and improved catalytic rate, lifetime and selectivity. Of the many reactions that have been investigated using NHC containing catalysts, hydrogenation and transfer hydrogenation have featured prominently, which is in part due to their wide ranging use in synthetic chemistry and continued industrial importance.

Whilst direct hydrogenation of unsaturated molecules is more widely applied, transfer hydrogenation is an attractive alternative because the use of a potentially dangerous high pressure of hydrogen is avoided, the protocols are simple and mild, and the reaction can be highly chemo- and enantioselective. In NHC chemistry transfer hydrogenation has been described for ruthenium,[8–20] rhodium,[21–26] iridium,[23,24,27–38] osmium[39] nickel[40] and palladium[41] precatalysts for the reduction of carbonyl, imine and nitro functionalities. NHC based ligands which have been investigated include mono-NHC, and chelating di-NHC and hybrid examples. Whilst excellent rates have been reported for NHC catalysts, a notable underdeveloped area is asymmetric transfer hydrogenation. There are very few reports describing catalytic asymmetric transfer hydrogenation using NHC catalysts and the enantioselectivities obtained to date are poor.[17,26,29,37,42] This is in contrast to hydrogenation with dihydrogen where chiral NHC containing catalysts can exhibit excellent enantioselectivities even for challenging substrates including unfunctionalised tri-substituted alkenes.[43–47]

Established asymmetric transfer hydrogenation catalysts are predominantly complexes of Ru, Rh or Ir that operate *via* a transition metal hydride or dihydride intermediate and may incorporate a coordinated NH functionality, which mediates protonation in a formal heterolytic H^+/H^- transfer from the donor to a substrate.[48,49] However, non-NH containing catalysts can also exhibit excellent activity and enantioselectivity.[50]

Previously we have reported the synthesis of imidazolium salt precursors to chiral NHC ligands derived from 1,2-diaminocyclohexane (Fig. 1) and subsequently prepared examples of transition metal complexes.[51–53] Palladium complexes incorporating an NHC–imine ligand gave a maximum enantiomeric excess (ee) of up to 92% for asymmetric allylic substitution[52] and iridium complexes of the NHC–phosphine and NHC–phosphite ligands were shown to be less successful for the asymmetric transfer hydrogenation of acetophenone, with a maximum ee of 38%.[29]

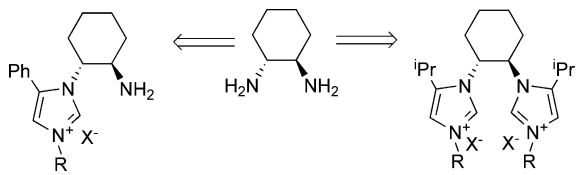


Fig. 1 Chiral imidazolium salt ligands derived from 1,2-diaminocyclohexane.

Here we report the synthesis of iridium NHC–phenoxyimine and rhodium and iridium NHC–amine complexes and investigate their catalytic application to enantioselective transfer hydrogenation. One motivation was to examine if the presence of a proximal alcohol or amine group in the NHC–hybrid complexes has a positive effect on enantioselectivity by mediating proton transfer to a substrate.

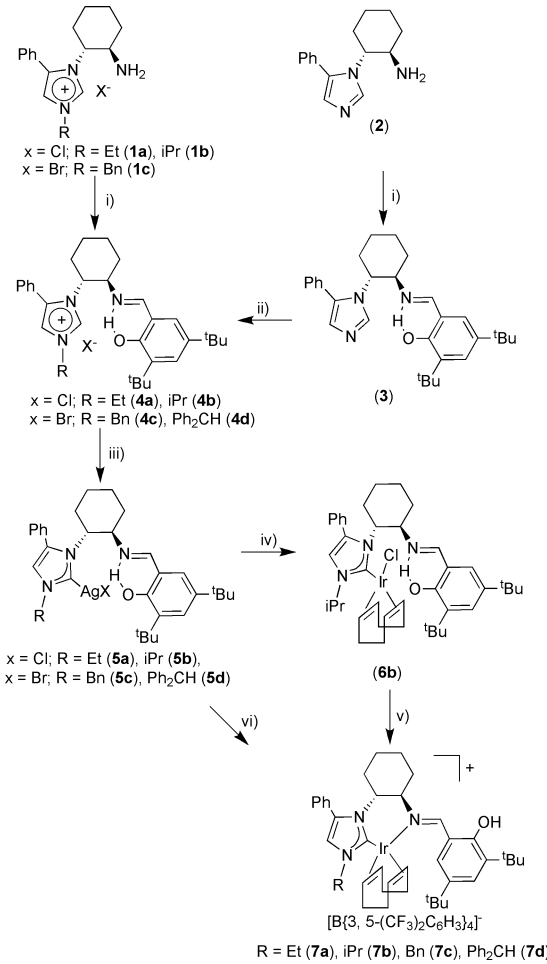
Results and discussion

Ligand and complex synthesis

The synthesis of two classes of hybrid NHC ligands and their metal complex derivatives are presented. Scheme 1 shows the synthetic route to chiral NHC–phenolimine ligands containing a Schiff base moiety analogous to the Salen class of ligands successfully used in several classes of enantioselective reactions.[54–59] We have recently

Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: red4@york.ac.uk; Fax: +44 (0)1904 434183

† CCDC reference numbers 731703–731706. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b909290k

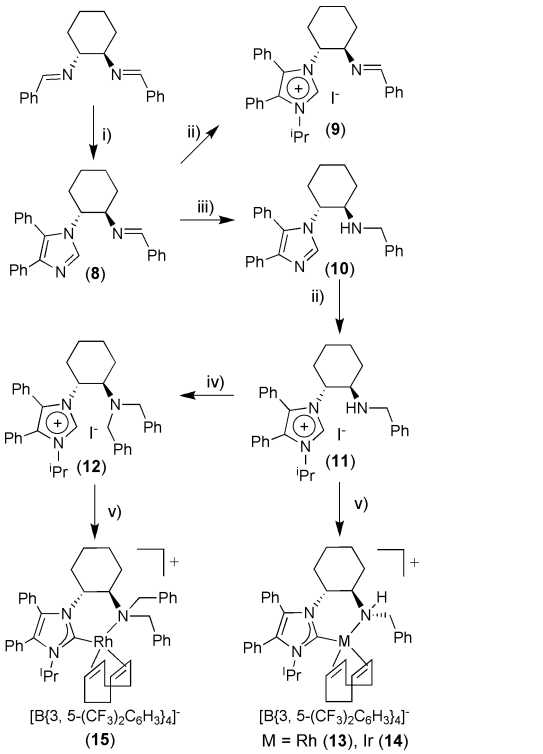


Scheme 1 Preparation of ligand precursors and silver(I) and iridium(I) complexes of NHC–phenolimines. Reaction conditions (i) 2-hydroxy-3,5-*t*-butyl benzaldehyde, EtOH, 80 °C; (ii) $BrC(H)Ph_2$, MeCN, 80 °C; (iii) Ag_2O, CH_2Cl_2, 25 °C; (iv) $[Ir(COD)Cl]_2$, CH_2Cl_2, 25 °C; (v) $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, CH_2Cl_2, 25 °C; (vi) $[Ir(COD)Cl]_2$, $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, CH_2Cl_2, 25 °C.

reported one example of a rhodium(I) complex derivative[53] of this class of ligand and here expand the synthetic chemistry to access new derivatives and a series of iridium(I) complexes. Scheme 2 shows the synthesis of a new class of ligand comprising an NHC and either a secondary or tertiary amine moiety. Imidazolium precursors have been prepared that do not contain C–H bonds in the C4 or C5 positions, in part, to avoid metal activation at these positions[60–66] and to possibly modify the conformation of the *N*-substituent in the resulting metal complex catalysts.

NHC–phenolimines

Imidazolium-amine (**1a–c**) and imidazole-amine (**2**) (Scheme 1) can serve as precursors to a range of NHC containing ligands *via* modification at the amine and imidazole moieties respectively,[29,51–53,67,68] and the synthesis of compounds **3** and **4** occurs in high yield. However, the close proximity of an imidazolium moiety appears to significantly attenuate the amine reactivity. For example compound **4d** could not be prepared from the $CHPh_2$ *N*-substituted analogue **1d** (not shown in Scheme 1) using the analogous method for **1a–c**. However, **4d**



Scheme 2 Preparation of ligand precursors and rhodium and iridium complexes of NHC–amines. Reaction conditions (i) 1-(isocyano-phenyl-methanesulfonyl)-4-methylbenzene, K_2CO_3, MeCN, 60 °C; (ii) $(CH_3)_2C(H)$ I, reflux; (iii) $NaBH_4$, MeOH, 0–25 °C; (iv) $PhCH_2Br$, K_2CO_3, MeCN, 80 °C; (v) **13** and **15** $[Rh(COD)Cl]_2$, KO*t*Bu, THF, $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, −78 to 25 °C. **14** $[Ir(COD)Cl]_2$, Ag_2O, THF, $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, 25 °C.

was synthesised from **2** *via* initial formation of the imine bond to give **3** followed by subsequent imidazolium salt synthesis. It was initially suspected that **1a–d** may exhibit intramolecular hydrogen bonding to account for the modified amine reactivity, however a single crystal diffraction study of a $[BPh_4]^-$ derivative of **1b** does not indicate any unusual features.‡ Unusually for imidazolium salt derivatives, compounds **4a–d** are very soluble in both polar and non-polar solvents with significant insolubility exhibited only in saturated hydrocarbons. All spectroscopic data is consistent with the formulations of **4a–d** and all exhibit a signal at *ca.* 13 ppm in the ^1H NMR spectrum characteristic of hydrogen bonding between the phenol and imine moiety.[69,70] Iridium(I) complex derivatives of ligand precursors **4a–d** are most readily accessed *via* silver(I) complexes **5a–d** that are prepared straightforwardly from reaction between **4a–d** and Ag_2O. Attempts to prepare free carbenes or imidazolium-phenoxide compounds *via* deprotonation using a variety of bases results in intramolecular cyclisation between NHC and imine.[71]

The ^1H NMR spectra of **5a–d** all exhibit a signal at *ca.* 13 ppm indicating that the phenol O*H* hydrogen atom is retained. Heating solutions of **5a–d** did not result in a loss of hydrogen halide to give a clean product as judged by ^1H NMR and addition of bases NEt_3, NaOH and BuLi led to insoluble products or decomposition. Reaction between **5b** and $[Ir(COD)Cl]_2$ (where COD = cyclo-1,4-diene) gives **6b** in high yield that undergoes chloride abstraction on addition of $Na[[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ to

give **7b** (Scheme 1). Alternatively **7a–d** can be prepared directly from **5a–d**, $[Ir(COD)Cl]_2$ and $Na[[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ in a single-pot reaction. Complex **6b** is an air and water stable solid, soluble in organic and chlorinated solvents and exhibits similar ^1H NMR spectroscopic signals as **5b** including a signal at 13.88 ppm for the O*H* proton. A characteristic signal at 181.2 ppm is observed in the ^{13}C NMR spectrum for the carbene carbon atom.

The molecular structure of **6b** was confirmed by a single crystal X-ray diffraction study and is shown in Fig. 2 with select data given in Table 1.‡§

Unfortunately single crystals of **7a–d** could not be grown, however NMR spectroscopy clearly indicates coordination of the imine moiety as exemplified by **7b**. In the ^1H NMR spectrum the O*H* hydrogen atom is observed at 6.32 ppm for **7b** that is typical for phenolic O*H* not participating in hydrogen bonding. In addition, the cyclohexyl hydrogen atom adjacent to the NHC moiety $^{c\text{-hex}}CH_{NHC}$ at 5.82 ppm is upfield by *ca.* 1.7 ppm with respect to **4–6b**.[53] This observation is consistent with previous work where metallocycle formation causes the $^{c\text{-hex}}CH_{NHC}$ proton to be projected into the vicinity of the metal atom resulting in a significant upfield shift.[52]

Table 1 Selected bond lengths (Å) and angles (°) for complexes **7b** and **13**

Complex **7b**			
Ir(1)–C(1)	2.059(2)	C(1)–Ir(1)–Cl(1)	92.76(5)
Ir(1)–Cl(5)	2.3635(5)	C(1)–Ir(1)–C(34)	91.06(8)
Ir(1)–C(34)	2.087(2)	C(1)–Ir(1)–C(39)	165.85(9)
Ir(1)–C(35)	2.120(2)	Cl(5)–Ir(1)–C(34)	152.13(7)
Ir(1)–C(38)	2.169(2)	Cl(5)–Ir(1)–C(39)	89.04(7)
Ir(1)–C(39)	2.203(2)		
C(34)–C(35)	1.413(3)		
C(38)–C(39)	1.391(4)		

Complex **13**			
Rh(1)–C(11)	2.025(8)	C(11)–Rh(1)–N(3)	81.6(3)
Rh(1)–N(3)	2.206(7)	C(1)–Rh(1)–C(l1)	99.9(4)
Rh(1)–C(1)	2.143(9)	C(11)–Rh(1)–C(6)	162.9(4)
Rh(1)–C(2)	2.072(11)	C(1)–Rh(1)–N(3)	176.5(4)
Rh(1)–C(5)	2.244(9)	C(6)–Rh(1)–N(3)	96.5(4)
Rh(1)–C(6)	2.168(9)	C(17)–N(3)–C(18)	113.0(7)
C(1)–C(2)	1.397(16)	C(17)–N(3)–Rh(1)	111.6(6)
C(5)–C(6)	1.345(16)	C(18)–N(3)–Rh(1)	113.5(5)

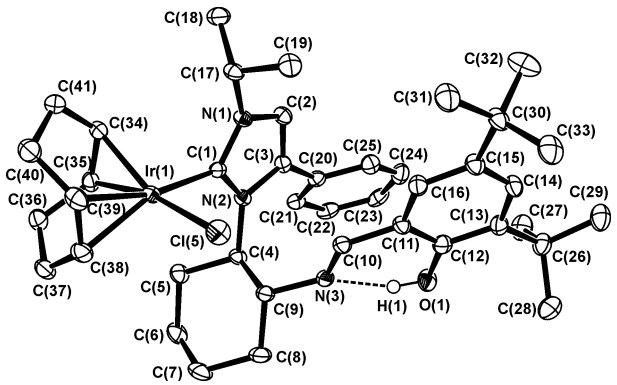


Fig. 2 Molecular structure of **6b**. Displacement ellipsoids are set at 50% probability. Hydrogen atoms except for H(1) have been omitted for clarity.

NHC–amines

Although hybrid NHC–amine ligands are an obvious target for ligand design there are relatively few structurally characterised examples of their complexes,[22,51,67,80–86] and there are reports in the literature to suggest NHC–amines are prone to decomposition.[86–89] It has also been shown that NHC ligands derived from imidazolium salts can result in metal–C bond formation *via* C–H activation at the C4 or C5 position giving abnormal carbenes.[60–66] To limit metal–C bond formation to C2, and potentially increase the kinetic stability of NHC–amine ligands compound **8** was prepared as a precursor to a new class of NHC–amine ligands. Reaction between phenylsubstituted tosylmethylisocyanide (Ph-TosMIC) and the dimine (1*R*,2*R*)-*N*,*N*'-bis-[1-phenyl-meth-(*E*)-ylidene]-cyclohexane-1,2-diamine gave compound **8** in good yield (Scheme 2).

Substitution at both C4 and C5 retards imidazolium salt formation and reactions between **8** and hydrocarbyl chlorides and bromides did not yield the corresponding imidazolium

‡ Crystallographic data for **1b**: Colourless crystals, $C_{102}H_{128}B_2N_6$, dimensions 0.30 × 0.20 × 0.20 mm; M_r = 1459.72; Monoclinic $P2_1$, a = 19.5255(14), b = 10.9535(8), c = 21.0834(15) Å, β = 114.9760(10)°, V = 4087.5(5) Å^3, Z = 2, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.186 g cm^{-3}, T = 110(2) K, $F(000)$ = 1584, θ range for data collection 2.19 to 27.98°, limiting indices $-26 \le h \le 25$, $-14 \le k \le 14$, $-28 \le l \le 28$, 42956/16572 collected/unique reflections (R(int) = 0.0244), absolute structure parameter 1(3), goodness of fit on F^2 = 1.015, $\Delta\rho_{max/min}$ = 1.480/–0.714 e Å^{-3}, final R indices ($I > 2\sigma(I)$) $R1$ = 0.0882, $wR2$ = 0.2570. The structure was solved using SHELXS-97 and refined using SHELXL-97.[103] Crystallographic data for **6b**: Yellow crystals, $C_{41}H_{57}ClN_3OIr$, dimensions 0.26 × 0.09 × 0.09 mm; M_r = 835.55; Orthorhombic $P2_12_12_1$, a = 12.7958(7), b = 16.4449(9), c = 18.4264(10) Å, V = 3877.4(4) Å^3, Z = 4, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.431 g cm^{-3}, T = 110(2) K, $F(000)$ = 1704, θ range for data collection 2.30 to 29.92°, limiting indices $-18 \le h \le 17$, $-23 \le k \le 22$, $-25 \le l \le 25$, 58607/10675 collected/unique reflections (R(int) = 0.0317), absolute structure parameter –0.009(3), goodness of fit on F^2 = 0.973, $\Delta\rho_{max/min}$ = 1.163/–0.299 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0186, $wR2$ = 0.0374. The structure was solved using SHELXS-97 and refined using SHELXL-97.[103] Crystallographic data for **9**: Colourless crystals, $C_{31}H_{34}IN_3$, dimensions 0.28 × 0.22 × 0.06 mm; M_r = 575.51; Orthorhombic $P2_12_12_1$, a = 9.3749(6), b = 11.8875(8), c = 51.257(4) Å, V = 5712.3(7) Å^3, Z = 8, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.338 g cm^{-3}, T = 110(2) K, $F(000)$ = 2352, θ range for data collection 2.31 to 24.94°, limiting indices $-11 \le h \le 11$, $-13 \le k \le 14$, $-60 \le l \le 60$, 44449/9414 collected/unique reflections (R(int) = 0.0440), absolute structure parameter 0.001(18), goodness of fit on F^2 = 1.244, $\Delta\rho_{max/min}$ = 0.866/–1.397 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0444, $wR2$ = 0.0884. The structure was solved using SHELXS-97 and refined using SHELXL-97.[103] Crystallographic data for **13**: Yellow crystals, $C_{152.5}H_{128}B_2F_{48}N_6Rh_2$, dimensions 0.38 × 0.18 × 0.10 mm; M_r = 3186.07; Orthorhombic $P2_12_12_1$, a = 13.297(3), b = 13.558(3), c = 80.440(16) Å, V = 14501(5) Å^3, Z = 4, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, ρ_{calc} = 1.459 g cm^{-3}, T = 110(2) K, $F(000)$ = 6476, θ range for data collection 1.81 to 22.55°, limiting indices $-14 \le h \le 14$, $-14 \le k \le 14$, $-86 \le l \le 86$, 104979/19029 collected/unique reflections (R(int) = 0.0495), absolute structure parameter 0.06(3), goodness of fit on F^2 = 1.205, $\Delta\rho_{max/min}$ = 0.975/–0.989 e Å^{-3}, final *R indices* ($I > 2\sigma(I)$) $R1$ = 0.0696, $wR2$ = 0.1611. The structure was solved using SHELXS-97 and refined using SHELXL-97.[103]

§ A distorted square planar geometry is observed at the iridium atom, if the COD ligand is considered as occupying two coordination sites, with the Ir–C_{NHC} distance (C(1)–Ir(1) 2.059(2) Å) similar to related iridium NHC complexes.[27,35,72–78] It is clear from the ligand conformation that the phenolimine moiety does not interact with the iridium atom and that the hydrogen bonding is retained between the phenol and imine group. The hydrogen atom was found in a difference map and bond lengths and angles clearly suggest a phenolimine and not the potential amine-one tautomer.[79]

salts in acceptable yield. Addition to the imidazole moiety of **8** can occur using neat isopropyl iodide giving compound **9**, however subsequent reduction chemistry of the imine group was problematic. NHC secondary/tertiary amine ligand precursors are most conveniently prepared *via* reduction of an imidazole imine and subsequent selective addition of a hydrocarbyl iodide or bromide. Borohydride reduction of **8** gives compound **10** that undergoes addition of isopropyl iodide exclusively at the imidazole moiety giving **11**. Reaction between **11** and benzyl bromide gives the tertiary amine **12** in 92% yield with no indication of quaternary ammonium salt formation. NMR spectroscopy of compounds **10** and **11** are consistent with a either a single diastereomer or rapid inversion at the secondary amine nitrogen atom. Variable temperature ^{1}H NMR spectroscopy of **11** in CD_2Cl_2 down to 160 K did not show any significant changes in chemical shift or the number of signals.

The preparation of iridium(I) and rhodium(I) transition metal complexes derived from **11** and **12** is shown in Scheme 2. Rhodium complexes **13** and **15** were synthesised in a one pot reaction from successive addition of $[Rh(COD)Cl]_2$, KO^{t}Bu, **11**(or **12**) in THF, followed by $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ and work-up with column chromatography to give **13** and **15** in 76 and 68% yield respectively. Iridium complex **14** was prepared *via* a putative intermediate silver(I) NHC complex salt in a similar procedure to **13** and **15** to give complex **14** in 54% yield. Frustratingly, the iridium analogue of **15** resisted attempts at purification.

NMR spectroscopy of complex **13** shows the number of signals consistent with a single diastereoisomer including a doublet at 176.5 ppm in the ^{13}C NMR spectrum assigned to the rhodium-coupled carbene atom and four other rhodium-coupled doublets assigned to the coordinating COD carbon atoms. The amine N*H* atom could not be unambiguously assigned but fortunately a single crystal structure could be obtained. The molecular structure is shown in Fig. 3 and select data are provided in Table 1.‡§ The amine nitrogen atom has an *S*-configuration that can be understood on the basis of minimising non-covalent interactions between the benzyl and cyclohexylamine substituents. A pseudo square planar geometry is observed at the rhodium atom with Rh–C bond lengths similar to other cationic Rh–NHC complexes containing a COD co-ligand[72,90–97] and a Rh–N bond

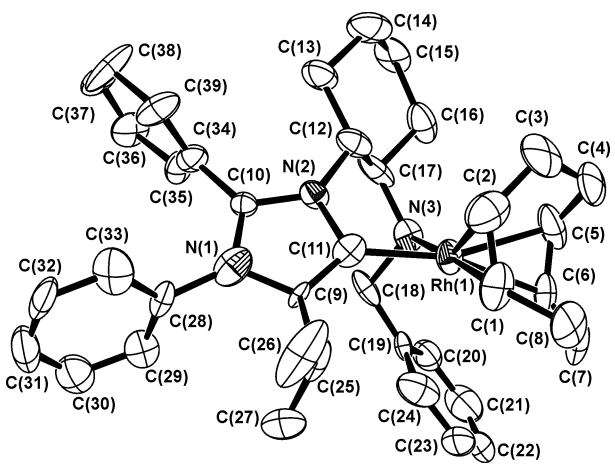


Fig. 3 Molecular structure of **13**. Displacement ellipsoids are set at 50% probability. Hydrogen atoms have been omitted for clarity.

(Rh(1)–N(3) = 2.206(7) Å) similar to the only other rhodium complex containing an NHC–amine ligand.[22] The metallocycle exhibits a boat-like conformation, with the NHC phenyl substituents orientated perpendicular to the NHC plane, and the isopropyl substituent appears to be orientated to minimise non-covalent interactions with the COD co-ligand.

The iridium complex **14** that is the analogue of **13** again exhibits in the ^{1}H and ^{13}C NMR spectra the number of signals expected for a single diastereoisomer with chemical shifts similar to **13**. For example in the ^{13}C NMR spectrum a single carbene signal at 173.7 ppm is observed and in the ^{1}H NMR spectrum two doublets for the diastereotopic isopropyl methyl groups, which have previously been shown to be sensitive to the stereochemistry in this class of ligand.[71] It is therefore assumed that the stereochemistry of **14** is analogous to **13** with an *RRS* configuration.

Complex **15** exhibits a doublet carbene signal in the ^{13}C spectrum at 173.5 ppm in addition to four other doublets attributable to the carbon atoms of the COD ligand. The most notable feature of the ^{1}H and ^{13}C signals are those due to the benzyl CH_2 group that are observed as a broad singlet at 3.47 and 51.2 ppm respectively. A signal attributable to $^{c\text{-hex}}CH_{NHC}$ is also observed at 3.89 ppm which is in contrast to complexes **13** and **14** where the corresponding signal is observed *ca.* 1.5 ppm further upfield. Collectively these data suggest that in $CDCl_3$ solution the amine group is not fully coordinated to the rhodium atom and is labile. Elemental analysis is consistent with the proposed formulation shown in Scheme 2 indicating that there is no additional ligand, but a single crystal structure has yet to be obtained.

Catalytic transfer hydrogenation

Initial test reactions using Rh and Ir NHC–amines **13–15** precatalysts for the transfer hydrogenation between acetophenone and 2-propanol at 20 °C and at reflux (80 °C) gave no enantioselectivity and very slow rates. These findings are analogous to those found for the only other related study using Rh NHC–imines and are consistent with the formation of colloidal rhodium metal.[22] It was also found that a rhodium analogue of **7b** exhibits significantly lower activity and enantioselectivity and therefore the current study was restricted to iridium complexes. Slower catalytic rates of transfer hydrogenation for NHC–rhodium in comparison to NHC–iridium catalysts has been noted previously.[28]

Complexes **7a–d** are precatalysts for transfer hydrogenation as shown in Tables 2 and 3. Reaction at 20 °C allowed differentiation of the activity between the precatalysts, whereas with acetophenone, reactions conducted at 80 °C gave products in > 95% yield within 1 h (Table 2, entries 5, 7, 9 and 11). A *ca.* 5% reduction in enantioselectivity was observed for reactions at 80 °C in comparison to those conducted at 20 °C. A previous study using chiral NHC–phosphine ligands has shown a similar reduction in enantioselectivity at 80 °C when comparing reaction times of 1 and 5 h respectively.[29]

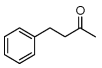
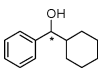
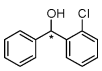
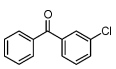
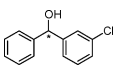
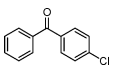
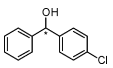
Table 2 shows data for the asymmetric transfer hydrogenation of acetophenone derivatives. Catalysis usually requires a base and hydroxide or alkoxide are the most commonly used. Entries 1–4 show that alkoxide, KO*t*Bu, gives the greatest yield and enantioselectivity with a small drop in enantioselectivity at extended reaction times. In the absence of a base or in the presence of $HCOOH/NEt_3$ the reaction rate is very low. Entries 3–11 show

Table 2 Asymmetric transfer hydrogenation of acetophenone and derivatives[a]

Entry	Precat.	R	Base	Yield (%)[b]	ee (%)[c]
1	**7b**	H	KOH	38	32(*S*)
2[d]	**7b**	H	KOH	72	28(*S*)
3	**7b**	H	KO*t*Bu	72	43(*S*)
4[d]	**7b**	H	KO*t*Bu	94	41(*S*)
5[e]	**7b**	H	KO*t*Bu	99	41(*S*)
6	**7a**	H	KO*t*Bu	64	0
7[e]	**7a**	H	KO*t*Bu	97	0
8	**7c**	H	KO*t*Bu	83	33(*S*)
9[e]	**7c**	H	KO*t*Bu	99	27(*S*)
10	**7d**	H	KO*t*Bu	21	41(*R*)
11[e]	**7d**	H	KO*t*Bu	95	36(*R*)
12	**7b**	2-Me	KO*t*Bu	18	10(*S*)
13	**7b**	3-Me	KO*t*Bu	83	36(*S*)
14	**7b**	4-Me	KO*t*Bu	39	31(*S*)
15	**7b**	3-OMe	KO*t*Bu	57	47(*S*)
16	**7b**	2-Cl	KO*t*Bu	18	12(*S*)
17	**7b**	3-Cl	KO*t*Bu	31	56(*S*)
18	**7b**	4-Cl	KO*t*Bu	47	22(*S*)

[a] 0.5 mol% **7**, 2 mol% base, 2 mL 2-propanol, 20 °C, 20 h; [b] Determined by ^{1}H NMR; [c] Determined by chiral HPLC; [d] 30 h; [e] 1 h, 80 °C.

Table 3 Asymmetric transfer hydrogenation of aryl ketones[a]

Entry	Substrate	Product	Yield(%)[b]	ee(%)[c]
1			64	41(*S*)
2			61	4(*S*)
3			0	0
4			0	0
5			0	0
6			42	23(*S*)
7			53	6(*R*)
8			68	3(*S*)

[a] 0.5 mol% **7b**, 2 mol% KO*t*Bu, 2 mL 2-propanol, 20 °C, 20 h; [b] Determined by ^{1}H NMR; [c] Determined by chiral HPLC.

the effect of modifying the NHC *N*-substituent indicating that the rate and particularly the enantioselectivity are very sensitive to changes at this position. Particularly noteworthy are the lack of significant enantioselectivity for **7a** (entries 6 and 7) and the inversion of stereochemistry observed for **7d** (entries 10 and 11). Complex **7d** also shows significantly lower activity in comparison to **7a–c**. Subsequent reactions were conducted using **7b** because **7b** exhibited the best overall performance.

Electron donating (entries 12–15) and withdrawing (entries 16–18) substituents on the phenyl ring modify yield and enantioselectivity. Groups *ortho* to the carbonyl (entries 12 and 16) gave significantly lower yield than substitution at the 3- or 4-position. All reactions resulted in predominant formation of the *S*-enantiomer where the 3-Cl substituent gives the highest ee of 56%. Although this is certainly modest with respect to what can be achieved using well developed transfer hydrogenation catalysts, this represents the highest ee to date for a transfer hydrogenation catalyst incorporating a chiral NHC ligand.

Table 3 shows catalytic transfer hydrogenation of a range of aryl containing ketones. It is clear from entries 3–4 that purely alkyl substituents possessing β-hydrogens are not amenable to transfer hydrogenation, whereas the presence of an aryl substituent (entry 2) allows reaction, although the enantioselectivity is significantly poorer than for aryl ketones (Table 2). Acetonaphthone (entry 1) gives the same ee as acetophenone although the yield is lower, presumably due to increased substrate bulk. Entries 6–7 show that biaryl ketones will undergo transfer hydrogenation and in contrast to the acetophenone derivatives (Table 2, entries 12–14) the 2-chloro derivative gives a comparable yield and the highest ee.

Conclusions

Asymmetric transfer hydrogenation using chiral NHC complexes remains a challenge. The mechanism of transfer hydrogenation is complex[48,49] and therefore it is difficult to correlate metal precatalyst structure with activity and enantioselectivity, however some broad features can be extracted. Clearly the development of NHC–amines for transfer hydrogenation does not appear to be promising given the results shown here and reported elsewhere.[22] Iridium NHC complexes are superior catalysts to their rhodium analogues for transfer hydrogenation and the enantioselectivity is very sensitive to the NHC *N*-substituent. At least a secondary substituent is required as evidenced by the lack of enantioselectivity for the ethyl substituted complex **7a** (Table 1 entry 5). The switch in the predominant isomer on introduction of a second aryl group (compare entries 6 and 7 in Table 1) would suggest aryl–substrate or aryl–alkoxide interactions are important. Noyori has shown for ruthenium based catalysts the importance of CH–π interactions for inducing high levels of enantioselectivity[98] that may also be operative here.

Experimental

General procedures

All manipulations were performed under argon using standard Schlenk techniques unless stated otherwise. All solvents were dried over the appropriate drying agent and distilled under dinitrogen according to literature methods.[99] Reagents were purchased from Aldrich, Acros or Lancaster and used as supplied. $[M(COD)Cl]_2$ (where M = Rh[100] and Ir[101]) and $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[102] were prepared using literature procedures. The synthesis of precursors **1b**[52] **2**[29] and **4b**[53] has been reported previously.

NMR spectra were recorded at probe temperature on a Jeol EX 270 (^{1}H, 270 MHz; ^{13}C, 67.9 MHz), Brüker AMX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) and Brüker AV-500 (^{1}H, 500 MHz; ^{13}C, 126 MHz); respectively. Chemical shifts are described in parts per million downfield shifted from SiMe4 and are reported consecutively as position (δH or δC), relative integral, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br = broad), coupling constant (J/Hz) and assignment. Proton NMR spectra were referenced to the chemical shift of residual proton signals ($CHCl_3$ δ 7.27, and C_6D_5H δ 7.16). Carbon spectra were referenced to a ^{13}C resonance of the solvent ($CDCl_3$ δ 77.16 and C_6D_6 δ 128.06). ^{13}C HSQC, PENDANT and Gradient HMBC experiments were performed using standard Brüker pulse sequences.

Mass spectra were recorded on VG 70-250E or Kratos MS-50 spectrometers. Electrospray (ES) was recorded using methanol or acetonitrile as the mobile phase. Major fragments were given as percentages of the base peak intensity (100%). Elemental analyses were performed at the University of North London.

2,4-Di-*tert*-butyl-6-{[(*E*)-(1*R*,2*R*)-2-(5-phenyl-imidazol-1-yl)-cyclohexylimino]-methyl}-phenol [C(H)N^{CHAr}] (3)

An ethanol solution (50 mL) of (1*R*,2*R*)-2-(5-phenyl-imidazol-1-yl)-cyclohexylamine (1.500 g, 6.22 mmol) and 3,5-di-*tert*-butyl 2-hydroxybenzaldehyde (2.18 g, 9.33 mmol) containing 4 Å molecular sieves (1.00 g) was heated at reflux for 16 h in a thick walled ampoule sealed with a Teflon stopcock. On cooling to 25 °C the mixture was filtered and the volatiles removed from the filtrate under reduced pressure and the resulting solid purified by flash chromatography on silica gel. The 1st band (3,5-di-*tert*-butyl 2-hydroxybenzaldehyde) was eluted with dichloromethane, the 2nd band (**3**) was eluted with 50:50 dichloromethane:ethyl acetate and the volatiles removed from the second band under reduced pressure to give **3** as an orange solid. Yield = 1.68 g, 60%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ = 1.25 (9 H, s, C(CH_3)$_3$), 1.41 (9 H, s, C(CH_3)$_3$), 1.87–2.23 (8 H, m, $^{c\text{-hex}}$CH_2), 3.36 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.08 (1 H, m, $^{c\text{-hex}}$CH_{imid}), 6.81 (1 H, s, NCHCPh), 6.87–7.39 (7 H, m, ^{Ph}CH), 7.71 (NCHN), 7.91 (1 H, s, ^{imine}CH). ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ = 24.0 ($^{c\text{-hex}}$CH_2), 25.2 ($^{c\text{-hex}}$CH_2), 29.4 (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 33.7 ($^{c\text{-hex}}$CH_2), 34.1 ($^{c\text{-hex}}$CH_2), 34.1 (C(CH$_3$)$_3$), 34.0 (C(CH$_3$)$_3$), 58.5 ($^{c\text{-hex}}$CH_{imid}), 74.1 ($^{c\text{-hex}}$CH_{imine}), 117.4 (NCHCPh), 126.2 (NCHCPh), 127.2, 128.1, 128.5, 129.7 (^{Ph}CH), 134.0, 134.3 (^{Ph}C$_{ipso}$), 136.3 (NCHN), 140.1 (^{Ph}C$_{ipso}$), 157.6 (COH), 165.7 (^{imine}CH); MS (ESI), m/z 458.3 ([M + H]$^+$) 100%; HRMS calc. for $C_{30}H_{40}N_3O$, 458.3171, found 458.3166.

3-((1*R*,2*R*)-2-{[1-(3,5-Di-*tert*-butyl-2-hydroxy-phenyl)-meth-(*E*)-ylidene]-amino}-cyclohexyl)-1-ethyl-4-phenyl-3*H*-imidazol-1-ium chloride [^{Et}C(H)N^{CHAr}][Cl] (4a)

An ethanol solution (40 mL) of 3-((1*R*,2*R*)-2-amino-cyclohexyl)-1-ethyl-4-phenyl-3*H*-imidazol-1-ium chloride (1a) (509 mg, 1.67 mmol) and 3,5-di-*tert*-butyl 2-hydroxybenzaldehyde (578 mg, 2.50 mmol) containing 4 Å molecular sieves (1.00 g) was heated at reflux for 16 h in a thick-walled ampoule sealed with a Teflon stopcock. On cooling to 25 °C the mixture was filtered and the solvent removed from the filtrate under reduced pressure. The resulting solid was dissolved in dichloromethane (2 mL) and added drop wise to 40–60 petroleum ether (100 mL) to give a pale yellow precipitate. The supernatant was decanted and the solid residue washed with cold 40–60 petroleum ether (2 × 20 mL) to give **4a** as a pale yellow solid. Yield = 789 mg, 90%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 1.26 (9 H, s, C(CH_3)$_3$), 1.41 (9 H, s, C(CH_3)$_3$), 1.60 (3 H, t, $^3J_{H\text{-}H}$ = 3.4, NCH$_2$CH_3), 1.75, 1.95, 2.12, 2.41 (8 H, m, $^{c\text{-hex}}$CH_2), 4.13 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.36 (3 H, m, $^{c\text{-hex}}$CH_{imid} + NCH_2CH$_3$), 6.90 (1 H, s, NCHCPh), 7.10–7.58 (7 H, m, ^{Ph}CH), 8.55 (1 H, s, ^{imine}CH), 11.55 (1 H, s, NCHN), 13.01 (1 H, s, OH); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 15.6 (NCH$_2$CH_3), 23.1 (CH_2), 25.1 (CH_2), 29.3 (C(CH_3)$_3$), 31.3 (C(CH_3)$_3$), 33.2 (CH_2), 34.1 (C(CH$_3$)$_3$), 34.3 (CH_2), 34.9 (C(CH$_3$)$_3$), 45.4 (NCH$_2$CH$_3$), 62.7 ($^{c\text{-hex}}$CH_{imid}), 70.8 ($^{c\text{-hex}}$CH_{imine}), 117.5 (NCHCPh), 117.7 (^{Ph}C$_{ipso}$), 124.6 (NCHCPh), 126.6, 127.4, 126.3, 130.1, 130.8 (^{Ph}CH), 136.0, 136.4 (^{Ph}C$_{ipso}$), 136.7 (NCHN), 140.7 (^{Ph}C$_{ipso}$), 157.5 (COH), 167.7 (^{imine}CH); MS (ESI), m/z 486 ([M − Cl]$^+$), 100%; HRMS calc. for $C_{32}H_{47}N_3O$ 486.3484, found 486.3479.

[^{Bn}C(H)N^{CHAr}][Br] (4c). Prepared and purified by an analogous method to **4a** using an ethanol solution (20 mL) of 3-((1*R*,2*R*)-2-amino-cyclohexyl)-1-benzyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1c**) (135 mg, 0.33 mmol) and 3,5-di-*tert*-butyl 2-hydroxybenzaldehyde (116 mg, 0.50 mmol) containing 4 Å molecular sieves (250 mg). Compound **4a** was isolated as a dark yellow solid. Yield = 191 mg, 92%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C), δ = 1.24 (9 H, s, C(CH_3)$_3$), 1.35 (9 H, s, C(CH_3)$_3$), 1.71, 1.91, 2.10, 2.35 (8 H, m, $^{c\text{-hex}}$CH_2), 4.14 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.38 (1 H, m, $^{c\text{-hex}}$CH_{imid}), 5.51 (1 H, s, NCH_2Ph), 6.72 (1 H, s, NCHCPh), 7.09–7.51 (12 H, m, ^{Ph}CH), 8.59 (1 H, s, ^{imine}CH), 11.72 (1 H, s, NCHN), 12.93 (1 H, s, OH); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C), δ = 23.2 ($^{c\text{-hex}}$CH_2), 25.1 ($^{c\text{-hex}}$CH_2), 29.4 (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 33.4 ($^{c\text{-hex}}$CH_2), 34.2 (C(CH$_3$)$_3$), 34.5 (C(CH$_3$)$_3$), 34.9 ($^{c\text{-hex}}$CH_2), 53.5 (NCH_2Ph), 62.9 ($^{c\text{-hex}}$CH_{imid}), 71.0 ($^{c\text{-hex}}$CH_{imine}), 117.5 (NCHCPh), 117.6 (^{Ph}C$_{ipso}$), 124.5 (NCHCPh), 126.8, 127.6, 128.7, 129.5, 130.1, 130.9, 132.8 (^{Ph}CH), 136.2, 136.4 (^{Ph}C$_{ipso}$), 137.3 (NCHN) 140.6 (^{Ph}C$_{ipso}$), 157.7 (COH), 168.1 (^{imine}CH); MS (ESI), m/z 548 ([M − Br]$^+$); HRMS calc. for $C_{37}H_{49}N_3O$ 548.3641, found 548.3635.

[^{Ph2CH}C(H)N^{CHAr}][Br] (4d). An acetonitrile solution (50 mL) of compound **3** (625 mg, 1.46 mmol) and bromodiphenylmethane (433 mg, 1.75 mmol) containing 4 Å molecular sieves (250 mg) was heated at reflux for 16 h in a thick-walled ampoule. On cooling to 25 °C the mixture was filtered and the volatiles removed from the filtrate under reduced pressure. The work up was analogous to **4a** giving **4d** as a yellow solid. Yield = 971 mg, 94%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 1.25 (9 H, s, C(CH_3)$_3$) 1.39 (9 H, s, C(CH_3)$_3$), 1.71, 1.91, 2.20, 2.43 (8 H, m, $^{c\text{-hex}}$CH_2), 4.21 (2 H, m, $^{c\text{-hex}}$CH_{2imine}, and $^{c\text{-hex}}$CH_{2imid}), 6.68–7.49 (17 H, m, ^{Ph}CH + NCHCPh), 7.61 (1 H, s, NCHPh$_2$), 8.52 (1 H, s, ^{imine}CH), 11.52 (1 H, s, NCHN), 12.88 (1 H, s, OH); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 23.2 (CH_2), 25.0 (CH_2), 29.3 (C(CH_3)$_3$), 31.4(C(CH_3)$_3$), 32.8 (CH_2), 34.1 (C(CH$_3$)$_3$), 34.3 (CH_2), 34.9 (C(CH$_3$)$_3$), 63.0 ($^{c\text{-hex}}$CH_{imid}), 66.3 (NCHPh$_2$), 71.1 ($^{c\text{-hex}}$CH_{imine}), 117.0 (NCHCPh), 117.3(^{Ph}C$_{ipso}$), 124.5 (NCHCPh), 126.7, 126.9, 127.5, 128.3, 128.8, 129.9, 129.1, 129.3, 130.0, 130.8 (^{Ph}CH), 136.1, 136.3, 136.4, 136.8 (^{Ph}CH_{ipso}), 137.4 (NCHN), 140.5 (^{Ph}CH_{ipso}), 157.5 (COH), 168.2 (^{imine}CH); MS (ESI), m/z 624 ([M − Br]$^+$), 100%; HRMS calc. for $C_{43}H_{53}N_3O$, 624.3954, found 624.3948.

[^{Et}C(AgCl)N] (5a). Silver(I) oxide (59 mg, 0.25 mmol) and 4 Å molecular sieves (200 mg) are added to a dichloromethane solution (20 mL) of **4a** (200 mg, 0.39 mmol) and the mixture stirred for 16 h at 25 °C in the absence of light. The mixture was filtered and the volatiles removed from the filtrate under reduced pressure to give **5a** as a light brown solid. Yield 240 mg, 98%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C), $\delta = 1.22$ (9 H, s, C(CH_3)$_3$), 1.38 (12 H, s, C(CH_3)$_3$ + NCH$_2$CH_3), 1.72, 1.84, 2.36, 2.47 (8 H, m, $^{c\text{-hex}}$CH_2), 3.98 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.08 (2 H, m, NCH_2CH$_3$), 4.22 (1 H, m, $^{c\text{-hex}}$CH_{NHC}), 6.68 (1 H, s, NCHCPh), 6.93–7.42 (7H, m, ^{Ph}CH), 8.14 (1 H, s, ^{imine}CH), 12.96 (1 H, s, OH); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C), δ = 17.0 (NCH$_2$CH_3), 23.8 (CH_2), 25.4 (CH_2), 29.3 (C(CH_3)$_3$), 31.5 (C(CH_3)$_3$), 34.2 (CH_2), 34.4 (C(CH$_3$), 34.7 (CH_2), 35.0 (C(CH$_3$)$_3$), 48.1 (NCH_2CH$_3$), 61.0 ($^{c\text{-hex}}$CH_{NHC}), 74.0 ($^{c\text{-hex}}$CH_{imine}), 117.2 (NCHCPh), 117.5 (^{Ph}C$_{ipso}$), 126.3, 127.2 (^{Ph}CH), 127.5 (NCHCPh), 128.9, 129.6, 130.3 (^{Ph}CH), 136.4, 137.0, 140.4 (^{Ph}C$_{ipso}$), 157.2 (COH), 166.2 (^{imine}CH); MS (ESI), m/z 1079 ([2M − Ag − 2Cl]$^+$), 100%; Anal. [Found (calc.)] $C_{32}H_{42}AgClN_3O$, C 60.99 (61.10), H 6.89 (6.74), N 6.68 (6.81).

[^{Bn}C(AgBr)N^{CHAr}] (5c). Prepared by an analogous method to **5a** using dichloromethane (10 mL), **4c** (85 mg, 0.14 mmol), silver(I) oxide (21 mg, 0.09 mmol) and 4 Å molecular sieves (100 mg) giving **5c** as a light brown solid. Yield = 102 mg, 99%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 1.30 (9 H, s, C(CH_3)$_3$), 1.42 (9 H, s, C(CH_3)$_3$), 1.81, 1.93, 2.17, 2.50 (8 H, m, $^{c\text{-hex}}$CH_2), 4.14 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.33 (1 H, m, $^{c\text{-hex}}$CH_{NHC}), 5.28 (2 H, s, NCH_2Ph), 6.68 (1 H, s, NCHCPh), 6.98–7.47 (12 H, m, ^{Ph}CH), 8.28 (1 H, s, ^{imine}CH), 13.00 (1 H, s, OH); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 23.9 (CH_2), 25.4 (CH_2), 29.3 (C(CH_3)$_3$), 31.5 (C(CH_3)$_3$), 34.2 (C(CH$_3$)$_3$), 34.6 (CH_2), 34.7 (CH_2), 34.9 (C(CH$_3$)$_3$), 56.6 (NCH_2Ph), 61.2 ($^{c\text{-hex}}$CH_{NHC}), 73.9 ($^{c\text{-hex}}$CH_{imine}), 117.5 (NCHCPh), 118.0 (^{Ph}C$_{ipso}$), 126.3, 127.2 (^{Ph}CH), 127.3 (NCHCPh), 128.3, 128.7, 129.0, 129.3, 129.7, 130.2 (^{Ph}CH) 135.3, 136.5, 137.5, 140.4 (^{Ph}C$_{ipso}$), 157.6 (COH), 166.5 (^{imine}CH); MS (ESI), m/z 1204 ([2M − Ag − 2Br]$^+$), 100%; Anal. [Found (calc.)] $C_{37}H_{46}AgBrN_3O$: C 60.53 (60.42), H 6.26 (6.17), N 5.56 (5.71).

[^{Ph2CH}C(AgBr)N^{CHAr}] (5d). Prepared by an analogous method to **5a** using dichloromethane (40 mL), **4d** (300 mg, 0.43 mmol), silver(I) oxide (100 mg, 0.43 mmol) and 4 Å molecular sieves (250 mg) giving **5d** as a light brown solid. Yield = 335 mg, 96%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 1.24 (9 H, s, C(CH$_3$)$_3$), 1.45 (9 H, s, C(CH$_3$)$_3$), 1.84, 1.95, 2.23, 2.45 (8 H, m, $^{c\text{-hex}}$CH_2), 4.22 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.30 (1 H, m, $^{c\text{-hex}}$CH$_{NHC}$), 6.61–7.47 (19 H, m, ^{Ph}CH + NCHCPh + NCH(Ph)$_2$), 8.24 (1 H, s, CH_{imine}), 12.99 (1 H, s, OH); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C): δ = 23.9 (CH_2), 25.5 (CH_2), 29.4 (C(CH_3)$_3$), 31.5 (C(CH_3)$_3$), 34.2 (C(CH$_3$)$_3$), 34.5 (CH_2), 34.6 (CH_2), 35.0 (C(CH$_3$)$_3$), 61.4 ($^{c\text{-hex}}$CH_{NHC}), 70.2 (NC(Ph)$_2$), 74.1 ($^{c\text{-hex}}$CH$_{imine}$), 117.4 (NCHCPh), 126.5 (NCHCPh), 127.0, 127.2, 127.4, 128.0, 128.9, 128.8, 128.9, 129.0, 129.1, 130.2 (^{Ph}CH), 136.9, 137.3 138.8, 138.7, 140.4 (^{Ph}C$_{ipso}$), 157.7 (COH), 166.7 (^{imine}CH); MS (ESI), m/z 1356 ([2M − Ag − 2Cl]$^+$), 100%; Anal. [Found (calc.)] $C_{43}H_{49}AgBrN_3O$, C 63.54 (63.63), H 6.19 (6.09), 5.15 (5.18).

[Ir(κ^1-^{iPr}CN^{CHAr})Cl(COD)] (6b). To a dichloromethane (10 mL) solution of **5b** (195 mg, 0.30 mmol) was added a dichloromethane (5 mL) solution of [Ir(COD)Cl]$_2$ (102 mg, 0.15 mmol) to immediately give a white precipitate. The mixture was stirred in the dark for 1 h, filtered and the solvent removed from the filtrate under reduced pressure to give an orange/yellow solid. Purification by flash chromatography on silica eluted with dichloromethane gave three yellow/orange bands. The third band was collected and the volatiles removed under reduced pressure to give **6b** as yellow/orange solid. Yield = 146 mg, 58%. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 1.08 (3 H, d, $^3J_{H\text{-}H}$ = 5.9, CH(CH_3)$_2$), 1.27 (9 H, s, C(CH_3)$_3$), 1.35 (3 H, d, $^3J_{H\text{-}H}$ = 5.9, CH(CH_3)$_2$), 1.70 (9 H, s, C(CH_3)$_3$), 1.87, 2.12, 2.19 (8 H, m, $^{c\text{-hex}}$CH_2), 2.36 (4 H, m, ^{COD}CH_2), 2.79 (1 H, m, ^{COD}CH, 2.99 (1 H, m, ^{COD}CH), 4.21 (1 H, m, $^{c\text{-hex}}$CH_{NHC}), 4.43 (1 H, m, ^{COD}CH_2), 4.93 (2H, m, ^{COD}CH + $^{c\text{-hex}}$CH_{imine}), 5.26 (1 H, m, ^{COD}CH), 5.91 (1 H, m, NCH(CH$_3$)$_2$), 6.12 (1 H, s, NCHCPh), 7.12–7.55 (7 H, m, ^{Ph}CH), 9.21 (1 H, s, ^{imine}CH), 13.88 (1 H, s, OH); ^{13}C NMR (126 MHz, C_6D_6, 25 °C): δ = 22.1 (CH(CH_3)$_2$), 24.3 (CH_2), 24.7 (C(CH_3)$_2$), 26.3 (CH_2), 28.0 (CH_2) 29.7 (CH_2), 29.9 (C(CH_3)$_3$), 31.6 (CH_2), 31.7 (C(CH_3)$_3$), 32.0 (CH_2), 34.0 (CH_2), 34.2 (C(CH$_3$)$_3$), 35.3 (C(CH$_3$)$_3$), 35.6 (CH_2), 51.6 (^{COD}CH), 54.6 (NCH(CH$_3$)$_2$), 54.7 (^{COD}CH), 63.4 ($^{c\text{-hex}}$CH_{NHC}), 70.0 ($^{c\text{-hex}}$CH_{imine}), 84.0 (^{COD}CH), 85.1 (^{COD}CH) 113.6 (NCHCPh) 119.1 (NCHCPh), 126.6, 127.3, 128.3, 128.9 129.9 (^{Ph}CH), 132.5, 136.4, 139.3, 139.8 (^{Ph}C$_{ipso}$), 158.5 (COH), 168.1 (^{imine}CH), 181.2 (IrC); MS (ESI), m/z 800 ([M − Cl]$^+$, 100%); Anal. [Found (calc.)] for $C_{41}H_{58}ClIrN_3O$. C 58.97 (58.86); H 6.93 (6.99); N 4.98 (5.02).

[Ir(κ^2-^{Et}CN^{CHAr})(COD)][B{3, 5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (7a). A dichloromethane solution (10 mL) of [Ir(COD)Cl]$_2$ (29 mg, 0.04 mmol) was added drop wise to a dichloromethane solution (10 mL) of **5a** (54 mg, 0.09 mmol), to immediately give a white precipitate. The mixture was stirred in the dark for 1 h, filtered and the volatiles were removed from the filtrate under reduced pressure to give an orange solid. Purification by flash chromatography on silica eluted with dichloromethane gave three yellow/orange bands. The third coloured band was collected and the solvent removed to give a red/yellow orange solid (38 mg, 0.05 mmol) that was dissolved in dichloromethane (10 mL) and Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (62 mg, 0.07 mmol) added. After stirring for 15 min the mixture was washed with water (2 × 10 mL) and the organic layer separated, dried over magnesium sulfate and the volatiles removed under reduced pressure to give **7a** as a red/brown solid. Yield = 42 mg, 63%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.47 (9 H, s, C(CH_3)$_3$), 1.49 (9 H, s, C(CH_3)$_3$), 1.60–2.40 (16 H, m, $^{c\text{-hex}}$CH_2 + ^{COD}CH_2), 3.54 (1 H, m, $^{c\text{-hex}}$CH_{imine}), 4.00 (2 H, m, NCH_2CH$_3$), 4.02, 4.15, 4.28, 4.39 (1 H, m, ^{COD}CH), 5.77 (1 H, m, $^{c\text{-hex}}$CH_{NHC}), 6.05 (1 H, s, OH), 6.75 (1 H, s, NCHCPh), 7.41–8.09 (19 H, m, ^{Ph}CH), 9.22 (1 H, s, ^{imine}CH); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 16.7 (NCH$_2$CH_3), 24.4 (CH_2), 25.5 (CH_2), 28.1 (CH_2), 29.7 (CH_2), 30.2 (C(CH_3)$_3$), 31.3 (CH_2), 31.6 (C(CH_3)$_3$), 31.9 (CH_2), 33.5 (C(CH$_3$)$_3$), 34.1 (CH_2), 34.6 (CH_2), 35.6 (C(C(CH_3)$_3$), 45.3 (NCH_2CH$_3$), 58.3 (^{COD}CH), 65.3 (^{COD}CH), 67.2 ($^{c\text{-hex}}$CH_{NHC}), 74.7 ($^{c\text{-hex}}$CH_{imine}), 83.2 (^{COD}CH), 87.1 (^{COD}CH), 117.5 (^{BArF}CH_{para}), 119.6 (NCHCPh), 120.6 (NCHCPh), 124.2 (^{Ph}CH), 124.5 (q, $^1J_{C\text{-}F}$ = 273, ^{BArF}CF_3), 127.8, 128.9 (m, ^{BArF}F$_3$CC_{ipso}), 128.8, 130.2, 130.5, 130.5 (^{Ph}CH), 134.8 (^{BArF}CH_{ortho}), 136.0, 143.6 (^{Ph}C$_{ipso}$), 153.5 (CO), 161.7 (q, $^1J_{B\text{-}C}$ = 51, ^{BArF}BC_{ipso}), 168.4 (^{imine}CH), 171.8 (IrC); MS (FAB), m/z 786 ([M − BAr$^F_4$]$^+$), 100%, 674 ([M − BAr$^F_4$ − COD]$^+$), 95%; HRMS calc. for $C_{40}H_{55}N_3OIr$ 786.3974, found 786.3969.

[Ir(κ²-^{iPr}*CN*^{CHAr})(COD)][B{3, 5-$(CF_3)_2C_6H_3$}$_4$] (7b). To a dichloromethane (10 mL) solution of **6** (80 mg, 0.01 mmol) was added Na[B{3,5-$(CF_3)_2C_6H_3$}$_4$] (126 mg, 0.14 mmol) and the mixture stirred for 15 min. The mixture was washed with water (2 × 10 mL) and the organic layer separated, dried over magnesium sulfate and the volatiles removed under reduced pressure to give **7b** as a red/brown solid. Yield = 156 mg, 98%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.23 (6 H, d, $^3J_{H\text{-}H}$ = 6.5, CH(CH_3)$_2$), 1.30 (2 H, m, ^{COD}CH_2), 1.46 (9 H, s, C(CH_3)$_3$), 1.49 (9 H, s, C(CH_3)$_3$), 1.88, 1.89 (8 H, m, $^{c\text{-}hex}$CH_2), 2.14, 2.18, 2.41 (6 H, s, ^{COD}CH_2), 3.57 (1 H, m, $^{c\text{-}hex}$CH_{imine}), 4.03 (2 H, m, ^{COD}CH), 4.15 (1 H, m, ^{COD}CH), 4.29 (1 H, m, ^{COD}CH), 4.97 (1 H, m, NCH(CH$_3$)$_2$), 5.82 (1 H, m, ($^{c\text{-}hex}$CH_{NHC}), 6.32 (1 H, s, OH), 6.79 (1 H, s, NCHCPh), 7.19–8.07 (19 H, m, ^{Ph}CH), 9.19 (1 H, s, ^{imine}CH); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 23.3 (CH(CH_3)$_2$), 24.4 (CH_2), 25.2 (C(CH_3)$_2$), 25.3 (CH_2), 25.5 (CH_2), 28.0 (CH_2), 29.3 (CH_2), 30.2 (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 31.8 (CH_2), 33.6 (CH_2), 34.2 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 35.6 (CH_2), 52.1 (NCH(CH$_3$)$_2$), 58.9 (^{COD}CH), 64.6 (^{COD}CH), 67.1 ($^{c\text{-}hex}$CH_{NHC}), 74.8 ($^{c\text{-}hex}$CH_{imine}), 83.1 (^{COD}CH), 87.0 (^{COD}CH), 116.6 (NCHCPh), 117.5 (^{BArF}CH_{para}), 120.5 (NCHCPh), 124.2 (^{Ph}CH), 124.5 (q, ^1J = 273, ^{BArF}CF_3), 127.5, 128.5 (^{Ph}CH) 128.9 (m, ^{BArF}F$_3$CC_{ipso}), 130.2, 130.6 (^{Ph}CH), 130.7 (^{Ph}C$_{ipso}$), 134.8 (^{BArF}CH_{ortho}), 135.0, 136.4, 143.7 (^{Ph}C$_{ipso}$), 153.8 (COH), 161.7 (q, $^1J_{B\text{-}C}$ = 51, ^{BArF}BC_{ipso}), 168.5 (^{imine}CH), 170.8 (IrC); MS (FAB), *m/z* 800 ([M – BAr$^F{}_4$]$^+$), 100%; Anal. [Found (calc.)] for $C_{73}H_{69}BF_{24}IrN_3O$, C 52.60 (52.71), H 4.07 (4.18), N 2.57 (2.53).

[Ir(κ²-^{Bn}*CN*^{CHAr})(COD)][B{3, 5-$(CF_3)_2C_6H_3$}$_4$] (7c). Prepared by an analogous method to **7a** using $[Ir(COD)Cl]_2$ (25 mg, 0.04 mmol) **5c** (54 mg, 0.07 mmol), and Na[B{3,5-$(CF_3)_2C_6H_3$}$_4$] (30 mg, 0.03 mmol) to give **7c** as a red/brown solid. Yield = 47 mg, 68%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.27 (2 H, m, ^{COD}CH_2), 1.39 (9 H, s, C(CH_3)$_3$), 1.44 (9 H, s, C(CH_3)$_3$), 1.72–2.31 (10 H, m, $^{c\text{-}hex}$CH_2 + ^{COD}CH_2), 3.54 (1 H, m, $^{c\text{-}hex}$CH_{imine}), 3.86, 3.99, 4.12, 4.26 (1 H, m, ^{COD}CH), 5.18 (1 H, d, ^2J = 15 Hz, NCH_2Ph), 5.66 (1 H, d, $^2J_{H\text{-}H}$ = 15, NCH_2Ph), 5.81 (1 H, m, $^{c\text{-}hex}$CH_{NHC}), 5.95 (1 H, s, OH), 6.55 (1 H, s, NCHCPh), 7.05–8.12 (24 H, m, ^{Ph}CH), 9.23 (1 H, s, ^{imine}CH); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 24.4 (CH_2), 25.5 (CH_2), 28.9 (CH_2), 29.5 (CH_2), 30.2 (C(CH_3)$_3$), 31.2 (CH_2), 31.5 (C(CH_3)$_3$), 32.2 (CH_2), 33.3 (CH_2), 34.1 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 35.8 (CH_2), 54.1 (NCH_2Ph), 58.1 (^{COD}CH), 65.6 (^{COD}CH), 67.4 ($^{c\text{-}hex}$CH_{NHC}), 74.9 ($^{c\text{-}hex}$CH_{imine}), 83.8 (^{COD}CH), 87.7 (^{COD}CH), 117.5 (^{BArF}CH_{para}), 120.5 (NCHCPh), 121.3 (NCHCPh), 124.1 (^{Ph}CH), 124.5 (q, $^1J_{C\text{-}F}$ = 273, ^{BArF}CF_3), 126.7 127.8, 128.5, 128.8 (^{Ph}CH), 128.9 (m, ^{BArF}F$_3$CC_{ipso}), 129.5 (^{Ph}C$_{ipso}$), 129.6, 130.3, 130.6 (^{Ph}CH), 130.7 (^{Ph}C$_{ipso}$), 134.8 (^{BArF}CH_{ortho}), 135.1, 136.0, 143.6 (^{Ph}C$_{ipso}$), 161.7 (q, $^1J_{B\text{-}C}$ = 51, ^{BArF}BC_{ipso}), 153.6 (COH),), 168.5 (^{imine}CH), 173.1 (IrC); MS (FAB), *m/z* 848 ([M – BAr$^F{}_4$]$^+$), 100%; Anal. [Found (calc.)] for $C_{77}H_{70}BF_{24}IrN_3O$, C 53.93 (54.04), H 3.95 (4.06), N 2.37 (2.46).

[Ir(κ²-Ph2CH*CN*^{CHAr})(COD)][B{3, 5-$(CF_3)_2C_6H_3$}$_4$] (7d). Prepared by an analogous method to **7a** using $[Ir(COD)Cl]_2$ (27 mg, 0.04 mmol) **5d** (66 mg, 0.008 mmol), and Na[B{3,5-$(CF_3)_2C_6H_3$}$_4$] (40 mg, 0.05 mmol) to give **7d** as a red/brown solid. Yield = 47 mg, 66%. ^{1}H NMR (500 MHz, $CDCl_3$. 25 °C): δ = 0.90 (2 H, m, ^{COD}CH_2), 1.24 (6 H, m, ^{COD}CH_2), 1.39 (9 H, s, C(CH_3)$_3$), 1.50 (9 H, s, C(CH_3)$_3$), 1.72–2.29 (8 H, m, $^{c\text{-}hex}$CH_2), 3.64 (1 H, m, $^{c\text{-}hex}$CH_{imine}), 3.82 (2 H, m, ^{COD}CH), 4.16 (1 H, m, ^{COD}CH), 4.35 (1 H, m, ^{COD}CH), 5.94 (1 H, m, $^{c\text{-}hex}$CH_{NHC}), 6.41 (1 H, s, NCHCPh), 6.91–8.43 (29 H, m, ^{Ph}CH + NCH(Ph)$_2$), 9.30 (^{imine}CH), OH not observed; ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ = 22.6 (CH_2), 24.4 (CH_2), 25.5 (CH_2), 27.9 (CH_2), 29.7 (C(CH_3)$_3$), 30.6 (CH_2), 31.2 (C(CH_3)$_3$), 31.7 (CH_2), 33.4 (CH_2), 34.3 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 35.7 (CH_2), 66.0 (^{COD}CH), 67.2 (^{COD}CH), 67.5 ($^{c\text{-}hex}$CH_{NHC}), 75.3 ($^{c\text{-}hex}$CH_{imine}), 83.3 (^{COD}CH), 87.6 (^{COD}CH), 117.5 (^{BArF}CH_{para}), 120.0 (NCHCPh), 120.6(NCHCPh), 124.3 (^{Ph}CH), 124.5 (q, $^1J_{C\text{-}F}$ = 273, ^{BArF}CF_3), 126.2, 128.6 (^{Ph}CH) 128.9 (m, ^{BArF}F$_3$CC_{ipso}), 129.0, 129.1, 129.2. 129.3, 129.5 (^{Ph}CH), 130.1 (^{Ph}C$_{ipso}$), 130.3, 130.8, 131.3 (^{Ph}CH), 134.6 (^{Ph}C$_{ipso}$), 134.8 (^{BArF}CH_{ortho}), 136.6, 138.3, 138.9, 143.8 (^{Ph}C$_{ipso}$), 153.8 (COH), 161.7 (q, $^1J_{B\text{-}C}$ = 51, ^{BArF}BC_{ipso}), 168.4 (^{imine}CH), 173.4 (IrC); MS (FAB), *m/z* 925 ([M – BAr$^F{}_4$]$^+$), 100%; Anal. [Found (calc.)] for $C_{83}H_{73}BF_{24}IrN_3O$, C 55.82 (55.77), H 4.42 (4.12), N 2.37 (2.35).

[(1*R*,2*R*)-2-(5-Phenyl-2*H*-imidazol-1-yl)-cyclohexyl]-[1-phenyl-meth-(*E*)-ylidene]-amine [C(H)N(CHPh)] (8). A 3-necked flask fitted with a reflux condenser, an addition funnel and a thermometer was charged with 4 Å molecular sieves (5.00 g), potassium carbonate (15.00 g) and (1*R*,2*R*)-*N*,*N*′-bis-[1-phenyl-meth-(*E*)-ylidene]-cyclohexane-1,2-diamine (10.00 g, 34 mmol) and dried under dynamic vacuum at 60 °C for 12 h. Acetonitrile (50 mL) was added and the mixture maintained at 60 °C whilst an acetonitrile solution (50 mL) of 1-(isocyano-phenyl-methanesulfonyl)-4-methylbenzene (Ph-TosMIC) (12.00 g, 44 mmol) was added dropwise. The mixture was stirred at 60 °C for *ca.* 36 h until complete disappearance of the starting diimine as judged by TLC and cooled to 25 °C. On removal of the volatiles under reduced pressure the solid residue was extracted with diethyl ether (3 × 200 mL) and the filtrates combined and cooled at 4 °C for 24 h to precipitate impurities. After filtration, the solution was concentrated to *ca.* 150 mL and dropped into hexane, resulting in the formation of an oily precipitate that was decanted and washed with hexane to give **8** as an off white waxy solid. Yield = 10.74 g, 78% ^{1}H (500 MHz, $CDCl_3$, 25 °C) δ = 1.25–2.20 (m, 8H, $^{c\text{-}hex}$CH_2), 3.39 (m, 1H, $^{c\text{-}hex}$CH_{imine}), 3.92 (m, 1H, $^{c\text{-}hex}$CH_{imid}), 6.90–7.60 (m, 15H, ^{Ph}CH), 7.64 (s, 1H, NCHN), 7.92 (s, 1H, ^{imine}CH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 22.7 ($^{c\text{-}hex}$CH_2), 25.4 ($^{c\text{-}hex}$CH_2), 33.8 ($^{c\text{-}hex}$CH_2), 33.9 ($^{c\text{-}hex}$CH_2), 58.5 ($^{c\text{-}hex}$CH_{imid}), 75.1 ($^{c\text{-}hex}$CH_{imine}), 125.9, 126.6, 127.9, 128.2, 128.4, 128.8, 129.4, 129.9, 130.7, 130.9, 131.5, 133.5, 134.7, 135.8, 137.0, 160.7 (^{imine}CH). M.S.: *m/z* = 405 ([M]$^+$), 100%; Anal. [Found (calc.)] for $C_{28}H_{27}N_3$, C 82.08 (82.93), H 7.04 (6.91), N 10.82 (10.36).

[^{iPr}C(H)N(CHPh)][I] (9). Compound **8** (4.05 g, 10 mmol) was refluxed in 2-iodopropane (17.3 g, 100 mmol) for 24 h in a thick-walled ampoule sealed with a Teflon stopcock. On cooling to 25 °C the volatiles were removed under reduced pressure to give a white foam that was dissolved in methanol (10 mL) and added dropwise into diethyl ether (100 mL) giving a yellow precipitate. The precipitate was isolated by filtration washed with diethyl ether (3 × 50 mL) and dried under reduced pressure at 60 °C for 24 h to give **9** as a white solid. Yield = 5.46 g, 95%. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 1.40–2.50 (m, 8H, $^{c\text{-}hex}$CH_2), 1.47 (d, J = 6.7 Hz, 3H, CH(CH_3)$_3$), 1.60 (d, J = 6.7 Hz, 3H, CH(CH_3)$_3$), 3.92 (m, 1H, $^{c\text{-}hex}$CH_{imine}), 4.40–4.25 (m, 2H, $^{c\text{-}hex}$CH_{imid} + CH(CH$_3$)$_3$), 7.01 (d, J = 7.0 Hz, 2H, ^{Ph}CH), 7.10–7.70 (m, 13H, ^{Ph}CH), 8.28 (s, 1H, ^{imine}CH), 9.78 (s, 1H, NCHN); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 23.0, 23.5, 24.1, 25.4, 32.3, 33.8, 51.9, 63.5, 72.7,

124.9, 125.0, 128.0, 128.6, 129.0, 129.1, 130.1, 130.3, 130.5, 130.9, 131.0, 132.6, 134.4, 135.7, 162.0 ($^{imine}CH$); MS (ESI): $m/z = 1023.7$ ([2M + I]$^+$), 100%; Anal. [Found (calc.)] for $C_{31}H_{34}N_3I$, C 64.82 (64.69), H 5.96 (5.95), N 7.20 (7.30).

[C(H)N(Bn)(H)] (10). To a stirring methanol (50 mL) solution of **8** (4.05 g, 10 mmol) cooled to 0 °C was added sodium borohydride (760 mg, 20 mmol) continually over 15 min. The solution was allowed to warm to 25 °C and stirred for 30 min. With stirring 1M sodium hydroxide (100 mL) was cautiously added and the majority of the methanol was removed under reduced pressure. The remaining aqueous phase was extracted with ethyl acetate (3 × 50 mL) and the combined organic layers dried over magnesium sulfate. On filtration through a short pad of neutral aluminium oxide the volatiles were removed to give **10** as a transparent glassy solid that is extremely hygroscopic. Yield = 3.30 g, 81%. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): $\delta = 1.18$–1.31 (m, 4H, $^{c\text{-hex}}CH_2$), 1.68 (m, 2H, $^{c\text{-hex}}CH_2$), 1.88 (m, 1H, $^{c\text{-hex}}CH_2$), 2.09 (m, 1H, $^{c\text{-hex}}CH_2$), 2.72 (m, 1H, $^{c\text{-hex}}CH_{imine}$), 3.44 (d, $J = 13.7$ Hz, 1H, PhCH_2), 3.56 (m, 1H, $^{c\text{-hex}}CH_{imid}$), 3.66 (d, $J = 13.7$ Hz, 1H, PhCH_2), 6.95–7.49 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 24.3$, 25.3, 26.9, 31.8, 34.6, 50.6, 60.0, 126.0, 126.8, 127.2, 127.8, 127.9, 128.0, 128.1, 128.2, 129.6, 130.9, 131.2, 133.8, 134.8, 137.6, 140.0; MS (EI): $m/z = 408$ ([M + H]$^+$), 100%; Anal. [Found (calc.)] for $C_{28}H_{29}N_3$, C 82.52 (82.52), H 7.14 (7.17), N 10.23 (10.31).

[^{iPr}C(H)N(Bn)(H)][I] (11). Was prepared by an analogous procedure to **9** using compound **10** (4.07 g, 10 mmol) and 2-iodopropane (17.3 g, 100 mmol) to give **11** as a white solid. Yield = 5.48 g, 95%. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): $\delta = 1.31$ (m, 1H, $^{c\text{-hex}}CH_2$), 1.49 (d, $J = 6.7$ Hz, 3H, CH(CH_3)$_3$), 1.50 (m, 3H, $^{c\text{-hex}}CH_2$), 1.76 (d, $J = 6.7$ Hz, 3H, CH(CH_3)$_3$), 1.87 (m, 1H, $^{c\text{-hex}}CH_2$), 2.04 (m, 1H, $^{c\text{-hex}}CH_2$), 2.48 (m, 1H, $^{c\text{-hex}}CH_2$), 2.55 (m, 1H, $^{c\text{-hex}}CH_2$), 4.08 (m, 1H, $^{c\text{-hex}}CH_{imine}$), 4.27 (m, 1H, $^{c\text{-hex}}CH_{imid}$), 4.37 (d, $J = 13.4$ Hz, 1H, PhCH_2), 4.45 (d, $J = 13.4$ Hz, 1H, PhCH_2), 4.48 (sep, $J = 6.7$ Hz, 1H, CH(CH$_3$)$_3$), 7.35–7.52 (m, 9H, ^{Ph}CH), 7.65–7.80 (m, 6H, ^{Ph}CH), 9.60 (s, 1H, NCHN); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): $\delta = 23.5$, 23.8, 24.0, 25.1, 28.7, 36.5, 47.9, 53.7, 58.2, 60.1, 126.0, 126.4, 129.9, 130.2, 130.5, 130.7 131.6, 131.8, 132.1, 132.4, 132.6, 132.7, 135.1; MS (ESI): $m/z =$ 450 ([M]$^+$), 100%.

[^{iPr}C(H)NBn$_2$][I] (12). A mixture of compound **11** (1.15 g, 2 mmol), benzyl bromide (400 mg, 2.25 mmol), potassium carbonate (417 mg, 3 mmol) and acetonitrile (50 mL) were heated at 80 °C for 16 h in a thick-walled ampoule sealed with a Teflon stopcock. On cooling to 25 °C the mixture was filtered into diethyl ether (100 mL) to give a white solid precipitate that was isolated by filtration and washed with diethyl ether (3 × 20 mL). The solid was dried under dynamic vacuum to give **12** as a white powder. Yield = 1.23 g, 92%. ^{1}H NMR (400 MHz, CD_3OD, 25 °C): $\delta =$ 1.31 (m, 2H, $^{c\text{-hex}}CH_2$), 1.47 (d, $J = 6.7$ Hz, 3H, CH(CH_3)$_3$), 1.50 (m, 1H, $^{c\text{-hex}}CH_2$), 1.67 (d, $J = 6.7$ Hz, 3H, CH(CH_3)$_3$), 1.82 (m, 2H, $^{c\text{-hex}}CH_2$), 1.98 (m, 1H, $^{c\text{-hex}}CH_2$), 2.25 (m, 1H, $^{c\text{-hex}}CH_2$), 2.48 (m, 1H, $^{c\text{-hex}}CH_2$), 3.38 (m, 1H, $^{c\text{-hex}}CH_{imine}$), 3.47 (dd, $J = 10.3$, 25.5 Hz, 4H, PhCH_2), 4.15 (m, 1H, $^{c\text{-hex}}CH_{imid}$), 4.61 (sep, $J =$ 6.7 Hz, 1H, CH(CH$_3$)$_3$), 6.83 (d, $J = 8.6$ Hz, 2H, ^{Ph}CH), 7.08–7.20 (m, 5H,^{Ph}CH), 7.30–7.55 (m, 13H, ^{Ph}CH), 8.91 (s, 1H, NCHC); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): $\delta = 23.0$, 24.9, 25.7, 26.2, 32.7, 36.1, 52.2, 54.0 (br, PhCH_2), 60.7, 62.5, 126.0, 126.4, 128.5, 129.9, 130.0, 130.1, 130.2, 131.7, 131.8, 132.1, 132.7, 133.0, 134.1, 140.2; M.S. (ESI): $m/z = 540$ ([M − I]$^+$), 100%; HRMS: Calc. for $C_{38}H_{42}N_3$ 540.3373, found 540.3369.

[Rh(κ$^{2\text{-iPr}}$*CN*(Bn)(H))(COD)][B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (13). At −78 °C, tetrahydrofuran (10 mL) was added to a mixture of [Rh(COD)Cl]$_2$ (62 mg, 0.125 mmol) and potassium *tert*-butoxide (70 mg, 0.625 mmol) at −78 °C and stirred for 15 min. Subsequently, a tetrahydrofuran (5 ml) solution of **11** (144 mg, 0.25 mmol) was added dropwise *via* cannula and the mixture allowed to warm to 25 °C and stirred for 12 h. On filtration, a tetrahydrofuran (5 mL) solution of Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (332 mg, 0.375 mmol) was added to the filtrate and stirred for 1 h. The volatiles were removed under reduced pressure and the residue purified by column chromatography on silica gel with 1:1 dichloromethane:hexane to give **13** as a yellow solid. Yield = 290 mg, 76%. ^{1}H (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.21$ (d, $J =$ 7.0 Hz, 3H, CH(CH_3)$_3$), 1.41 (d, $J = 7.0$ Hz, 3H, CH(CH_3)$_3$), 1.45–1.70 (m, 6 H, $^{c\text{-hex}}CH_2$ + ^{COD}CH), 1.76 (m, 1H, $^{c\text{-hex}}CH_2$), 1.95–2.25 (m, 8H, $^{c\text{-hex}}CH_2$ + ^{COD}CH), 2.38 (m, 1H, $^{c\text{-hex}}CH_2$), 2.52 (m, 1H, $^{c\text{-hex}}CH_{imine}$), 2.84 (m, 1H, PhC$H_2$), 3.22 (m, 1H,^{COD}CH), 3.43 (m, 1H, PhCH_2), 3.83 (m, 1H, ^{COD}CH), 4.0 (m, 1H, ^{COD}CH), 4.51 (m, 1H, ^{COD}CH), 5.25 (sep, $J = 6.9$ Hz, 1H, CH(CH$_3$)$_3$), 5.49 (m, 1H, $^{c\text{-hex}}CH_{imid}$), 6.96 (d, $J = 7.6$ Hz, 2H, ^{Ph}CH), 7.00–7.35 (m, 9H, ^{Ph}CH), 7.40–7.50 (m, 8H, ^{Ph}CH), 7.64 (brs, 8H, PhCH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 22.5$, 24.5, 24.9, 25.5, 26.3, 28.9, 29.9, 31.5, 33.4, 35.1, 54.7, 60.5, 65.3, 69.8, 70.6 (d, $^1J_{Rh\text{-}C} =$ 13.5 Hz, ^{COD}CH), 77.8 (d, $^1J_{Rh\text{-}C} = 13.5$ Hz, ^{COD}CH), 95.4 (d, $^1J_{Rh\text{-}C} = 13.5$ Hz,^{COD}CH), 95.6 (d, $^1J_{Rh\text{-}C} = 13.5$ Hz,^{COD}CH) 117.4, 121.4, 125.9, 128.3, 128.5, 128.7, 129.0, 129.6, 130.9, 131.8, 133.4, 133.5, 134.8, 160.9, 161.4, 161.9, 162.4, 176.5 (d, $^1J_{Rh\text{-}C} = 51.1$ Hz, Rh^{NHC}C); MS (FAB): $m/z = 661$ ([M − B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^+$), 100%; Anal. [Found (calc.)] for $C_{71}H_{60}BF_{24}N_3Rh$, C 56.07 (55.92), H 3.91 (3.97), N 2.69 (2.76).

[Ir(κ$^{2\text{-iPr}}$*CN*(Bn)(H))(COD)][B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (14). A tetrahydrofuran (10 mL) solution of **11** (150 mg, 0.26 mmol) and Ag_2O (46 mg, 0.2 mmol) and were stirred at 25 °C for 16 h. The resulting green mixture was filtered *via* cannula into a tetrahydrofuran (10 mL) solution of [Ir(COD)Cl]$_2$ (87 mg, 0.13 mmol) immediately giving an off white precipitate and the mixture stirred for 24 h. Subsequently, the mixture was filtered and Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (310 mg, 0.35 mmol) added to the solution and stirred for 1 h. The volatiles were removed under reduced pressure and the residue purified by column chromatography on silica gel with dichloromethane to give **14** as a yellow solid. Yield = 227 mg, 54%. ^{1}H (400 MHz, $CDCl_3$, 25 °C): $\delta = 0.90$–2.10 (m, 16H, $^{c\text{-hex}}CH_2$ + ^{COD}CH), 1.18 (d, $J =$ 6.4 Hz, 3H, CH(CH_3)$_3$), 1.45 (d, $J = 6.4$ Hz, 3H, CH(CH_3)$_3$), 2.74 (m, 1H, $^{c\text{-hex}}CH_{imine}$), 3.10 (m, 3H, ^{COD}CH + PhCH_2), 3.47 (m, 1H, ^{COD}CH), 3.56 (m, 1H, ^{COD}CH), 3.64 (m, 1H, PhCH_2), 4.26 (m, 1H, ^{COD}CH), 5.24 (m, 1H, $^{c\text{-hex}}CH_{imid}$), 5.31 (sep, $J = 6.9$ Hz, 1H CH(CH$_3$)$_3$), 6.95 (d, $J = 8.9$ Hz, 2H, ^{Ph}CH), 7.00–7.35 (m, 13H, ^{Ph}CH), 7.44 (brs, 4H, ^{Ph}CH), 7.63 (brs, 8H, ^{Ph}CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 22.5$, 24.3, 25.2, 26.8, 29.7, 29.8, 31.6, 32.2, 33.1, 35.8, 54.8, 56.7, 62.0, 63.7, 65.8, 68.3, 81.1, 81.2, 117.4, 122.3, 126.2, 128.0, 128.5, 128.7, 129.6, 129.8, 130.2, 131.5, 131.6, 131.8, 133.8, 134.2, 134.8, 160.9, 161.4, 161.9, 162.4, 173.7 (Ir^{NHC}C); MS (FAB): $m/z = 751$ ([M − B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^+$)

100%; Anal. [Found (calc.)] for $C_{71}H_{60}BF_{24}N_3Ir$, C 53.01 (52.86), H 3.87 (3.69), N 2.61 (2.60).

[Rh(κ$^{2\text{-iPr}}$*C*,*N*Bn$_2$)(COD)][B{3, 5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (15). Was prepared by an analogous method to **13** using [Rh(COD)Cl]$_2$ (62 mg, 0.125 mmol), potassium *tert*-butoxide (70 mg, 0.625 mmol) and **12** (167 mg, 0.25 mmol). Purification by column chromatography on silica gel with 1:2 dichloromethane:hexane to give **15** as a yellow solid. Yield = 275 mg, 68%. ^{1}H (400 MHz, $CDCl_3$, 25 °C): δ = 1.25–2.25 (m, 14H, $^{c\text{-hex}}CH_2$), 1.28 (d, J = 6.8 Hz, 3H, CH(CH_3)$_3$), 1.36 (d, J = 6.8 Hz, 3H, CH(CH_3)$_3$), 2.40–2.65 (m, 3H, $^{c\text{-hex}}CH_2$ + $^{c\text{-hex}}CH_{imine}$), 3.47 (br, 4H, PhC$H_2$), 3.89 (m, 1H, $^{c\text{-hex}}CH_{imid}$), 4.21 (m, 1H, ^{COD}CH), 4.30 (m, 1H, ^{COD}CH), 4.74 (m, 1H, ^{COD}CH), 5.50 (m, 1H, ^{COD}CH), 6.00 (sep, J = 6.9 Hz, 1H, CH(CH$_3$)$_3$), 6.86 (d, J = 7.5 Hz, 2H, ^{Ph}CH), 6.90–7.35 (m, 18H, ^{Ph}CH), 7.44 (br, 4H, ^{Ph}CH), 7.63 (br, 8H, ^{Ph}CH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 22.6, 23.2, 25.4, 26.5, 27.0, 29.7, 30.2, 31.4, 34.6, 38.1, 52.1 (br, PhCH_2), 55.8, 64.4, 66.3, 75.6 (d, $^1J_{Rh\text{-}C}$ = 13 Hz, ^{COD}CH), 82.4 (d, $^1J_{Rh\text{-}C}$ = 14 Hz, ^{COD}CH), 96.2 (d, $^1J_{Rh\text{-}C}$ = 14 Hz, ^{COD}CH), 97.0 (d, $^1J_{Rh\text{-}C}$ = 14 Hz, ^{COD}CH), 117.4, 123.2, 125.9, 129.0, 128.7, 128.5, 128.3, 129.6, 129.7, 130.9, 131.8, 133.4, 133.5, 134.8, 139.4, 160.9, 161.4, 161.9, 162.4, 173.5 (d, $^1J_{Rh\text{-}C}$ = 51 Hz, Rh^{NHC}C); MS (FAB): m/z = 752 ([M − B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$]$^+$), 100%; Anal. [Found (calc.)] for $C_{78}H_{66}BF_{24}N_3Rh$, C 57.93 (58.01), H 4.05 (4.12), N 2.48 (2.60).

General procedure for catalytic asymmetric hydrogenation. To a reaction vial was added 2-propanol (2 mL), precatalyst complex (0.5×10^{-5} mol) from a 2-propanol stock solution, the substrate (1×10^{-3} mol) and potassium *t*-butoxide (2.5 mg, 2×10^{-5} mol). After 20 h stirring at 20 °C an aliquot (100 μL) was then taken and diluted with 40–60 petroleum ether (1 mL), passed through a silica plug and analysed by ^{1}H NMR and chiral HPLC.

Chiral separation conditions: **Phenyl ethanol**. 1.0 mL/min (95% hexane, 5% 2-propanol), 20 °C, Chiralcel OD column. 13.05 min phenylethan-1-ol (*R*), 18.39 min phenylethan-1-ol (*S*); **2-methylphenyl ethanol**. 1.0 mL/min (99% hexane, 1% 2-propanol), 20 °C, Chiralcel OD column. 17.32 min 2-methylphenylethan-1-ol (*R*), 19.32 min 2-methylphenylethan-1-ol (*S*); **3-methylphenyl ethanol**. 1.0 mL/min (98% hexane, 2% 2-propanol) 20 °C, Chiralcel OD column. 11.93 min 3-methylphenylethan-1-ol (*R*), 18.41 min 3-methylphenylethanol (*S*); **4-methylphenyl ethanol**. 1.0 mL/min (99% hexane, 1% 2-proanol), 20 °C, Chiralcel OD column. 14.85 min 4-methylphenylethan-1-ol (*R*), 16.04 min 4-methylphenylethan-1-ol (*S*); **2-Chlorophenyl ethanol**. 1.0 mL/min (99% hexane, 1% 2-propanol), 20 °C, Chiralcel OD column. 14.04 min 2-chlorophenylethan-1-ol (*R*), 15.60 min 2-chlorophenylethan-1-ol (*S*); **3-Chlorophenyl ethanol**. 0.5 mL/min (96% hexane, 4% 2-propanol), 20 °C, Chiralcel OD column. 18.06 min 3-chlorophenylethan-1-ol (*R*), 18.89 min 3-chlorophenylethan-1-ol (*S*); **4-Chlorophenyl ethanol**. 1.0 mL/min (99% hexane, 1% 2-propanol), 20 °C, Chiralcel OD column. 20.07 min 4-chlorophenylethan-1-ol (*S*), 21.63 min 4-chlorophenylethan-1-ol (*R*); **2-naphthylalcohol** (Table 3 **entry 4)**. 1.0 mL/min (98% hexane, 2% 2-propanol), 20 °C, Chiralcel OC column, detected at 210 nm. 28.34 min naphthyl-2-ethan-1-ol (*S*), 31.47 min naphthyl-2-ethan-1-ol (*R*); **4-phenyl butan-2-ol (**Table 3 **entry 5)**. 1.0 mL/min (95% hexane, 5% 2-propanol), 20 °C, Chiralcel OD column, detected at 210 nm. 8.75 min 4-phenyl butan-1-ol (*S*), 12.55 min 4-phenyl butan-1-ol (*R*); **2-chlorophenyl benzylmethanol**. 1.0 mL/min (90% hexane, 10% 2-propanol), 20 °C, Chiralcel OD column, detected at 210 nm. 9.74 min (3-chlorophenyl)(phenyl)methanol (*S*), 10.40 min (3-chlorophenyl)(phenyl)methanol (*R*); **3-chlorophenyl benzylmethanol**. 1.0 mL/min (90% hexane, 10% 2-propanol), 20 °C, Chiralcel OD column, detected at 210 nm. 9.74 min (3-chlorophenyl)(phenyl)methanol (*S*), 10.40 min (3-chlorophenyl)(phenyl)methanol (*R*).; **4-chlorophenyl benzylmethanol**. 1.0 mL/min (98% hexane, 2% 2-propanol), 20 °C, Chiralcel OD column, detected at 210 nm. 31.00 min (4-chlorophenyl)(phenyl)methanol (*R*), 32.20 min (4-chlorophenyl)(phenyl)methanol (*S*).

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