# Dalton Transactions

Accepted Manuscript






ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

ARTICLE

# Ruthenium(II) Complexes of Hemilabile Pincer Ligands: Synthesis and Catalysing the Transfer Hydrogenation of Ketones

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ashwin G. Nair,[a,b] Roy T. McBurney,[b] D. Barney Walker,[a,b] Michael J. Page,[a] Mark R. D. Gatus,[a,b] Mohan Bhadbhade,[c] and Barbara A. Messerle[a,b,†]

A series of Ru(II) complexes were synthesised based on a hemilabile pyrazole-*N*-heterocyclic carbene (NHC)-pyrazole (C-$_3N_2H_5$)$CH_2$($C_3N_2H_2$)$CH_2$($C_3N_2H_5$) NCN pincer ligand **1**. All complexes were fully characterised using single crystal X-ray crystallography and multinuclear NMR spectroscopy. Hemilabile ligands provide flexible coordination modes for the coordinating metal ion which can play a significant effect on the efficiency and mechanism of catalysis by the resulting complex. Here we observed and isolated mono-, bi- and tri-dentate complexes of both Ag(I) and Ru(II) with **1** in which the resultant coordination mode was controlled by careful reagent selection. The catalytic activity of the Ru(II) complexes for the transfer hydrogenation reaction of acetophenone with isopropanol was investigated. The unexpected formation of the pentaborate anion, $[B_5O_6(OH)_4]^-$, during the synthesis of complex **6a** was found to have an unexpected positive effect by enhancing the catalysis rate. This work provides insights into the roles different co-ordination modes, counterions and ligand hemilability play on the catalytic activity in transfer hydrogenations.

## Introduction

In an effort to create organometallic complexes with diverse coordination modes pincer ligands which incorporate hemilability with a mix of strongly donating donors and weakly donating pendant arms that may or may not coordinate to a metal ion have received significant attention. Complexes with pincer ligands have been used successfully as catalysts for promoting a wide range of transformations, and selected coordination motifs may significantly improve catalysis rates and/or selectivities.[1] Our research focuses on pincer ligands containing a central *N*-heterocyclic carbene (NHC) donor[2] together with labile pendant pyrazole donors. NHCs are an increasingly common motif, competing with the central aryl unit prominent in the work of van Koten[1b,c] and others. The carbene moiety should provide a strong σ-donor,[1a] therefore stabilising metal complexes of these ligands giving access to different coordination modes. Complexes of such hemilabile pincer ligands are known to display enhanced catalytic activity over analagous complexes where the pendant arms are strongly binding. For instance, an Ir(I) carbene-based complex with two pendant pyridyl donor groups, hence potentially a $\kappa^2$ or $\kappa^3$ complex, demonstrated enhanced catalytic turnovers for transfer hydrogenation (Chart 1a) in comparison to other Ir(I) NHC complexes.[2a] Similar to the ligand system under investigation here, Shreeve and co-workers reported Pd(II) complexes with bidentate ligands containing the strongly donating carbene donor as well as the weakly coordinating pyrazole donors as catalysts for the Heck and Suzuki reactions in ionic liquids, (Chart 1b).[3] The hemilability of this ligand facilitates the weakly coordinating pyrazole to dissociate from the metal centre, allowing the catalyst to pass through the key Pd(0) intermediate for enhancing catalysis.

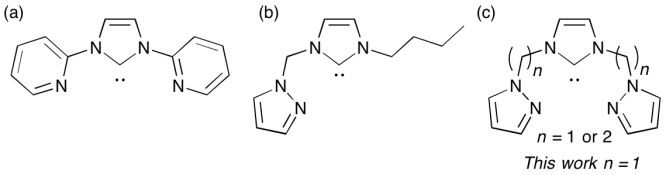



**Chart 1** Comparison of other carbene-based ligands with pendant *N*-heterocyclic donor groups. This work is (c) where *n* = 1.

We have recently reported the coordination chemistry and catalytic activity of Rh(I) and Ir(I) complexes containing a pincer ligand with a central NHC and a pair of weakly coordinating pyrazole pendant donors (Chart 1c).[4] As with many other hemilabile carbene containing ligands, the complexes exhibited varied and diverse coordination chemistry, where even the less flexible ligands (*n* = 1) underwent conformational exchange. The Ir(I) and Rh(I) complexes with the ligand featuring a methylene bridge (*n* = 1) were shown to be good catalysts for both hydroamination and hydroacyloxylation but not hydrosilylation reactions. It was found that an increase in hemilability of the pendant donors,

[a] School of Chemistry, University of New South Wales, Sydney 2052, Australia.
[b] Department of Chemistry and Biomolecular Sciences, Macquarie University, North Ryde 2109.
[c] Mark Wainwright Analytical Centre, University of New South Wales, Sydney 2052, Australia.
† Email: barbara.messerle@mq.edu.au
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

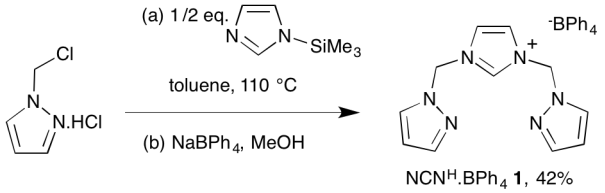
achieved using a longer linker between the pendant donor and the central NHC donor (ethylene vs methylene bridge), resulted in much poorer catalytic activity for hydrocarboxylation reactions, though a similar reactivity was observed in hydroamination reactions.

Herein, we report the co-ordination chemistry of Ru(II) with the hemilabile pincer ligand **1**, an NHC-based bis-pyrazole NCN pincer, (Chart 1c, $n$ = 1).[4] The most efficient hemilable Ru(II) pincer catalyst reported to date for the transfer hydrogenation of acetophenone is a Ru(II) based complex with a tridentate pyrazole-pyridyl-benzimidazole ligand which achieves substrate conversions of 95% in 1 minute under very mild conditions (room temperature, in air, catalyst loading of only 0.2 mol%).[5] We were interested in how Ru(II) catalysts with a central strong σ-donor carbene pincer ligand would impact on the efficiency of catalysed transfer hydrogenation catalysis of ketones. During the synthesis of the complexes we encountered formation of a rare tetrahydroxypentaborate $[B_5O_6(OH)_4]^-$ anion. The pentaborate anion had an unexpected effect during the transfer hydrogenation where its presence actually increased the catalysis rate compared to just the tetraphenylborate $[BPh_4]^-$ anion.

## Results and Discussion

### Synthesis and Characterisation

The imidazolium pro-ligand **1** was synthesised according to our previous report from chloromethylpyrazole and half an equivalent of trimethylsilyl imidazole in refluxing toluene, see Scheme 1.[4] After 16 h a viscous brown oil had formed; upon anion exchange with $NaBPh_4$, $NCN^H.BPh_4$, **1**, was isolated as colourless crystals in 42% yield. Crystals suitable for crystallographic analysis were grown by slow evaporation of an acetone solution of **1**. As expected the solid state structures confirmed the chemical structure with the pro-ligand essentially in a straight conformation, see Figure 1.




**Scheme 1** Synthesis of imidazolium bis-pyrazole pro-ligand **1** from chloromethylpyrazole and trimethylsilyl imidazole.[4]

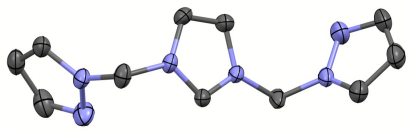
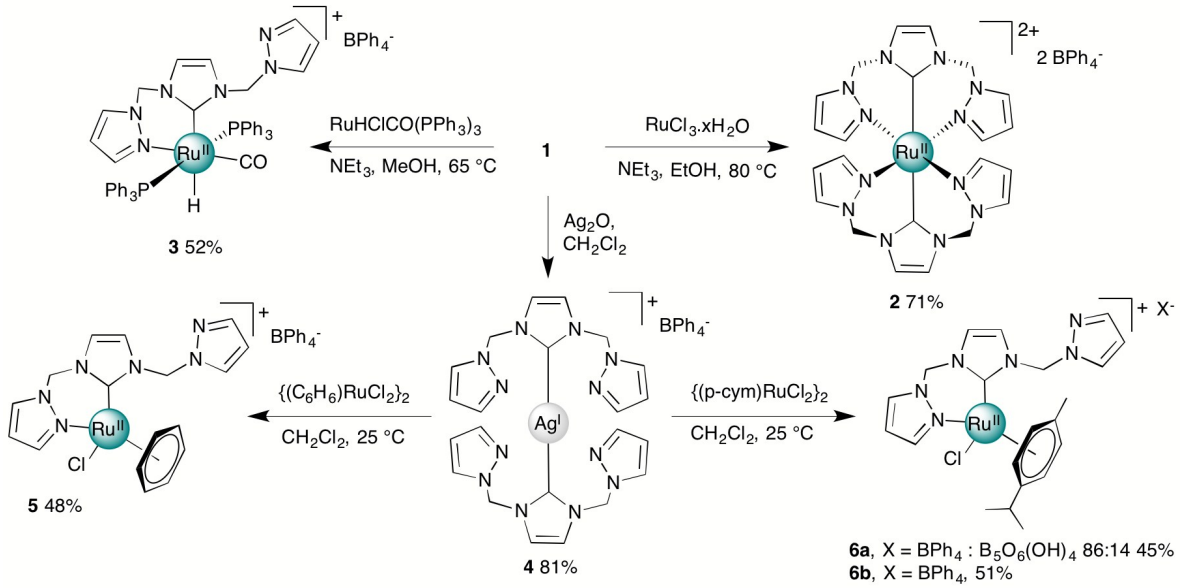


**Figure 1** X-ray crystal structure of the imidazolium bis-pyrazole pro-ligand **1**. Ellipsoids shown with 50% probability, hydrogen atoms and $BPh_4$ anions have been omitted for clarity.

Our experience with this imidazolium pro-ligand (**1**) has proved it to be capricious during attempts to introduce a metal ion.[4] We wanted to create a general and robust methodology that would be able to select for different coordination motifs with the ligand. We attempted numerous approaches to achieving complexation to Ru(II), including carbene transmetallation via Ag(I), as detailed in Scheme 2. Deprotonation of the imidazolium salt **1** with $NEt_3$, followed by complexation with $RuCl_3.xH_2O$ in refluxing ethanol led to a bis-$\kappa_3$-NCN complex **2** in a good 71% yield. Treatment of **1** with $Ru(H)Cl(CO)(PPh_3)_3$ in refluxing methanol resulted in the production of complex **3** in a moderate yield of 52%.

In an effort to achieve better complexation yields we attempted a slightly different approach to the final Ru(II) complexes where an intermediate bis-$\kappa_1$-NCN Ag(I) complex, **4**, was synthesised by reaction of **1** with $Ag_2O$ in $CH_2Cl_2$ with the intention of using complex **4** as a carbene transfer reagent.[6] Treatment of **4** with $\{(C_6H_6)\}RuCl_2\}_3$ in $CH_2Cl_2$ at room temperature led to the Ru(II) $\kappa_2$-NCN $\eta$-6-benzene chloro complex **5** in 48% yield. It was expected that treatment of **4** with $[Ru(\eta^6\text{-}p\text{-cym})Cl_2]_2$ (where $p$-cym = $p$-cymene) would led to a pure $BPh_4$ complex. Instead, upon elucidation of the solid state structure of **6a**, it was found that rather than the expected $BPh_4$ anion there was a rare tetrahydroxypentaborate $[B_5O_6(OH)_4]^-$ anion present. This was then revealed to be a mixed counterion system in the bulk sample, with both $BPh_4$ and a rare tetrahydroxypentaborate $[B_5O_6(OH)_4]^-$ anion present in an 86:14 ratio as determined by $^1H$ NMR analysis.[7] $^{11}B$ NMR proved unable to verify this ratio due to extremely broad resonances, see ESI. The ratio of boron-based anions varied in each synthesis batch and it is unclear as to how exactly the pentaborate anion formed as our conditions vary from those reports in which the synthesis of this molecule is reported.[8] In an effort to obtain the Ru(II) complex containing solely the $[BPh_4]^-$ counterion, an *in situ* silver transmetallation method was utilised where **1** was reacted with $[Ru(\eta^6\text{-}p\text{-cym})Cl_2]_2$ in the presence of $Ag_2O$. Complex **6b** was isolated in 51% yield and the purity of the anion was confirmed by NMR and elemental analysis, with no pentaborate anion being detected.

The $^1H$ NMR spectrum of a bis-$\kappa_3$-NCN Ru(II) complex **2** contained two sets of ligand proton resonances, which were attributed to the formation of two isomers. Variable NMR temperature experiments revealed that upon heating the complex to 40 °C the two sets of NMR resonances approached pairwise coalescence, indicating that a single species was present (see ESI). The ratio of ligand to $BPh_4$ proton resonances was 1:1 indicating that **2** was likely to be a Ru(II) NCN homoleptic complex, this was confirmed in the solid state by crystallographic analysis (Figure 3a). The solid state structure showed the expected octahedral coordination geometry of Ru(II) with the NCN ligands occupying tridentate *fac* orientations, with the carbene groups located *trans* to each other. It is likely that the pincer ligand can coordinate to the Ru centre in either *fac* or *mer* coordination modes, although only the *fac* structure was observed in the solid state using X-ray crystallography. Mass spectrometry showed the presence of a single molecular ion and elemental analysis was in agreement with the calculated value of complex **2**.




**Scheme 2** Complexation routes from pro-ligand **1** to generate complexes **2** to **6**.

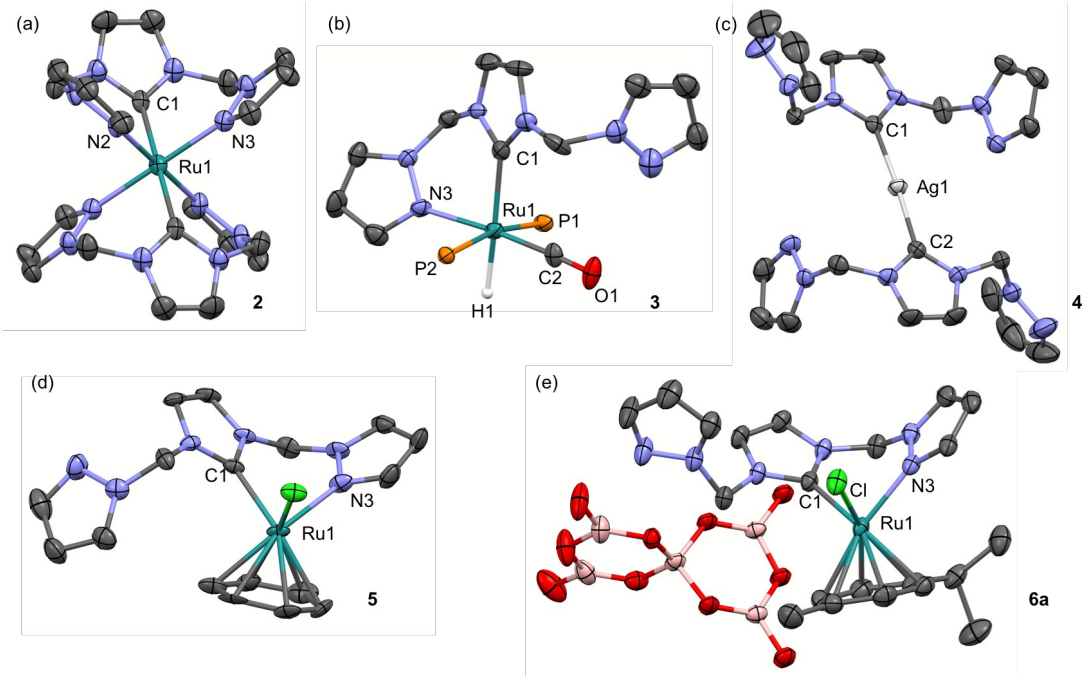



**Figure 2** X-ray crystal structures of complexes (a) **2**, (b) **3**, (c) **4**, (d) **5**, and (e) **6a**. Complex **6a** crystallised with the $[B_5O_6(OH)_4]^-$ anion, the $BPh_4$ anion was not observed in the solid state. Ellipsoids shown with 50% probability, hydrogen atoms and $BPh_4$ anions have been omitted for clarity, as have the $Ph_3$ groups present in complex **3**.

The $^1$H NMR spectrum of complex **3**[9] contained a triplet resonance at -6 ppm due to a Ru(II) bound hydride with $^2J_{H-P}$ coupling of 21.9 Hz to two chemically equivalent phosphine atoms ($^{31}$P NMR, δ = -48 ppm). The Ru-H triplet and a single $^{31}$P NMR resonance indicated the presence of two phosphine ligands *trans* to one another.[10] The IR spectrum contained two distinct strong signals for the Ru-H (1606.2 cm$^{-1}$) and Ru-CO (1938.3 cm$^{-1}$) stretches. The solid state structure of **3** confirmed the *trans* geometry of the phosphine groups and revealed that the CO unit lies *trans* to N3 contained in the NCN ligand which was bound to the Ru centre in a bidentate fashion though N3 and C1 atoms.

The solid state structures of Ru(II) complexes **2** and **3** each exhibit an octahedral geometry, with the main difference being that the NCN ligand is bound to Ru(II) in a bidentate co-ordination mode in complex **3** while in complex **2** the ligand

**Table 1** Selected bond lengths(Å) and angles(°) for **2**, **3**, **5**, and **6a**.

| Atoms | 2 | 3 | 5 | 6a |
|---|---|---|---|---|
| Ru(1)-C(1) | 2.049(5) | 2.117(6) | 2.04(1) | 2.046(2) |
| Ru(1)-C(2) | ---- | 1.810(5) | ---- | ---- |
| Ru(1)-N(2) | 2.076(4) | ----- | ----- | ----- |
| Ru(1)-N(3) | 2.088(4) | 2.122(5) | 2.096(7) | 2.085(2) |
| Ru(1)-Cl | ----- | ----- | 2.399(2) | 2.408(1) |
| Ru(1)-P(1) | ----- | 2.368(1) | ----- | ----- |
| Ru(1)-P(2) | ----- | 2.369(1) | ----- | ----- |
| C(1)-Ru(1)-N(3) | 84.2(2) | 86.6(2) | 83.3(3) | 83.58(9) |
| C(1)-Ru(1)-N(2) | 82.1(2) | ----- | ----- | ----- |

adopts a tridentate co-ordination mode to the metal centre (Figure 3). The Ru-C(1) and Ru-N(3) bond lengths are slightly longer in complex **3** in comparison to the analogous bond lengths in **2**, indicating stronger bonding interaction between Ru and pyrazole in **2** as strong π back-donation from Ru to CO in **3** weakens the Ru-pyrazole bond located in a *trans* position, see Table 1. The carbene carbons and pyrazole nitrogens (N2, N3) in complex **3** show no distortion from linearity as the Ru atom lies on an inversion centre (C-Ru-C/N-Ru-N: 180.00(2)°). However, similar alignments in complex **3** (X-Ru-Y, where X=N, Y=C, or X=Y=P)) exhibit heavy distortion from linearity (P-Ru-P: 168.77(2)°) likely due to the steric bulk of the two $PPh_3$ groups.

The proton NMR spectra of complexes **5**, **6a** and **6b** all exhibited a large number of proton resonances, indicative of complexes with a single, asymmetrically bound ligand. The solid state structures for complexes **5** and **6a** confirmed the initial assignment, revealing that both complexes featured bidentate coordination of the NCN ligand to the Ru centre, with a bound chloride and a *η*-6-aromatic ligand completing the first coordination sphere. As in complex **3** the NCN ligand coordinates to the metal centre through though its N3 and C1 atoms in both complexes **5** and **6a**. Complexes **5** and **6a** each adopt a psuedo-octahedral geometry and are similar in structure, for example, the Ru-C(1) bond lengths are the same within 1 esd. Structural similarity of complexes **5** and **6a** is further confirmed by comparison of the Ru-N(3) or Ru-Cl bond lengths, which fall within 0.01 Å of each other, as well as the C(1)-Ru-N(3) angle which differs by only 0.2° between complexes **5** and **6a**. The Ru-C1 bond lengths of complexes **3a**-**6a** are comparable to those of similar Ru complexes reported in the literature.[11] The boron counterion $[B_5O_{10}H_4]^-$ in **6a** was identified using X-ray crystallography. The counterion is composed of a central tetrahedral boron as the apex of two 6-membered rings composed of alternating boron and oxygen atoms, the counterion is terminated by four hydroxyl groups.

As expected the crystal structure of Ag(I) complex **4** showed two NCN ligands coordinated the Ag(I) ion through the carbene unit. In the solid state the pendant pyrazole arms are directed toward the same face such that the complex has centre of inversion through the silver centre. The Ag-C1 and Ag-C2 each have a bond length of 2.08 Å typical of other similar silver *bis*-NHC complexes and the angle between C1-Ag-C2 is 4° off linearity (180°).[12] There is also slight rotation of one of the NHC ligands out of the plane relative to the other giving a torsion angle of 17°. The $^1$H NMR spectra was simpler, with only one species present and a 1:1 ratio of ligand to $BPh_4$ counterion.

### Transfer Hydrogenation Catalysis

The Ru(II) complexes **2**, **3**, **5**, **6b**, and the complex containing the mixture of $BPh_4$ and $[B_5O_6(OH)_4]$ counterions, **6a**, were tested as catalysts for the transfer hydrogenation of acetophenone using a catalyst loading of 1.5 mol% in propan-2-ol and KOH. The catalysis reactions were followed both at room temperature and under reflux conditions using GC-MS and $^1$H NMR spectroscopy to monitor reaction progress. Interestingly the complexes with the pseudo-octahedral coordination geometry proved to be the most active and also gave the highest yield of hydrogenated products, see Figure 3. The mixed anion catalyst, **6a**, containing the unusual boron counterion achieves over 90% conversion of acetophenone to 1-phenylethan-1-ol in less than 30 minutes at 83 °C, and complete conversion on heating for four hours. The efficacy of **6a** as a catalyst for transfer hydrogenation is comparable to some of the best Ru(II) catalysts reported for this reaction, such as $[Ru(OTf)(PCP)PPh_3]$.[13]

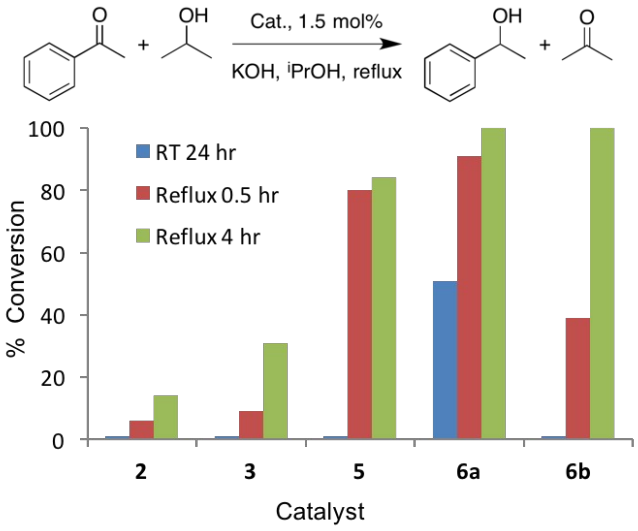



**Figure 3** Catalytic transfer hydrogenation of ketones. % Conversion refers to conversion of acetophenone to 1-phenylethan-1-ol.

Comparing the efficacy of complex **6a** containing a mixed anion with that of complex **6b** containing pure $BPh_4$ anion, we found **6a** was more active with conversion of substrate at 0.5 hours 91% vs. 39% for **6b**, (Figure 3 and Table 2). This indicates that the presence of $[B_5O_6(OH)_4]^-$ enhances the overall catalytic activity for the transfer hydrogenation reaction and is therefore non-innocent, acting as a catalyst in its own right. Polyborate anions have been reported in the literature for promoting transfer hydrogenation reactions.[14] Thus it seems very likely that the increase in catalytic activity for **6a** is as a result of the pentaborate anion.

Catalysts **5** and **6b** display different catalytic rates despite the similarity in structure of the two complexes, with the only difference being a change of the bound co-ligand (benzene, **5**, vs. *p*-cym, **6b**). Whilst complex **6b** achieves complete (>99%) substrate conversion within four hours at 83 °C, complex **5** only reaches a maximum of 80% conversion. The stronger electron donating properties of the *p*-cym co-ligand may stabilise **6b** more effectively than the benzene co-ligand of complex **5**, resulting in a longer catalyst lifetime and hence higher conversion of the substrate.

Catalyst **3** catalysed the formation of the 1-phenylethan-1-ol product with only 24% conversion after four hours at reflux, increasing to >99% conversion after 24 hours at reflux. This was unexpected as the complex contains a pre-existing hydrido group which should enable more efficient transfer hydrogenation reaction, as one of the key steps in the catalytic

cycle is the transfer of a hydride from the catalyst to the substrate.

The *bis*-NHC dimer complex **2** was expected to possess a low catalytic activity due to the metal centre being enclosed by two pincer ligands which occupy all six available co-ordination sites. Indeed, complex **2** only promoted the transfer hydrogenation reaction to a conversion of 14% after 4 hours at 83 °C, and after 24 hours to approximately 30% (see Figure 3). As complex **2** is coordinatively saturated, any conversion of the substrate must result from the hemilability of the pyrazole side arms.

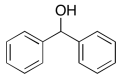
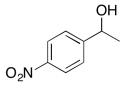
When the high activity of catalyst **6a**, which we attribute in part to the pentaborate anion, is set aside, it is clear that the "pure" organometallic catalysts **5** and **6b** outperform catalyst **3** for the transfer hydrogenation of acteophenone. Thus the reason for the difference in catalytic efficiency between catalysts **3**, and **5** and **6b** must lie in the structural features between **3**, that contains well defined carbonyl and hydride ligands, and the pseudo-octahedral, chloride bearing catalysts **5** and **6b**. The mechanisms in operation must therefore proceed *via* slightly different initiation stages. Complexes **5** and **6b** could be operating via an inner-sphere mechanism similar to that postulated by Bhattacharjee, where an initial chloride exchange with alkoxide is followed by β-hydride elimination to give a ruthenium hydride species and acetone.[15] Catalyst **3**, despite possessing a pre-existing hydride, must follow a similar inner-sphere mechanism, however, the reaction proceeds at a slower rate as there is no chloride which can be lost to allow binding of the alkoxide.[16] Additionally, a recent study has shown that half-sandwich Ru(II) NHC complexes containing a hemilabile picolyl sidearm are able to catalyse the transfer hydrogenation reaction efficiently.[17] This is achieved through a stepwise process in which the hemilabile arm is lost generating a 16 $e^-$ Ru centre, before coordination of the alkoxide and delivery of the hydride to the metal centre.[17]

Of all the catalysts tested here the mixed anion complex **6a** was the only active catalyst at room temperature (25 °C), resulting in a 51% conversion within 24 hours (Figure 3). Complexes **2**, **3**, and **5** and **6b** did not catalyse the reaction at room temperature even after 24 hours. This would suggest that the pentaborate anion does indeed play a non-innocent role in the transfer hydrogenation and likely has an entirely separate mechanism from the carbene pincer based catalyst. All efforts to isolate the pentaborate anion (via salt exchange and chromatography) failed, otherwise a potassium or sodium pentaborate salt would have provided an interesting set of control experiments. While most Ru(II) complexes have been reported to catalyse the transfer hydrogenation reaction of ketones to alcohols at elevated temperatures (> 50 °C), there are relatively few reports of Ru(II) complexes capable of catalysing the reaction at room temperature. The catalyst containing the pentaborate anion (**6a**) is indeed a unique system which requires further mechanistic investigation.

Whilst using complex **6b** for the transfer hydrogenations it transpired that this complex was not completely soluble in propan-2-ol, indicating that the catalytic activity may be reduced due poor solubility. Addition of THF as a co-solvent in a propan-2-ol:THF ratio of 9:1 aided solubility of the catalyst. The catalytic activity of complex **6b** in either neat propan-2-ol or in the propanol-2-ol/THF mix for the transfer hydrogenation of acetophenone proved to be nearly identical (45% at 0.5 h, >99% at 4 h). For exact comparison and to ensure THF was not affecting the reaction, complex **5** was tested for the transfer hydrogenation of acetophenone using the 9:1 propan-2-ol:THF solvent ratio. The addition of THF to the reaction mixture resulted in complete conversion of the substrate (87% after 0.5 h, >99% at 4 hours at reflux), the catalytic rate remains relatively constant in comparison to using neat propan-2-ol as solvent. It is likely that the complete conversion achieved by catalyst **5** was a result of co-ordination of THF to the Ru metal centre, stabilising the complex and thus prolonging the lifetime of the catalyst.

The most active catalysts, **6a** and **6b**, were investigated for the transfer hydrogenation reaction of a number of different ketone substrates (both aromatic and aliphatic, see Table 2). Both catalysts successfully catalysed the reactions at reflux and were able to achieve complete conversion of substrate in each case with the exception of the *p*-nitroacetophenone (Table 2, entry 3). Again, catalyst **6a** was more efficient for the conversion of all substrates in comparison to **6b**. Catalyst **6a** was tested for the transfer hydrogenation reaction of acetophenone, benzophenone and cyclohexanone at room temperature and reasonable yields of 51%, 41% and 59% were achieved respectively after 24 hours. (Table 2, entries 1, 2 and 4).

**Table 2.** Catalytic transfer hydrogenation of ketones using complexes 6a and 6b.

| entry | product | catalyst | % conv. at time (h) | | | |
|---|---|---|---|---|---|---|
| | | | 0.5[b] | 2[b] | 4[b] | 24[c] |
| 1 |  | **6a** | 91 | 96 | >99 | 51 |
| | | **6b** | 39 | 82 | >99 | - |
| 2 |  | **6a** | 91 | 91 | >99 | 41 |
| | | **6b** | 69 | 97 | >99 | - |
| 3 |  | **6a** | 0 | 0 | 0 | - |
| | | **6b** | 0 | 0 | 0 | - |
| 4 |  | **6a** | 92 | >99 | >99 | 59 |
| | | **6b** | 72 | >99 | >99 | - |
| 5 |  | **6a** | 51 | 94 | >99 | - |
| | | **6b** | 44 | 78 | >99 | - |

[a] Reaction conditions: 1.5 mol% catalyst, isopropanol, KOH; [b] 40 °C; [c] 25 °C. % conversion refers to conversion of aldehyde substrate to product alcohol shown.

## Conclusions

The coordination chemistry of NCN pincer ligand precursor **1** with Ru(II) and Ag(I) salts was investigated. The Ru(II)

complexes were tested as catalysts for transfer hydrogenation reactions. A series of coordination motifs were observed in the solid state, ranging from a fully saturated tridentate Ru(II) dimer to a mono-dentate Ag(I) dimer, all of which could be preferentially selected for by careful reagent choice. It was through crystallographic analysis that the rare pentaborate anion was observed in complex **6a**. Indeed, this mixed anion complex was found be the most active catalyst for the transfer hydrogenation reaction, promoting the conversion of a range of aromatic and aliphatic ketone substrates to alcohols with high yields in reasonable times at elevated temperature. The catalysed transfer hydrogenation reaction could also be conducted at room temperature using catalyst **6a**. Complexes **2**, **3a**, **3b**, **5**, and **6b** were catalytically inactive at room temperature. Comparison of the catalytic activities of the mixture **6a** and complex **6b** revealed that the presence of the $[B_5O_6(OH)_4]^-$ counterion enhanced the rate of reaction, most probably by catalysing transfer hydrogenations via a separate mechanism from the organometallic catalyst. Despite not being amongst the most active hemilabile Ru(II) in the literature, the discovery and catalytic activity of the pentaborate anion warrants further investigation.

## Experimental Section

### Materials and Methods

All manipulations were carried out under a nitrogen atmosphere using standard schlenk techniques or in a nitrogen or argon filled glovebox unless otherwise stated. Imidazolium pro-ligand **1** was prepared according to literature method.[4] Commercially available reagents were purchased from Sigma-Aldrich or Alfa Aesar Inc. and used as received. Solvents were acquired using a solvent purification system. Propan-2-ol, methanol and THF were freshly distilled from standard drying reagents. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on Bruker DPX300, DMX500 and DMX400 spectrometers. Chemical shifts (δ) are quoted in ppm. $^1$H, $^{13}$C and $^{31}$P NMR chemical shifts were referenced internally to residual solvent resonances. IR spectra were recorded using an Avatar 370 FTIR spectrometer. Elemental analyses were carried out at the Campbell Microanalytical Labaoratory, University of Otago, New Zealand and the Elemental Analysis Unit, The Research School of Chemistry, Australian National University. Single crystal X-ray analyses were carried out at the Mark Wainwright Analytical Centre, University of New South Wales, Sydney. X-ray diffraction measurements were carried out on a Bruker Kappa APEXII CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710723 Å). All structures were solved by direct methods and the full-matrix least-square refinements were carried out using SHELXL. Absorption correction was performed using Multi-scan SADABS and H-atom parameters were treated as constrained. CCDC 1480997 – 1481002 contains supplementary X-ray crystallographic data for complexes **1**, **2**, **3**, **4**, **5** and **6a**. The yields of hydrogenation products were determined using GCMS - QP2010 ULTRA.

### Synthesis of $[Ru(NCN)_2](BPh_4)_2$ (2)

$NCN^H.BPh_4$ (**1**) (0.05 g, 0.092 mmol) and $RuCl_3.xH_2O$ (0.024 g, 0.092 mmol) and $NEt_3$ (1 mL) were suspended in 15 mL of dry ethanol. The mixture was refluxed for 16 hours. The resulting dark green solid, $[Ru(NCN)_2](BPh_4)_2$ was separated from a pale yellow solution using glass fibre (GF/C) filter paper. Yield: 65%. Single crystals were grown by slow evaporation of a saturated acetone solution of **2**. $^1$H NMR (400 MHz, $(CD_3)_2CO$): $\delta$ 8.14 (d, $^3J$ = 2.6 Hz, 4H, **H**1), 7.85 (s, 4H, **H**5), 7.28 (m, 16H, *o*-$BPh_4$), 6.88 (t, $^3J$ = 7.3 Hz, 16H, *m*-$BPh_4$), 6.85 (d, 4H,**H**4), 6.73 (t, $^3J$ = 7.2 Hz, 8H, *p*-$BPh_4$), 6.52 (d, $^3J$ = 1.6 Hz, 4H, **H**3), 6.17 (br dd, 4H, **H**2), 5.97 (d, $^3J$ = 13.7Hz, 4H, **H**4) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2SO$): $\delta$ 195.4 (**C**6), 164.3-162.3 (q, $^1J$ = 49.8 Hz, *ipso*-**C** of $BPh_4$), 147.0 (**C**1), 136.1 (**C**3), 135.5 (*o*-$BPh_4$), 125.2 (*m*-$BPh_4$), 121.4 (*p*-$BPh_4$), 120.8 (**C**5), 107.2 (**C**2), 62.4 (**C**4) ppm. Elemental analysis found: C, 70.17; H, 5.50; N, 14.05. Calc for $Ru_1C_{70}H_{64}N_{12}B_2$: C, 70.18; H, 5.55; N, 14.03. ESI MS: (m/z 279.08) $[M\text{-}2BPh_4]^{2+}$ amu.

### Synthesis of $[Ru(H)CO(NCN)(PPh_3)_2]BPh_4$ (3a)

$NCN^H.BPh_4$ (**1**) (0.040 g, 0.073 mmol) and $[Ru(H)COCl(PPh_3)_3]$ (0.070 g, 0.073 mmol) were suspended in 20 mL of dry MeOH and $NEt_3$ (1 mL). The mixture was refluxed for 2 hours. The resulting pale yellow solution was filtered using glass fibre (GF/B) filter paper. The filtered solution was reduced to half its initial volume under reduced pressure resulting in the precipitation of $[Ru(H)CO(NCN)(PPh_3)_2]BPh_4$ as a white solid. The solvent was removed and the product was washed with diethylether (2 x 20 mL) and dried under vacuum. Yield: 40%. Single crystals were grown by vapour diffusion of diethyl ether into saturated dichloromethane solution of **3a**. $^1$H NMR (300 MHz, $(CD_3)_2CO$): $\delta$ 7.60 (d, $^3J$ = 1.8 Hz, 1H, **H**1), 7.57 (d, $^3J$ = 2.1 Hz, 1H, **H**5), 7.49 (d, $^3J$ = 2.1 Hz, 1H, **H**6), 7.48-7.30 (m, 43H, *o*-$BPh_4$, $PPh_3$, **H**3, **H**9), 6.92 (t, $^3J$ = 7.2 Hz, 9H, *m*-$BPh_4$, **H**11), 6.77 (br tt, $^3J$ = 7.2 Hz, 4H, *p*-$BPh_4$), 6.26 (dd, 1H, **H**2), 5.67 (br s, $^2$H, **H**8), 5.53 (dd, $^1$H, **H**10) 5.30 (br s, 2H, **H**4), -6.03 (t, $^3J$ = 22.0 Hz, 1H, Ru-**H**) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CD_2Cl_2$): $\delta$ 206.7 (Ru-**C**O), 189.3 (**C**7), 149.3 (**C**9), 141.6 (**C**3), 136.3 (**C**1), 134.7-133.7 (4 x **C**) 130.7 (3 x **C**), 130.2 (**C**11), 129.3-129.0 (3 x **C**) 126.2 (*m*-**C** of $BPh_4$) 124.7 (**C**5), 122.4 (*o*-**C** of $BPh_4$), 122.0 (**C**6), 107.5 (**C**2) 107.2 (**C**10), 62.1 (**C**8), 61.8 (**C**4) ppm.$^{31}$P NMR (121 MHz, $(CD_3)_2CO$): $\delta$ 47.7 (**P**-Ru) ppm. ESI-MS: (m/z 883.26) $[M\text{-}BPh_4]^+$ amu. IR (Solution): Ru-H: 1606.2 $cm^{-1}$, Ru-CO: 1938.3 $cm^{-1}$.

### Synthesis of $[Ag(NCN)_2]BPh_4$ (4)

The imidazolium salt $NCN^H.BPh_4$ (**1**) (0.155 g, 0.287 mmol) and $Ag_2O$ (0.090 g, 0.388 mmol) were suspended in 20 mL of dry $CH_2Cl_2$. The suspension was stirred for 16 hours at room temperature. The colourless solution was filtered using glass fibre (GF/C) filter paper and the solvent removed under vacuum yielding a white precipitate. Yield: 81%. Single crystals were grown by vapour diffusion of pentane into saturated dichloromethane solution of complex **4**. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.73 (d, $^3J$ = 2.4 Hz, 4H, **H**1), 7.58 (d, $^3J$ = 1.8 Hz, 4H, **H**3), 7.38 (m, 8H, *o*-$BPh_4$), 7.20 (s, 4H, **H**5), 6.98 (t, $^3J$ = 7.0 Hz, 8H, *m*-$BPh_4$), 6.89 (t, $^3J$ = 7.2 Hz, 4H, *p*-$BPh_4$), 6.38 (dd, 4H, **H**2), 6.36 (s, 8H, **H**4) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 183.9 (**C**6,

identified through HMBC), 141.9 (**C**1), 136.3 (*o*-**C** of $BPh_4$), 130.5 (**C**3), 126.1 (*m*-**C** of $BPh_4$), 122.3 (*p*-**C** of $BPh_4$), 122.2 (**C**5), 108.1 (**C**2), 65.3 (**C**4) ppm.

**Synthesis of $[Ru(\eta^6\text{-}C_6H_6)(NCN)Cl]BPh_4$ (5)**

$[Ag(NCN)_2]BPh_4$ (**1**) (0.060 g, 0.068 mmol) and $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (0.034 g, 0.068 mmol) were dissolved in 20 mL of $CH_2Cl_2$. The mixture was stirred overnight at room temperature under an atmosphere of Argon. The resulting yellow solution was filtered and pentane (40 mL) was slowly added to the filtrate resulting in the precipitation of the complex $[Ru(\eta^6\text{-}C_6H_6)(NCN)Cl]BPh_4$ (**5**) as a yellow powder. Yield: 48%. Single crystals were grown by slow evaporation of a saturated methanol solution of **5**. $^1$H NMR (300 MHz, $(CD_3)_2CO$): $\delta$ 8.19 (d, $^3J$ = 2.2 Hz, 1H, **H**1), 8.16 (d, $^3J$ = 2.4 Hz, 1H, **H**11), 8.14 (d, $^3J$ = 2.8 Hz, 1H, **H**3), 7.68 (d, $^3J$ = 1.8 Hz, 1H, **H**9), 7.63 (d, $^3J$ = 2.2 Hz, 1H, **H**5), 7.40 (d, $^3J$ = 2.2 Hz, 1H, **H**6), 7.37-7.30 (m, 8H, *o*-$BPh_4$), 6.92 (t, $^3J$= 7.3 Hz, 8H, *m*-$BPh_4$), 6.86 (d, $^2J$ = 13.9 Hz, 1H, **H**4), 6.77 (t, $^3J$= 7.3 Hz, 4H, *p*-$BPh_4$), 6.75 (d, $^2J$ = 13.9 Hz, 1H, **H**8), 6.55 (t, $^3J$ = 2.4 Hz, 1H, **H**2), 6.49 (d, $^2J$ = 13.9 Hz, 1H, **H**8), 6.40 (d, $^3J$ = 2.1 Hz, 1H, **H**10), 6.21 (s, 6H, Ru-$C_6$**H**$_6$), 6.08 (d, $^2J$ = 13.9 Hz, 1H, **H**4) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$): $\delta$ 177.8 (**C**7), 165.9-164.0 (q, $^1J_{C\text{-}B}$ = 48.9 Hz, *ipso*-**C** of $BPh_4$), 149.4, (**C**1), 142.1 (**C**9) 137.0 (*o*-**C** of $BPh_4$), 135.4 (**C**3), 132.2 (**C**11), 126.1 (*m*-$BPh_4$), 124.1 (**C**5), 122.3 (p-$BPh_4$ & **C**6), 108.8 **C**2), δ 107.7 (**C**10), 89.7 (Ru-$\mathbf{C}_6H_6$), 64.9 (**C**8), 63.3 (**C**4) ppm. Elemental Analysis found: C, 64.69; H, 5.42; N, 10.85. Calc for $Ru_1C_{41}H_{38}N_6B_1$: C, 64.83; H, 5.44; N, 10.80. ESI MS: (m/z 443.03) $[M\text{-}Cl]^+$ amu.

**Synthesis of $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN)Cl]BPh_4.[B_5O_6(OH)_4]$ (6a)**

$[Ag(NCN)_2]BPh_4$ (**4**) (0.050 g, 0.056 mmol) and $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2]_2$ (0.035 g, 0.056 mmol) were dissolved in 20 mL of dry $CH_2Cl_2$. The mixture was left stirring overnight at room temperature under an $N_2$ atmosphere. The resulting yellow solution was filtered using glass fibre (GF/C) filter paper and reduced to 10 mL. 40 mL of diethylether was slowly added to the solution resulting in the precipitation of $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN)Cl]BPh_4.[B_5O_6(OH)_4]$ as a yellow powder. Yield: 51%. Elemental Analysis found: C, 40.05; H, 4.08; N, 11.64. Calc. for $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN)Cl]14\%BPh_4.86\%[B_5O_6(OH)_4]$: C, 40.01; H, 4.44; N, 11.49 ESI MS: (m/z 499.19) $[M\text{-}BPh_4/B_5O_6(OH)_4]^+$ amu.

**Synthesis of $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN)Cl]BPh_4$ (6b)**

$Ag_2O$ (0.1g, 0.432 mmol), $NCN.BPh_4$ (**1**) (0.061g, 0.12mmol) and $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2]_2$ (0.035g, 0.056mmol) were dissolved in 20 mL of dry $CH_2Cl_2$. The mixture was left stirring overnight at room temperature under an $N_2$ atmosphere. The resulting dark suspension was filtered using glass fibre (GF/C) filter paper producing a yellow solution which was reduced to 10 mL. 40 mL of diethyl ether was slowly added to the solution resulting in the production of $[Ru(\eta^6\text{-}C_{10}H_{14})(NCN)Cl]BPh_4$ as a yellow powder. Yield: 51%. $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 7.87 (br d, 1H, **H**1), 7.77 (d, $^3J$ = 2.4 Hz, 1H, **H**9), 7.71 (br d, 1H, **H**3), 7.40 (br t, 8H, *o*-$BPh_4$), 7.09 (d, $^3J$ = 2.6 Hz, 1H, H**11**), 7.06 (t, $^3J$ = 7.5 Hz, 8H, *m*-$BPh_4$), 6.95 (t, $^3J$ = 7.5 Hz, 5H, *p*-$BPh_4$ & **H**5), 6.64 (d, $^3J$ = 2.0 Hz, 1H, **H**6), 6.53 (d, $^2J$ = 13.8 Hz, 1H, **H**4), 6.42 (br dd, 1H, **H**2), 6.38 (br dd, 1H, **H**10), 6.09 (d, $^2J$ = 13.8 Hz, 1H, **H**4), 5.90 (d, $^3J$ = 6.2 Hz, 1H, **H**20), 5.78 (d, $^3J$ = 5.8 Hz, 1H, **H**14), 5.47 (d, $^3J$ = 6.2 Hz, 1H, **H**21), 5.24 (d, $^3J$ = 6.1 Hz, 1H, **H**15), 4.75 (d, $^2J$ = 14.1 Hz, 1H, **H**8), 4.64 (d, $^2J$ = 14.1 Hz, 1H, **H**8), 2.64 (sept, $^3J$ = 7.0 Hz, 1H, **H**17), 2.07 (s, 3H, **H**12), 1.22-1.21 (2 x d, 2H, **H**18 & **H**19) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$): $\delta$ 177.7 (**C**7), 164.8-163.4 (q, $^1J$ = 49.3 Hz *ipso*-**C** of $BPh_4$), 148.4 (**C**1), 142.2 (**C**11), 136.4 (*o*-**C** of $BPh_4$), 134.8 (**C**3), 131.2 (**C**9), 126.3 (*m*-**C** of $BPh_4$), 123.4 (**C**5), 122.7 (*p*-**C** of $BPh_4$), 121.2 (**C**6), 112.5 (**C**16), 108.6 (**C**2), 107.8 (**C**10), 102.6 (**C**13), 89.1 (**C**20), 86.9 (**C**21), 86.6 (**C**14), 84.3 (**C**15), 64.5 (**C**8), 61.8 (**C**4), 31.9 (**C**17), 23.7 (**C**19), 21.4 (**C**18), 18.9 (**C**12) ppm. Elemental Analysis found: C, 65.86; H, 5.77; N, 9.83 %. calculated for $Ru_1C_{45}H_{46}N_6B_1$: C,65.97; H, 5.78; N, 10.26. ESI MS: (m/z 499.19) $[M\text{-}BPh_4/B_5O_6(OH)_4]^+$ amu.

**General Procedure for Transfer Hydrogenation Reactions**

The transfer hydrogenation experiments were carried out under standard schlenk conditions. The substrates (0.25 mmol), catalyst (1.5 mol%) and base (KOH, 0.045 mmol) were mixed in 10 mL of 2-propanol. The mixture was heated to reflux (82 °C) for 24 hours. Aliquots were taken at regular intervals, which were quenched with cold isopropanol (1 mL) and filtered through a plug of silica. The crude products (2-3 drops) were diluted in dichloromethane and collected for GC-MS analysis. Selected aliquots were also analysed using $^1$H NMR spectra. Integration of selected resonance signals were compared in quantitative ratio between substrates and respective products. The GC-MS product yield values were consistently within 2% of the $^1$H NMR analysed yield values.

## Acknowledgements

This work was supported under Australian Research Council's Discovery Projects funding scheme (project number DP110101611). AGN is grateful for an Australian Postgraduate Award (APA) awarded by the Australian Government, administered by the University of New South Wales and Macquarie University. We thank the University of New South Wales and the Australian Government for financial support. We acknowledge Dr Samantha Binding for useful discussions on the preparation of this manuscript. We acknowledge the Campbell Microanalytical Laboratory, University of Otago, New Zealand, and the Research School of Chemistry, Australian National University, for elemental analyses.

## Notes and references

1 (*a*) A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27; (*b*) M. H. P. Rietveld, D. M. Grove and G. van Koten, *New J. Chem.*, 1997, **21**, 751; (*c*) M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 375;. (*d*) P. Y. Shi, Y. H. Liu, S. M. Peng and S. T. Liu, *Organometallics*, 2002, **21**, 3203; (*e*) M. Bassetti, A. Capone and M. Salamone, *Organometallics*, 2004, **23**, 247; (*f*) E. Poverenov, M. Gandelman, L. J. W. Shimon, H. Rozenberg, Y. Ben-David and D. Milstein, *Organometallics*, 2005, **24**, 1082; (*g*)

J.-L. Niu, X.-Q. Hao, J.-F. Gong and M.-P. Song, *Dalton Trans.*, 2011, **40**, 5135.

2 (*a*) K. Riener, M. J. Bitzer, A. Pöthig, A. Raba, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Inorg. Chem.*, 2014, **53**, 12767; (*b*) F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (*c*) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev.*, 2004, **248**, 2247.

3 (*a*) R. Wang, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2006, **71**, 426; (*b*) R. Wang, Z. Zeng, B. Twamley, M. M. Piekarski and J. M. Shreeve, *Eur. J. Org. Chem.*, 2007, 655.

4 G. Mancano, M. J. Page, M. Bhadbhade and B. A. Messerle, *Inorg. Chem.*, 2014, **53**, 10159.

5 M. Zhao, Z. Yu, S. Yan and Y. Li, *Tetrahedron Lett.*, 2009, **50**, 4624.

6 (*a*) O. Santoro, F. Lazreg, D. B. Cordes, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans.*, 2016, **45**, 4970; (*b*) H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972; (*c*) I. J. B. Lin and C. S. Vasam, *Coord. Chem. Rev.*, 2007, **251**, 642; (*d*) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561.

7 The ratio of $BPh_4^-$ to $[B_5O_6(OH)_4]^-$ was determined using $^1H$ NMR spectroscopy by taking into account the ratio of integrals of the *ortho*-hydrogens on $BPh_4$ anion to ligand and calculating what was missing which was then attributed to solely $[B_5O_6(OH)_4]^-$ anion present.

8 (*a*) M. A. Beckett, C. C. Bland, P. N. Horton, M. B. Hursthouse and K. S. Varma, *J. Organometallic Chem.*, 2007, **692**, 2832; (*b*) Q. Wu, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2011, **67**, i67; (*c*) G. C. Fortman, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2011, **30**, 5487.

9 It was found that the Ru-H and Ru-CO groups of complex **3** undergo *cis-trans* isomerisation in the presence of heat. On heating the complex to 73 °C, the hydride resonance shifted upfield from -6 ppm to -13 ppm ($^2J_{H-P}$ = 21 Hz). Whilst the hydride chemical shift changes, the coupling constants and the chemical shifts of the resonances in the $^{31}P$ NMR spectrum remain the same, which suggests that the two phosphine ligands remain *trans* to one another in the new isomer. See ESI for VT NMR spectra and catalysis results of this isomer.

10 J. G. Malecki and A. Maron, *Transition Met. Chem.*, 2012, **37**, 727.

11 (*a*) S. Horn, C. Gandolfi and M. Albrecht, *Eur. J. Inorg. Chem.*, 2011, 2863; (*b*) I. del Río, G. van Koten, M. Lutz and A. L. Spek, *Organometallics*, 2000, **19**, 361; (*c*) M. Poyatos, A. Mata, E. Falomir, R. H. Crabtree, and E. Peris, *Organometallics*, 2003, **22**, 1110.

12 Z. He, S.-H. Zhang, J.-R. Xue, Y. Liang, X. Zhang, L.-H. Jing and D.-B. Qin, *J. Organomet. Chem.*, 2016, **808**, 12.

13 (*a*) P. Dani, T. Karlen, R. A. Gossage, S. Gladiali and G. van Koten, *Angew. Chem., Int. Ed.*, 2000, **39**, 743; (*b*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290; (*c*) M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233; (*d*) A. A. Danopoulos, S. Winston and W. Motherwell, *Chem. Commun.,* 2002, **36**, 1376; (*e*) T. Steinke, B. K. Shaw, H. Jong, B. O. Patrick and M. D. Fryzuk, *Organometallics*, 2009, **28**, 2830; (*f*) C. Chen, H. Qiu and W. Chen, *J. Organomet. Chem.*, 2012, **696**, 4166; (*g*) W. Weng, S. Parkin and O. V. Ozerov, *Organometallics*, 2006, **25**, 5345.

14 (*a*) A. Kilic, M. Aydemir, M. Durgun, N. Meriç, Y. S. Ocak, A. Keles and H. Temel, *J. Fluor. Chem.*, 2014, **162**, 9; (*b*) A. Kilic, C. Kayan, M. Aydemir, F. Durap, M. Durgun, A. Baysal, E. Tas and B. Gümgüm, *Appl. Organomet. Chem.*, 2011, **25**, 390; (*c*) A. A. Desai, Y. Guan, A. L. Odom, S. Majumder, W. D. Wulff and M. J. Vetticatt, *Tetrahedron Lett.*, 2015, **56**, 3481.

15 S. Naskar and M. Bhattacharjee, *J. Organomet. Chem.*, 2005, **690**, 5006.

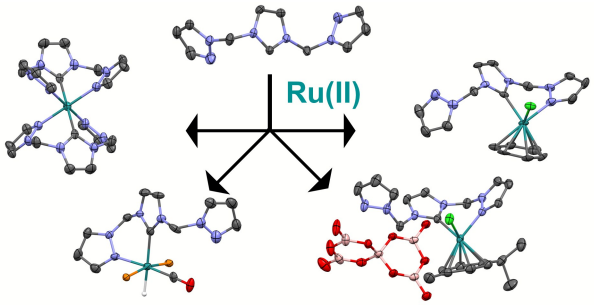
16 B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294.

17 J. Ning, Z. Shang and X. Xu, *Catal. Lett.*, 2015, **145**, 1331.

## Journal Name

## ARTICLE

TOC Entry




A series of hemilabile NHC Ru(II) complexes were synthesised and assessed for their catalytic activity for transfer hydrogenation reactions.