Rhodium(I) and iridium(I) complexes of pyrazolyl-*N*-heterocyclic carbene ligands

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Received 7th March 2006, Accepted 25th May 2006
First published as an Advance Article on the web 9th June 2006
DOI: 10.1039/b603455a

Several Rh(I) and Ir(I) complexes containing an *N*-heterocyclic carbene-pyrazolyl chelate ligand have been synthesised. Determination of the single-crystal X-ray structure of the Ir(I) complex showed a novel binding mode with the iridium centre coordinated to two ligands *via* two carbene donors in preference to one ligand forming the entropically favoured chelate. The hydrogenation activity of several of these complexes was investigated along with that of previously synthesised Rh(I) and Ir(I) complexes containing an analogous phosphine-pyrazolyl chelate.

Introduction

N-Heterocyclic carbene (NHC) ligands are known to be effective and versatile donors in homogeneous transition-metal catalysts.[1] It was first noted by Hermann and co-workers that a close similarity existed between NHCs and electron-rich organophosphines in terms of their metal coordination chemistry.[2] This led to an initial application of NHCs as phosphine substitutes in homogeneous catalysts of proven efficiency, most notably in the Pd(0) catalysed Heck reaction[3] and Ru(III) Grubbs type catalysts,[4] where the use of NHC donors resulted in a vast improvement to catalytic activity. In contrast to this impact on C–C bond forming catalysts, early work on incorporating NHC ligands into analogues of Wilkinson's ([RhCl(PPh$_3$)$_3$]) and Crabtree's ([Ir(PCy$_3$)(pyridine)(COD)]) hydrogenation catalysts generally resulted in little improvement to catalytic activity.[5] Recent work by Burgess and co-workers, however, on chiral NHC-oxazolyl chelates has resulted in the development of some highly active and enantioselective Ir(I) hydrogenation catalysts with carbene donor ligands (**1**) (Chart 1).[6] These systems showed an increased activity and much improved enantioselectivity when compared to analogous Ir(I) phosphine-oxazolyl systems,[7] although the activity and selectivity of these Ir(I) systems was highly dependent on the steric environment around iridium.

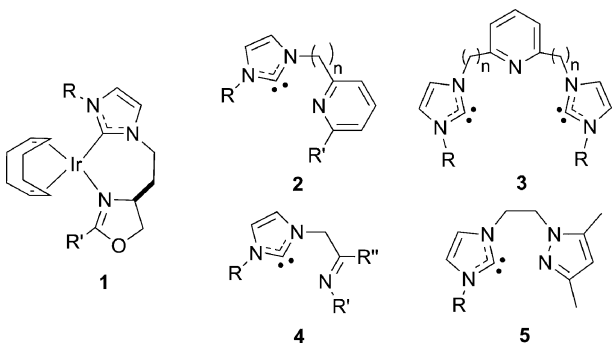

Chart 1

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Research into mixed donor NHC–N chelates, such as the NHC-oxazolyl ligand in **1**, has attracted considerable attention. NHCs are strong σ-donor ligands that form very stable metal–ligand bonds. N-Donor ligands on the other hand form weaker more labile bonds.[8] While it is often advantageous to incorporate these weaker N donors into the metal catalyst, the ligand lability can provide a route for catalyst decomposition. When tethered to a stable NHC donor a relatively labile sp^2 N donor will become anchored to the metal centre thereby allowing only partial ligand dissociation.[9] Much early work in the development of such heterotopic NHC–N ligands was aimed at the development of Pd(0) complexes of NHC-pyridyl chelates (**2** and **3**)[10] for use as C–C bond forming catalysts. Later work has focused on including non-heterocyclic imino groups into the ligand (**4**)[11] that increase the proximity of the sterically shielding R′ group to the N donor. More recently NHC-pyrazolyl ligands (**5**),[12] related to those reported here, and their complexes with Pd(II) and Ag(I) have also been reported.

Herein we report the synthesis of the NHC-pyrazolyl ligand precursors: methyl-1-[(1-pyrazolyl)methyl]imidazolium tetraphenylborate, [PzMeImH][BPh$_4$] (**6**) and 3-methyl-1-[2-(1-pyrazolyl)-ethyl]imidazolium tetraphenylborate, [PzEtImH][BPh$_4$] (**7**). The NHC derivatives PzMeIm and PzEtIm were generated *in situ* to form complexes with Rh(I) and Ir(I): [Rh(PzMeIm)(COD)][BPh$_4$] (**8**), [Rh(PzEtIm)(COD)][BPh$_4$] (**9**), [Rh(PzMeIm)(CO)$_2$][BPh$_4$] (**10**), [Rh(PzEtIm)(CO)$_2$][BPh$_4$] (**11**) and [Ir(PzMeIm)$_2$(COD)][BPh$_4$] (**12**) where COD = 1,5-cyclooctadiene. Complexes **8**, **9** and **12** were investigated as potential hydrogenation catalysts, as were the analogous phosphine-pyrazolyl complexes [Rh(PyP)(COD)]BPh$_4$ (**13**) and [Ir(PyP)(COD)]BPh$_4$ (**14**) (Chart 2).[13]

Results and discussion

Ligand precursor synthesis

The imidazolium salts **6** and **7** were synthesised *via* S$_N$2 displacement of the halide from 1-chloromethylpyrazole and 1-(2-bromoethyl)pyrazole, respectively, with *N*-methylimidazole. From a solution of toluene the halide salt precipitates as a pale yellow oil, and counterion exchange with NaBPh$_4$ *in situ* affords the desired

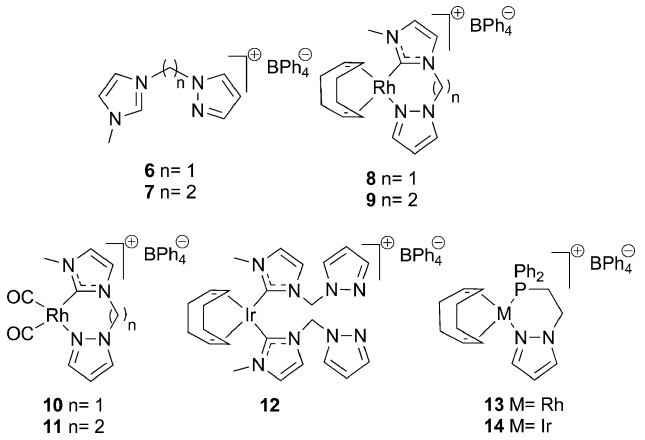


Chart 2

salt as an amorphous beige solid which can be recrystallised from acetone–diethyl ether to yield fine white crystals of the product. It was observed that nucleophiles such as DMF, acetonitrile and triethylamine competed with *N*-methylimidazole in displacing the halide from the pyrazolyl precursor.

The length of the alkyl chain bridging the ligand was increased from one to two carbons (**6** to **7**) to investigate the influence of the structure on the catalytic activity of the complex. Changing the bridge length can influence the steric environment around the metal centre by altering the bite angle of the chelate as well as the orientation of the donor groups relative to the metal centre. Ring-strain within the metallocycle can also affect the stability of the chelate and the lability of the weaker pyrazolyl donor.

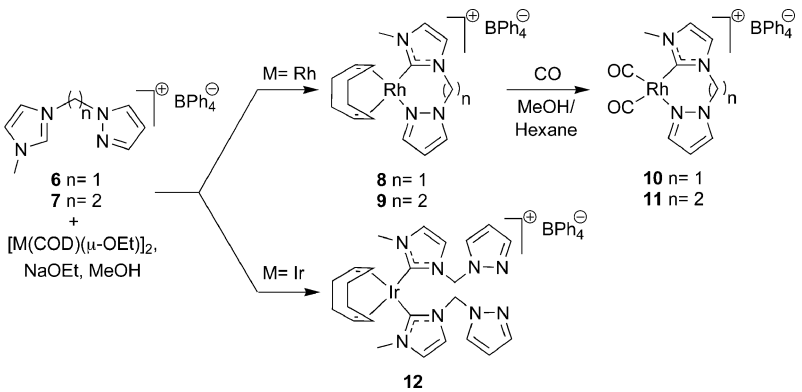
Unlike most analogous mixed donor NHC–N systems the ligand derivatives of **6** and **7** are surrounded by very little steric bulk leaving the coordinated metal centre largely unshielded. However, the ligand design does allow for facile inclusion of bulky substituents onto each of the pyrazolyl and the imidazolium rings at the 3 position.[14]

Complex synthesis

The Rh(I) complexes **8** and **9** were synthesised *via* deprotonation of the corresponding imidazolium salt *in situ* by reaction with the metal precursor $[Rh(COD)(\mu\text{-}OEt)]_2$ in the presence of an excess of NaOEt (Scheme 1). Both **8** and **9** were isolated as air-stable bright yellow solids in high yield and characterised by ^1H and ^{13}C NMR spectroscopy, MS and microanalysis. Complex **8** was also characterised by X-ray crystal structure determination (Fig. 2(a)). In the ^1H NMR spectra of **8** the COD resonances are observed as four broad lines between 1.8 and 4.8 ppm due to fluxionality in the conformation of the COD chelate. Conformational exchange was no longer observed at 220 K at which temperature the COD resonances sharpen up to form a set of 12 multiplets. At this temperature a diastereotopic splitting of the bridgehead protons of the NHC-pyrazolyl ligand and the COD CH_2 protons is observed. The ^1H NMR spectra of **9** shows resolved COD resonances and diastereotopic splitting of the ligand bridgehead protons and COD CH_2 protons, at room temperature. Conformational exchange within complex **9** is therefore considerably slower than in complex **8**, possibly due to an increased steric interaction between the COD ligand and the NHC-pyrazolyl ligand.

The Ir(I) complex **12** was synthesised in an analogous fashion to **8** and **9** *via* the reaction of two equivalents of ligand precursor **6** with $[Ir(COD)(\mu\text{-}OEt)]_2$ and an excess of NaOEt. It was observed that reacting $[Ir(COD)(\mu\text{-}OEt)]_2$ with a sub-stoichiometric amount of ligand precursor resulted in the formation of the same complex. Complex **12** was isolated as an air stable orange solid in good yield and characterised by ^1H and ^{13}C NMR spectroscopy, MS, microanalysis and X-ray crystal structure determination (Fig. 2(b)). The X-ray structure shows **12** to have a highly unusual bonding mode with two potentially bidentate PzMeIm ligands coordinated to the metal centre in a monodentate fashion through the carbene donor alone, leaving both pyrazolyl donors uncoordinated. The ^1H NMR spectra reveals two distinct sets of resonances for each PzMeIm ligand and four distinct COD ethylidene resonances. The methylene protons from each PzMeIm ligand are also diastereotopic suggesting a strong steric interaction restricting the mobility of the ligand arms. 2D ^1H NOESY experiments at 298 K revealed that the conformation of **12** was still fluxional at this temperature with exchange peaks observed between both sets of PzMeIm resonances and between COD resonances (Fig. 1). At 200 K this exchange was no longer observed.

Unlike the reaction with ligand precursor **6**, the reaction of ligand precursor **7** with $[Ir(COD)(\mu\text{-}OEt)]_2$ under similar conditions led to the formation of an amorphous red precipitate which ^1H NMR spectroscopy revealed to be a mixture of several PzEtIm containing species, and which could not be sufficiently purified and characterised. This result indicates the degree to



Scheme 1

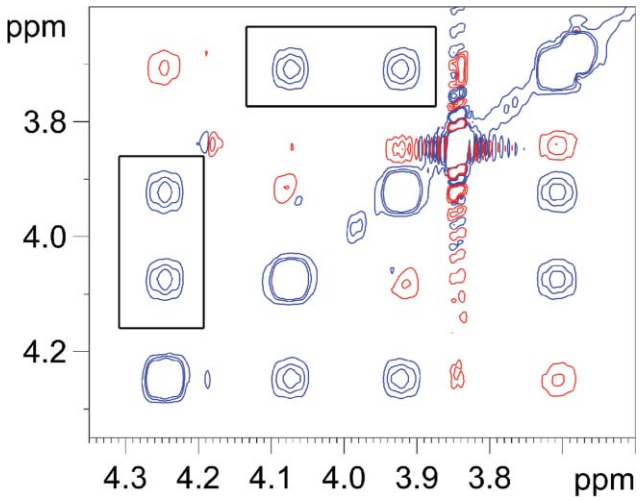


Fig. 1 2D ^{1}H NOESY spectra of **12** at 298 K showing exchange peaks between COD ethylidene proton resonances.

which complex structure and stability is influenced by altering the alkyl bridge length within the ligand.

The rhodium dicarbonyl complexes **10** and **11** were synthesised by the displacement of COD from complexes **8** and **9**, respectively, by stirring a suspension of the complex under an atmosphere of CO. Both **10** and **11** were isolated as mildly air sensitive pale yellow solids. The complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy, MS, microanalysis and FTIR spectroscopy. Two strong bands were observed in the IR spectra at 2092 and 2017 cm^{-1}, and 2093 and 2032 cm^{-1} for complexes **10** and **11** respectively, indicating the presence of two inequivalent, metal bound, carbonyl groups. Attempted displacement of COD from **12** with CO resulted in complex decomposition.

X-Ray crystal structure determination

The solid-state structures of **8** and **12** were determined using single-crystal X-ray diffraction analyses (Table 1). Crystals suitable for analysis were obtained by vapour diffusion of hexane into a THF solution of **8**, and by vapour diffusion of diethyl ether into a DCM solution of **12**, under N_2. ORTEP depictions of the cations of **8** and **12** are shown in Fig. 2.

The crystal structure of **8** reveals a square planar geometry around the metal centre with one PzMeIm ligand bound in a chelate fashion to rhodium as expected. The Rh(1)–C(15) bond distance of 2.053(2) Å is in the range expected for such bonds.[5b,15,17c] The bite angle of 85.14(7)° for N(4)–Rh(1)–C(15) is quite low due to ring-strain within the metallocycle, which adopts a pseudo-boat conformation. The bite angles of the six-membered metallocycles formed by the analogous pyrazolylphosphine chelate (PyP in **13**)[13] and *N*,*N*-bispyrazolylmethane chelate (Bpm)[16] ligands bound to Rh(I) are significantly higher (88.9 and 88.4° respectively). The increased ring-strain in **8** can be attributed to the anisotropy of NHC coordination which directs the carbene ring towards an orthogonal orientation relative to the plane of the complex. Two factors contribute to this anisotropy, firstly in presenting the slim axis of the carbene ring to the bulky plane of the complex any steric interaction with the ligand is minimized. Secondly, orbital interactions between the vacant carbene *p*-orbital and either a free metal d-orbital and/or a metal–ligand σ-bonding orbital are maximised in such an orthogonal arrangement. The details of these interactions, and in particular the validity of any dπ–pπ back donation, have been discussed in detail elsewhere.[17]

Table 1 Crystallographic data for [Ir(PzMeIm)$_2$(COD)]BPh$_4$ (**12**) and [Rh(PzMeIm)(COD)]BPh$_4$ (**8**)

	12	**8**
Empirical formula	$C_{48.50}H_{53.25}BIrN_8O_{0.38}$	$C_{40}H_{42}BN_4Rh$
M/g mol^{-1}	957.25	692.50
Crystal system	Monoclinic	Monoclinic
Space group (no.)	$C2/c$ (15)	$P2_1/n$ (14)
a/Å	31.705(6)	9.396(5)
b/Å	13.512(3)	19.599(11)
c/Å	24.585(5)	18.476(11)
β/°	117.508(3)	93.911(10)
V/Å^3	9341(3)	3394(3)
D_c/g cm^{-3}	1.361	1.355
Z	8	4
T/K	150(2)	150(2)
λ(Mo-Kα)/Å	0.71073	0.71073
μ(Mo-Kα)/mm^{-1}	2.900	0.537
Crystal size/mm	0.347 × 0.204 × 0.049	0.366 × 0.119 × 0.078
Crystal colour	Orange	Yellow
Crystal habit	Blade	Prism
$2\theta_{max}$/°	56.68	56.62
hkl Range	−42 40, −17 17, −32 31	−12 12, −25 25, −23 24
N	44772	33922
N_{ind} (R_{merge})	11157 (0.0666)	8150 (0.0612)
N_{obs} ($I > 2\sigma(I)$)	7636	6019
GoF (all)	1.213	1.026
$R1$ (F, $I > 2\sigma(I)$)	0.0375	0.0324
$wR2$ (F^2, all data)	0.0916	0.0749

$R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections, $w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

On binding to Ir(I), the PzMeIm ligand is bound in a very different manner to that observed for Rh(I). The crystal structure of **12** shows a square planar geometry about iridium. The Ir(1)–C(9) and Ir(1)–C(17) bond distances are 2.053(4) and 2.045(4) Å, respectively. The angle of 93.57(16)° for C(9)–Ir(1)–C(17) is significantly larger than the ideal 90° and is probably due to steric crowding between the uncoordinated pyrazolyl arms. The NHC ring planes in **12** are oriented perpendicular to the square plane of the complex, consistent with the binding anisotropy noted above and free rotation of the ligand about the Ir–C bond.

We have previously observed pyrazolyl donors to have only a slightly weaker coordinating strength to Rh(I) than to Ir(I).[13] There should be a negligible difference between the steric nature of PzMeIm when chelated to either Rh(I) or Ir(I). This suggests that the orbital interactions described above are more favourable for Ir(I) complexes than Rh(I) complexes (at least with COD as coligand), thereby inducing the NHC to adopt an orthogonal orientation to the plane of the metal complex and disrupting the formation of the chelate. This phenomenon is not observed in analogous chelates with an NHC ligand tethered to a stronger donor such as phosphine or even pyridine, in which case the desired chelate is always formed.[18]

Hydrogenation reactions

The Rh(I) and Ir(I) NHC complexes **8**, **9** and **12** were investigated as potential hydrogenation catalysts, as were the analogous

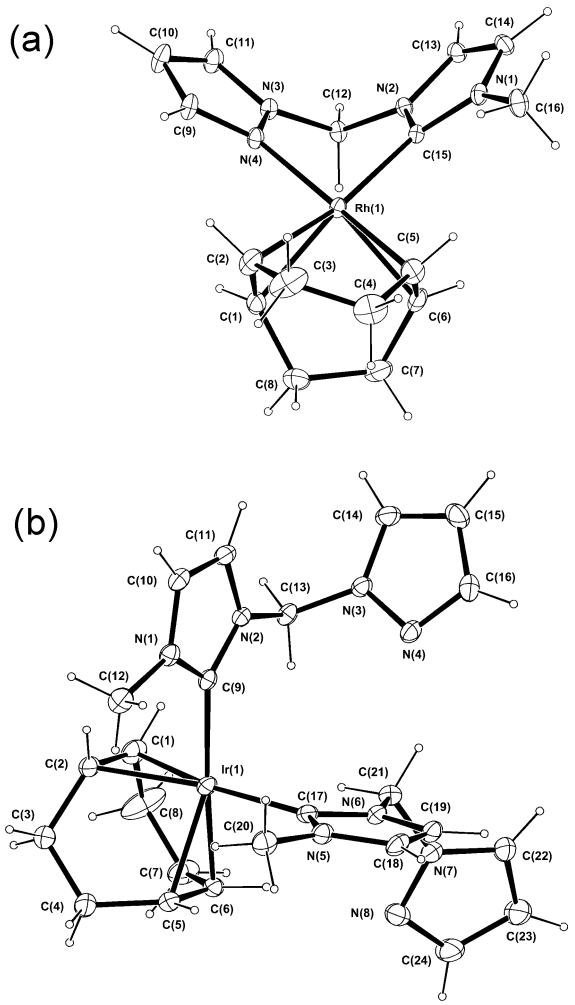
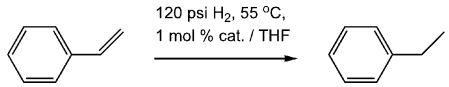


Fig. 2 The ORTEP depictions of (a) $[Rh(PzMeIm)(COD)]^+$ (**8**) and (b) $[Ir(PzMeIm)_2(COD)]^+$ (**12**) at 20% thermal ellipsoids for non-hydrogen atoms.

complexes containing pyrazolylphosphine ligands (**13** and **14**). The reactions were performed under 120 psi of H_2 gas, at 55 °C, using 1 mol% of catalyst in THF; the results are summarized in Table 2. Catalysts **8**, **9**, **13** and **14** all showed a moderate activity with complete conversion of the substrate within 50 min in all cases. No change in activity was observed between complexes **8** and **9**, *i.e.* in going from the six membered to the seven-membered metallocycle, nor is any change in activity observed between the analogous pair of rhodium and iridium complexes **13** and **14**. Interestingly,

Table 2 Hydrogenation of styrene



Catalyst	% Conversion (time/min)
12 $[Ir(PzMeIm)_2(COD)]BPh_4$	0 (180)
8 $[Rh(PzMeIm)(COD)]BPh_4$	100 (50)
9 $[Rh(PzEtIm)(COD)]BPh_4$	100 (50)
13 $[Rh(PyP)(COD)]BPh_4$	100 (35)
14 $[Ir(PyP)(COD)]BPh_4$	100 (35)

the Rh(I) complex containing the phosphine-pyrazolyl chelate (**13**) showed a significantly higher activity than the Rh(I) NHC-pyrazolyl analogues (**8** and **9**) with the hydrogenation reactions reaching completion in only 35 min in the case of **13** and 50 min when using complexes **8** and **9**. The biscarbene complex **12** showed absolutely no activity after several hours. This was unexpected as similar bisphosphine complexes reported in the literature exhibit a moderate activity under similar conditions.[19] It is possible that in complex **12** the uncoordinated pyrazolyl donors interfere with the reaction progress *via* a transient coordination to the iridium centre.

The hydrogenation of simple olefins such as styrene is achieved in less time and under milder conditions (*e.g.* at 25 °C and 1 atm H_2), using commercially available complexes such as Crabtree's catalyst and its analogues,[5,19] than the rate of hydrogenation reported here for complexes **8**, **9**, **12**, **13** and **14**. The hydrogenation activity of complexes with chelating NHC–N ligands is strongly influenced by the steric environment about the metal, with a greater steric shielding of the metal centre generally leading to an improved catalytic activity.[6] This suggests that there is considerable potential to improve the activity of these complexes, with the possibility of developing these complexes as catalysts for the hydrogenation of more substituted, sterically demanding substrates.

Conclusions

Two new mixed donor NHC-pyrazolyl ligand precursors **6** and **7** were synthesised and their coordination chemistry with Ir(I) and Rh(I) was investigated. An unusual binding mode was observed in complex **12** with two potentially chelating NHC-pyrazolyl ligands binding to iridium in a monodentate fashion through the carbene donor. Complexes **8**, **9**, **13** and **14** were shown to be efficient catalysts for the hydrogenation of styrene. A more comprehensive hydrogenation study is currently underway to fully investigate the potential catalytic activity of these complexes and their derivatives.

Experimental

General procedures

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. 1-Chloromethylpyrazole,[20] 1-(2-Bromoethyl)pyrazole,[21] $[Ir(COD)(\mu\text{-}Cl)]_2$,[22] $[Rh(COD)(\mu\text{-}Cl)]_2$,[23] $[Ir(COD)(\mu\text{-}OEt)]_2$[24] and $[Rh(COD)(\mu\text{-}OEt)]_2$[24] were prepared by literature methods.

^1H and ^{13}C NMR spectra were recorded on Bruker DPX300 and DMX500 spectrometers, operating at 300 and 500 MHz (^1H) and 75 and 125 MHz (^{13}C), respectively. ^1H and ^{13}C chemical shifts are referenced to internal solvent resonances. The following subscripted abbreviations are used to assign resonances: Pz = pyrazolyl, Im = imidazolyl, COD = 1,5-cyclooctadiene and BPh = tetraphenylborate counterion. IR spectra were recorded on an Avatar 370 FT-IR (Thermo Nicolet) spectrometer. Melting points were determined using a Mel-Temp (Laboratory Devices) apparatus. ESI-MS were carried out in the Mass Spectrometry Unit, School of Chemistry, University of Sydney, Australia. Microanalyses were carried out at the Campbell Analytical Laboratory, the University of Otago, New Zealand. The X-ray

structures of **12** and **8** were obtained by Dr Peter Turner at the X-ray crystallography centre, University of Sydney.

CCDC reference numbers 600823 and 600824.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603455a

Synthesis of 3-methyl-1-[(1-pyrazolyl)methyl]imidazolium tetraphenylborate, 6. A solution of 1-chloromethylpyrazole hydrogen chloride (1.09 g, 7.12 mmol) in toluene (15 mL) was added to a solution of 1-methylimidazole (1.50 mL, 18.8 mmol) in toluene (15 mL) and the mixture was left to reflux for 24 h. $NaBPh_4$ (2.50 g, 7.31 mmol) was then added and the mixture refluxed for a further 3 h, after which time a beige precipitate had formed. The precipitate was recrystallised from acetone–diethyl ether to yield fluffy white crystals of **6** (2.22 g, 65%), mp 208–210 °C.

^{1}H NMR (300 MHz, acetone-d_6): δ 9.08 (br s, 1H, $H2_{Im}$), 8.01 (d, 1H, $^3J_{H3/5–H4} = 2.3$, $H3_{Pz}$ or $H5_{Pz}$), 7.81 (dd, 1H, $^3J_{H4–H5} = 1.9$, $^4J_{H4/5–H2} = 1.5$, $H4_{Im}$ or $H5_{Im}$), 7.64 (dd, 1H, $^3J_{H5–H4} = 1.9$, $^4J_{H5/4–H2} = 1.5$, $H5_{Im}$ or $H4_{Im}$), 7.62 (d, 1H, $^3J_{H5/3–H4} = 1.9$, $H5_{Pz}$ or $H3_{Pz}$), 7.34 (m, 8H, *o*-CH_{BPh}), 6.91 (dd, 8H, $^3J_{m\text{-}CH–o\text{-}CH} = 7.5$, $^3J_{m\text{-}CH–p\text{-}CH} = 7.2$, *m*-$CH_{BPh}$), 6.76 (t, 4H, $^3J_{p\text{-}CH–m\text{-}CH} = 7.2$, *p*-$CH_{BPh}$), 6.23 (s, 2H, CH_2), 6.38 (dd, 1H, $^3J_{H4–H3/5} = 2.3$, $^3J_{H4–H5/3} = 1.9$, $H4_{Pz}$), 4.01 (s, 3H, CH_3) ppm. ^{13}C NMR (300 MHz, acetone-d_6): δ 164.00 (q, $^1J_{B–C} = 49.4$, B–C), 141.85 ($C3_{Pz}$ or $C5_{Pz}$), 136.75 ($C2_{Im}$), 136.00 (*o*-C_{BPh}), 130.95 ($C5_{Pz}$ or $C3_{Pz}$), 125.05 (*m*-C_{BPh}), 124.25 ($C4_{Im}$ or $C5_{Im}$), 121.90 ($C5_{Im}$ or $C4_{Im}$), 121.25 (*p*-C_{BPh}), 107.20 ($C4_{Pz}$), 61.95 (CH_2), 36.00 (CH_3) ppm. IR (KBr): ν 3053, 1295, 1174, 1090, 843, 766, 707 cm^{-1}. MS (electrospray) *m*/*z*: (ES^+) 163.1 (100%, $[PzMeImH]^+$), (ES^-) 319.6 (100%, $[BPh_4]^-$). Microanalysis: found: C 78.46, H 6.52, N 11.63%; calc.: C 79.67, H 6.48, N 11.61%.

Synthesis of 3-methyl-1-[2-(1-pyrazolyl)ethyl]imidazolium tetraphenylborate, 7. A solution of 1-(2-bromoethyl)pyrazole (1.50 g, 8.57 mmol) in toluene (15 mL) was added to a solution of 1-methylimidazole (1.5 mL, 18.8 mmol) in toluene (15 mL) and the mixture heated under reflux for 24 h. $NaBPh_4$ (3.00 g, 8.77 mmol) was then added and the mixture refluxed for a further 3 h, after which time a beige precipitate had formed. The precipitate was recrystallised from acetone–diethyl ether to yield fluffy white crystals of **7** (4.17 g, 97%), mp 174–176 °C.

^{1}H NMR (300 MHz, acetone-d_6): δ 8.49 (br s, 1H, $H2_{Im}$), 7.56 (dd, 1H, $^3J_{H5–H4} = 1.9$, $^4J_{H5/4–H2} = 1.5$, $H5_{Im}$ or $H4_{Im}$), 7.54 (d, 1H, $^3J_{H3/5-H4} = 2.3$, $H3_{Pz}$ or $H5_{Pz}$), 7.46 (d, 1H, $^3J_{H5/3–H4} = 1.9$, $H5_{Pz}$ or $H3_{Pz}$), 7.39 (dd, 1H, 1H, $^3J_{H4–H5} = 1.9$, $^4J_{H4/5–H2} = 1.5$, $H4_{Im}$ or $H5_{Im}$), 7.34 (m, 8H, *o*-CH_{BPh}), 6.91 (dd, 8H, $^3J_{m\text{-}CH–o\text{-}CH} = 7.5$, $^3J_{m\text{-}CH–p\text{-}CH} = 7.5$, *m*-$CH_{BPh}$), 6.76 (t, 4H, $^3J_{p\text{-}CH–m\text{-}CH} = 7.5$, *p*-$CH_{BPh}$), 6.22 (dd, 1H, $^3J_{H4–H3/5} = 1.9$, $^3J_{H4–H5/3} = 2.3$, $H4_{Pz}$), 4.77 (m, 2H, N_{Im}–CH_2 or N_{Pz}–CH_2), 4.66 (m, 2H, N_{Pz}–CH_2 or N_{Im}–CH_2), 3.91 (s, 3H, CH_3) ppm. ^{13}C NMR (300 MHz, acetone-d_6): δ 164.00 (q, $^1J_{B–C} = 49.4$, B–C), 139.80 ($C5_{Pz}$ or $C3_{Pz}$), 136.00 (*o*-C_{BPh}), 130.30 ($C3_{Pz}$ or $C5_{Pz}$), 125.05 (*m*-C_{BPh}), 123.70 ($C5_{Im}$ or $C4_{Im}$), 122.65 ($C4_{Im}$ or $C5_{Im}$), 121.25 (*p*-C_{BPh}), 105.65 ($C4_{Pz}$), 50.70 (N_{Im}–C or N_{Pz}–C), 49.45 (N_{Pz}–C or N_{Im}–C), 35.65 (CH_3) ppm. IR (KBr): ν 3074, 1277, 1170, 1090, 843, 738, 712, 605 cm^{-1}. MS (electrospray) *m*/*z*: (ES^+) 177.2 (100%, $[PzEtImH]^+$), (ES^-) 319.7 (100%, $[BPh_4]^-$). Microanalysis: found: C 79.42, H 6.55, N 11.43%; calc.: C 79.84, H 6.70, N 11.29%.

Synthesis of Rh complex 8. A suspension of **6** (0.198 g, 0.410 mmol) in methanol (20 mL) was added to a solution of $[Rh(COD)(\mu\text{-}OEt)]_2$ (0.102 g, 0.199 mmol) and sodium ethoxide (0.028 g, 0.411 mmol) in methanol (20 mL) and the mixture stirred for 3 h. A bright yellow solution formed and a beige solid remained undissolved. The solid was filtered off and the filtrate reduced *in vacuo*, to *ca.* 20 mL, to precipitate a bright yellow solid. This precipitate was washed with hexane and dried *in vacuo* to yield **8** (0.253 g, 89%), mp 176–178 °C (decomp.).

^{1}H NMR (500 MHz, CD_2Cl_2, 220 K): δ 7.38 (m, 8H, *m*-CH_{BPh}), 7.32 (d, $^3J_{H3–H4} = 2.2$, 1H, $H3_{Pz}$), 7.16 (d, $^3J_{H5–H4} = 2.6$, 1H, $H5_{Pz}$), 7.03 (t, $^3J_{o\text{-}CH–m\text{-}CH} = 7.3$, 8H, *o*-$CH_{BPh}$), 6.90 (t, $^3J_{p\text{-}CH–m\text{-}CH} = 7.3$, 4H, *p*-$CH_{BPh}$), 6.63 (d, $^3J_{H4–H5} = 2.0$, 1H, $H4_{Im}$), 6.57 (d, $^3J_{H5–H4} = 2.0$, 1H, $H5_{Im}$), 6.23 (app. t, $^3J_{H4–H3/H5} = 2.4$, 1H, $H4_{Pz}$), 5.44 (d, $^2J_{CH–CH} = 13.8$, 1H, N–CH[a]), 4.92 (app. t, $^3J_{H1–H2/H8} = 7.3$, 1H, $H1_{COD}$-*trans* to C), 4.48 (dt, $^3J_{H2–H1} = 7.3$, $^3J_{H2–H3} = 7.5$, 1H, $H2_{COD}$), 4.42 (app. t, $^3J_{H5–H6/H4} = 7.3$, 1H, $H5_{COD}$), 4.27 (d, $^3J_{CH–CH} = 13.8$, 1H, N–CH[b]), 4.18 (dt, $^3J_{H6–H5} = 5.7$, $^3J_{H6–H7} = 7.3$, 1H, $H6_{COD}$), 3.65 (s, 3H, CH_3), 2.70 (m, 1H, $H8_{COD}$[a]), 2.54 (m, 1H, $H4_{COD}$[a]), 2.34 (m, 1H, $H8_{COD}$[b]), 2.31 (m, 1H, $H4_{COD}$[b]), 2.25 (m, 1H, $H7_{COD}$[a]), 2.11 (m, 1H, $H3_{COD}$[a]), 1.81 (m, 1H, $H7_{COD}$[b]), 1.77 (m, 1H, $H3_{COD}$[b]) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 220 K): δ 174.72 (d, $^1J_{C2–Rh} = 50.0$, $C2_{Im}$), 163.75 (q, $^1J_{B–C} = 49.4$, B–C), 141.55 ($C3_{Pz}$), 135.60 (*m*-C_{BPh}), 132.69 ($C5_{Pz}$), 126.08 (*o*-C_{BPh}), 122.72 ($C4_{Im}$), 122.14 (*p*-C_{BPh}), 120.99 ($C5_{Im}$), 107.21 ($C4_{Pz}$), 97.87 ($C2_{COD}$), 96.87 ($C1_{COD}$), 80.16 ($C5_{COD}$), 70.75 ($C6_{COD}$), 62.31 (CH_2), 38.15 (CH_3), 35.13 ($C4_{COD}$), 30.78 ($C8_{COD}$), 29.30 ($C7_{COD}$), 26.92 ($C3_{COD}$) ppm. IR (KBr): ν 3052, 1477, 1269, 1221, 735, 709 cm^{-1}. MS *m*/*z*: (ES^+) 373.1 (12%, $[Rh(PzMeIm)(COD)]^+$), 371.0 (100%). Microanalysis: found: C 66.29, H 5.96, N 7.82%; calc.: (**3** + 2MeOH) C 66.67, H 6.66, N 7.41%.

Synthesis of Rh complex 9. Complex **9** was synthesised in a similar fashion to **8** from the ligand precursor **7**. A bright yellow powder of **9** was isolated in good yield (0.089 g, 86%), mp 178–180 °C (decomp.).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.39 (m, 8H, *m*-CH_{BPh}), 7.28 (d, $^3J_{H5–H4} = 2.6$, 1H, $H5_{Pz}$), 7.20 (d, $^3J_{H3–H4} = 1.8$, 1H, $H3_{Pz}$), 7.06 (t, $^3J_{o\text{-}CH–m\text{-}CH} = 7.3$, 8H, *o*-$CH_{BPh}$), 6.91 (tt, $^3J_{p\text{-}CH–m\text{-}CH} = 7.3$, $^4J_{p\text{-}CH–o\text{-}CH} = 1.3$, 4H, *p*-$CH_{BPh}$), 6.71 (d, $^3J_{H4–H5} = 1.8$, 1H, $H4_{Im}$), 6.56 (d, $^3J_{H5–H4} = 1.1$, 1H, $H5_{Im}$), 6.24 (app. t, $^3J_{H4–H3/H5} = 2.2$, 1H, $H4_{Pz}$), 6.14 (m, 1H, N_{Im}–CH[a]), 4.91 (m, 1H, $H1_{COD}$-*trans* to C), 4.42 (m, 1H, N_{Pz}–CH[a]), 4.38 (m, 1H, $H2_{COD}$), 4.31 (m, 1H, $H5_{COD}$), 4.22 (dt, $^2J_{CH–CH} = 15.2$, $^3J_{CH–CH2} = 4.8$, 1H, N_{Im}–CH[b]), 3.94 (s, 3H, CH_3), 3.79 (m, 1H, $H6_{COD}$), 3.76 (m, 1H, N_{Pz}–CH[b]), 2.66 (m, 1H, $H8_{COD}$[a]), 2.56 (m, 1H, $H4_{COD}$[a]), 2.46 (m, 1H, $H7_{COD}$[a]), 2.33 (m, 1H, $H3_{COD}$[a]), 2.25 (m, 1H, $H8_{COD}$[b]), 2.24 (m, 1H, $H4_{COD}$[b]), 2.05 (m, 1H, $H7_{COD}$[b]), 1.98 (m, 1H, $H3_{COD}$[b]) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ 163.90 (q, $^1J_{B–C} = 49.4$, B–C), 140.36 ($C3_{Pz}$), 135.83 (*m*-C_{BPh}), 133.41 ($C5_{Pz}$), 125.60 (*o*-C_{BPh}), 122.94 ($C4_{Im}$), 122.86 ($C5_{Im}$), 121.78 (*p*-C_{BPh}), 107.90 ($C4_{Pz}$), 97.48 ($C1_{COD}$), 95.19 ($C2_{COD}$), 80.04 ($C5_{COD}$), 72.76 ($C6_{COD}$), 50.02 (N_{Im}–C), 48.30 (N_{Pz}–C), 38.60 (CH_3), 33.59 ($C4_{COD}$), 30.36 ($C7_{COD}$), 29.97 ($C8_{COD}$), 27.97 ($C3_{COD}$) ppm ($C2_{Im}$ undefined). IR (KBr): ν 3054, 1477, 768, 735, 707 cm^{-1}. MS *m*/*z*: (ES^+) 387.1 (29%, $[Rh(PzEtIm)(COD)]^+$), 375.0 (100%). Microanalysis: found: C 69.70, H 6.51, N 8.30%; calc.: C 69.70, H 6.28, N 7.93%.

Synthesis of Rh complex 10. A suspension of **8** (0.093 g, 0.134 mmol) in hexane (10 mL) and methanol (1 mL) was degassed *via* three freeze–pump–thaw cycles. An atmosphere of CO was introduced over the reaction mixture, which was stirred at room

temperature for 3 h. The bright yellow solid turned pale yellow, this solid was collected and washed with hexane and dried *in vacuo* to afford **10** (0.077 g, 90%), mp 125–126 °C (decomp.)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (m, 8H, *m*-CH_{BPh}), 7.42 (d, $^3J_{H3-H4} = 2.3$, 1H, $H3_{Pz}$), 7.00 (t, $^3J_{o\text{-}CH\text{–}m\text{-}CH} = 7.2$, 8H, *o*-$CH_{BPh}$), 6.93 (d, $^3J_{H5-H4} = 2.6$, 1H, $H5_{Pz}$), 6.88 (t, $^3J_{p\text{-}CH\text{–}m\text{-}CH} = 7.2$, 4H, *p*-$CH_{BPh}$), 6.35 (m, 2H, $H4_{Im}$ and $H5_{Im}$), 6.19 (t, $^3J_{H4-H3/H5} = 2.6$, 1H, $H4_{Pz}$), 4.13 (br s, 2H, CH_2), 3.46 (s, 3H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.02 (q, $^1J_{B-C}$ = 49.4, B–C), 145.33 ($C3_{Pz}$), 136.03 (*m*-C_{BPh}), 134.61 ($C5_{Pz}$), 125.93 (*o*-C_{BPh}), 122.78 ($C4_{Im}$), 122.18 (*p*-C_{BPh}), 122.07 ($C5_{Im}$), 107.83 ($C4_{Pz}$), 61.49 (CH_2), 38.23 (CH_3) ppm ($C2_{Im}$ and C≡O's undefined). IR (KBr): *ν* 2092 (CO), 2017 (CO) cm^{-1}. MS *m*/*z*: (ES$^+$) 265.6 (37%, [Rh(PzMeIm)]$^+$), 293.6 (76%, [Rh(PzMeIm)(CO)]$^+$), 320.9 (100%, [Rh(PzMeIm)$(CO)_2$]$^+$). Microanalysis: found: C 64.95, H 5.15, N 9.59%; calc.: C 63.77, H 4.72, N 8.75%.

Synthesis of Rh complex 11. Complex **11** was prepared in a similar manner to **10** *via* displacement of COD from **9**. **11** was isolated as a pale yellow solid in high yield (0.115 g, 92%), mp 114–116 °C (decomp.).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.40 (m, 9H, *m*-CH_{BPh} and $H3_{Pz}$), 7.27 (d, $^3J_{H5-H4}$ = 2.6, 1H, $H5_{Pz}$), 7.05 (t, $^3J_{o\text{-}CH\text{–}m\text{-}CH}$ = 7.3, 8H, *o*-CH_{BPh}), 6.90 (m, H5, *p*-CH_{BPh} and $H4_{Im}$), 6.58 (d, $^3J_{H5-H4}$ = 2.0, 1H, $H5_{Im}$), 6.37 (app. t, $^3J_{H4-H3/H5} = 2.6$, 1H, $H4_{Pz}$), 4.48 (br s, 2H, N_{Im}–CH_2), 3.86 (s, 3H, CH_3), 3.63 (br t, $^{2/3}J_{CH\text{–}CH/CH2}$ = 5.9, 2H, N_{Pz}–CH_2) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ 163.87 (q, $^1J_{B-C}$ = 49.4, B–C), 142.87 ($C3_{Pz}$), 135.79 (*m*-C_{BPh}), 133.79 ($C5_{Pz}$), 125.66 (*o*-C_{BPh}), 123.90 ($C5_{Im}$), 123.64 ($C4_{Im}$), 121.83 (*p*-C_{BPh}), 109.07 ($C4_{Pz}$), 49.24 (N_{Im}–C), 49.12 (N_{Pz}–C), 39.72 (CH_3) ppm ($C2_{Im}$ and C≡O's undefined). IR (KBr): *ν* 2093 (CO), 2032 (CO) cm^{-1}. MS *m*/*z*: (ES$^+$) 279.6 (51%, [Rh(PzEtIm)]$^+$), 307.6 (64%, [Rh(PzEtIm)(CO)]$^+$), 334.9 (100%, [Rh(PzEtIm)$(CO)_2$]$^+$). Microanalysis: found: C 63.98, H 5.01, N 8.60%; calc.: C 64.24, H 4.93, N 8.56%.

Synthesis of Ir complex 12. A suspension of **6** (0.200 g, 0.415 mmol) in methanol (15 mL) was added to a solution of $[Ir(COD)(\mu\text{-}OEt)]_2$ (0.070 g, 0.101 mmol) and sodium ethoxide (0.040 g, 0.588 mmol) in methanol (15 mL) and the mixture stirred for 3 h. The solution changed from yellow to orange and a beige solid remained undissolved. The solid was filtered off and the filtrate reduced *in vacuo*, to *ca.* 5 mL, to precipitate a pale orange solid. This precipitate was washed with hexane and dried *in vacuo* to yield **12** as a pale orange powder (0.056 g, 59%), mp 155–160 °C.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.58 (d, 1H, $^3J_{H3-H4}$ = 1.7, $H3_{Pz}{}^a$), 7.54 (d, 1H, $^3J_{H5-H4} = 2.4$, $H5_{Pz}{}^a$), 7.52 (d, 1H, $^3J_{H3-H4} = 1.8$, $H3_{Pz}{}^b$), 7.31 (m, 9H, *o*-CH_{BPh} and $H5_{Pz}{}^b$), 7.00 (dd, 8H, $^3J_{m\text{-}CH\text{–}o\text{-}CH}$ = 7.5, $^3J_{m\text{-}CH\text{–}p\text{-}CH} = 7.2$, *m*-$CH_{BPh}$), 6.85 (m, 6H, $H4_{Im}{}^a$, $H4_{Im}{}^b$ and *p*-CH_{BPh}), 6.80 (d, 1H, $^3J_{H5-H4} = 2.0$, $H5_{Im}{}^b$), 6.75 (d, 1H, $^3J_{H5-H4}$ = 2.0, $H5_{Im}{}^a$), 6.52 (d, 1H, $^2J_{CH\text{–}CH} = 13.4$, N–$CH^{ax}$), 6.41 (d, 1H, $^2J_{CH\text{–}CH} = 13.4$, N–$CH^{ay}$), 6.38 (dd, 1H, $^3J_{H4-H3} = 2.0$, $^3J_{H4-H5}$ = 2.0, $H4_{Pz}{}^a$), 6.32 (d, 1H, $^2J_{CH\text{–}CH} = 13.2$, N–$CH^{bx}$), 6.30 (dd, 1H, $^3J_{H4-H3} = 2.0$, $^3J_{H4-H5} = 2.0$, $H4_{Pz}{}^b$), 6.21 (d, 1H, $^2J_{CH\text{–}CH} = 13.2$, N–$CH^{by}$), 4.24 (m, 1H, $H1_{COD}$), 4.07 (m, 1H, $H5_{COD}$), 3.92 (m, 1H, $H6_{COD}$), 3.85 (s, 3H, $CH_3{}^a$), 3.84 (s, 3H, $CH_3{}^b$), 3.71 (m, 1H, $H2_{COD}$), 2.31 (m, 4H, $H3_{COD}{}^a$, $H4_{COD}{}^a$, $H7_{COD}{}^a$ and $H8_{COD}{}^a$), 2.04 (m, 4H, $H3_{COD}{}^b$ and $H4_{COD}{}^b$ and $H7_{COD}{}^b$ and $H8_{COD}{}^b$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ 163.90 (q, $^1J_{B-C} = 49.4$, B–C), 141.75 ($C3_{Pz}{}^a$), 141.45 ($C3_{Pz}{}^b$), 135.85 (*o*-C_{BPh}), 130.40 ($C5_{Pz}{}^a$), 129.50 ($C5_{Pz}{}^b$), 125.50 (*m*-C_{BPh}), 124.10 ($C4_{Im}{}^b$), 123.75 ($C4_{Im}{}^a$), 121.65 (*p*-C_{BPh}), 120.10 and 119.95 ($C5_{Im}{}^a$ and $C5_{Im}{}^b$), 107.20 ($C4_{Pz}{}^a$ and $C4_{Pz}{}^b$), 80.05 ($C1_{COD}$), 78.35 ($C5_{COD}$ and $C6_{COD}$), 77.05 ($C2_{COD}$), 63.95 ($CH_2{}^a$), 63.70 ($CH_2{}^b$), 38.28 and 38.05 ($CH_3{}^a$ and $CH_3{}^b$), 32.35–29.90 ($C3_{COD}$, $C4_{COD}$, $C7_{COD}$ and $C8_{COD}$) ppm. ($C2_{Im}{}^a$ and $C2_{Im}{}^b$ undefined). IR (KBr): *ν* 3054, 1387, 1224, 734, 707, cm^{-1}. MS *m*/*z*: (ES$^+$) 463.4 (63%, [Ir(PzMeIm)(COD)]$^+$), 517.1 (23%, [Ir(PzMeIm)$_2$]$^+$), 625.1 (10%, [Ir(PzMeIm)$_2$(COD)]$^+$), 355.1 (2.5%, [Ir(PzMeIm)]$^+$), 456.9 (100%). Microanalysis: found: C 59.13, H 5.34, N 11.14%; calc.: C 61.07, H 5.55, N 11.87%.

General procedure for catalytic hydrogenation

A solution of 0.015 mmol of catalyst, 1.50 mmol of styrene and 0.3 mmol of mesitylene in 5 mL of THF in a glass vial was sealed inside a 320 ml steel bomb reactor (Parr Instrument Co. USA) under nitrogen. The reactor was flushed three times with 120 psi of H_2 gas. The solutions were stirred under 120 psi of H_2 at 55 °C for the duration of the reaction. The solutions were then concentrated to 0.5 ml under reduced pressure (water aspirator), made up to 1.5 ml with $CDCl_3$ and analysed *via* ^{1}H NMR spectroscopy. Percent conversions were reported relative to remaining substrate. Comparison of substrate/product peak integrals relative to mesitylene, used as an internal standard, indicated approximately 85% of substrate/product was recovered after workup. This difference was assumed to have a minimal influence on reported conversions due to a similarity in boiling points between ethylbenzene (136 °C) and styrene (145–146 °C).

Acknowledgements

We gratefully acknowledge financial support from the University of New South Wales, the Australian Research Council (ARC) and the Australian government for an Australian Postgraduate Award (M. J. P).

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