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Chelating N-heterocyclic carbene-carboranes offer flexible ligand coordination to Ir^{III}, Rh^{III} and Ru^{II}: effect of ligand cyclometallation in catalytic transfer hydrogenation

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Imidazolium salts linked by an ethyl tether to *closo*-dicarbadodecaboranes were reacted with $[IrCp^*Cl_2]_2$, $[RhCp^*Cl_2]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$ in the presence of Ag_2O to prepare complexes of the type $[MCp^*(NHC)Cl_2]$ (M = Ir, Rh; NHC = N-heterocyclic carbene) or $[Ru(p\text{-cymene})(NHC)Cl_2]$. When the NHC contained an N-^{t}Bu substituent, C-H activation of the ^{t}Bu and subsequent alkyl coordination was observed at Ir. Coordination of the *closo*-dicarbadodecaborane moiety to Ir was possible to give 7-membered metallacycles, coordinated through the carbenic carbon of the NHC and either a carbon atom or a boron atom of the carborane. Examination of the Ir complexes in the transfer hydrogenation of acetophenone to 1-phenylethanol reveals that cyclometallation of the carborane moiety is important for catalytic efficacy, indicating a bifunctional mechanism and involvement of the dicarbadodecaborane anion.

Introduction

N-Heterocyclic carbenes (NHCs) represent an attractive alternative to phosphines as ligands in many organometallic-catalysed reactions, and are showing promise in the biomedical field.[1-6] Advantages of NHCs over common ligand types include the strong metal-carbene bond which is able to stabilise an array of metals in various oxidation states, and the ability to fine-tune the steric and electronic effects of the ligand through modification of nitrogen substituents and backbone substituents respectively. Nitrogen substituents on NHCs are usually alkyl or aryl groups, with neutral (*e.g.* pyridyl, oxazoline)[7-15] or anionic (*e.g.* alkoxide, amide)[16-20] donor functionalities often being incorporated into the substituents. These tethering groups enable ligands to chelate a metal centre, allowing fine control over stability, steric and electronic properties. The N-substituents may further become involved in catalysis in a bifunctional manner, for example in academically and industrially viable hydrogenation and transfer hydrogenation reactions.[21-24]

Lavallo and co-workers have previously reported NHC ligands bearing a *closo*-carbadodecaborate substituent.[25, 26] Coordination of the ligands to Au through the NHC yields zwitterionic and anionic complexes.[27] We have recently introduced a new class of NHC ligands which contain either a *closo*-dicarbadodecaborane (neutral and anionic) or a *nido*-dicarbaundecaborane dianion.[28] Versatile coordination to Rh^I through both the NHC and either a *closo*-dicarbadodecaborane anion, or a *nido*-dicarbaundecaborane dianion was demonstrated. The *nido*-carborane ligands furnish homo-bimetallic complexes, whereas the *closo*-carborane ligand chelates the Rh^I centre, coordinating through both the NHC and a carbon atom of the carborane. Herein, we report a valuable addition to the NHC-carborane ligand class, and their reactivity with Ir^{III}, Rh^{III} and Ru^{II}. Examination of the Ir^{III} complexes in the transfer hydrogenation of acetophenone to 1-phenylethanol demonstrates that the complexes are catalytically viable, with a profound ligand effect observed upon cyclometallation.

Results and discussion

Ligand precursors **1a**-**1c** were identified for this study and were prepared using a convenient nucleophilic substitution reaction.[28] Reaction of 1-bromoethyl-1,2-dicarba-*closo*-dodecaborane with a stoichiometric amount of N-^{t}butyl or N-methyl imidazole in a minimal amount of anhydrous toluene at 100 °C gave the corresponding imidazolium bromide salts **1a** and **1b** respectively (Scheme 1). (1-Bromoethyl)(2-methyl)-1,2-dicarba-*closo*-dodecaborane was prepared from 1-methyl-1,2-dicarba-*closo*-dodecaborane (see experimental) and reacted with N-methyl imidazole to give imidazolium bromide **1c**. The novel salts **1b** and **1c** were fully characterised using multinuclear NMR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography. The solid-state structures of **1b** and **1c** show an ethyl tether linking a nitrogen atom of the imidazolium with a carbon atom of each carborane (Figure 1). The carboranyl carbon atoms were identified using the VCD method,[29] with the carboranyl C-H proton in **1b** resonating at 5.37 ppm in the ^{1}H NMR spectrum (500 MHz, dmso-d_6).

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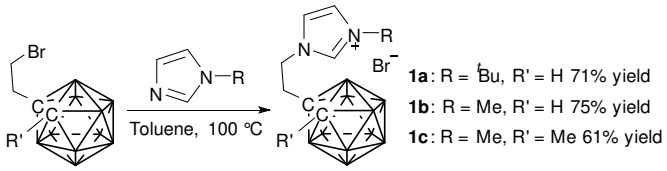


Scheme 1 Synthesis of imidazolium ligand precursors **1a**-**1c**.

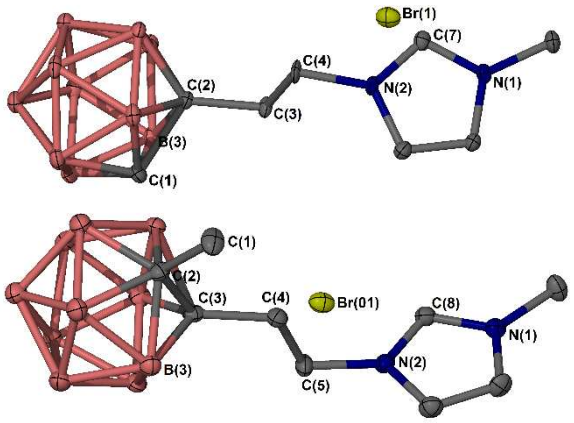
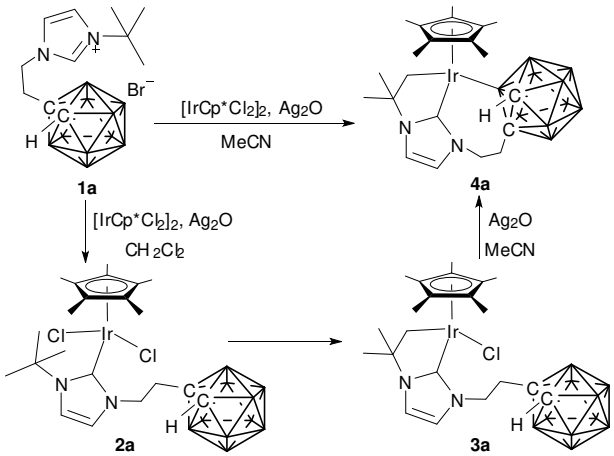


Fig 1 Molecular structure of imidazolium bromide salts **1b** (top) and **1c** (bottom). H atoms are omitted for clarity and thermal ellipsoids are depicted at 50% probability.

Reaction of compound **1a** with $[IrCp^*Cl_2]_2$ in the presence of Ag_2O in CH_2Cl_2 gave an Ir^{III}-NHC complex **3a** (Scheme 2). In addition to NHC formation, the ^1H NMR spectrum revealed that C-H activation of a methyl of the ^{t}Bu group had occurred, with concomitant coordination to the metal. The non-equivalent diastereotopic protons of the metallated CH_2 group appear at 3.06 and 2.39 ppm in the ^1H NMR spectrum (300 MHz, CD_2Cl_2), with a coupling of 12.0 Hz. The non-cyclometallated complex **2a** was not observed in this reaction, indicating that aliphatic C-H activation is facile, as previously seen in related Ir^{III}-NHCs.[30]



Scheme 2 Reaction of imidazolium **1a** with an Ir^{III} precursor and Ag_2O to yield cyclometallated complexes **3a** and **4a**.

Our previous work has shown that solvent-assisted C-H activation/deprotonation of the carborane moiety occurs in MeCN,[28] hence the reaction with **1a** was carried out in MeCN with excess Ag_2O. In addition to Ir-NHC formation, cyclometallation through the carborane did occur to give **4a**, though in this case the *closo*-dicarbadodecaborane anion coordinates to the metal through a boron atom, rather than a carbon atom as observed in Rh^I complexes.[28] This was confirmed through the observation of a broad resonance at 3.21 ppm, integrating to 1H in the ^1H NMR spectrum (500 MHz, C_6D_6), indicative of the carboranyl C-H remaining protonated. The ^1H NMR spectrum of **4a** exhibits two sets of resonances in a 7:3 ratio due to diasteroisomers, as a result of the sterogenic metal centre and a mixture of B3 and B6 metallation.[31, 32] Crystals of complex **4a** suitable for X-ray diffraction analysis were obtained from slow evaporation of a MeCN solution, and provide unambiguous confirmation that intramolecular C-H activation of the ^{t}Bu group had occurred to give a five-membered metallacycle, with a C-Ir-C bite angle of 76.27(12) ° (Figure 2). In addition, coordination through a boron atom of the *closo*-carborane results in a seven-membered metallacycle, with a C-Ir-B bite angle of 85.65(14) °, forming an interesting and structurally distinct (7,5)-bicyclo-metallated system. The molecular structure of **4a** can be regarded as a distorted piano stool geometry, with an Ir-$C_{carbene}$ bond length of 1.956(3) Å, which is comparatively short for IrCp*(NHC)-type complexes.[33-37] The Ir-CH_2 distance of 2.128(3) Å is moderately long compared to other Ir^{III}-alkyl-cyclometallated complexes.[30, 33, 38] The carboranyl carbon atoms were determined using the VCD method, and revealed a particularly elongated B3 vertex to centroid distance of 1.89 Å, which are typically in the range 1.72-1.78 Å.[31, 39] It can be proposed that the metallated carborane B vertex elongates to relieve steric encumbrance close to the metal centre.

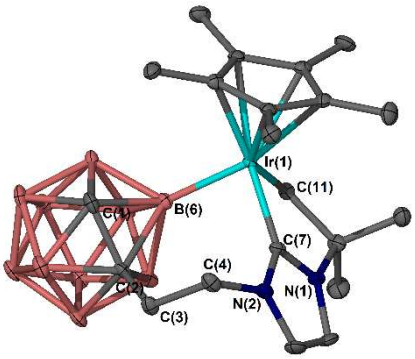
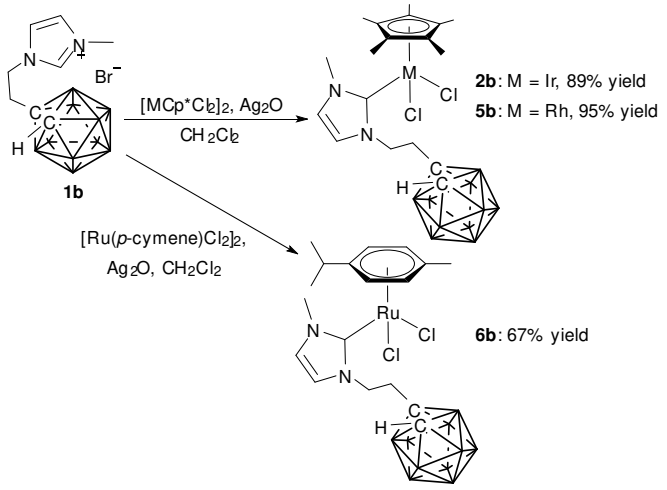


Fig 2 Molecular structure of Ir^{III}-NHC complex **4a**. H atoms are omitted for clarity and thermal ellipsoids are depicted at 50% probability.

Complexes **3a** and **4a** were isolated in relatively low (but useable) yields, with attempts to improve them unsuccessful. Therefore, to increase yield and enable isolation of a non-cyclometallated $Ir^{III}Cp^*(NHC)Cl_2$-type complex of an NHC-carborane ligand, the sterics were reduced by replacing the ^{t}Bu substituent of the NHC with a methyl group (**1b**). Ligand precursor **1b** was reacted with $[IrCp^*Cl_2]_2$ under the same conditions as previously to give the desired $Ir^{III}Cp^*(NHC)Cl_2$ complex **2b** in excellent yield (Scheme 3). The corresponding $RhCp^*(NHC)Cl_2$ (**5b**) and Ru(*p*-cymene)$(NHC)Cl_2$ (**6b**) complexes

were also synthesised in good yield using analogous procedures. Complexes **2b**, **5b** and **6b** were fully characterised by multinuclear NMR spectroscopy, mass spectrometry and elemental analysis. As expected, upon deprotonation and subsequent coordination of the NHC group, the imidazolium C2-proton resonance is absent from the ^{1}H NMR spectra in each case. The CH_2 protons of the ethyl linkers are diastereotopic, indicating hindered rotation about the M-$C_{carbene}$ bonds at room temperature. Furthermore, there appears to be a second minor product in the ^{1}H NMR spectrum, with two resonances that appear close together for both the N-Me and Cp* groups. This may be due to the complexes being in equilibrium with cyclometallated derivatives in solution,[40] though mass spectrometry and elemental analysis data are indicative of only the non-cyclometallated products. The carboranyl C-H resonances appear at 4.45 ppm (**2b**), 4.62 ppm (**5b**) (300MHz, $CDCl_3$) and 4.54 ppm (**6b**) (500MHz, CD_2Cl_2), and the ^{11}B{^{1}H} NMR spectra display characteristic resonances for *closo*-carboranes, with peaks ranging from -2 to -13 ppm.



Scheme 3 Reaction of imidazolium **1b** with Ir^{III}, Rh^{III} and Ru^{II} precursors to give complexes **2b**, **5b** and **6b**.

Crystals of **2b** and **6b** suitable for X-ray diffraction analysis were obtained from CH_2Cl_2/hexane and slow evaporation of a concentrated MeCN solution respectively. The solid-state structures (Figure 3) show piano stool geometry around the metal centres, with each metal bearing two chloride atoms, an NHC and either Cp* (**2b**) or *p*-cymene (**6b**). The M-$C_{carbene}$ bond lengths of 1.92(3) Å (**2b**) and 2.064(7) Å (**6b**) are relatively short when compared to other $IrCp^*(NHC)Cl_2$ and Ru(*p*-cymene)$(NHC)Cl_2$ complexes in the literature,[37, 41-45] which may be an effect of the carborane substituent causing the carbenic carbon to be more nucleophilic than other NHCs.

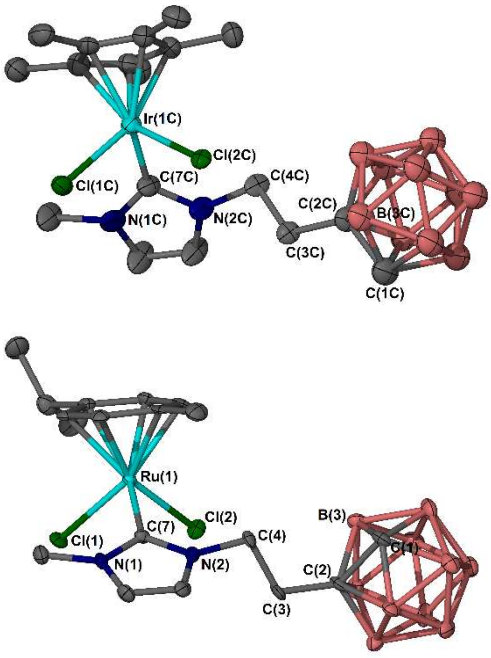
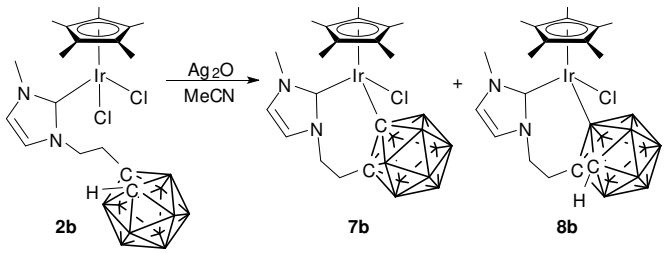


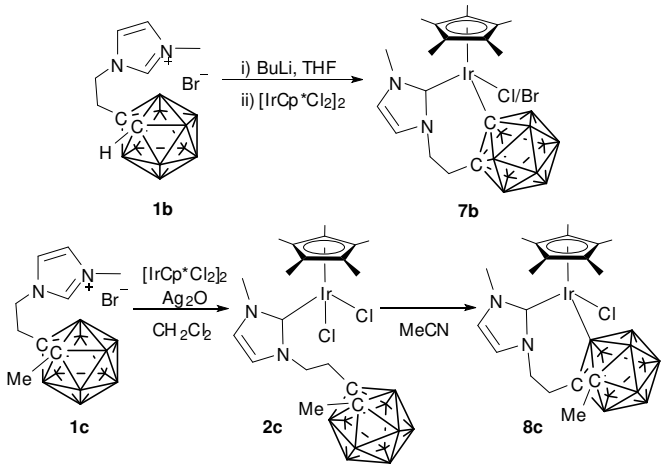
Fig. 3 Molecular structure of complexes **2b** (top) and **6b** (bottom). H atoms are omitted for clarity and thermal ellipsoids are depicted at 30% (**2b**) and 50% (**6b**) probability.

Similarly to complex **3a**, the Ir complex **2b** underwent cyclometallation upon reaction with Ag_2O in MeCN. Following cyclometallation, the NMR data revealed two overlapping sets of resonances, which were assigned as a mixture of $C_{carborane}$- and $B_{carborane}$-cyclometallated complexes **7b** and **8b** (Scheme 4). The carboranyl C-H appears as two resonances in the ^{1}H NMR spectrum, attributable to a diasterotopic mixture of B3 and B6 metallation. Mass spectrometry data revealed just one signal at 579.3350, attributable to [**7b**/**8b**-Cl]$^{+}$, with elemental analysis providing evidence for the presence of only **7b** and/or **8b**. It is intriguing that the N-^{t}Bu substituted ligand leads selectively to only B-cyclometallation (**4a**), whereas a mixture of B- and C-cyclometallation is observed with the N-Me substituted ligand. Such selectivity in **4a** is likely due to elongation of the B vertex allowing reduction of steric encumbrance around the metal, which is not necessary in the case of the N-Me substituted ligand. Surprisingly, Rh and Ru complexes **5b** and **6b** do not cyclometallate under the same reaction conditions, which may indicate that an M-C/B interaction occurs prior to deprotonation, with the higher charge density of Ir^{III} compared to Rh^{III} and Ru^{II} rendering the C-H/B-H proton more acidic.



Scheme 4 Synthesis of mixed metallacycles **7b** and **8b**.

To negate the formation of a mixture of cyclometallated products, an alternative route was developed to furnish complex **7b** (Scheme 5). Ligand precursor **1b** was reacted with ^{n}BuLi to deprotonate both the imidazolium NCHN proton and the carboranyl CH proton, followed by reaction with $[IrCp^*Cl_2]_2$. Analysis of the resulting product revealed NHC coordination and Ir-$C_{carborane}$ cyclometallation, however, halide exchange had also occurred to give a mixture of Ir-Cl and Ir-Br (originating from LiBr). X-ray crystallography analysis showed 70% bromide and 30% chloride occupancy in the solid-state (Figure 4). To remove bromide ions from the reaction, attempts were made to synthesise the imidazolium chloride ligand precursor from 1-chloroethyl-1,2-dicarba-*closo*-dodecaborane, though the nucleophilic substitution reaction was sluggish, furnishing 7% product which was contaminated with *nido*-carborane species.



Scheme 5 Synthesis of Ir-NHC-$C_{carborane}$ metallacycle **7b** (top), and Ir-NHC-$B_{carborane}$ metallacycle **8c** *via* non-cyclometallated complex **2c** (bottom).

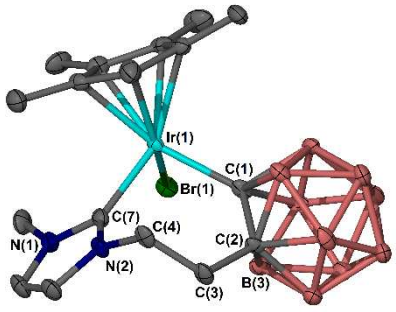


Fig. 4 Molecular structure of complex **7b**. H atoms are omitted for clarity and thermal ellipsoids are depicted at 50% probability. The halide labelled Br(1) was found to be a mixture of Br (70%) and Cl (30%).

To prepare a cyclometallated complex that coordinates through a carboranyl boron atom, C-Me protected ligand precursor **1c** was reacted with $[IrCp^*Cl_2]_2$ in the presence of Ag_2O. As previously observed, reaction in CD_2Cl_2 furnishes the non-cyclometallated product **2c**. X-ray diffraction analysis of complex **2c** showed the expected $IrCp^*(NHC)Cl_2$ species, with an Ir-$C_{carbene}$ bond length of 2.002(18) Å (Figure 5). As observed in **2b**, complex **3c** undergoes cyclometallation upon reaction with Ag_2O in MeCN to give **8c** in 44% yield.

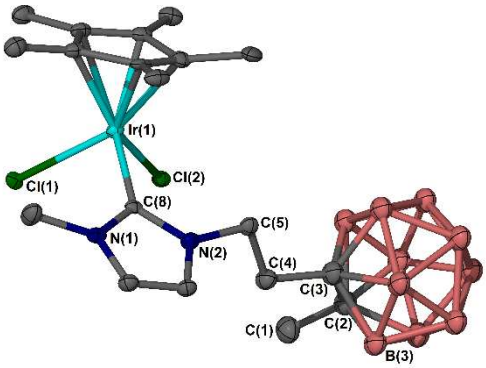
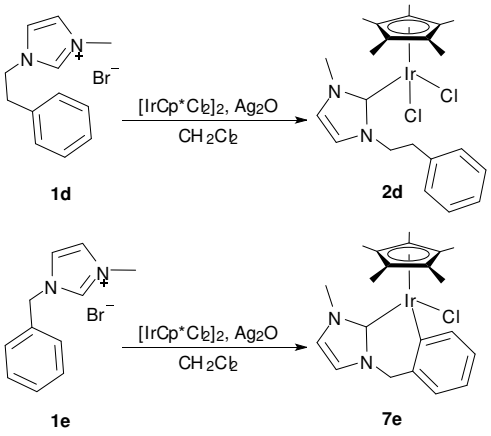


Fig. 5 Molecular structure of complex **2c**. H atoms are omitted for clarity and thermal ellipsoids are depicted at 50% probability.

Catalytic viability in transfer hydrogenation

The reduction of ketones *via* transfer hydrogenation provides a mild route to secondary alcohols without the need for pressurised H_2 gas.[46] Several different metals have been shown to catalyse the transfer hydrogenation reaction, including Ir, Rh and Ru, many of which contain NHC ligands.[21-23, 36] To assess the catalytic feasibility of our novel Ir^{III} complexes bearing NHC-carborane ligands, complexes **2b**, **7b**/**8b** mixture, **7b** and **8c** were examined in the transfer hydrogenation of acetophenone, alongside $[IrCp^*Cl_2]_2$ as a benchmark reaction (Table 1). Furthermore, as a dicarbadodecaborane is thought to mimic the sterics created by rotation of a planar phenyl group through 360°, the phenyl derivative **2d** was prepared and examined for useful comparison, in addition to the cyclometallated phenyl complex **7e** (Scheme 6).



Scheme 6 Synthesis of phenyl-derivatives **2d** and **7e**.

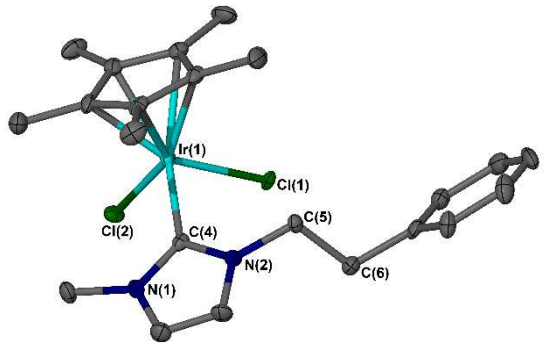
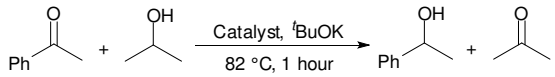


Fig. 6 Molecular structure of complex **2d**. H atoms are omitted for clarity and thermal ellipsoids are depicted at 50% probability.

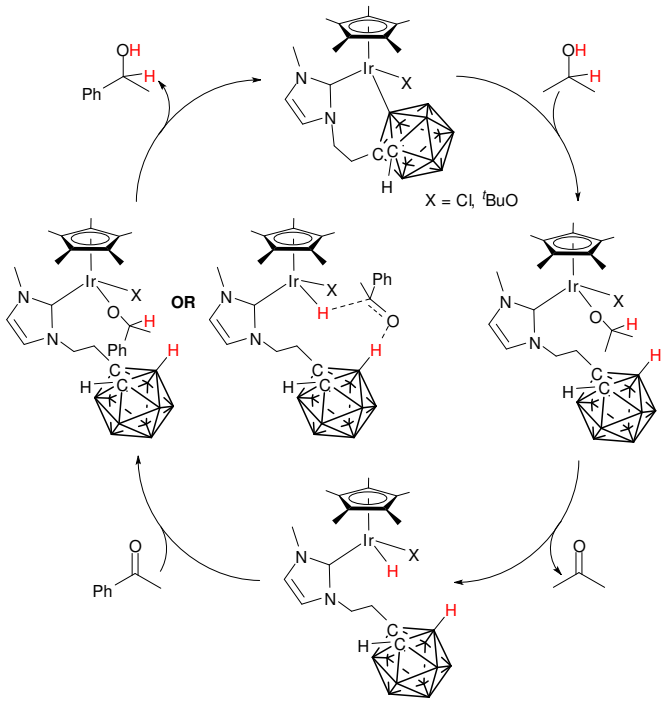
Table 1 Examination of a range of Ir^{III} catalysts in the transfer hydrogenation of acetophenone to 1-phenylethanol.



	Catalyst	Catalyst Loading (mol%)	Conversion (%)[#]
1	No catalyst	0	8
2	$[IrCp^*Cl_2]_2$	1[Δ]	68
3	**2b**	1	33
4	**2d**	1	25
5	**7b/8b**	1	>99
6	**7b/8b**	0.5	91
7	**7b**	1	75
8	**8c**	1	>99
9	**8c**	0.5	82
10	**7e**	1	39
11	**7b/8b**[‡]	1	0

Conditions: Acetophenone (1 mmol), 2-propanol (2.3 mL, 30 mmol), tBuOK (0.1 mmol, [‡]no base added), catalyst ([Δ]1.0 mol% per Ir), internal standard = 1,3,5-trimethoxybenzene (0.33 mmol), 82 °C, 1 hour. [#]Conversion was calculated by ^{1}H NMR spectroscopy, by measuring the integration of the methyl resonance of 1-phenylethanol and comparing to the TMB internal standard. Conversion values are an average of two separate runs.

The transfer hydrogenation reaction with $[IrCp^*Cl_2]_2$ as the catalyst gave a reasonable conversion of 68% after 1 hour (entry 2). Incorporating an NHC ligand with a dicarbadodecaborane substituent (**2b**) into the complex had a significant deactivating effect, with a conversion of 33% after 1 hour (entry 3), which decreased further to 25% when exchanging the dicarbadodecaborane group for phenyl (**2d**) (entry 4). However, cyclometallation of the carborane moiety enhances catalysis greatly compared to the non-cyclometallated counterparts (entries 5-9). The C/B-cyclometallated mixture **7b/8b** catalyses the hydrogenation of acetophenone to 1-phenylethanol quantitatively after 1 hour (entry 5), with a 91% conversion when the catalyst loading is lowered to 0.5 mol% (entry 6). When using 1.0 mol% of the C-cyclometallated complex **7b**, a conversion of 75% was achieved after 1 hour (entry 7), which indicates that the B-cyclometallated complex is more active than the C-cyclometallated. Indeed, when B-cyclometallated complex **8c** was tested, quantitative conversion was observed with 1.0 mol% after 1 hour (entry 8). However, 0.5 mol% **8c** yielded 82% conversion (entry 9), which is lower than the C/B-cyclometallated mixture **7b/8b**. This indicates that either the Ir-halide has an effect on catalysis, with Cl being more activating than Br, or that the mixed C/B-cyclometallated complexes work synergistically. Cyclometallation of a phenyl group has little effect upon the outcome of the reaction, with a conversion of only 39% when using complex **7e** (entry 10). The significant enhancement in activity upon cyclometallation of a carborane substituent, which is not observed upon cyclometallation of a phenyl substituent, is likely a result of metal-ligand bifunctional catalysis, in which the carborane anion becomes involved. Conducting the transfer hydrogenation reaction in the absence of tBuOK shuts down catalysis (entry 11), which may suggest that the active catalyst is an alkoxide rather than a chloride species. Based upon these findings, a proposed mechanism for the transfer hydrogenation reaction is given in Scheme 7, which may proceed *via* an inner-sphere[22] or an outer-sphere[47] mechanism.



Scheme 7 Proposed inner-sphere or outer-sphere mechanism for the transfer hydrogenation of acetophenone catalysed by an Ir^{III} complex bearing a cyclometallated NHC-dicarbadodecaborane ligand.

Conclusion

In summary, we have reported a series of complexes bearing NHC-carborane ligands. Variable coordination has been observed through the NHC and through either a carbon atom or a boron atom of the carborane, which highlights their potential as a flexible and distinct ligand class. Through judicious choice of reaction conditions and ligand precursor, selective C- or B-

cyclometallation can be effected. The cyclometallated complexes are validated active catalysts in the transfer hydrogenation of acetophenone, with a bifunctional mechanism proposed in which the dicarbadodecaborane moiety is involved.

Experimental

General

All manipulations were carried out under an inert atmosphere by means of standard Schlenk line or Glovebox techniques. Anhydrous solvents were prepared by passing over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water, *via* the Dow-Grubbs solvent system, and then freeze-pump-thaw degassed prior to use. 1-^{t}Butylimidazole,[48] 6,9-bis(acetonitrile)decaborane,[49] 1-bromoethyl-1,2-dicarba-closo-dodecaborane,[50] 1-methyl-1,2-dicarba-*closo*-dodecaborane,[50] $[Ir(Cp^*)Cl_2]_2$,[51] $[Rh(Cp^*)Cl_2]_2$,[51] $[Ru(p\text{-cymene})Cl_2]_2$,[52] **1d**,[53] **1e**[41] and **7e**[41] were prepared using literature methods. All other reagents were purchased and used without further purification. NMR spectra were recorded on a Bruker AV500 or a Bruker DPX300 spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts were referenced against residual solvent peaks. The ^{11}B{^{1}H} NMR spectra were referenced externally to $BF_3.OEt_2$. Assignment of ^{1}H and ^{13}C{^{1}H} NMR spectra for all complexes was aided by the use of 2D ^{1}H^{1}H COSY, ^{1}H^{13}C HMQC, ^{1}H^{13}C HMBC and ^{13}C{^{1}H} DEPT 135 experiments. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Elemental analyses were performed by Mr Stephen Boyer at London Metropolitan University.

(1-Hydroxyethyl)(2-methyl)-1,2-dicarba-*closo*-dodecaborane

1-Methyl-1,2-dicarba-*closo*-dodecaborane (300 mg, 1.90 mmol) was added to a Schlenk flask and degassed. Anhydrous THF (10 mL) was added and cooled to -78°C. A 1.6 M solution of ^{n}BuLi in hexane (1.17 mL, 1.87 mmol) was added dropwise and stirred for 30 minutes at -78°C. The temperature was raised to 0°C and a 2.5 M solution of ethylene oxide in THF (1.13 mL, 2.81 mmol) was added dropwise and stirred at 0°C for 1 hour. The reaction was quenched by adding a saturated solution of NH_4Cl (5 mL), and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The organic fractions were combined and dried over $MgSO_4$, filtered and solvent removed *in vacuo*. Hexane (3 mL) was added and cooled to -15°C for 3 hours. The resulting white crystals were filtered, washed with hexane at 0°C (5 mL) and dried *in vacuo*. Yield: 325 mg, 1.61 mmol (85 %). ^{1}H NMR (500 MHz, dmso-d_6): δ 4.87 (s, 1H, O*H*), 3.56 (t, J = 5 Hz, 2H, CH_2OH), 2.44 (t, J = 5 Hz, 2H, CH_2), 2.09 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, dmso-d_6): δ 77.2 (carboranyl quaternary *C*), 76.0 (carboranyl quaternary *C*), 59.5 (*C*H$_2$OH), 36.9 (*C*H$_2$), 22.6 (*C*H$_3$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d_6): δ -4.9 (1B), -6.4 (1B), -8.9 (2B), -10.0 (2B), -10.9 (4B). Anal. Calcd for $C_5H_{18}B_{10}O$: C, 29.69; H, 8.97. Found: C, 29.77; H, 9.02.

(1-Bromoethyl)(2-methyl)-1,2-dicarba-*closo*-dodecaborane

To a Schlenk flask was added (1-hydroxyethyl)(2-methyl)-1,2-dicarba-*closo*-dodecaborane (360 mg, 1.78 mmol) and anhydrous CH_2Cl_2 (5 mL). This was cooled to 0°C and PPh_3 (543 mg, 2.07 mmol) and N-bromosuccinimide (368 mg, 2.07 mmol) was added and stirred at 0°C for 3 hours. The organic phase was washed with H_2O (4 × 10 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. Et_2O (10 mL) was added and the suspension was filtered through a 5 cm silica plug which was flushed with Et_2O (2 × 10 mL). The solvent was removed from the filtrate *in vacuo* to give the product as a white crystalline solid. Yield: 365 mg, 1.38 mmol (78 %). ^{1}H NMR (500 MHz, dmso-d_6): δ 3.60 (t, J = 10 Hz, 2H, CH_2Br), 2.86 (t, J = 10 Hz, 2H, CH_2), 2.12 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (126 MHz, dmso-d_6): δ 76.9 (carboranyl quaternary *C*), 76.2 (carboranyl quaternary *C*), 36.5 (*C*H$_2$Br), 28.9 (*C*H$_2$), 22.4 (*C*H$_3$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d_6): δ -4.4 (1B), -6.3 (1B), -9.0 (2B), -9.9 (2B), -10.9 (4B). Anal. Calcd for $C_5H_{17}B_{10}Br$: C, 22.65; H, 6.46. Found: C, 22.77; H, 6.48.

Compound 1a

1-Bromoethyl-1,2-dicarba-closo-dodecaborane (500 mg, 1.99 mmol), 1-^{t}butylimidazole (246 mg, 1.98 mmol) and anhydrous toluene (3 mL) were added to an ampoule and heated at 100°C for 18 hours. The reaction was cooled to room temperature, filtered, and the solid washed with toluene (3 × 10 mL) to give an off white crystalline solid. This was recrystallised from MeOH (3 mL) / Et_2O (30 mL), filtered and dried *in vacuo* to give **1a** as a white crystalline solid. Yield: 529 mg, 1.41 mmol (71 %). ^{1}H NMR (500 MHz, dmso-d_6): δ 9.41 (s, 1H, imidazolium NC*H*N), 8.03 (t, J = 1.9 Hz, 1H, imidazolium NC*H*), 7.90 (t, J = 1.9 Hz, 1H, imidazolium NC*H*), 5.38 (br. s, 1H, carboranyl C*H*), 4.33 (m, 2H, CH_2), 2.99 (m, 2H, CH_2), 1.57 (s, 9H, (CH_3)$_3$). ^{13}C{^{1}H} NMR (126 MHz, dmso-d_6): δ 134.9 (imidazolium N*C*N), 122.6 (imidazolium N*C*H), 120.2 (imidazolium N*C*H), 72.4 (carboranyl quaternary *C*), 63.2 (carboranyl *C*H), 59.6 (*C*(CH$_3$)$_3$), 47.0 (*C*H$_2$), 35.3 (*C*H$_2$), 28.9 ((*C*H$_3$)$_3$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d_6): δ -2.8 (1B), -5.5 (1B), -9.6 (2B), -11.8 (6B). HRMS (ESI+): *m/z* 295.3188 $[C_{11}H_{27}B_{10}N_2]^+$, Calcd for $[M\text{-}Br]^+$ 295.3177.

Compound 1b

Compound **1b** was prepared as described for **1a**, from 1-bromoethyl-1,2-dicarba-closo-dodecaborane (500 mg, 1.99 mmol) and 1-methylimidazole (162 mg, 1.97 mmol). Following purification the product was isolated as a fluffy crystalline white solid. Yield: 490 mg, 1.47 mmol (75 %). ^{1}H NMR (500 MHz, dmso-d_6): δ 9.21 (s, 1H, imidazolium NC*H*N), 7.84 (t, J = 2.0 Hz, 1H, imidazolium NC*H*), 7.71 (t, J = 2.0 Hz, 1H, imidazolium NC*H*), 5.37 (br. s, 1H, carboranyl C*H*), 4.35 (m, 2H, CH_2), 3.86 (s, 3H, CH_3), 2.94 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (126 MHz, dmso-d_6): δ 137.0 (imidazolium N*C*N), 123.6 (imidazolium N*C*H), 122.3 (imidazolium N*C*H), 72.5 (carboranyl quaternary *C*), 63.1 (carboranyl *C*H), 46.9 (*C*H$_2$), 35.8 (*C*H$_3$), 35.3 (*C*H$_2$). ^{11}B{^{1}H} NMR (161 MHz, dmso-d_6): -3.0 (1B), -5.6 (1B), -9.7 (2B), -11.8 (4B), -12.9 (2B). HRMS (ESI+): *m/z* $[C_8H_{21}B_{10}N_2]^+$ 253.2714, Calcd for $[M\text{-}Br]^+$ 253.2706. Anal. Calcd for $C_8H_{21}B_{10}N_2Br$: C, 28.83; H, 6.35; N, 8.41. Found: C, 28.72; H, 6.41; N, 8.27. Crystals suitable for X-ray diffraction analysis were grown *via* slow diffusion of Et_2O into a concentrated solution of **1b** in MeCN.

Compound 1c

Compound **1c** was prepared as described for **1a**, from (1-bromoethyl)(2-methyl)-1,2-dicarba-closo-dodecaborane (100 mg, 0.38 mmol) and 1-methylimidazole (31 mg, 0.38 mmol) in anhydrous toluene (1 mL), with a reaction time of 6 hours. After purification the product was obtained as a fluffy crystalline white solid. Yield: 79 mg, 0.23 mmol (61 %). ^{1}H NMR (300 MHz, CD_3OD): δ 9.07 (s, 1H, imidazolium NC*H*N), 7.75 (m, 1H, imidazolium NC*H*), 7.59 (m, 1H, imidazolium NC*H*), 4.46 (m, 2H, C*H*$_2$), 3.93 (s, 3H, C*H*$_3$), 2.95 (m, 2H, C*H*$_2$), 2.15 (s, 3H, carboranyl CH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ 138.5 (imidazolium N*C*N), 125.1 (imidazolium N*C*H), 123.8 (imidazolium N*C*H), 77.5 (carboranyl quaternary *C*), 75.6 (carboranyl quaternary *C*), 48.9 (*C*H$_2$), 36.6 (*C*H$_2$), 35.2 (*C*H$_3$), 23.6 (carboranyl-*C*H$_3$). ^{11}B{^{1}H} NMR (96 MHz, CD_3OD): -3.9 (1B), -5.9 (1B), -9.6 (4B), -10.5 (4B). HRMS (ESI+): *m/z* $[C_9H_{23}B_{10}N_2]^+$ 267.2875, Calcd for [M-Br]$^+$ 267.2863. Anal. Calcd for $C_9H_{23}B_{10}N_2Br$: C, 31.13; H, 6.68; N, 8.07. Found: C, 31.02; H, 6.79; N, 8.12. Crystals suitable for X-ray diffraction analysis were grown *via* slow diffusion of Et_2O into a concentrated solution of **1c** in MeCN.

Ir complex 3a

To a Schlenk flask was added **1a** (100 mg, 0.27 mmol), Ag_2O (34 mg, 0.15 mmol), $[Ir(Cp^*)Cl_2]_2$ (120 mg, 0.15 mmol) and anhydrous CH_2Cl_2 (5 mL) along with some 4Å molecular sieves. The reaction was heated at 40°C for 16 hours, filtered through a 2 cm silica plug and flushed with CH_2Cl_2 (3 × 10 mL). The solvent was removed from the filtrate *in vacuo* and the solid added to Et_2O (10 mL). This was filtered and removal of the solvent from the filtrate *in vacuo* gave **3a** as an orange powder. Yield: 63 mg, 0.10 mmol (37 %). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.87 (d, J = 3.0 Hz, 1H, NC*H*), 6.80 (d, J = 3.0 Hz, 1H, NC*H*), 4.56 (td, J = 12.0 Hz, 6.0 Hz, 1H, C*H*$_2$), 4.13 (br. s, 1H, carboranyl C*H*), 3.95 (m, 1H, C*H*$_2$), 3.06 (d, J = 12.0 Hz, 1H, C*H*$_2$-Ir), 2.98 (m, 1H, C*H*$_2$), 2.63 (m, 1H, C*H*$_2$), 2.39 (d, J = 12.0 Hz, 1H, C*H*$_2$-Ir), 1.78/1.74 (Cp*), 1.53 (s, 3H, C*H*$_3$), 1.15 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 164.0 (N*C*N), 119.7 (N*C*H), 117.3 (N*C*H), 89.7/89.4 (quaternary Cp*), 73.0 (carboranyl quaternary *C*), 65.9 (*C*H$_3$), 62.7 (carboranyl *C*H), 49.3 (*C*H$_2$), 39.7 (*C*H$_2$), 31.4/31.0 (*C*H$_3$), 28.3 (Ir-*C*H$_2$), 10.1/10.0 (Cp*). ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ -2.3, -5.4, -9.5, -11.1, -12.6. HRMS (ESI+): *m/z* $[C_{21}H_{40}B_{10}N_2Ir]^+$ 621.3803, Calcd for [M-Cl]$^+$ 621.3811. Anal. Calcd for $C_{22}H_{42}B_{10}ClN_2Ir$: C, 38.43; H, 6.14; N, 4.27. Found: C, 38.50; H, 6.21; N, 4.35.

Ir complex 4a

To a Schlenk flask was added **1a** (100 mg, 0.27 mmol), Ag_2O (94 mg, 0.41 mmol), $[Ir(Cp^*)Cl_2]_2$ (108 mg, 0.14 mmol) and anhydrous MeCN (5 mL) along with some 4Å molecular sieves. The reaction was heated at 70°C for 24 hours, filtered through a 2 cm silica plug and flushed with MeCN (3 × 10 mL). The solvent volume was reduced to 5 mL *in vacuo* resulting in **4a** as colourless crystals, which were filtered, washed with pentane (5 mL) and dried *in vacuo*. Yield: 41 mg, 0.06 mmol (22 %). ^{1}H NMR (500 MHz, C_6D_6): Major isomer (70 %) δ 6.11 (d, 1H, J = 2.0 Hz, NC*H*), 5.96 (d, J = 2.0 Hz, 1H, NC*H*), 4.06 (td, J = 13.1 Hz, 3.0 Hz, 1H, C*H*$_2$), 3.24 (d, J = 10.0 Hz, 1H, C*H*$_2$-Ir), 3.21 (br. s, 1H, carboranyl C*H*), 2.64 (m, 2H, C*H*$_2$), 2.63 (d, J = 10.0 Hz, 1H, C*H*$_2$-Ir), 1.87 (m, 1H, C*H*$_2$), 1.61 (Cp*), 1.44 (s, 1H, C*H*$_3$), 1.06 (s, 1H, C*H*$_3$). Minor isomer (30 %) δ 5.86 (d, 1H, J = 2.0 Hz, NC*H*), 5.74 (d, 1H, J = 2.0 Hz, NC*H*), 4.35 (td, J = 13.8 Hz, 3.0 Hz, 1H, C*H*$_2$), 3.07 (d, J = 10.5 Hz, 1H, C*H*$_2$-Ir), 3.21 (br. s, 1H, carboranyl C*H*), 2.64 (m, 2H, C*H*$_2$), 2.63 (d, J = 10.5 Hz, 1H, C*H*$_2$-Ir), 2.18 (m, 1H, C*H*$_2$), 1.98 (m, 1H, C*H*$_2$), 1.73 (Cp*), 1.26 (s, 1H, C*H*$_3$), 0.98 (s, 1H, C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 117.6/117.5 (N*C*H), 116.7/116.6 (N*C*H), 93.5/93.0 (quaternary Cp*), 65.8/65.5 (carboranyl quaternary C), 59.9/58.3 (carboranyl *C*H), 45.1/44.3 (*C*H$_2$), 41.3 (*C*H$_2$), 31.9/31.2 (CH_3), 30.7/30.5 (*C*H$_3$), 20.6/18.4 (Ir-*C*H$_2$), 9.7/9.7 (Cp*). ^{11}B{^{1}H} NMR (96 MHz, C_6D_6): δ -1.4, -4.0, -7.8, -11.3, -15.3. HRMS (ESI+): *m/z* $[C_{21}H_{39}B_{10}N_2Ir]^+$ 620.3766, Calcd for [M]$^+$ 620.3733. Anal. Calcd. for $C_{21}H_{39}B_{10}N_2Ir$: C, 40.69; H, 6.34; N, 4.52. Found: C, 40.80; H, 6.47; N, 4.30. Crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of **4a** in MeCN.

Ir complex 2b

To a Schlenk flask was added **1b** (50 mg, 0.15 mmol), Ag_2O (17 mg, 0.075 mmol), $[Ir(Cp^*)Cl_2]_2$ (60 mg, 0.073 mmol) and anhydrous CH_2Cl_2 (5 mL), along with some 4 Å molecular sieves. The reaction was heated at 40°C for 16 hours, filtered through celite and flushed with CH_2Cl_2 (3 × 5 mL). The solvent was removed from the filtrate *in vacuo* and the residue was recrystallised from acetone (5 mL) / pentane (30 mL), filtered and dried *in vacuo* to give **2b** as a yellow solid. Yield: 86 mg, 0.13 mmol (89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (d, J = 3.0 Hz, 1H, NC*H*), 6.90 (d, J = 3.0 Hz, 1H, NC*H*), 4.94 (m, 1H, C*H*$_2$), 4.45 (br. s, 1H, carboranyl C*H*), 3.97/3.95 (s, 3H, C*H*$_3$), 3.71 (m, 1H, C*H*$_2$), 3.21 (m, 1H, C*H*$_2$), 2.59 (m, 1H, C*H*$_2$), 1.64/1.61 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.2 (N*C*N), 124.3 (N*C*H), 121.3 (N*C*H), 89.2 (quaternary Cp*), 71.9 (carboranyl quaternary *C*), 60.9 (carboranyl *C*H), 49.7 (*C*H$_2$), 39.1 (*C*H$_2$), 38.8 (*C*H$_3$), 9.5/9.3 (Cp*). ^{11}B{^{1}H} NMR (96 MHz, CDCl3): δ -2.2, -5.0, -9.6, -13.0. HRMS (ESI+): *m/z* $[C_{18}H_{35}B_{10}N_2IrCl]^+$ 615.3121, Calcd for [M-Cl]$^+$ 615.3106. Anal. Calcd for $C_{18}H_{35}B_{10}N_2IrCl_2$: C, 33.22; H, 5.42; N, 4.31. Found: C, 33.12; H, 5.34; N, 4.37. Crystals suitable for X-ray diffraction analysis were grown by the slow diffusion of hexane into a concentrated solution of **2b** in CH_2Cl_2.

Rh complex 5b

To a Schlenk flask was added **1b** (50 mg, 0.15 mmol), Ag_2O (17 mg, 0.075 mmol), $[Rh(Cp^*)Cl_2]_2$ (46 mg, 0.074 mmol) and anhydrous CH_2Cl_2 (5 mL), along with some 4 Å molecular sieves. The reaction was heated at 40°C for 16 hours, filtered through celite and flushed with CH_2Cl_2 (3 × 5 mL). The solvent was removed from the filtrate *in vacuo* and the residue was recrystallised from acetone (5 mL) / pentane (30 mL), filtered and dried *in vacuo* to give **5b** as a yellow solid. Yield: 79 mg, 0.14 mmol (95 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (d, J = 3.0 Hz, 1H, NC*H*), 6.99 (d, J = 3.0 Hz, 1H, NC*H*), 5.02 (m, 1H, C*H*$_2$), 4.62 (br. s, 1H, carboranyl C*H*), 4.00 (s, 3H, C*H*$_3$), 3.76 (m, 1H, C*H*$_2$), 3.20 (m, 1H, C*H*$_2$), 2.50 (m, 1H, C*H*$_2$), 1.60 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 171.9 (d, $^{1}J_{Rh-C}$ = 52.5 Hz, N*C*N), 125.3 (N*C*H), 122.2 (N*C*H), 96.6 (d, $^{1}J_{Rh-C}$ = 7.5 Hz, quaternary Cp*), 71.9

(carboranyl quaternary *C*), 61.0 (carboranyl *C*H), 50.0 (*C*H_2), 39.3 (*C*H_2), 38.8 (*C*H_3), 9.6 (Cp*). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -2.2, -5.1, -9.7, -12.8. HRMS (ESI+): *m/z* 526.2550 $[C_{18}H_{35}B_{10}N_2RhCl]^+$, Calcd for $[M\text{-}Cl]^+$ 526.2525. Anal. Calcd for $C_{18}H_{35}B_{10}Cl_2N_2Rh$: C, 38.51; H, 6.28; N, 4.99. Found: C, 38.63; H, 6.32; N, 5.13.

Ru complex 6b

To a Schlenk flask was added **2b** (50 mg, 0.15 mmol), Ag_2O (17 mg, 0.075 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (46 mg, 0.075 mmol) and anhydrous CH_2Cl_2 (5 mL), along with some 4 Å molecular sieves. The reaction was heated at 40°C for 3 hours, filtered through celite and flushed with CH_2Cl_2 (3 × 5 mL). The solvent was removed from the filtrate *in vacuo* and the residue subjected to column chromatography on silica using a gradient elution with CH_2Cl_2 / MeOH (2%). Recrystallisation from MeCN gave **6b** as a microcrystalline orange solid. Yield: 58 mg, 0.10 mmol (67 %). ^1H NMR (500 MHz, CD_2Cl_2): Major δ 7.08 (d, J = 2.0 Hz, 1H, NC*H*), 7.03 (d, J = 2.0 Hz, 1H, NC*H*), 5.40 (d, J = 5.0 Hz, 2H, *p*-cymene Ar-*H*), 5.06 (d, J = 5.0 Hz, 2H, *p*-cymene Ar-*H*), 4.93 (br. s, 1H, C*H*$_2$), 4.54 (br. s, 1H, carboranyl C*H*), 3.94 (s, 3H, C*H*$_3$), 3.82 (br. s, 1H, C*H*$_2$), 2.93 (br. s, 1H, C*H*$_2$), 2.90 (septet, J = 10 Hz, 1H, isopropyl-C*H*), 2.64 (br. s, 1H, C*H*$_2$), 1.93 (s, 3H, C*H*$_3$), 1.26 (d, J = 10 Hz, 6H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 175.6 (N*C*N), 125.3 (N*C*H), 122.0 (N*C*H), 110.4 (*p*-cymene quaternary *C*), 99.4 (*p*-cymene quaternary *C*), 86.4 (*p*-cymene *C*H), 82.4 (p-cymene *C*H), 72.6 (carboranyl quaternary *C*), 61.5 (carboranyl *C*H), 50.5 (*C*H_2), 39.9 (*C*H_3), 39.0 (*C*H_2), 31.2 (*p*-cymene isopropyl-*C*H), 23.0 (*p*-cymene *C*H_3), 21.9 (*p*-cymene *C*H_3), 18.8 (*p*-cymene *C*H_3). $^{11}B\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ -2.4, -5.4, -9.8, -12.9. HRMS (ESI+): *m/z* $[C_{18}H_{34}B_{10}N_2RuCl]^+$ 523.2460, Calcd for $[M\text{-}Cl]^+$ 523.2455. Anal. Calcd for $C_{18}H_{34}B_{10}N_2RuCl_2$: C, 38.71; H, 6.14; N, 5.02. Found: C, 38.63; H, 6.02; N, 5.12. Crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of **6b** in MeCN.

Ir complex 7b/8b mixture

To a Schlenk flask was added **2b** (100 mg, 0.15 mmol), Ag_2O (52 mg, 0.22 mmol) and anhydrous MeCN (5 mL) along with some 4Å molecular sieves. The reaction was heated at 70°C for 16 hours, filtered through a 2 cm silica plug and flushed with MeCN (2 × 10 mL). The solvent was reduced to 5 mL and the desired product was precipitated with Et_2O (30 mL), filtered and the solvent removed *in vacuo* to give a mixture of **7b** and **8b**. Yield: 52 mg, 0.08 mmol (53 %). The NMR spectra contain several sets of overlapping resonances (see Supporting Information) hence are not interpreted here. HRMS (ESI+): *m/z* $[C_{18}H_{34}B_{10}N_2Ir]^+$ 579.3350, Calcd for $[M\text{-}Cl]^+$ 579.3340. Anal. Calcd for $C_{18}H_{34}B_{10}N_2IrCl$: C, 35.20; H, 5.58; N, 4.56. Found: C, 35.34; H, 5.57; N, 4.63.

Ir complex 7b

To a Schlenk flask was added **1b** (50 mg, 0.15 mmol) and anhydrous THF (5 mL). The solution was cooled to -78 °C and a 1.6 M solution of ^{n}BuLi in hexane (133 µL, 0.32 mmol) was added dropwise. This was stirred at -78 °C for 30 minutes, then the temperature was then raised to 0 °C and stirred for a further 1 hour. A solution of $[IrCp^*Cl_2]_2$ in THF (3 mL) was added at 0°C and the reaction was stirred at room temperature for 12 hours. The solvent was removed *in vacuo*, CH_2Cl_2 (5 mL) added and filtered through a 2 cm silica plug which was flushed with CH_2Cl_2 (2 × 10 mL). The solvent volume was reduced to 5 mL and the product precipitated with pentane (30 mL), filtered and dried *in vacuo* to give **7b** as a yellow solid. Yield: 68 mg, 0.11 mmol (73 %). ^1H NMR (300 MHz, CD_2Cl_2): δ 6.97 (m, 1H, NC*H*), 6.90 (s, 1H, NC*H*), 4.54 (m, 1H, C*H*$_2$), 3.98/3.94 (s, 3H, C*H*$_3$), 3.72 (m, 1H, C*H*$_2$), 2.82 (m, 1H, C*H*$_2$), 2.66 (m, 1H, C*H*$_2$), 1.53/1.48 (Cp*). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ carbenic C not observed, 126.0/125.9 (N*C*H), 121.2 (N*C*H), 93.8/93.5 (quaternary Cp*), 46.2 (*C*H_2), 42.3, 41.0, 39.2 (*C*H_3), 9.6/9.3 (Cp*). HRMS (ESI+): *m/z* $[C_{22}H_{29}B_{10}N_2Ir]^+$ 549.1650, Calcd for $[M\text{-}X]^+$ 549.1635. Crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of **7b** in MeCN.

Ir complex 2c

2c was prepared as described for **2b**, starting from **1c** (50 mg, 0.14 mmol), Ag_2O (16 mg, 0.07 mmol), $[Ir(Cp^*)Cl_2]_2$ (56 mg, 0.07 mmol) and anhydrous CH_2Cl_2 (5 mL). After purification the product was obtained as a yellow solid. Yield: 80 mg, 0.12 mmol (86 %). ^1H NMR (300 MHz, $CDCl_3$): δ 6.99 (d, J = 2.1 Hz, NC*H*), 6.92 (d, J = 2.1 Hz, NC*H*), 5.04 (m, 1H, C*H*$_2$), 3.99/3.97 (s, 3H, C*H*$_3$), 3.84 (td, J = 12.0 Hz, 3 Hz, 1H, C*H*$_2$), 3.41 (m, 1H, C*H*$_2$), 2.48 (m, 1H, C*H*$_2$), 2.15 (s, 3H, C*H*$_3$), 1.67/1.63 (Cp*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.6 (N*C*N), 121.3 (N*C*H), 89.4/89.1 (quaternary Cp*), 74.9 (carboranyl quaternary *C*) (only one carboranyl quaternary C observed), 49.9 (*C*H_2), 38.9 (*C*H_3), 36.6 (*C*H_2), 23.9 (carboranyl *C*H_3), 9.5/9.3 (Cp*). $^{11}B\{^1H\}$ NMR (96 MHz, $CDCl_3$): δ -3.7, -6.1, -10.0. HRMS (ESI+): *m/z* $[C_{19}H_{37}B_{10}N_2IrCl]^+$ 629.3283, Calcd for $[M\text{-}Cl]^+$ 629.3263.

Ir complex 8c

This complex was prepared as described for **7b**/**8b**, starting from **2c** (60 mg, 0.09 mmol), Ag_2O (16 mg, 0.07 mmol) and anhydrous MeCN (5 mL). After purification **8c** was obtained as a yellow solid. Yield, 25 mg, 0.04 mmol (44 %). ^1H NMR (500 MHz, CD_3CN): δ 7.23 (d, J = 2.0 Hz, 1H, NC*H*), 7.19 (d, J = 2.0 Hz, 1H, NC*H*), 7.14 (d, J = 2.0 Hz, 1H, NC*H*), 7.11 (d, J = 2.0 Hz, 1H, NC*H*), 5.01 (td, J = 12.5 Hz, 6 Hz, 1H, C*H*$_2$), 4.25 (m, 1H, C*H*$_2$), 4.02-3.95 (m, 1H, C*H*$_2$), 3.73/3.71/3.61 (s, 3H, C*H*$_3$), 3.17 (m, 1H, C*H*$_2$), 2.72 (m, 1H, C*H*$_2$), 2.30 (m, 1H, C*H*$_2$), 2.17 (s, 1H, C*H*$_3$), 1.72/1.68/1.63 (Cp*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN): δ 124.4 (N*C*H), 122.8 (N*C*H), 95.5/89.6 (quaternary Cp*), 50.5 (*C*H_2), 37.9, (*C*H_2), 36.9 (*C*H_3), 23.9 (*C*H_3), 9.3, 9.2, 9.0, 8.8. $^{11}B\{^1H\}$ NMR (161 MHz, CD_3CN): δ -4.2, -6.3, -8.5, -9.8, -10.6. HRMS (ESI+): *m/z* $[C_{19}H_{36}B_{10}N_2Ir]^+$ 593.3513, Calcd for $[M\text{-}Cl]^+$ 593.3497. Anal. Calcd for $C_{19}H_{36}B_{10}ClN_2Ir$: C, 36.32; H, 5.78; N, 4.46. Found: C, 36.45; H, 5.77; N; 4.60.

Ir complex 2d

To a Schlenk flask was added **1d** (50 mg, 0.19 mmol), Ag_2O (22 mg, 0.095 mmol), $[Ir(Cp^*)Cl_2]_2$ (76 mg, 0.095 mmol) and anhydrous CH_2Cl_2 (5 mL) along with some 4Å molecular sieves. The reaction was heated at 40°C for 16 hours and filtered over celite, which was flushed with CH_2Cl_2 (3 × 5 mL). The solvent was removed from the filtrate *in vacuo* and the residue was

recrystallised from acetone (5 mL) with pentane (30 mL), filtered and dried *in vacuo* to give **2d** as a yellow solid. Yield: 97 mg, 0.17 mmol (89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.20 (m, 5H, benzyl), 6.95-6.89 (m, 2H, NC*H*), 5.08 (dt, J = 12.0, 6.0 Hz, 1H, CH_2), 4.00/3.98 (s, 3H, CH_3) 3.89 (dt, J = 12.0, 6.0 Hz, 1H, CH_2), 3.50 (dt, J = 12.0, 6.0 Hz, 1H, CH_2) 2.99 (dt, J = 12.0, 6.0 Hz, 1H, CH_2), 1.62/1.59 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 157.0 (N*C*N) 138.7 (benzyl), 129.4 (benzyl), 128.7 (benzyl), 126.7 (benzyl), 123.5 (N*C*H), 121.5 (N*C*H), 88.8 (quaternary Cp*), 52.2 (*C*H$_2$), 38.7 (*C*H$_3$), 38.4 (*C*H$_2$), 9.5/9.3 (Cp*). HRMS (ESI+): *m/z* $[C_{22}H_{29}N_2IrCl]^+$ 549.1650, Calcd for $[M\text{-}Cl]^+$ 549.1635. Anal. Calcd for $C_{22}H_{29}N_2IrCl_2$: C, 45.20; H, 5.00; N, 4.79. Found: C, 45.06; H, 4.93; N, 4.85.

Catalytic transfer hydrogenation general procedure

Catalyst (0.01 or 0.005 mmol) and 1,3,5-trimethoxybenzene (55.5 mg, 0.33 mmol) were added to an ampoule and degassed. In a Glovebox, ^{t}BuOK (14 mg, 0.1 mmol) and acetophenone (117 µL, 1 mmol) were added to the ampoule. Under an atmosphere of N_2, anhydrous ^{i}PrOH (2.30 mL, 30 mmol) was added and the reaction was heated at 82 °C for 1 hour. The reaction mixture was quenched by cooling in an ice bath and an aliquot (0.1 mL) was added to an NMR tube with $CDCl_3$ (0.4 mL). Conversion was calculated using ^{1}H NMR spectroscopy by comparing the integration of the methyl resonance of 1-phenylethanol with the internal standard, and values are an average of two separate runs.

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