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Axially chiral dimeric Ir and Rh complexes bridged by flexible NHC ligands

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ABSTRACT

A family of Ag complexes of the type [{BnN($CH_2CH_2{}^RIm)_2$}Ag]·[AgX_2] (X = I, ^{R}Im = 1-methylimidazole (**3a**); X = Cl, ^{R}Im = 1-*tert*-butylimidazole (**3b**), 1-benzylimidazole (**3c**) or 1-methylbenzimidazole (**3d**)) or [{BnN($CH_2CH_2CH_2{}^RIm)_2$}Ag]·[$AgCl_2$] (^{R}Im = 1-methylimidazole (**4a**), 1-*tert*-butylimidazole (**4b**), 1-benzylimidazole (**4c**) or 1-methylbenzimidazole (**4d**)) with a flexible unsaturated linker connecting the two NHC ligands has been prepared. These silver complexes undergo facile transmetalliation with $[Ir(COD)Cl]_2$ to generate the bimetallic species (COD)ClIr{BnN($CH_2CH_2{}^RIm)_2$}IrCl(COD) (^{R}Im = 1-methylimidazole (**5a**), 1-*tert*-butylimidazole (**5b**), 1-benzylimidazole (**5c**) or 1-methylbenzimidazole (**5d**)) or (COD)ClIr{BnN($CH_2CH_2CH_2{}^RIm)_2$}IrCl(COD) (^{R}Im = 1-methylimidazole (**6a**), 1-*tert*-butylimidazole (**6b**), 1-benzylimidazole (**6c**) or 1-methylbenzimidazole (**6d**)) with a bridging bidentate NHC ligand. A similar reaction can be performed using $[Rh(COD)Cl]_2$ to generate the analogous Rh species (COD)ClRh {BnN($CH_2CH_2CH_2{}^RIm)_2$}RhCl(COD) (^{R}Im = 1-methylimidazole (**7a**), 1-benzylimidazole (**7c**) or 1-methylbenzimidazole (**7d**)). Complexes **5d**, **6d** and **7d** were characterized by X-ray crystallography. All of our new Rh and Ir species possess axial chirality and are prepared as a mixture of isomers. However, crystals of **5d**, **6d** and **7d** contain only one diastereomer. Dissolution of the diastereometrically pure crystals results in epimerization and the formation of an equilibrium mixture. Our new Ir complexes are active catalysts for both olefin and transfer hydrogenation and we present a comparison of their catalytic activity based on the linker length of the ligand.

1. Introduction

Over the last 20 years the coordination chemistry of *N*-heterocyclic carbenes has been explored in significant detail [1–7]. A wide range of different NHC ligands have now been prepared, including numerous systems which incorporate NHCs in chelate [8–11], pincer [8,12] and tripodal [9,10,13,14] scaffolds. It has been shown that these ligands coordinate to most transition metals and the resulting complexes have been utilized in a number of catalytic reactions [1,2,10–12,15]. In general, it is believed that NHCs are extremely strong σ-donors and weak π-acceptors, although there is some dispute on the latter point [16–18]. Surprisingly, given the plethora of NHC ligands that have been designed for monomeric species, reports of bimetallic complexes are less common. The vast majority of reports of bidentate and polydentate NHC supported bimetallic species involve Rh or Ir. Broadly speaking these complexes fall into four main classes: (i) species with bidentate carbenes containing flexible saturated linkers [19–23], (ii) species with bidentate carbenes containing semi-rigid unsaturated linkers [24–38], (iii) species with bidentate carbenes containing completely rigid linkers, often described as 'Janus' type carbenes [39–41]; and (iv) species with three or more NHC ligands, which often contain more than two metal centers [42–45]. Representative examples of each of these types of complex are shown in Fig. 1. At this stage, reactivity studies are not as extensive as structural studies, however these bimetallic and multimetallic systems are catalysts for hydrosilylation reactions [26,30,42,46], hydrogen transfer reactions [46], the hydroformylation of olefins [24,38], and the cyclization of acetylenic carboxylic acids [43].

Currently the handful of reports describing bimetallic Ir and Rh complexes with saturated linkers [19–23], are restricted to systems which contain an unsubstituted alkyl chain as the linker. Recently both Douthwaite and our group have reported bidentate NHC ligands with flexible amine linkers (Fig. 2) [47–49]. Douthwaite has described ligands with a two carbon linker (**a**) (linker length is defined as the number of carbons between the imidazole and the central amine) while our group has prepared species with a three carbon linker (**b**). Depending on the length of the linker and the size of the amine substituent, when these ligands coordinate to $PdCl_2(MeCN)_2$, the ligand either binds in a tridentate pincer fashion with coordination of the central amine or as a bidentate *trans*-spanning ligand with no coordination of the central amine [47–49]. In both cases the resulting complexes are active catalysts for the Heck and Suzuki reactions. As part of our studies exploring the coordination chemistry of ligands of the type **a** and **b** we were interested in preparing Rh and Ir complexes supported by these ligands. Here, we describe the synthesis of dimeric Ir and Rh

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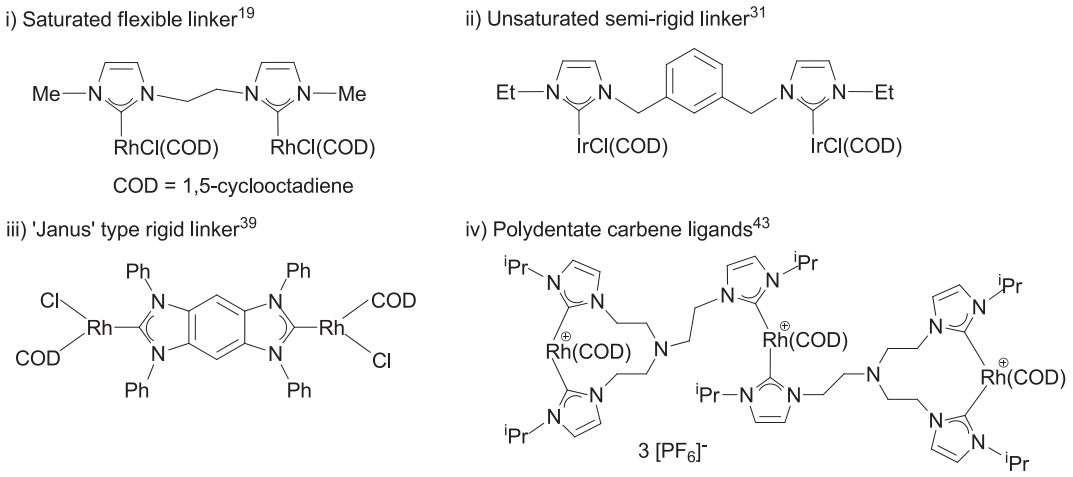


Fig. 1. Representative examples of the four different types of carbene linkers utilized to make multinuclear Ir and Rh complexes.

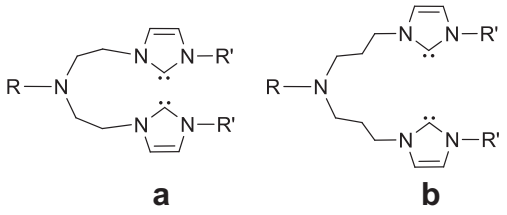


Fig. 2. Bidentate carbene ligands with flexible amine containing linkers [47–49].

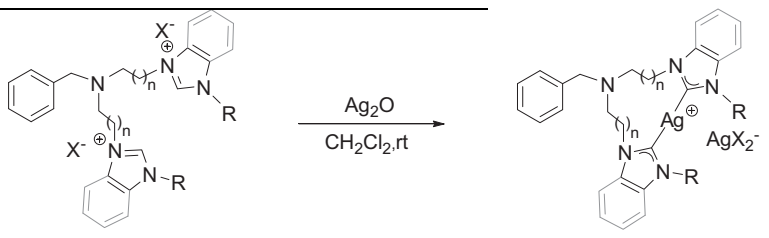
complexes supported by ligands **a** and **b**. The resulting species possess axial chirality and are unusual amongst Rh and Ir species bridged by a flexible bidentate NHC ligand because they contain a functional group in the linker. Furthermore, we demonstrate that our complexes are active catalysts for both olefin and transfer hydrogenation and present a comparison of their catalytic activity based on the linker length of the ligand.

2. Results and discussion

2.1. Ligand synthesis and preparation of Ir and Rh complexes

As part of a previous study we prepared the imidazolium salts **2a**–**2d** [49], while Douthwaite had previously reported an analogous species to **2b** with a two carbon linker **1b** [47,48]. Using an analogous synthetic route to that described by Douthwaite, the imidazolium salts **1a**, **1c** and **1d** were prepared in good yield using an S_N2 reaction between the appropriate free imidazole and bis(2-chloroethyl)benzylamine. This reaction was significantly slower when 1-methylbenzimidazole was used as the substrate and both a high concentration and an elevated temperature were required to obtain a satisfactory yield. In the case of the methyl substituted imidazolium salt **1a**, the Cl^- salt was extremely hygroscopic and was converted into the PF_6^- salt to allow for easy handing in air. Treatment of **1c** and **1d** with Ag_2O generated the silver salts **3c** and **3d** (Eq. (1)), as reported earlier for **1b** and **2a**–**2d**. In the case of **1a** the PF_6^- was first converted into the I^- salt (see Supporting information for X-ray structure) before being treated with Ag_2O to generate the silver species **3a**. The new silver salts were characterized by ^1H and ^{13}C NMR spectroscopy and have similar spectroscopic properties to those previously reported. Although they were not characterized by X-ray crystallography, it is likely that the ligand binds in a bidentate fashion to one cationic Ag center, with an $AgCl_2^-$ or AgI_2^- anion, as described for **2d** [49].

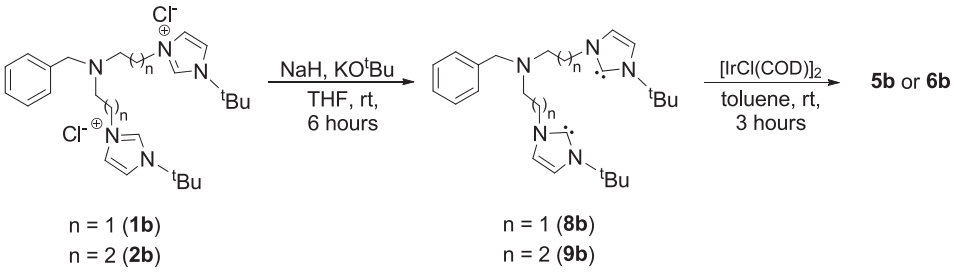
Reaction of the silver salts **3a–3d** and **4a–4d** with $[IrCl(COD)]_2$ resulted in facile transmetallation and the formation of the new dimeric Ir complexes **5a-5d** and **6a-6d**, respectively (Eq. (2)). When a similar reaction was performed between the representative silver salts **4a**, **4c** and **4d** and $[RhCl(COD)]_2$ the analogous Rh complexes **7a**, **7c** and **7d** were obtained (Eq. (2)). All of the Rh and Ir complexes were fully characterized. If two equivalents of the silver salts were reacted with $[IrCl(COD)]_2$ or $[RhCl(COD)]_2$, one



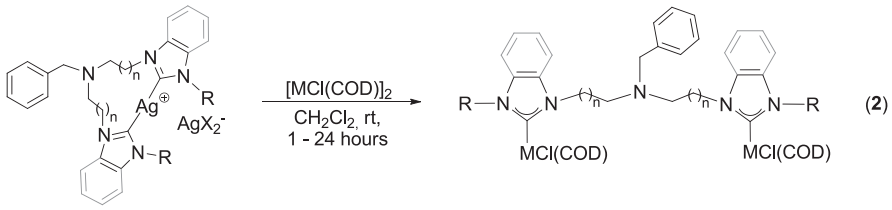
(1)

For imidazole
n=1, X=PF_6, R=Me (**1a**)
n=1, X=Cl, R=^{t}Bu (**1b**), Bn (**1c**)
n=2, X=Cl, R=Me (**2a**),^{t}Bu (**2b**), Bn (**2c**)
For benzimidazole
n=1, X=Cl, R=Me (**1d**)
n=2, X=Cl, R=Me (**2d**)

For imidazole
n=1, X=I, R= Me (**3a**)
n=1, X=Cl, R=^{t}Bu (**3b**),Bn (**3c**)
n=2, X=Cl, R=Me (**4a**),^{t} Bu (**4b**), Bn (**4c**)
For benzimidazole
n=1, X=Cl, R=Me (**3d**)
n=2, X=Cl, R=Me (**4d**)



Scheme 1. Synthesis of Ir complexes **5b** and **6b** from the free carbenes **8b** and **9b**.



For imidazole
n = 1 R = Me (**3a**), ^{t}Bu (**3b**), Bn (**3c**)
n = 2 R = Me (**4a**), ^{t}Bu (**4b**), Bn (**4c**)
For benzimidazole
n = 1 R = Me (**3d**)
n = 2 R = Me (**4d**)

M = Ir
For imidazole
n = 1 R = Me (**5a**), ^{t}Bu (**5b**), Bn (**5c**)
n = 2 R = Me (**6a**), ^{t}Bu (**6b**), Bn (**6c**)
For benzimidazole
n = 1 R = Me (**5d**)
n = 2 R = Me (**6d**)

M = Rh
For imidazole
n = 2 R = Me (**7a**), Bn (**7c**)
For benzimidazole
n = 2 R = Me (**7d**)

equivalent of the silver salt remained unreacted, consistent with the proposed coordination of one equivalent of the ligand per equivalent of the Ir dimer. In some cases the yields of the Rh and Ir complexes (after purification by column chromatography) were relatively low and an alternative synthetic method was pursued. Douthwaite had demonstrated that **1b** could be deprotonated to generate the free carbene **8b** [48], and we were able to perform a similar reaction using **2b** to form the free carbene **9b** (Scheme 1). The free carbene **9b** was unstable for prolonged periods at room temperature and needed to be stored under N_2. Reaction of the free carbenes **8b** and **9b** with $[IrCl(COD)]_2$ generated **5b** and **6b** in high initial yield and purity, however further purification by column chromatography was still required, which resulted in modest yields. This route could not be generalized to imidazoles with other substituents, as successful deprotonation to generate the free carbene was not possible due to the low solubility of the imidazolium salts, **1a** and **1d** and **2a** and **2d** in organic solvents.

Complexes **5d**, **6d** and **7d** were characterized by X-ray crystallography (Figs. 3–5). The structure of **5d** clearly shows that the ligand is bridging between the two Ir centers with no interaction between the central amine and either metal center. The coordination geometry around Ir is the same at both metal centers and within experimental error the bond lengths and angles around Ir are identical. The geometric parameters around Ir are consistent with those reported in other related species [22,31,34,43] and the NHC ligands are oriented perpendicular to the coordination plane around Ir. The most interesting aspect of the solid state structure is that it demonstrates that the molecule possesses axial chirality around the Ir–NHC bond [50], with both metal centers being part of a separate center of axial chirality. The (R,R) diastereomer is shown in Fig. 3, although as the space group, $P2(1)/n$, is non-enantiomorphic, each unit cell contains two molecules of the (S,S) and (R,R) enantiomers. Interconversion between the (R,R) and (S,S) isomers could be achieved by rotation around both Ir–NHC bonds, while rotation around one Ir–NHC bond would give the equivalent meso (R,S) or (S,R) diastereomers.

The solid-state structures of **6d** and **7d** are iso-structural (within esd) and both molecules possess axial chirality. In both cases the (R,R) configuration is depicted in Figs. 4 and 5. Unsurprisingly, there is almost no variation in bond lengths and angles between the Ir and Rh structures and the structures are superimposable (see Fig. S1).[1] The major difference between the structures with a three carbon linker and **5d** relates to the orientation of the nitrogen lone pair on the central amine. This results in the inversion of the direction of the lone pair on nitrogen atom between the two carbon linked species **5d** and the three carbon linked species **6d** and **7d**.

The ^1H and ^{13}C NMR spectra of **5a–5d** and **6a–6d** were complicated. For example in the ^{13}C spectrum of a pure (by elemental analysis) amorphous sample of **6d**, 16 different resonances corresponding to both the vinylic and aliphatic COD environments and two different carbene resonances at δ 191.5 and 191.6 ppm were observed. In fact for all complexes **5a–5d** and **6a–6d** double the expected number of carbon resonances were obtained and it appeared that the molecules have no symmetry. However, when a crystalline sample of **6d** was dissolved in CD_2Cl_2 and a ^{13}C NMR spectrum recorded immediately, only eight COD environments and one carbene resonance were initially detected. Subsequently, over the course of several hours, eight new COD resonances and an additional carbene resonance grew in (changes in the number of linker resonances were also observed). The ^1H NMR spectrum of crystals of **6d** showed similar behaviour. When crystals of **6d** were dissolved in CD_2Cl_2 and the spectrum immediately recorded, the CH_2 protons in the benzyl substituent on the central amine of the linker appeared as two doublets at δ 3.82 and 3.67 ppm (Fig. 6b). However, over 6 h at room temperature a new singlet grew in at δ 3.75 ppm along with the doublets (Fig. 6c). We believe that equilibration between the (R,R) or (S,S) and (R,S) diastereomers of **6d** accounts for this phenomenon. As explained above, a crystalline sample of **6d** comprises of only the

[1] See supporting information for more details.

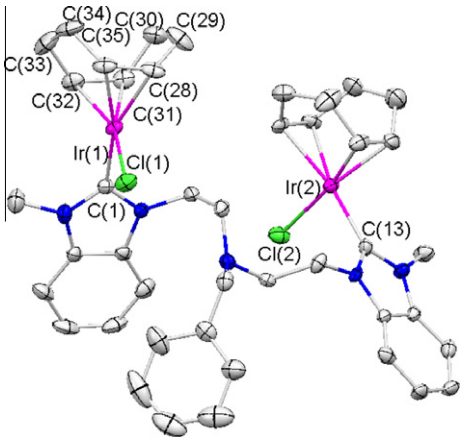


Fig. 3. Molecular structure of **5d**. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–Cl(1) 2.352(2), Ir(1)–C(1) 2.001(8), Ir(1)–C(28) 2.156(9), Ir(1)–C(32) 2.077(9), Ir(1)–C(31) 2.084(9), Ir(1)–C(35) 2.190(9), Ir(2)–Cl(2) 2.352(2), Ir(2)–C(13) 2.026(8), Ir(2)–C(36) 2.065(9), Ir(2)–C(37) 2.096(10), Ir(2)–C(40) 2.177(8), Ir(2)–C(41) 2.151(9), C(28)–C(29) 1.494(15), C(28)–C(35) 1.365(15), C(29)–C(30) 1.485(14), C(30)–C(31) 1.512(13), C(31)–C(32) 1.428(14), C(32)–C(33) 1.494(16), C(33)–C(34) 1.488(15), C(34)–C(35) 1.492(14), Cl(1)–Ir(1)–C(1) 87.5(2), Cl(1)–Ir(1)–C(28) 91.9(3), Cl(1)–Ir(1)–C(31) 165.1(3), C(1)–Ir(1)–C(28) 156.8(4), C(1)–Ir(1)–C(31) 94.0(3), C(28)–Ir(1)–C(31) 80.9(3).

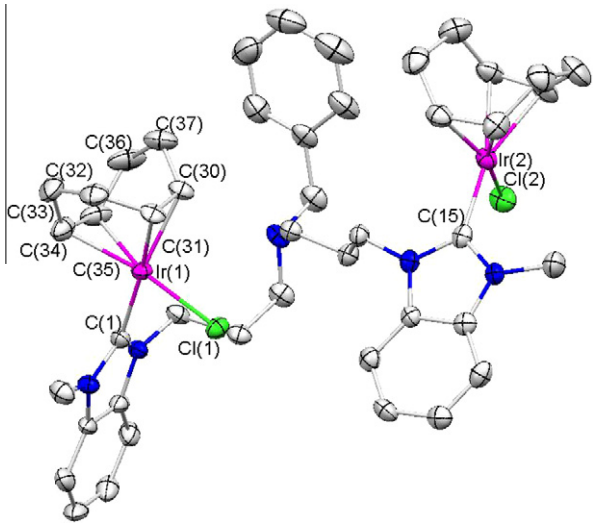


Fig. 4. Molecular structure of **6d**. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–Cl(1) 2.3542(17), Ir(1)–C(1) 2.014(7), Ir(1)–C(30) 2.191(8), Ir(1)–C(31) 2.187(8), Ir(1)–C(34) 2.092(8), Ir(1)–C(35) 2.082(8), Ir(2)–Cl(2) 2.3623(20), Ir(2)–C(15) 2.026(8), Ir(2)–C(40) 2.107(8), Ir(2)–C(41) 2.110(8), Ir(2)–C(44) 2.163(10), Ir(2)–C(45) 2.181(9), C(30)–C(31) 1.389(11), C(30)–C(37) 1.510(11), C(31)–C(32) 1.511(10), C(32)–C(33) 1.507(12), C(33)–C(34) 1.525(12), C(34)–C(35) 1.382(13), C(35)–C(36) 1.503(14), C(36)–C(37) 1.546(13), Cl(1)–Ir(1)–C(1) 86.34(19), Cl(1)–Ir(1)–C(30) 94.47(19), Cl(1)–Ir(1)–C(34) 160.9(2), C(1)–Ir(1)–C(31) 162.3(3), C(1)–Ir(1)–C(34) 96.6(3), C(31)–Ir(1)–C(34) 81.9(3).

(R,R) or (S,S) diastereomers (the NMR spectra of these species would be expected to be equivalent). In the (R,R) or (S,S) diastereomer the benzylic protons are diastereotopic and should appear as two doublets (Fig. 6a). Immediately after dissolution of crystalline **6d** in solution, only these equivalent diastereomers are present. Over time, presumably through rotation around the Ir–NHC bonds, some of the (R,R) and (S,S) diastereomers are converted to the meso (R,S) diastereomer. The benzylic protons in the (R,S) diastereomer are equivalent and should appear as a singlet, which explains the growth in the peak at δ 3.75 ppm. Along with the

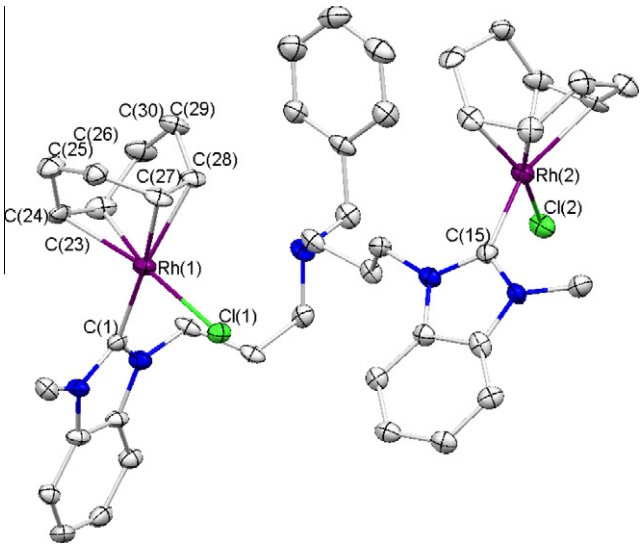


Fig. 5. Molecular structure of **7d**. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–Cl(1) 2.363(2), Rh(1)–C(1) 2.027(10), Rh(1)–C(23) 2.073(11), Rh(1)–C(24) 2.155(9), Rh(1)–C(27) 2.220(11), Rh(1)–C(28) 2.223(11), Rh(2)–Cl(2) 2.386(3), Rh(2)–C(15) 2.030(11), Rh(2)–C(38) 2.093(10), Rh(2)–C(41) 2.215(12), Rh(2)–C(42) 2.203(12), Rh(2)–C(45) 2.147(11), C(23)–C(30) 1.517(18), C(24)–C(25) 1.522(16), C(25)–C(26) 1.520(15), C(26)–C(27) 1.491(14), C(27)–C(28) 1.390(15), C(28)–C(29) 1.542(15), C(29)–C(30) 1.543(17), C(31)–C(32) 1.525(16), C(32)–C(33) 1.386(14), C(32)–C(37) 1.401(16), Cl(1)–Rh(1)–C(1) 85.8(2), Cl(1)–Rh(1)–C(24) 160.2(3), Cl(1)–Rh(1)–C(27) 90.4(3), C(1)–Rh(1)–C(24) 96.1(4), C(1)–Rh(1)–C(27) 162.9(4), C(24)–Rh(1)–C(27) 82.0(4).

major change in the benzylic protons, and the growth of a second set of peaks in the ^{13}C spectrum, several other more subtle changes occur in the ^{1}H NMR spectrum. For example several new peaks appear in the aromatic region, and the complexity of the multiplets corresponding to some of the coordinated COD and linker peaks increases as the second isomer grows in.[1]

The rate of rotation around the Ir–NHC bond was measured by monitoring the growth of the singlet at δ 3.75 ppm with time. Eyring analysis indicates that $\Delta H^{\ddagger} = 52 \pm 3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -162 \pm 15$ J mol^{-1}K^{-1}. The $\Delta G^{\ddagger}_{298}$ value of 101 ± 6 kJ mol^{-1} is consistent with the measured rate of rotation in Rh supported NHC complexes [51,52]. The large negative entropy is surprising but a similar value has been reported by Doyle and Lappert [52]. Crystalline samples of the three carbon linked Rh species **7d** displayed similar NMR properties to **6d** and the rate of equilibration appears to be similar. Unfortunately crystals of **7d** could not be grown on a large enough scale to perform an Eyring analysis and the rate of rotation could not be accurately measured. In contrast dissolution of a crystalline sample of the two carbon linked species **5d** in CD_2Cl_2 resulted in the observation of both the R,R and R,S isomers by ^{1}H NMR spectroscopy immediately after dissolution. The rate was too fast to accurately measure, which suggests that rotation around the Ir–NHC bond is significantly faster in the two carbon linked species **5d** compared with the three carbon linked species **6d**.

Despite repeated attempts, X-ray quality crystals of species supported by imidazole, instead of benzimidazole ligands could not be obtained. In all cases the ^{1}H NMR spectrum of **5a**–**5c** and **6a**–**6c** displayed two doublets and a singlet for the CH_2 protons of the benzyl group and 16 signals for the COD carbons in the ^{13}C NMR spectrum. On this basis we believe that these species are formed as a mixture of diastereomers and the approximate ratio of the isomers is 1:1 (from integration of the ^{1}H NMR spectrum). Presumably, the lower solubility of the (R,R) and (S,S) isomers of **5d**, **6d** and **7d** allowed them to be crystallized and separated from the meso (R,S) isomer, but they are clearly not configurationally stable

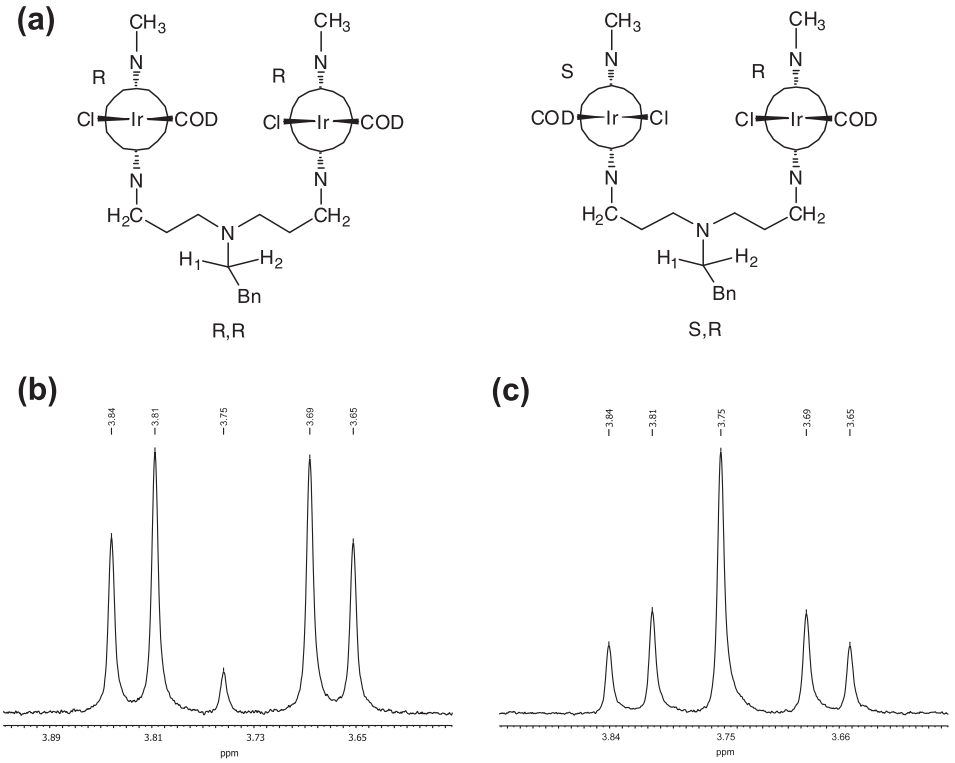
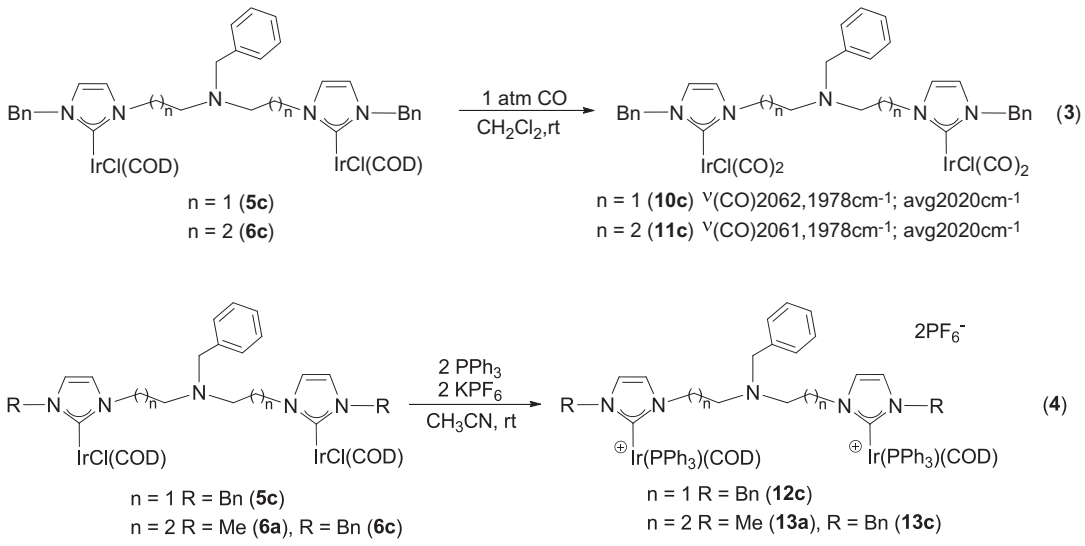


Fig. 6. (a) Modified Newman projections of **6d** looking down the Ir–NHC bond. In the R,R (or S,S) isomer H_1 and H_2 are diastereotopic, whereas they are equivalent in the S,R (or R,S). (b) Selected region of the ^{1}H NMR spectrum of crystals of **6d** immediately after dissolution in CD_2Cl_2 at room temperature. (c) Selected region of the ^{1}H NMR spectrum of crystals of **6d** 24 h after dissolution in CD_2Cl_2 at room temperature. In the case of the R,R isomer, the inequivalence of H_1 and H_2 gives rise to a pair of doublets. Conversely, the R,S isomer contains a mirror plane making H_1 and H_2 equivalent and gives rise to a singlet.

in solution at room temperature. To the best of our knowledge this is the first example of bimetallic Rh or Ir complexes supported by NHC ligands in which one isomer of an axially chiral pair has been separated. Crabtree and Faller have previously reported that dimeric Rh complexes supported by a bidentate NHC with a flexible linker give rise to two sets of signals in their ^{1}H NMR spectra, but were unable to separate the isomers or confirm the structure of either isomer by X-ray crystallography [20].

Treatment of **5c** and **6c** with 1 atm of CO at room temperature, resulted in rapid displacement of the COD ligands and the formation of the tetra(carbonyl) complexes **10c** and **11c** (Eq. (3)). Compounds **10c** and **11c** were not fully characterized but were identified using ^{1}H and ^{13}C NMR spectroscopy, high resolution mass spectrometry and IR spectroscopy. The length of the linker did not affect the average ν(CO) values suggesting that the size of the linker length does not greatly perturb the electronic properties of the complexes. Furthermore, the average ν(CO) values are consistent with those observed in monomeric complexes of the type $IrCl(CO)_2(NHC)$ [53], indicating that there is little electronic effect of having a second metal center in relatively close proximity. Attempts to further compare the electronic properties of complexes with two carbon and three carbon linkers using electrochemistry failed, as only broad



irreversible waves were observed and a solid material deposited on the electrode.

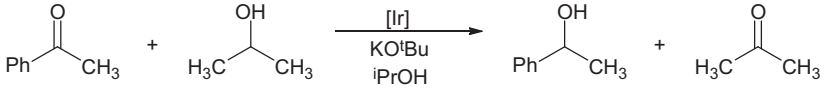
Cationic Ir complexes have been shown to be vastly more effective catalysts for olefin hydrogenation compared with neutral species. Treatment of the representative neutral Ir complexes **5c**, **6a** and **6c** with KPF_6 and PPh_3 in CH_3CN, resulted in rapid displacement of the Cl ligand with PPh_3 on both Ir centers (Eq. (4)). The resulting complexes **12c**, **13a** and **13c** were fully characterized. The ^1H NMR spectra of these complexes featured both two sets of doublets and a singlet at the characteristic resonance for the benzylic protons in the ^1H NMR spectrum and all resonances in the ^{13}C NMR spectrum were doubled. This strongly suggests that these species were formed as a mixture of diastereomers with an approximate ratio of 1:1. X-ray quality crystals of these species could not be obtained.

2.2. Catalysis

Ir(I) and Ir(III) complexes supported by NHC ligands have been shown to catalyze hydrogen transfer reactions to oxidize alcohols to aldehydes and ketones and reduce ketones, aldehydes, and imines to alcohols and amines, respectively [54]. We tested our systems for hydrogen transfer reactions to gauge the performance of the bimetallic systems relative to reported catalysts with high TON [54–59]. Initially we probed the reduction of acetophenone using standard conditions [59]. Our results demonstrate that our new complexes are active for transfer hydrogenation (Table 1). In general it appears that the three carbon linked species are more efficient catalysts than the two carbon linked species, although mechanistically it is not clear what factors make a certain linker length desirable. Consistent with our results at high substrate conversion, when time course experiments were performed, it was clear that that the three carbon linked species was faster than the two carbon linked species at short reaction times as well. There is also some variation in the rates of reaction when the imidazole substituent is changed, suggesting that in agreement with previous results the reaction is sensitive to the electronic properties around the metal [59]. Imines are more difficult to reduce than ketones and we were interested in testing our catalysts for the transfer hydrogenation of imines. A higher catalyst loading was required to achieve imine reduction within 24 h at 80 °C (Table 2). The three carbon linked systems were again faster than the two carbon linked systems. Overall our bimetallic catalysts are fairly effective for transfer hydrogenation but the rate of catalysis is slower than the best catalysts in the literature [58,59]. Notably our observation that changing from imidazole to benzimidazole makes a bigger difference to catalytic activity than changing the linker length is consistent with Crabtree's hypothesis that electronic effects make a larger different to catalytic activity than steric effects [1].

Since the early 1970s cationic Ir complexes have been utilized as homogeneous olefin hydrogenation catalysts [60]. One of the main pathways for catalyst deactivation involves the formation of bi and trimetallic Ir polyhydrides [60] and we hypothesized that by starting with a bimetallic system decomposition pathways involving the formation of dimeric species might be circumvented. The phosphine supported dimers **12c** and **13c** were screened as olefin hydrogenation catalysts (Table 3). Both complexes were able to hydrogenate (Z)-cyclooctene to cyclooctane at room temperature, with no apparent difference in activity between the two carbon and three carbon linked system. However, the complexes are far less active than the best Ir catalysts [60]. Lower conversions were obtained with more substituted olefins. Only a small amount

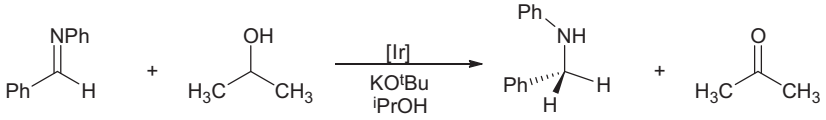
Table 1
Results for hydrogen transfer between acetophenone and acetone using different bimetallic Ir catalysts.



Entry	Catalyst	Time (h)	Yield (%)[a]
1	**5b**	10	92
2	**6b**	9	92
3	**5d**	36	74
4	**6d**	36	92

[a] Yield measured using ^1H NMR spectroscopy (average of two runs), no by-products were detected. Reagents and conditions: 4.16 mmol acetophenone, catalyst loading 0.021 mol%, 0.43 mol% KO^{t}Bu, 25 mL ^{i}PrOH, 80 °C.

Table 2
Results for hydrogen transfer between *N*-benzylideneaniline and acetone using different bimetallic Ir catalysts.



Entry	Catalyst	Time (h)	Conversion (%)[a]
1	**5b**	4	99
2	**6b**	2	98
3	**5d**	12	75
4	**6d**	12	87

[a] Yield measured using ^1H NMR spectroscopy (average of two runs), no by-products were detected. Reagents and conditions: 4.16 mmol *N*-benzylideneaniline, catalyst loading 0.043 mol%, 0.43 mol% KO^{t}Bu, 25 mL ^{i}PrOH, 80 °C.

Table 3
Results for catalytic hydrogenation using different bimetallic Ir catalysts.

Entry	Catalyst	Substrate	Time (h)	Temp (°C)	Yield (%)[a]
1	**12c**	(Z)-Cyclooctene	4	25	100
2	**13c**	(Z)-Cyclooctene	4	25	100
3	**12c**	(Z)-stilbene	21	40	5[b]
4	**13c**	(Z)-stilbene	21	40	4[b]
5	**12c**	(E)-stilbene	168	40	12
6	**13c**	(E)-stilbene	168	40	12
7	**12c**	1-methylcyclohexene	168	40	0
8	**13c**	1-methylcyclohexene	168	40	0

[a] Yield measured using ^{1}H NMR spectroscopy (average of two runs), no by-products were detected.
[b] In this case the (Z)-stilbene was completely isomerized to the thermodynamically more stable (E)-stilbene. Reagents and conditions: 0.091 mmol substrate, catalyst loading 2.5 mol%, 1 atm H_2, 0.5 mL CD_2Cl_2.

of (E)-stilbene was converted to bibenzyl and no conversion was obtained with 1-methylcyclohexene as the substrate. When (Z)-stilbene was used as the substrate, complete isomerization to thermodynamically preferred (E)-stilbene occurred prior to any hydrogenation. At this stage there is little information about the mechanism of hydrogenation using our bimetallic systems but we believe the standard pathway of oxidative addition of H_2, olefin coordination, insertion and then reductive elimination is occurring [61].

3. Conclusions

We have synthesized a series of bimetallic Rh and Ir complexes bridged by a flexible bidentate NHC ligand containing an amine in the linker. The new complexes are axially chiral and in several cases one diastereomer can be isolated selectively through recrystallization. To the best of our knowledge this is the first time a single isomer of a species of this type has been isolated in a pure form. Our new bimetallic complexes are active catalysts for both transfer hydrogenation and olefin hydrogenation and the length of the linker between the metal centers influences the catalytic activity in the case of transfer hydrogenation reactions. At this stage it is unclear why the linker length affects catalysis and further work will look to understand this interesting phenomenon.

4. Experimental

4.1. General methods

Experiments were performed under air unless otherwise noted. Solvents were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received except where noted. Acetophenone, ammonium hexafluorophosphate, benzyl amine, *N*-benzylideneaniline, 1-methylimidazole, 1-benzylimidazole, 1-methylbenzimidazole, silver(I) oxide, potassium tert-butoxide, sodium iodide, sodium hydride, and triphenylphosphine were purchased from Aldrich. Deuterated solvents were obtained from Cambridge Isotope Laboratories. CD_2Cl_2 and $CDCl_3$ were dried using P_2O_5 and vacuum transferred prior to use. NMR spectra were recorded on Bruker AMX-400 or AMX500 spectrometers at ambient probe temperatures. Chemical shifts are reported with respect to residual internal *protio* solvent for ^{1}H and ^{13}C{^{1}H} NMR spectra. All assignments are based on two dimensional ^{1}H,^{13}C-HMQC and HMBC experiments. HRMS were recorded at The Mass Spectrometry (MS) and Proteomics Resource of the W.M. Keck Foundation Biotechnology Resource Laboratory at Yale University. Robertson Microlit Laboratories, Inc. performed the elemental analyses. Literature procedures were followed to prepare the following compounds: **1b** [48], **2a**–**2d** [49], **3b** [48], **4a**–**4d** [49], **8b** [48], 1-*tert*-butylimidazole [62], $BnN(CH_2CH_2Cl)_2$ [63], $[Ir(COD)Cl]_2$ [64] and $[Rh(COD)Cl]_2$ [65].

4.2. X-ray crystallography

Crystal samples were mounted in MiTeGen polyimide or Hampton Research nylon loops with immersion oil. The diffraction experiments were carried out on either a Rigaku SCXMini diffractometer using filtered Mo Kα radiation (λ = 0.71073 Å) or a Rigaku diffractometer equipped with a Saturn 944+ detector and rotating anode Cu Kα source (λ = 1.54187 Å). The data frames were processed using Rigaku CrystalClear [66] and corrected for Lorentz and polarization effects. The structures were solved by direct methods [67] and expanded using Fourier techniques [68]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Details of the crystal and refinement data for complexes **5d**, **6d**, **7d** and $[^{Me}(H)C_{Et}N(Bn)_{Et}C.(H)^{Me}]\cdot 2[I]$ are given in the supporting information.

4.3. Synthesis and characterization of compounds

4.3.1. $[^{Me}(H)C_{Et}N(Bn)_{Et}C(H)^{Me}]\cdot 2[PF_6]$ (**1a**)

1-methylimidazole (1.40 g, 17.2 mmol) and $BnN(CH_2CH_2Cl)_2$ (2.00 g, 8.60 mmol) were mixed with dioxane (20 mL) and heated at reflux for 18 h with stirring. The pale solid that precipitated out of the reaction mixture was isolated by filtration, and then quickly dissolved in methanol (20 mL). (The solid is presumably the Cl salt of **1a** which is extremely hygroscopic.) NH_4PF_6 (4.77 g, 10.0 mmol) was then added to the methanol solution and a white solid instantly precipitated. The solid was isolated by filtration, washed with methanol (2 × 10 mL) and then dried in vacuo to give **1a** as a white solid. Yield: 4.23 g, 80%.

^{1}H NMR (400 MHz, d_6-DMSO): 2.86 (4H, t, CH_2CH_2NBn, $^3J_{H-H}$ = 6.0), 3.64 (2H, s, NCH_2Ar), 3.85 (6H, s, CH_3), 4.26 (4H, t, $NCNCH_2CH_2$, $^3J_{H-H}$ = 6.0), 7.01 (2H, m, C_6H_5), 7.26 (3H, m, C_6H_5), 7.54 (2H, br t, HC=C*H*), 7.63 (2H, br t, HC=C*H*), 8.88 (2H, s, NC*H*N). ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO): 35.7, 46.4, 52.4, 56.8, 122.5, 123.2, 127.1, 128.2, 128.6, 136.4, 137.9. ^{19}F NMR (376 MHz, d_6-DMSO): −70.1 (d, $^1J_{P-F}$ = 711, PF_6). HR FT–ICR MS: Found (Calc. for $C_{19}H_{27}F_{12}N_5P_2$): *m*/*z* = (M–PF_6) 470.1892 (470.1903).

4.3.2. $[^{Bn}(H)C_{Et}N(Bn)_{Et}C(H)^{Bn}]\cdot 2[Cl]$ (**1c**)

1-benzylimidazole (1.36 g, 8.60 mmol) and $BnN(CH_2CH_2Cl)_2$ (1.00 g, 4.30 mmol) were mixed with dioxane (15 mL) and heated at reflux for 18 h with stirring. The pale solid that precipitated out of the reaction mixture was isolated by filtration, dissolved in water and washed with dichloromethane (3 × 20 mL) and hexane (3 × 20 mL). The water was removed by heating to 70 °C under reduced pressure to yield **1c** an orange glassy solid. Yield: 1.80 g, 76%.

^{1}H NMR (400 MHz, D_2O): 2.93 (4H, t, CH_2CH_2NBn, $^3J_{H-H}$ = 6.0), 3.55 (2H, s, NCH_2Ar), 4.10 (4H, t, $NCNCH_2CH_2$, $^3J_{H-H}$ = 6.5), 5.22 (4H, s, $NCNCH_2CH_2$), 6.91 (2H, d, HC=C*H*, $^3J_{H-H}$ = 8.0), 7.08 (2H, t, HC=C*H*, $^3J_{H-H}$ = 1.6), 7.19–7.23 (4H, m, C_6H_5), 7.29–7.31 (1H, m, C_6H_5), 7.38–7.48 (12H, m, C_6H_5), 9.07 (2H, s, NC*H*N). ^{13}C{^{1}H} NMR

(101 MHz, D_2O): 47.4, 52.8, 52.9, 57.2, 121.9, 122.5, 127.5, 128.5, 128.7, 128.9, 129.4, 129.4, 133.5, 135.0, 138.0. HR FT–ICR MS: Found (Calc. for $C_{31}H_{35}Cl_2N_5$): *m/z* = (M–Cl) 512.2556 (512.2576).

4.3.3. [^{Me}Bz(H)C$_{Et}$N(Bn)$_{Et}$C(H)Bz^{Me}]·2[Cl] (**1d**)

1-methylbenzimidazole (1.32 g, 10.00 mmol) and BnN(CH_2CH_2Cl)$_2$ (1.16 g, 4.99 mmol) were mixed with dioxane (5 mL) and heated at reflux for 48 h with stirring. The pale solid that precipitated out of the reaction mixture was isolated by filtration, dissolved in water and washed with dichloromethane (3 × 20 mL) and hexane (3 × 20 mL). The water was removed by heating to 70 °C under reduced pressure to yield **1d** an orange glassy solid. Yield: 1.60 g, 65%.

^{1}H NMR (400 MHz, D_2O): 3.20 (4H, t, CH_2CH_2NBn, $^3J_{H-H}$ = 5.6), 3.71 (2H, s, NCH_2Ar), 3.85 (6H, s, NCNCH_3), 4.42 (4H, t, NCNCH_2CH$_2$, $^3J_{H-H}$ = 5.4), 7.02–7.71 (13H, m, Ar), 8.61 (2H, s, NC*H*N). ^{13}C{^{1}H} NMR (101 MHz, D_2O): 32.9, 45.0, 51.9, 57.6, 112.6, 113.2, 126.9, 127.0, 127.7, 128.3, 129.3, 130.9, 131.4, 137.4, 140.7. HR FT–ICR MS: Found (Calc. for $C_{27}H_{31}ClN_5$) *m/z* (M–Cl) 460.2209 (460.2268).

4.3.4. [(^{Me}C$_{Et}$N(Bn)$_{Et}$C^{Me})Ag]·[AgI$_2$] (**3a**)

[^{Me}(H)C$_{Et}$N(Bn)$_{Et}$C(H)^{Me}]·2[PF_6] (**1a**) (129 mg, 0.21 mmol) was dissolved in acetone (10 mL) and NaI (63.0 mg, 0.42 mmol) was added with stirring. A white solid immediately precipitated out of solution. The solid, presumably [^{Me}(H)C$_{Et}$N(Bn)$_{Et}$C(H)^{Me}]·2[I] (see supporting information for X-ray structure) was isolated via filtration, dried under reduced pressure and then dissolved in dichloromethane (15 mL). Ag_2O (53.2 mg, 0.23 mmol) was added to the reaction mixture and the reaction vessel was covered in aluminum foil and left to stir for 14 h. The reaction mixture was then filtered through Celite and the filtrate dried under reduced pressure to give **3a** as a white powder. Yield = 75 mg, 38%.

^{1}H NMR (400 MHz, CD_2Cl_2): 3.00 (4H, t, CH_2CH_2NBn, $^3J_{H-H}$ = 6.8), 3.68 (2H, s, NCH_2Ar), 3.88 (6H, s, CH_3), 4.23 (4H, t, NCNCH_2CH$_2$, $^3J_{H-H}$ = 6.8), 6.80 (2H, HC=C*H*, $^3J_{H-H}$ = 1.6), 6.88 (2H, HC=C*H*, $^3J_{H-H}$ = 1.6), 7.18–7.31 (5H, m, C$_6H_5$). ^{13}C{^{1}H} NMR (126 MHz, d_6-DMSO): 38.0, 48.3, 54.0, 57.8, 122.0, 122.1, 126.8, 128.0, 128.5, 138.3, 181.4.

4.3.5. [(^{Bn}C$_{Et}$N(Bn)$_{Et}$C^{Bn})Ag]·[AgCl$_2$] (**3c**)

Under an N_2 atmosphere [^{Bn}(H)C$_{Et}$N(Bn)$_{Et}$C(H)^{Bn}]·2[Cl] (**1c**) (429 mg, 0.78 mmol) was dissolved in dichloromethane (10 mL) and Ag_2O (218 mg, 0.94 mmol) was added. The reaction vessel was covered in aluminum foil and left to stir for 14 h. The reaction mixture was then filtered through Celite and the filtrate dried under reduced pressure to give **3c** as a white powder. Yield = 0.40 g, 69%.

^{1}H NMR (400 MHz, CD_2Cl_2): 2.95 (4H, t, CH_2CH_2NBn, $^3J_{H-H}$ = 6.8), 3.67 (2H, s, NCH_2Ar), 4.13 (4H, t, NCNCH_2CH$_2$, $^3J_{H-H}$ = 6.8), 5.29 (4H, s, NCNCH_2Ar), 6.92 (2H, d, HC=C*H*, $^3J_{H-H}$ = 1.6), 6.97 (2H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 7.15–7.16 (2H, m, C$_6H_5$), 7.20–7.22 (3H, m, C$_6H_5$), 7.27–7.29 (4H, m, C$_6H_5$), 7.32–7.36 (6H, m, C$_6H_5$); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): 50.8, 55.8, 56.2, 60.0, 121.6, 122.6, 127.9, 128.5, 129.0, 129.0, 129.3, 129.5, 136.6, 138.7, 180.7.

4.3.6. [(^{Me}BzC$_{Et}$N(Bn)$_{Et}$CBz^{Me})Ag]·[AgCl$_2$] (**3d**)

Under an N_2 atmosphere [^{Me}BzC(H)$_{Et}$N(Bn)$_{Et}$C(H)Bz^{Me}]·2[Cl] (**1d**) (0.36 mg, 0.73 mmol) was dissolved in dichloromethane (60 mL) containing activated molecular sieves and Ag_2O (0.54 g, 2.33 mmol) added. The reaction vessel was covered in aluminum foil and stirred for 4 days. The resultant orange solution was filtered and the filtrate dried under reduced pressure and washed with pentane to yield **3d** as an orange solid. Yield: 0.38 g, 76%.

^{1}H NMR (500 MHz, CD_2Cl_2): 3.12 (4H, t, CH_2CH_2NBn, $^3J_{H-H}$ = 7.1), 3.68 (2H, s, NCH_2Ar), 4.03 (6H, s, NCNCH_3), 4.57 (4H, t, NCNCH_2CH$_2$, $^3J_{H-H}$ = 7.2), 7.06 (5H, br s, Ar), 7.25 (2H, d, Ar, J_{H-H} = 8.0), 7.32 (2H, t, Ar, J_{H-H}=), 7.38 (2H, t, Ar, J_{H-H}=), 7.44 (2H, d, Ar, J_{H-H} = 8.0). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 35.9, 47.5, 53.6, 60.3, 111.0, 111.1, 123.7, 123.7, 127.3, 128.3, 129.0, 133.6, 134.3, 138.4, 192.0.

4.3.7. (COD)ClIr{^{Me}C$_{Et}$N(Bn)$_{Et}$C^{Me}}IrCl(COD) (**5a**)

The following representative procedure was used for the synthesis of **5a**–**5d**:

[Ir(COD)Cl]$_2$ (10.3 mg, 15 μmol) and [(^{Me}C$_{Et}$N(Bn)$_{Et}$C-^{Me})Ag]·[AgI_2] (**3a**) (10 mg, 15 μmol) were dissolved in 2 mL of dichloromethane. The reaction was stirred for 1 h and the solution filtered through Celite. The solvent was removed under reduced pressure and the yellow solid washed with pentane (2 × 2 mL). The precipitate was collected as a yellow crystalline solid. The solid was purified using column chromatography (acetone/pentane (30:70 v/v)). Yield: 10.0 mg, 63%.

^{1}H NMR (500 MHz, $CDCl_3$): 1.52–1.77 (8H, m, COD CH_2), 2.09–2.25 (8H, m, COD CH_2), 2.77 (2H, m, COD C*H*), 2.93–3.06 (4H, m, COD C*H* and CH_2CH_2NBn), 3.18 (2H, m, CH_2CH_2NBn), 3.87 (2H, m, CH_2C$_6H_5$), 3.91 (3H, s, NCH_3), 3.92 (3H, s, NCH_3), 3.98 (1H, m, NCNCH_2CH$_2$), 4.12 (1H, m, NCNCH_2CH$_2$), 4.53 (4H, s br, COD C*H*), 4.56 (1H, m, NCNCH_2CH$_2$), 4.70 (1H, m, NCNCH_2CH$_2$), 6.72 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.74 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.91 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.91 (1H, d, HC=C*H*, $^3J_{H-H}$ = 1.5), 7.27–7.38 (5H, m, C$_6H_5$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 29.1, 29.6, 29.8, 33.0, 33.8, 37.3, 49.0, 49.2, 51.3, 51.8, 55.2, 59.8, 84.2, 84.3, 84.6, 121.2, 121.3, 121.7, 121.9, 127.4, 128.6, 129.2, 139.0, 180.3. HR FT–ICR MS: Found (Calc. for $C_{35}H_{49}Cl_2Ir_2N_5$): *m/z* = (M–Cl) 960.2880 (960.2935). Despite repeated attempts satisfactory elemental analysis could not be achieved for this compound.

4.3.8. (COD)ClIr{^{tBu}C$_{Et}$N(Bn)$_{Et}$C^{tBu}}IrCl(COD) (**5b**)

This reaction was performed in toluene instead of dichloromethane. Yield: 40 mg, 47%.

^{1}H NMR (400 MHz, $CDCl_3$): 1.27 (4H, m, COD CH_2), 1.46 (4H, m, COD CH_2), 1.62 (8H, m, COD CH_2), 2.15 (18H, s, NCCH_3), 2.70 (2H, m, CH_2CH_2NBn), 2.75 (2H, m, CH_2CH_2NBn), 2.87 (2H, m, COD C*H*), 3.00 (2H, m, COD C*H*), 3.82–3.98 (3H, m, NCH_2Ar and NCNCH_2CH$_2$), 4.18 (1H, m, NCNCH_2CH$_2$), 4.41–4.51 (4H, m, COD C*H*), 5.23 (2H, m, NCNCH_2CH$_2$) 6.92 (2H, d, HC=CH), 6.95 (1H, d, HC=CH), 7.03 (1H, d, HC=CH), 7.31–7.38 (5H, m, C$_6H_5$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 29.5, 29.6, 29.7, 29.9, 32.8, 32.8, 33.1, 33.3, 33.7, 33.8, 50.3, 50.8, 51.5, 51.7, 53.6, 53.6, 55.4, 55.6, 58.7, 60.0, 60.3, 79.5, 79.6, 81.8, 81.9, 118.8, 119.1, 121.4, 127.3, 127.3, 128.5, 128.5, 129.1, 129.2, 140.0, 140.1, 179.0, 179.1. HT FT-ICR MS: Found (Calc. for $C_{41}H_{61}Cl_2Ir_2N_5$) *m/z* (M+H) 1080.3609 (1079.2965). *Anal.* Calc. for $C_{41}H_{61}Cl_2Ir_2N_5$: C, 45.63; H, 5.70; N, 6.49. Found: C, 46.22; H, 5.62; N, 6.07%.

4.3.9. (COD)ClIr{^{Bn}C$_{Et}$N(Bn)$_{Et}$C^{Bn}}IrCl(COD) (**5c**)

Yield: 177 mg, 78%. ^{1}H NMR (500 MHz, $CDCl_3$): 1.52 (4H, br m, COD CH_2), 1.65 (4H, br m, COD CH_2), 2.06 (4H, br m, COD CH_2), 2.14 (4H, br m, COD CH_2), 2.67 (1H, m, CH_2CH_2NBn), 2.80–2.94 (3H, m, COD C*H* and CH_2CH_2NBn), 3.00–3.25 (4H, m, COD C*H* and CH_2CH_2NBn), 3.88 (3H, m, CH_2C$_6H_5$ and NCNCH_2CH$_2$), 4.13 (1H, m, NCNCH_2CH$_2$), 4.54 (4H, m, COD C*H*), 4.64 (2H, m, NCNCH_2CH$_2$), 5.44 (1H, d, NCNCH_2Ar, J_{H-H} = 3.7), 5.47 (1H, d, NCNCH_2Ar, J_{H-H} = 3.8), 5.71 (1H, d, NCNCH_2Ar, J_{H-H} = 14.8), 5.76 (1H, d, NCNCH_2Ar, J_{H-H} = 14.8), 6.47 (1H, d, HC=C*H*, $^3J_{H-H}$ = 1.9), 6.59 (1H, d, HC=C*H*, $^3J_{H-H}$ = 1.9), 6.84 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.99 (1H, d, HC=C*H*, $^3J_{H-H}$ = 1.9), 7.22–7.38 (15H, m, C$_6H_5$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 29.4, 29.4, 29.7, 29.8, 33.5, 33.5, 33.6, 33.7, 48.3, 48.3, 51.8, 51.8, 52.3, 52.4, 55.0, 55.7, 59.5, 60.3, 84.4, 84.4, 84.4, 84.4, 119.2, 119.5, 122.3, 122.5, 127.2, 127.3, 128.1, 128.1, 128.3, 128.4, 128.8, 128.8, 129.0, 129.1, 136.6, 136.6, 139.1, 139.4, 180.1, 180.2. HR FT–ICR MS: Found (Calc. for $C_{47}H_{57}Cl_2Ir_2N_5$):

m/z = (M+H) 1148.3241 (1148.3369). *Anal.* Calc. for $C_{47}H_{57}Cl_2Ir_2N_5$: C, 46.63; H, 4.77; N, 5.67. Found: C, 46.30; H, 5.01; N, 6.11%.

4.3.10. (COD)ClIr{^{Me}BzC$_{Et}$N(Bn)$_{Et}$CBz^{Me}}IrCl(COD) (**5d**)

Yield: 57 mg, 69%. X-ray quality crystals were grown by slow evaporation from an acetone/pentane (30:70 v/v) solution.

^{1}H NMR (500 MHz, $CDCl_3$): 1.74 (6H, m, COD C*H*$_2$), 2.03 (2H, m, COD C*H*$_2$), 2.14 (2H, m, COD C*H*$_2$), 2.28 (4H, m, COD C*H*$_2$), 2.85 (1H, m, COD C*H*$_2$), 2.89 (1H, m, COD C*H*$_2$), 3.07 (4H, m, COD C*H*), 3.19 (2H, m, CH$_2$C*H*$_2$NBn), 3.48 (2H, m, CH$_2$C*H*$_2$NBn), 4.15 (5H, m and br s, NCNC*H*$_3$ and NC*H*$_2$Ar), 4.15 (3H, s, NCNC*H*$_3$), 4.51–4.71 (5H, m, COD C*H* and NCNC*H*$_2$CH$_2$), 4.76 (1H, m, NCNC*H*$_2$CH$_2$), 5.11 (2H, m, NCNC*H*$_2$CH$_2$), 7.12–7.52 (13H, m, Ar). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 29.0, 29.2, 30.0, 30.4, 31.7, 33.1, 33.2, 34.2, 34.3, 34.4, 46.0, 46.5, 52.1, 52.3, 53.1, 53.1, 53.2, 53.7, 59.4, 60.7, 86.4, 86.6, 87.1, 87.2, 109.5, 109.5, 110.4, 110.5, 122.5, 122.6, 122.8, 122.8, 127.4, 127.5, 128.5, 128.7, 129.3, 129.4, 134.8, 135.0, 135.4, 135.5, 191.7, 191.8. HT FT–ICR MS: Found (Calc. for $C_{43}H_{53}Cl_2Ir_2N_5$) *m/z* (M+H) 1096.2914 (1095.2937). *Anal.* Calc. for $C_{43}H_{53}Cl_2Ir_2N_5$: C, 47.15; H, 4.88; N 6.39. Found: C, 47.41; H, 4.93; N 6.22%.

4.3.11. (COD)ClIr{^{Me}C$_{Pr}$N(Bn)$_{Pr}$C^{Me}}IrCl(COD) (**6a**)

The following representative procedure was used for the synthesis of **6a**–**6d**:

[Ir(COD)Cl]$_2$ (108 mg, 0.160 mmol) and [(^{Me}C$_{Pr}$N(Bn)$_{Pr}$C^{Me})Ag]·[$AgCl_2$] (**4a**) (100 mg, 0.160 mmol) were dissolved in dichloromethane (10 mL). The reaction was stirred for 3 h and then the solution was filtered through Celite. The solvent was removed under reduced pressure and the yellow solid washed with pentane (2 × 2 mL). The precipitate was collected as a yellow crystalline solid. The solid was purified using column chromatography (acetone/hexane (30:70 v/v)). Yield: 95 mg, 58%.

^{1}H NMR (500 MHz, CD_2Cl_2): 1.45–1.75 (10H, br m, COD C*H*$_2$ and NCH$_2$C*H*$_2$CH$_2$N), 1.96 (2H, m, NCH$_2$C*H*$_2$CH$_2$N), 2.17 (8H, br m, COD C*H*$_2$), 2.59 (4H, m, CH$_2$CH$_2$C*H*$_2$NBn), 2.88 (2H, br, COD C*H*), 2.96 (2H, br, COD C*H*), 3.65 (2H, m, NC*H*$_2$Ar), 3.91 (6H, s, NC*H*$_3$), 4.14 (2H, m, COD C*H*), 4.45 (4H, br, NCNC*H*$_2$CH$_2$CH$_2$), 4.54 (2H, m, COD C*H*), 6.81 (2H, br, HC=C*H*), 6.85 (2H, m, HC=C*H*), 7.25 (1H, t, *para*-C$_6$*H*$_5$, $^3J_{H-H}$ = 7.4), 7.33 (2H, m, *meta*-C$_6$*H*$_5$), 7.41 (2H, m *ortho*-C$_6$*H*$_5$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 28.6, 28.8, 29.5, 29.6, 30.0, 30.1, 33.5, 33.6, 34.0, 34.1, 37.6, 49.0, 49.0, 51.4, 51.5, 51.9, 51.9, 58.8, 84.1, 84.2, 84.2, 84.3, 120.8, 120.8, 121.7, 121.7, 127.1, 128.5, 129.3, 129.3, 139.9, 140.0, 180.1, 180.2. HR FT–ICR MS: Found (Calc. for $C_{37}H_{53}Cl_2Ir_2N_5$): *m/z* = (M+H) 1024.2986 (1024.3015). *Anal.* Calc. for $C_{37}H_{53}Cl_2Ir_2N_5$: C, 42.15; H, 4.88; N, 6.38. Found: C, 42.70; H, 5.22; N, 6.85%.

4.3.12. (COD)ClIr{^{tBu}C$_{Pr}$N(Bn)$_{Pr}$C^{tBu}}IrCl(COD) (**6b**)

This reaction was performed in toluene instead of dichloromethane. Yield: 38 mg, 38%.

^{1}H NMR (400 MHz, $CDCl_3$): 1.47 (4H, m, COD C*H*$_2$), 1.61 (4H, m, COD C*H*$_2$), 1.84 (18H, s, NCC*H*$_3$), 1.92 (4H, m, COD C*H*$_2$ and CH$_2$C*H*$_2$CH$_2$), 2.12 (6H, m, COD C*H*$_2$), 2.30 (2H, m, CH$_2$C*H*$_2$CH$_2$), 2.61 (4H, CH$_2$CH$_2$C*H*$_2$NBn), 2.71 (2H, m, COD C*H*), 2.79 (2H, m, COD C*H*), 3.64 (2H, m, NC*H*$_2$Ar), 4.27 (2H, m, NCNC*H*$_2$CH$_2$CH$_2$), 4.45 (2H, m, COD C*H*), 4.52 (2H, m, COD C*H*), 5.12 (2H, m, NCNC*H*$_2$CH$_2$CH$_2$), 6.87 (1H, d, HC=CH, $^2J_{H-H}$ = 2.1), 6.93 (1H, d, HC=CH, $^2J_{H-H}$ = 2.1), 6.97 (1H, d, HC=CH, $^2J_{H-H}$ = 2.1), 6.98 (1H, d, HC = CH, $^2J_{H-H}$ = 2.1), 7.23–7.39 (5H, m, C$_6$*H*$_5$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 28.1, 28.6, 29.5, 29.5, 29.6, 29.7, 32.8, 33.0, 33.2, 33.6, 33.8, 50.4, 50.7, 51.1, 51.2, 51.2, 51.2, 53.3, 52.4, 58.7, 58.9, 59.0, 79.2, 79.4, 81.6, 81.7, 119.5, 119.5, 120.2, 127.0, 128.3, 129.2, 129.2, 139.8, 140.0, 178.9, 179.0. HT FT-ICR MS: Found (Calc. for $C_{41}H_{61}Cl_2Ir_2N_5$) *m/z* (M+H) 1108.3924 (1107.3876). *Anal.* Calc. for $C_{41}H_{61}Cl_2Ir_2N_5$: C, 46.64; H, 5.92; N, 6.32. Found: C, 46.39; H, 5.75; N, 6.04%.

4.3.13. (COD)ClIr{^{Bn}C$_{Pr}$N(Bn)$_{Pr}$C^{Bn}}IrCl(COD) (**6c**)

Yield: 55 mg, 64%. ^{1}H NMR (500 MHz, $CDCl_3$): 1.45–1.71 (8H, m, COD C*H*$_2$), 1.90–2.30 (12H, m, COD C*H*$_2$ and NCH$_2$C*H*$_2$CH$_2$N), 2.62 (4H, m, CH$_2$CH$_2$C*H*$_2$NBn), 2.90 (4H, m, COD C*H*), 3.65 (2H, m, NC*H*$_2$Ar), 4.16 (2H, m, COD C*H*), 4.50–4.65 (6H, m, COD C*H* and NCNC*H*$_2$CH$_2$CH$_2$), 5.53 (1H, d, NCNC*H*$_2$Ar, $^3J_{H-H}$ = 1.8), 5.53 (1H, d, NCNC*H*$_2$Ar, $^3J_{H-H}$ = 1.8), 5.68 (1H, d, NCNC*H*$_2$Ar, $^3J_{H-H}$ = 7.3), 5.71 (1H, d, NCNC*H*$_2$Ar, $^3J_{H-H}$ = 7.3), 6.59 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.61 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.80 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 6.81 (1H, d, HC=C*H*, $^3J_{H-H}$ = 2.0), 7.20–7.40 (15H, m, C$_6$*H*$_5$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 28.6, 28.8, 29.7, 29.8, 29.8, 33.7, 33.8, 33.8, 33.9, 49.1, 49.2, 50.8, 50.9, 51.9, 51.9, 52.1, 52.2, 54.5, 58.9, 58.9, 84.4, 84.5, 84.7, 84.7, 120.2, 121.2, 121.3, 127.2, 128.3, 128.4, 128.4, 128.5, 129.1, 129.2, 129.3, 136.7, 139.9, 140.0, 180.4, 180.5. HR FT-ICR MS: Found (Calc. for $C_{49}H_{61}Cl_2Ir_2N_5$): *m/z* = (M+H) 1176.3613 (1176.3641). *Anal.* Calc. for $C_{49}H_{61}Cl_2Ir_2N_5$: C, 49.78; H, 5.09; N, 5.91. Found: C, 50.05; H, 5.23; N, 5.96%.

4.3.14. (COD)ClIr{^{Me}BzC$_{Pr}$N(Bn)$_{Pr}$CBz^{Me}}IrCl(COD) (**6d**)

Yield = 36 mg, 71%. X-ray quality crystals were grown by slow evaporation from an ethyl acetate/pentane (60:40 v/v) solution.

^{1}H NMR (500 MHz, $CDCl_3$): 1.67 (4H, m, COD C*H*$_2$), 1.79 (4H, m, COD C*H*$_2$), 2.04 (2H, m, CH$_2$C*H*$_2$CH$_2$), 2.24 (8H br m, COD C*H*$_2$), 2.40 (2H, m, CH$_2$C*H*$_2$CH$_2$), 2.78 (4H, br m, CH$_2$CH$_2$C*H*$_2$NBn), 2.90 (2H, m, COD C*H*), 3.00 (2H, m, COD C*H*), 3.75 (2H, see axial chirality section, NC*H*$_2$Ar), 4.17 (3H, s, NC*H*$_3$), 4.17 (3H, s, NC*H*$_3$), 4.43 (2H, m, NCNC*H*$_2$ CH$_2$CH$_2$), 4.71 (4H, m, COD C*H*), 4.98 (2H, m, NCNC*H*$_2$ CH$_2$CH$_2$), 7.16–7.51 (13H, m, Ar). R,R-(COD)ClIr{^{Me}BzC$_{Pr}$N(Bn)$_{Pr}$CBz^{Me}}IrCl(COD) ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 26.2, 29.4, 29.8, 33.5, 34.0, 34.5, 46.7, 50.1, 52.4, 52.7, 58.5, 86.5, 86.6, 109.6, 110.4, 122.5, 127.0, 128.4, 129.2, 134.8, 135.7, 140.1, 191.5 R,S-(COD)ClIr{^{Me}BzC$_{Pr}$N(Bn)$_{Pr}$ CBz^{Me}}IrCl(COD) ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 27.1, 29.2, 30.0, 33.3, 34.1, 34.5, 46.8, 51.0, 52.2, 52.9, 58.5, 86.4, 86.9, 109.6, 110.4, 122.6, 122.7, 127.1, 128.4, 129.2, 134.7, 139.7, 139.8, 191.6. HR FT ICR MS Found: (Calc. for $C_{45}H_{57}Cl_2Ir_2N_5$) *m/z* 1123.3315 (1123.32 50). *Anal.* Calc. for $C_{45}H_{57}Cl_2Ir_2N_5$: C, 48.12; H, 5.11; N, 6.23. Found: C, 47.35; H, 4.96; N, 5.92%.

4.3.15. (COD)ClRh{^{Me}C$_{Pr}$N(Bn)$_{Pr}$C^{Me}}RhCl(COD) (**7a**)

The following representative procedure was used for the synthesis of **7a**, **7c** and **7d**:

[Rh(COD)Cl]$_2$ (50 mg, 0.101 mmol) and [(^{Me}C$_{Pr}$N(Bn)$_{Pr}$C^{Me})Ag]·[$AgCl_2$] (**3a**) (63 mg, 0.101 mmol) were dissolved in dichloromethane (10 ml) and the reaction mixture stirred for 1 h. The yellow solution was filtered through Celite and the filtrate collected. The solvent was removed under reduced pressure and the resulting solid washed with pentane (2 × 10 mL) to give **7a** as a yellow crystalline solid. The solid was purified using column chromatography (acetone/hexane (30:70 v/v)). Yield: 83 mg, 95%.

^{1}H NMR (500 MHz, $CDCl_3$): 1.85 (8H, br m, COD C*H*$_2$), 1.98 (2H, m, NCH$_2$C*H*$_2$CH$_2$N), 2.24 (8H, br m, COD C*H*$_2$), 2.38 (2H, m, NCH$_2$C*H*$_2$CH$_2$N), 2.60 (4H, m, CH$_2$CH$_2$C*H*$_2$NBn), 3.14 (2H, br, COD C*H*), 3.23 (2H, br, COD C*H*), 3.63 (2H, m, NC*H*$_2$Ar), 3.98 (6H, s, NC*H*$_3$), 4.15 (2H, m, COD C*H*), 4.67 (2H, m, COD C*H*), 4.90 (4H, br, NCNC*H*$_2$CH$_2$CH$_2$), 6.69 (2H, br, HC=C*H*), 6.75 (1H, d, HC=C*H*, $^3J_{H-H}$ = 1.8), 6.76 (1H, d, HC=C*H*, $^3J_{H-H}$ = 1.8), 7.18 (1H, m, *para*-C$_6$*H*$_5$), 7.27 (2H, m, *meta*-C$_6$*H*$_5$), 7.37 (2H, m *ortho*-C$_6$*H*$_5$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 28.6, 28.8, 28.8, 28.8, 29.3, 29.3, 32.8, 32.8, 33.4, 33.4, 37.9, 49.2, 49.2, 50.7, 50.9, 58.8, 67.6 (d, $^1J_{Rh-C}$ = 7.6), 67.8 (d, $^1J_{Rh-C}$ = 7.6), 68.3 (d, $^1J_{Rh-C}$ = 14.5), 98.2 (m), 121.0, 121.1, 122.0, 127.1, 128.4, 129.2, 129.3, 139.9, 140.0, 181.8 (d, $^1J_{Rh-C}$ = 16.1), 182.2 (d, $^1J_{Rh-C}$ = 16.3). HR FT-ICR MS: Found (calcd for $C_{37}H_{53}C_{l2}N_5Rh_2$): *m/z* = (M-Cl) 808.2083 (808.2100).

Anal. calcd (found) for $C_{37}H_{53}Cl_2N_5Rh_2$: C, 52.36 (52.60); H, 6.20 (6.33); N, 8.24 (8.29).

4.3.16. (COD)ClRh{$^{Bn}C_{Pr}N(Bn)_{Pr}C^{Bn}$}RhCl(COD) (**7c**)

Yield: 101 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): 1.79 (8H, m, COD CH_2), 1.98 (2H, m, $NCH_2CH_2CH_2N$), 2.10–2.35 (10H, m, COD CH_2 and $NCH_2CH_2CH_2N$), 2.62 (4H, m, $CH_2CH_2CH_2NBn$), 3.18 (2H, m, NCH_2Ar), 3.62 (2H, m, COD CH), 4.19 (2H, m, $NCNCH_2CH_2CH_2$), 4.69 (2H, m, $NCNCH_2CH_2CH_2$), 4.98 (4H, br, COD CH), 5.68 (4H, m, N$CNCH_2$Ar), 6.50 (1H, d, HC=CH, $^3J_{H-H}$ = 1.90), 6.52 (1H, d, HC=CH, $^3J_{H-H}$ = 1.8), 6.73 (1H, d, HC=CH, $^3J_{H-H}$ = 1.9), 6.76 (1H, d, HC=CH, $^3J_{H-H}$ = 1.9), 7.12–7.40 (15H, m, C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 28.6, 28.8, 29.0, 29.0, 29.1, 29.1, 33.1, 33.1 (br), 33.2, 49.4, 49.4, 50.9, 51.0, 53.6, 58.9, 68.1 (d, $^1J_{Rh-C}$ = 5.6), 68.2 (d, $^1J_{Rh-C}$ = 5.6), 68.6 (d, $^1J_{Rh-C}$ = 14.1), 98.4 (d, $^1J_{Rh-C}$ = 6.6), 98.5 (d, $^1J_{Rh-C}$ = 6.6), 98.7 (d, $^1J_{Rh-C}$ = 6.4), 98.7 (d, $^1J_{Rh-C}$ = 6.6), 120.6, 121.5, 121.6, 127.1, 128.2, 128.4, 128.4, 128.5, 129.1, 129.2, 129.3, 136.8, 140.0, 140.0, 182.5 (d, $^1J_{Rh-C}$ = 14.3), 182.7 (d, $^1J_{Rh-C}$ = 14.7). HR FT–ICR MS: Found (Calc. for $C_{49}H_{61}Cl_2N_5Rh_2$): *m/z* = (M+H) 996.2461 (996.2492). *Anal.* Calc. for $C_{49}H_{61}Cl_2N_5Rh_2$: C, 58.75; H, 6.09; N, 6.82. Found: C, 59.02; H, 6.17; N, 7.03%.

4.3.17. (COD)ClRh{$^{Me}BzC_{Pr}N(Bn)_{Pr}CBz^{Me}$}RhCl(COD) (**7d**)

Yield = 11 mg, 28%. X-ray quality crystals were grown by slow evaporation from an acetone/pentane (30:70 v/v) solution.

^{1}H NMR NMR (400 MHz, $CDCl_3$): 1.87–2.15 (10H, br m COD CH_2 and $CH_2CH_2CH_2$), 2.25–2.46 (6H, m, COD CH_2 and $CH_2CH_2CH_2$), 2.51 (4H, m, COD CH_2), 2.86 (3H, m, $CH_2CH_2CH_2NBn$), 3.02 (1H, ddd, $NCH_2CH_2CH_2NBn$, *J* = 12.8, 7.6, 5.1), 3.27 (2H, m, COD CH), 3.38 (2H, m, COD CH), 3.81 (2H, see above, NCH_2Ar), 4.30 (3H, s, NCH_3), 4.30 (3H, s, NCH_3), 4.52 (2H, m, $NCNCH_2CH_2CH_2$), 5.04–5.24 (6H, br m, COD CH and $NCNCH_2CH_2CH_2$), 7.19–7.56 (13H, m, Ar). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 26.3, 27.2, 28.7, 28.8, 29.3, 29.4, 32.7, 32.9, 33.5, 33.6, 34.9, 47.2, 47.3, 50.2, 51.2, 58.7, 68.4 (d, $^1J_{Rh-C}$ = 14.6), 68.5 (d, $^1J_{Rh-C}$ = 14.5), 69.0 (d, $^1J_{Rh-C}$ = 14.5), 69.2 (d, $^1J_{Rh-C}$ = 14.5), 100.0 (d, $^1J_{Rh-C}$ = 6.3), 100.1 (d, $^1J_{Rh-C}$ = 6.6), 100.2 (d, $^1J_{Rh-C}$ = 6.4). 100.3 (d, $^1J_{Rh-C}$ = 6.4), 109.4, 109.5, 110.3, 122.4, 122.4, 122.6, 122.6, 127.1, 127.1, 128.4, 128.5, 129.2, 129.3, 134.7, 134.7, 135.6, 140.0, 140.2, 194.9 (d, $^1J_{Rh-C}$ = 18.1), 194.4 (d, $^1J_{Rh-C}$ = 18.2). HR FT–ICR MS Found: (Calc. for $C_{45}H_{57}Cl_2Rh_2N_5$) *m/z* 943.2134 (943.2101). *Anal.* Calc. for $C_{45}H_{57}Cl_2Rh_2N_5$: C, 57.21; H, 6.08; N, 7.41. Found: C, 57.48; H, 6.93; N, 7.46%.

4.3.18. [$^{tBu}C_{Pr}N(Bn)_{Pr}C^{tBu}$]·toluene (**9b**)

Under an N_2 atmosphere a 50 mL schlenk flask was charged with a mixture of [^{tBu}(H)$C_{Pr}N(Bn)_{Pr}C$(H)^{tBu}]·2[Cl] (**2b**) (0.87 g, 1.73 mmol) and NaH (0.12 g, 5.04 mmol, 2.9 equivalents) and THF (200 mL) was added. A solution of KO^{t}Bu (0.33 g, 2.93 mmol, 1.7 equivalents) in THF (20 mL) was then added over 20 min and the reaction mixture stirred vigorously for 6 h. The solution was filtered on a frit through dry Celite and the volatiles removed under reduced pressure. The resultant oil was extracted with toluene (30 mL) and the solution filtered. The toluene was removed under reduced pressure to yield **9b** as orange oil. Yield: 0.89 g, 97%.

^{1}H NMR (400 MHz, C_6D_6): 1.56 (18H, s, NCCH_3), 1.93 (4H, p, $CH_2CH_2CH_2$, J_{H-H} = 5.0), 2.17 (3H, s, $C_6H_5CH_3$), 2.34 (4H, t, $CH_2CH_2CH_2NBn$, $^3J_{H-H}$ = 6.8), 3.34 (2H, s, NCH_2Ar), 4.01 (4H, t, $NCNCH_2CH_2CH_2$, $^3J_{H-H}$ = 7.3), 6.59 (2H, d, HC=CH, $^2J_{H-H}$ = 1.6), 6.77 (2H, d, HC=CH, $^2J_{H-H}$ = 1.6), 7.07–7.31 (10H, m, $C_6H_5CH_2N$, $C_6H_5CH_3$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): 21.8 ($C_6H_5CH_3$), 30.1, 31.8, 49.8, 51.6, 56.0, 59.5, 115.7, 118.8, 126.0 (*para*-$C_6H_5CH_3$), 127.4, 128.8 (*meta*-$C_6H_5CH_3$), 128.9, 129.6 (*ortho*-$C_6H_5CH_3$), 129.7, 138.2 (*ipso*-$C_6H_5CH_3$), 140.9, 214 (carbene, located by ^{1}H, ^{13}C HMBC). This compound was too unstable to obtain elemental analysis.

4.3.19. Synthesis of **6b** using **9b**

Under a N_2 atmosphere [$^{tBu}C_{Pr}N(Bn)_{Pr}C^{tBu}$]·toluene (**9b**) (51.1 mg, 0.09 mmol) and $[IrCODCl]_2$ (65.0 mg, 0.09 mmol) were mixed in toluene (10 mL). The reaction mixture was stirred for 3 h and then the solution was filtered through Celite. The solvent was removed under reduced pressure and the yellow solid washed with pentane (2 × 2 mL). The precipitate was collected as a yellow crystalline solid. The solid was purified using column chromatography (acetone/hexane (30:70 v/v)). Yield: 38 mg, 38%. (Characterizing data as described above).

An analogous procedure was used to synthesize **5b** using **8b**.

4.3.20. $(CO)_2$ClIr{$^{Bn}C_{Et}N(Bn)_{Et}C^{Bn}$}IrCl$(CO)_2$ (**10c**)

The following representative procedure was used for the synthesis of **10c** and **11c**:

[(COD)ClIr{$^{Bn}C_{Et}N(Bn)_{Et}C^{Bn}$}IrCl(COD)] (**5c**) (4.5 mg, 3.8 μmol) was dissolved in CD_2Cl_2 (0.5 mL) in a J. Young NMR tube. The solution was degassed using three consecutive freeze–pump-thaw cycles and then excess 1 atm CO was added via a dual manifold Schlenk line. The solution was left to stand for 4 h and the solvent was then removed under reduced pressure. The resulting solid was washed with pentane (3 × 5 mL) to give $(CO)_2$ClIr{$^{Bn}C_{Et}N(Bn)_{Et}C^{Bn}$}IrCl$(CO)_2$ (**10c**) as a yellow powder in essentially quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$): 3.10 (4H, m, CH_2CH_2NBn), 3.82 (2H, s, NCH_2Ar), 4.26 (4H, m, $NCNCH_2CH_2$), 5.47 (4H, m, N$CNCH_2$Ar), 6.80 (2H, s br, HC=CH), 7.00 (2H, s br, HC=CH), 7.29–7.36 (m, 15H, C_5H_5). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): 49.7, 55.2, 55.4, 59.7, 121.3, 123.6, 128.7, 128.8, 128.9, 129.0, 129.1, 129.4, 136.2, 168.5, 182.2. IR (Diamond Tip, cm^{-1}): 2061.7 (νCO), 1978.4 (νCO). HR FT–ICR MS: Found (Calc. for $C_{35}H_{33}Cl_2Ir_2N_5O_4$): *m/z* = (M+H) 1044.1146 (1044.1220).

4.3.21. $(CO)_2$ClIr{$^{Bn}C_{Pr}N(Bn)_{Pr}C^{Bn}$}IrCl$(CO)_2$ (**11c**)

^{1}H NMR (400 MHz, $CDCl_3$): 1.97–2.16 (4H, m, $CH_2CH_2CH_2$), 2.56 (4H, m, $CH_2CH_2CH_2NBn$), 3.62 (2H, m, NCH_2Ar), 4.32–4.41 (4H, m, $NCNCH_2CH_2CH_2$), 5.50 (4H, m, N$CNCH_2$Ar), 6.86 (2H, s, HC=CH), 6.92 (2H, s, HC=CH), 7.32–7.44 (15H, m, C_6H_5). ^{13}C{^{1}H} NMR (126 MHz, CD_3Cl): 29.1, 51.2, 54.5, 55.3, 59.0, 121.7, 122.7, 127.6, 128.7, 128.8, 128.9, 129.4, 129.5, 129.9, 136.3, 168.7, 180.3. IR (Diamond Tip, cm^{-1}): 2061.5 (νCO), 1977.7 (νCO). HR FT-ICR MS: Found (Calc. for $C_{37}H_{37}Cl_2Ir_2N_5O_4$): *m/z* = (M+H) 682.1514 (682.1543).

4.3.22. [(COD)(PPh_3)Ir{$^{Bn}C_{Et}N(Bn)_{Et}C^{Bn}$}Ir($PPh_3$)(COD)]·2[$PF_6$] (**12c**)

The following representative procedure was used for the synthesis of **12c**, **13a** and **13c**:

[(COD)ClIr{$^{Bn}C_{Et}N(Bn)_{Et}C^{Bn}$}IrCl(COD)] (**5c**) (30.0 mg, 0.027 mmol) was dissolved in acetonitrile and then triphenylphosphine (14.0 mg, 0.054 mmol) and KPF_6 (9.82 mg, 0.054 mmol) were added. After 30 min of stirring the solution was deep red with a white precipitate. The solution was filtered and the filtrate collected. The solvent was removed under reduced pressure and the resulting solid washing with hexane (2 × 10 mL) to give **12c** as a red solid. Yield: 40 mg, 80%.

^{1}H NMR (400 MHz, CD_3CN): 3.35 (2H, m, $NCNCH_2CH_2CH_2$), 3.53 (2H, m, NCH_2Ar), 3.58 (2H, m, COD CH), 3.71 (2H, br m, COD CH), 4.06 (1H, br m, COD CH), 4.12 (3H, br s, COD CH), 4.42 (2H, m, $NCNCH_2CH_2CH_2$), 4.62 (1H, d, N$CNCH_2$Ar, J_{H-H} = 3.8), 4.66 (1H, d, N$CNCH_2$Ar, J_{H-H} = 3.7), 6.83 (1H, d, HC=CH, $^3J_{H-H}$ = 2.0), 5.50 (1H, d, N$CNCH_2$Ar, J_{H-H} = 3.1), 5.54 (1H, d, N$CNCH_2$Ar, J_{H-H} = 3.2), 6.83 (1H, d, HC=CH, $^3J_{H-H}$ = 2.0), 6.86 (1H, d, HC=CH, $^3J_{H-H}$ = 2.0), 6.99 (1H, d, HC=CH, $^3J_{H-H}$ = 2.0), 7.04 (1H, d, HC=CH, $^3J_{H-H}$ = 2.0), 7.05 (4H, m, HC=CH) 7.25–7.60 (41H, m, C_6H_5 and PPh_3). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 30.3 (s, br), 31.0, 31.0, 31.1, 31.2, 31.4 (s, br), 48.0, 48.1, 53.8, 54.2, 58.7, 58.7, 79.6 (d, $^2J_{P-C}$ = 6.1), 81.2 (d,

$^2J_{P-C}$ = 7.3), 86.4 (t, $^2J_{P-C}$ = 10.0), 87.0 (d, $^2J_{P-C}$ = 12.0), 87.1 (d, $^2J_{P-C}$ = 11.8), 122.3, 122.3, 123.4, 123.7, 127.5, 127.6, 127.9 (d, $^1J_{P-C}$ = 5.1), 128.6, 128.7, 128.8, 129.3 (d, $^3J_{P-C}$ = 10.0), 129.4, 130.0, 130.0, 130.4, 130.4, 131.5, 133.9 (d, $^2J_{P-C}$ = 12.0), 134.1, 134.7, 134.8, 138.8, 139.0, 173.8, 173.9. $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): −144.6 (sep, PF_6, $^1J_{P-F}$ = 706.4) 17.83 (s, PPh_3), 17.86 (s, PPh_3). HR FT–ICR MS: Found (Calc. for $C_{83}H_{87}Ir_2N_5P_2$): m/z = 800.7839 (800.7847). *Anal.* Calc. for $C_{83}H_{87}F_{12}Ir_2N_5P_4$: C, 49.38; H, 4.43; N, 3.02. Found: C, 50.70; H, 4.64; N, 3.70%.

*4.3.23. [(COD)(PPh$_3$)Ir{^{Me}C$_{Pr}$N(Bn)$_{Pr}$C^{Me}}Ir(PPh$_3$)(COD)]·2[PF$_6$] (**13a**)*

Yield: 98 mg, 85%. ^1H NMR (300 MHz, CD_3CN): 1.47 (2H, br m, $NCH_2CH_2CH_2N$), 1.72 (2H, br m, $NCH_2CH_2CH_2N$), 1.90–2.50 (20H, br m, COD CH_2 and $NCH_2CH_2CH_2N$), 3.43 (2H, m, NCH_2Ar), 3.44 (6H, s, NCH_3), 3.59 (2H, br, $NCNCH_2CH_2CH_2$), 3.76 (4H, br, COD C*H*), 4.12 (2H, br, $NCNCH_2CH_2CH_2$), 4.25 (2H, m, COD C*H*), 4.42 (2H, m, COD C*H*), 6.86 (2H, s br, HC=C*H*), 6.91 (2H, t, HC=C*H*, J_{H-H} = 2.4), 7.10–7.50 (35H, m, C_6H_5 and PPh_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): 27.7, 30.8 (d, $^3J_{P-C}$ = 3.0), 30.9 (d, $^3J_{P-C}$ = 2.9), 31.1 (d, $^3J_{P-C}$ = 2.8), 31.2 (d, $^3J_{P-C}$ = 3.0), 31.3, 31.4, 31.8, 31.9, 37.7, 49.1, 51.4, 59.2, 80.4 (d, $^2J_{P-C}$ = 3.4), 81.1, 86.0, 86.1, 86.8 (d, $^2J_{P-C}$ = 2.8), 87.0 (d, $^2J_{P-C}$ = 2.7), 122.0, 122.0, 124.2, 129.0 (d, $^1J_{P-C}$ = 5.4), 129.1, 129.2, 129.5 (d, $^4J_{P-C}$ = 10.0), 130.5, 131.0, 131.7, 132.5, 134.2 (d, $^3J_{P-C}$ = 10.8), 140.2, 174.1 (d, $^2J_{P-C}$ = 2.1), 174.1 (d, $^2J_{P-C}$ = 2.0). $^{31}P\{^1H\}$ NMR (162 MHz, CD_3CN): −144.3 (sep, PF_6, $^1J_{P-F}$ = 707.1) 18.81 (s, PPh_3). HR FT–ICR MS: Found (Calc. for $C_{73}H_{83}Ir_2N_5P_2$): m/z = 738.7687 (738.7691). *Anal.* Calc. for $C_{73}H_{83}F_{12}Ir_2N_5P_4$: C, 50.37; H, 4.47; N, 3.28. Found: C, 49.95; H, 4.74; N, 3.60%.

*4.3.24. [(COD)(PPh$_3$)Ir{^{Bn}C$_{Pr}$N(Bn)$_{Pr}$C^{Bn}}Ir(PPh$_3$)(COD)]·2[PF$_6$] (**13c**)*

Yield: 49 mg, 70%. ^1H NMR (500 MHz, CD_2Cl_2): 1.55 (2H, m, $CH_2CH_2CH_2$), 1.79 (2H, m, $CH_2CH_2CH_2$), 2.01(10H, m, COD CH_2), 2.26 (6H, m, COD CH_2), 2.44 (4H, m, $BnNCH_2CH_2CH_2$), 3.42 (2H, m, NCH_2Ar), 3.67 (2H, m, $CH_2CH_2CH_2NCN$), 3.77 (2H, m, COD C*H*), 3.82 (2H, m, COD C*H*), 4.19 (2H, m, $CH_2CH_2CH_2NCN$), 2.28 (2H, m, COD C*H*), 4.37 (1H, d, $NCNCH_2Ar$, $^2J_{H-H}$ = 2.9), 4.40 (3H, m, COD C*H* and $NCNCH_2Ar$), 5.44 (1H, s, $NCNCH_2Ar$), 5.47 (1H, s, $NCNCH_2Ar$), 6.69 (1H, m, HC=CH), 6.94 (2H, m, HC=CH), 7.02 (1H, dd, HC=CH, $^2J_{H-H}$ = 2.1 and 2.4), 7.23–7.52 (45H, m, C_6H_5 and PPh_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): 27.8, 30.2, 30.2, 30.8 (m), 31.8, 31.8, 49.5, 51.4 (d, $^1J_{P-C}$ = 2.6), 59.4, 81.0 (m), 86.7 (d, $^1J_{P-C}$ = 3.6), 86.9 (d, $^1J_{P-C}$ = 3.5), 122.2, 128.3, 129.0 (d, $^1J_{P-C}$=3.11), 129.2, 129.5, 129.6, 129.7, 130.4, 130.9, 131.8 (d, $^1J_{P-C}$ = 2.1), 134.2, 134.2, 135.1, 140.4, 174.3 (d, $^1J_{P-C}$ = 3.0), 174.4 (d, $^1J_{P-C}$ = 2.9). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): −144.4 (sep, PF_6, $^1J_{P-F}$ = 716.8), 18.2 (s, PPh_3). HR FT–ICR MS: Found (Calc. for $C_{85}H_{91}Ir_2N_5P_2$): m/z = 814.7994 (814.8004). *Anal.* Calc. for $C_{85}H_{91}F_{12}Ir_2N_5P_4$: C, 47.59; H, 4.61; N, 4.08. Found: C, 48.50; H, 4.78; N, 3.65%.

4.4. Representative procedure for measuring rate of Ir–NHC rotation in **6d**

For a standard kinetics experiment the NMR probe was pre-heated to the desired temperature prior to introduction of a sample. Crystals of (COD)ClIr{^{Me}BzC$_{Pr}$N(Bn)$_{Pr}$CBz^{Me}}IrCl(COD) (**6d**, 4 mg, 3.6 μmol) (prepared by slow evaporation from an ethyl acetate/pentane (60:40 v/v) solution) were dissolved in 700 μl $CDCl_3$ immediately before placing the sample into the NMR spectrometer. The time between the placement of the sample in the probe and the first data point was recorded. The increase in the area of the singlet at δ 3.76 ppm corresponding to the R,S isomer and the decrease in the area of the doublets at δ 3.68 and 3.85 ppm corresponding to the R,R isomer were measured by integration of a series of ^1H NMR spectra at different times. In order to generate an Eyring plot this experiment was repeated at several different temperatures.

4.5. Conditions for catalytic reactions

4.5.1. Transfer hydrogenation

The following represents a general procedure for transfer hydrogenation between acetophenone and acetone:

0.021 mol% of a stock solution of the appropriate Ir catalyst in CH_2Cl_2 was syringed into a 50 mL round-bottom flask and the solvent removed. Trimethoxybenzene (15 mg, internal standard), KO^{t}Bu (2.0 mg, 0.43 mol%), acetophenone (487 μL, 4.16 mmol) and ^{i}PrOH (25 mL) were then added and the degassed solution heated under nitrogen at 80 °C for the specified time. Aliquots were taken under a flow of nitrogen gas and concentrated *in vacuo* before their ^1H NMR spectrum was recorded in $CDCl_3$.

The following represents a general procedure for transfer hydrogenation between *N*-benzylidineaniline and acetone:

0.042 mol% of a stock solution of the appropriate Ir catalyst in CH_2Cl_2 was syringed into a 50 mL round-bottom flask and the solvent removed. Trimethoxybenzene (15 mg, internal standard), KO^{t}Bu (2.0 mg, 0.43 mol%), *N*-benzylidineaniline (0.754 g, 4.16 mmol) and ^{i}PrOH (25 mL) were then added and the degassed solution heated under nitrogen at 80 °C for the specified time. Aliquots were taken under a flow of nitrogen gas and concentrated *in vacuo* before their ^1H NMR spectrum was recorded in $CDCl_3$.

4.5.2. Olefin hydrogenation

The following represents a general procedure for catalytic olefin hydrogenation reactions:

(Z)-Cyclooctene (10 mg, 0.091 mmol) and 2.5 mol% **12c** (4.3 mg, 2.3 μmol) were dissolved in CD_2Cl_2 (0.5 mL) in a J. Young NMR tube. The tube was degassed using three consecutive freeze–pump-thaw cycles and then 1 atm H_2 was introduced using a dual-manifold Schlenk line. The reaction was monitored using ^1H NMR spectroscopy. In all reactions no by-products were observed and conversion was estimated by integration of the starting material versus the product.

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Appendix A. Supplementary material

X-ray information for **5d**, **6d**, **7d** and [^{Me}(H)C$_{Et}$N(Bn)$_{Et}$C.(H)^{Me}]·2[I], an overlay of the solid state structures of **6d** and **7d**, a comparison of the ^1H NMR spectra of freshly dissolved crystals of **6d** versus a solution of crystals that has been standing for 24 h and the Eyring plot for measuring the rate of rotation around the Ir-NHC bond in **6d** is available free of charge via the Internet at http://pubs.acs.org. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.034.

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