A Robust Method to Heterogenise and Recycle Group 9 Catalysts

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General

L1, **1a**, and **2a** were prepared according to the literature method.[1, 2] The Wang resin, with particle sizes of 100-200 mesh, 1% cross linking of divinylbenzene and a 1.51 mmol/g loading, was purchased from Bioproducts Ltd. All other reagents are commercially available and were used as received.

All manipulations involving the synthesis of **L1**, **L2**, **1a**, **1b**, **4a**, **4b**, **4c** and **4d**, were conducted using standard Schlenk line techniques under an inert atmosphere of dry dinitrogen using a dual vacuum/dinitrogen line or in a Braun Labmaster100 glove box. Dry dinitrogen was obtained by passing dinitrogen gas through a double column of self-indicating phosphorus pentoxide and activated 4Å molecular sieves. Dichloromethane, diethyl ether and methanol were dried using a Pure Solvent MD Solvent Purification System, with solvents purified by copper catalysts and activated alumina columns. All solvents were subsequently stored in ampoules under dinitrogen.

^{1}H- and ^{13}C-NMR spectra were recorded on Bruker DPX 300 spectrometer. Gas chromatography (GC) analyses were performed on a Hewlett Packard HP 6890 Series GC System. Microanalyses were obtained by Mr. Ian Blakeley at the University of Leeds Microanalytical Service. X-ray data was collected by Stephanie Lucas. A suitable single crystal was selected and immersed in an inert oil. The crystal was then mounted onto a glass capillary and attached to a goniometer head on a Bruker X8 Apex diffractor using graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) and 1.0° ϕ-rotation frames. The crystal was then cooled to 150K by an Oxford cryostream low temperature device.[3] The full data set was recorded and the images processed using DENZO and SCALEPACK programs.[4] The structures were solved by Stephanie Lucas. Structure solution by direct methods was achieved through the use of SHELXS86[5], SIR92[6] or SIR97[7] programs, and the structural model defined by full matrix least squares on F^2 using SHELX97.[5] Molecular graphics were plotted using POV-Ray[8] *via* the XSeed program. Editing of Crystallographic Information files and construction of tables of bond lengths and angles was achieved using WC[9] and PLATON.[10] Hydrogen atoms were placed using idealised geometric positions (with free

rotation for methyl groups), allowed to move in a "riding model" along with the atoms to which they were attached, and refined isotropically.

ICP analysis was performed by Matthew Stirling at the University of Huddersfield using the following procedure:

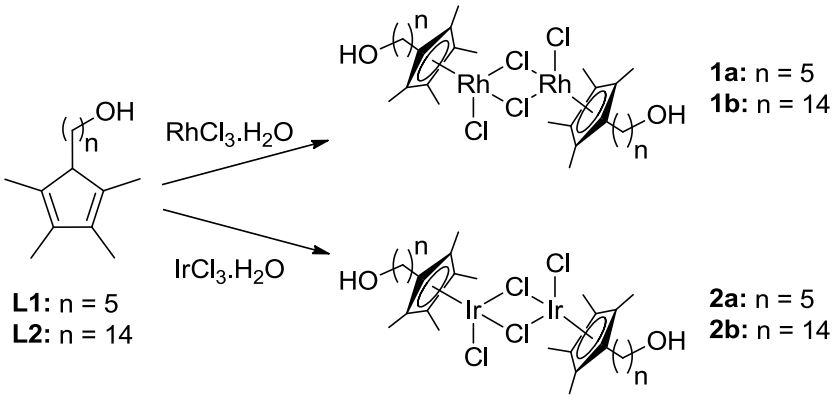
Between 15 – 30 mg of each sample was accurately weighed into a microwave digestion tube. 1.5 ml trace-metal concentrated sulfuric acid was pipetted into each tube and the samples digested. 10 ml trace-metal concentrated nitric acid and 3.0 ml trace-metal concentrated hydrochloric acid were added to each vessel, any effervescence allowed to subside then the samples were digested. The samples were allowed to cool to room temperature then transferred to 100 ml plastic volumetric flasks and made up to volume with ultra-pure water. 2.0 ml of each sample was then pipetted into 100 ml plastic volumetric flasks containing ~10 ml ultra-pure water 2.0 ml trace-metal concentrated nitric acid, 1.0 ml trace-metal concentrated hydrochloric acid and 1.0 ml of the 50 ppm internal standard solution. The samples were made up to volume with ultra-pure water, mixed well and transferred to ICP sample tubes for analysis.

Solid state NMR analysis was performed by Dr. D. C. Apperley and Mr A. F. Markwell at the University of Durham using the following methods:

A solid-state ^{13}C spectrum of complex **2a** was recorded at 100.56 MHz using a Varian VNMRS spectrometer and a 6 mm (rotor o.d.) magic-angle spinning probe. It was obtained using cross-polarisation with a 5 s recycle delay, 3 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 6.8 kHz. 136 repetitions were accumulated. Spectral referencing was with respect to an external sample of neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm).

Carbon spectra from the immobilised complex **4c** and Wang resin swollen in $CDCl_3$ were obtained using the same instrument but with direct excitation (using a 90° pulse of duration 4.4 μs), proton decoupling a 0.5 s recycle and at a spin rate of 3 kHz. Spectral referencing is with respect to neat tetramethylsilane in both cases.

Synthesis



ESI Scheme 1 Synthesis of functionalised Cp* iridium and rhodium dimers

Synthesis of L2 ($C_5(CH_3)_4C_{14}H_{28}OH$)

Under a nitrogen atmosphere, lithium wire (2 g, 0.29 mol, washed with hexane) was added to anhydrous diethyl ether (100 ml) and the lithium suspension was vigorously stirred. 2-Bromo-2-butene (20 g, 0.15 mol, mixture of *cis* and *trans* isomers) was added to a dropping funnel and a small portion added to the reaction mixture to initiate the reaction. Diethyl ether (70 ml) was also added to the remaining 2-bromo-2-butene, which was then added at a rate that maintained a gentle reflux. After complete addition of 2-bromo-2-butene the reaction was stirred at r.t. for 2 hours. Pentadecanolide (16.8 ml, 0.06 mol) in diethyl ether (50 ml) was then added dropwise and the mixture stirred for 1 hour. The resulting mixture was poured into saturated NH_4Cl (aq) (300 ml) and after separating the ether layer, the aqueous layer was extracted with *tert*-butyl methyl ether (3 x 100 ml). The combined ether layers were washed with brine, dried over $MgSO_4$ and concentrated to *ca*. 100 ml. 10% aqueous HCl (150 ml) was added to the resulting concentrate and the biphasic mixture was stirred for 3h at r.t. After separating the ether layer, the aqueous layer was extracted with *tert*-butyl methyl ether (3 x 50 ml). The combined organic layers were washed with water (2 x 100 ml), dried over Na_2SO_4, and the solvent evaporated to leave a brown oil, which was purified through a large plug of silica (hexane/EtOAc 3:1 as eluent) gave the product **L2** as a pale yellow oil, which was a mixture of 3 regioisomers (15.7 g, 0.05 mol, 83%). **L2** was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 3.62 (t, ^3J = 6.6 Hz, 2 H, CH_2OH), 2.13-2.65 (m, 2 H, CH_2), 1.81 (s, 3 H, CH_3), 1.77 (s, 6 H, 2 × CH_3), 1.66-1.72 (m, 2 H, CH_2), 1.50-1.63 (m, 3 H, CH_2 and allyl CH), 1.20-1.40 (m, 20H, 10 × CH_2), 1.00 (2 × d, ^3J = 7.6 Hz, 3H, CH_3).

Synthesis of 1b ([Rh{η^5-$C_5(CH_3)_4C_{14}H_{28}OH$}$Cl_2$])

Under a nitrogen atmosphere, rhodium trichloride hydrate (0.10 g, 0.38 mmol) was added to 1-(14-hydroxytetradecyl)-2,3,4,5-tetramethylcyclopentadiene (**L2**) (0.26 g, 0.78 mmol) in MeOH (30 ml) and the mixture was heated under reflux for 15 h. After evaporation of the solvent, the powder was dissolved in a minimum amount of DCM and the product precipitated using hexane, collected by filtration and dried *in vacuo* to give the product as a red powder (0.18 g, 0.18 mmol, 47%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 3.64 (t, $^3J(^1H\text{-}^1H)$ = 6.6 Hz, 4 H, 2 × CH_2OH), 2.25 (m, $^1J(^1H\text{-}^1H)$ = 7.4 Hz,4 H, 2 × CH_2), 1.63 (s, 12 H, 4 × CH_3), 1.62 (s, 12 H, 4 × CH_3), 1.55 (m, 4 H, 2 × CH_2), 1.49 (br. s, 4H, 2 × CH_2), 1.20-1.40 (m, 40 H, 20 × CH_2). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) 96.3 (d, ^1J ($^{13}C\text{-}^{103}Rh$) = 9.8 Hz, Q), 94.5 (d, ^1J ($^{13}C\text{-}^{103}Rh$) = 9.3 Hz, Q), 94.1 (d, ^1J ($^{13}C\text{-}^{103}Rh$) = 9.3 Hz, Q), 63.1 (s, *C*H_2OH), 32.8 (s,CH_2), 29.7 (s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 29.4 (s, CH_2), 29.4 (s, CH_2), 29.4 (s, CH_2), 29.3 (s, CH_2), 27.5 (s, CH_2), 25.7 (s, CH_2), 9.4 (s, CH_3), 9.4 (s, CH_3). Anal. Calcd for $C_{46}H_{82}Cl_4O_2Rh_2$: C, 54.5; H, 8.1; Cl, 14.0%. Found: C, 54.0; H, 8.1; Cl, 13.8%.

Synthesis of 2b (Ir{η^5-$C_5(CH_3)_4C_{14}H_{28}OH$}$Cl_2$]$_2$)

Under a nitrogen atmosphere, iridium trichloride hydrate (0.10 g, 0.28 mmol) and sodium bicarbonate (0.02 g, 0.24 mmol) were added to degassed methanol (3 ml) in a 10 ml capacity microwave tube and the suspension was purged with nitrogen for 10 minutes. After adding 1-(14-hydroxytetradecyl)-2,3,4,5-tetramethylcyclopentadiene (**L2**) (0.19 g, 0.57 mmol), the suspension was purged for a further 5 minutes. The tube was then sealed and microwave heating was applied at 150 °C for 10 minutes. After effervescence from the solution had subsided, the tube was opened and the solution was diluted with DCM (20 ml), washed with water (10 ml), brine (10 ml), dried over Na_2SO_4 and the solvent evaporated. The resulting oily red residue was dissolved in DCM, precipitated with hexane and left overnight to yield an orange powder (0.14 g, 0.12 mmol, 42%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 3.64 (t, $^3J(^1H\text{-}^1H)$ = 6.6 Hz, 4 H, 2 × CH_2OH), 2.12 (t, $^3J(^1H\text{-}^1H)$ = 7.6 Hz, 4 H, 2 × CH_2), 1.80-2.04 (m, 4 H, 2 × CH_2), 1.61 (s, 12 H, 4 × CH_3), 1.59 (s, 12 H, 4 × CH_3), 1.50-1.58 (m, 4 H, 2 × CH_2), 1.20-1.45 (m, 40 H, 10 × CH_2). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 300 K) 88.2 (s, Q), 86.5 (s, Q), 86.4 (s, Q), 63.1 (s, *C*H_2OH), 32.8 (s,CH_2), 29.7 (s, CH_2), 29.6 (s, CH_2), 29.5 (s,

CH_2), 29.4 (s, CH_2), 29.3 (s, CH_2), 27.7 (s, CH_2), 25.7 (s, CH_2), 24.1 (s, CH_2) 9.4 (s, CH_3), 9.4 (s, CH_3). Anal. Calcd for $C_{46}H_{82}Cl_4O_2Ir_2$: C, 46.3; H, 6.9; Cl, 11.9%. Found: C, 46.7; H, 7.0; Cl, 10.9%.

Control reaction

A solution of 2,6-di-tert-butylpyridine (0.39 ml, 1.80 mmol) in dichloromethane (0.83 ml) was added to trifluoromethanesulfonic anhydride (0.15 ml, 0.89 mmol) in dichloromethane (0.91 ml) at -10 °C. A solution of $[IrCp^*Cl_2]_2$ (0.17 g, 0.22 mmol) in dichloromethane (1.00 ml) was slowly added over 30 minutes. After stirring for an hour, the solution was evaporated to dryness to remove excess trifluoromethanesulfonic anhydride. The residue was dissolved in dichloromethane (1.00 ml), and transferred to Wang resin (0.28 g, 0.42 mmol) and agitated. After 22 hours the suspension was filtered and washed with dichloromethane until the filtrate was colourless. The residue was added to H_2O (10 ml) and the slurry filtered. This was repeated with 1M HCl, H_2O and methanol respectively. The resulting dark red resin was repeatedly washed with dichloromethane/*iso*propanol (1:1, 10 ml) at 60°C for 1 hour until no colour was seen in solution, followed by acetone (3 × 10 ml) for 1 hour, filtered and dried overnight in a vacuum oven (0.25g)

Synthesis of 4a

A solution of 2,6-di-tert-butylpyridine (0.39 ml, 1.80 mmol) in dichloromethane (0.83 ml) was added to trifluoromethanesulfonic anhydride (0.15 ml, 0.89 mmol) in dichloromethane (0.91 ml) at -10 °C. A solution of **1a** (0.17 g, 0.22 mmol) in dichloromethane (1 ml) was slowly added over 30 minutes. After stirring for an hour, the solution was evaporated to dryness to remove excess trifluoromethanesulfonic anhydride, leaving a brown residue containing **3a**. The residue was redissolved in 1.06 ml DCM and 0.06 ml was transferred to an ampoule and evaporated for an NMR sample. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 4.56 (t,$^3J(^1H\text{-}^1H)$ = 6.1 Hz, 4 H, 2 × CH_2OTf), 2.25 (t, $^3J(^1H\text{-}^1H)$ = 7.0 Hz, 4 H, 2 × CH_2), 1.90-1.75 (m, 4 H, 2 × CH_2), 1.71 (br. s, 24 H, 8 × CH_3), 1.40-1.60 (m, 8 H, 4 × CH_2).

The resulting solution containing **3a** was transferred to Wang resin (0.28 g, 0.42 mmol) and agitated. After 22 hours the suspension was filtered and washed with dichloromethane until the filtrate was colourless. The residue was added to H_2O (10 ml) and the slurry filtered. This was repeated with 1M HCl, H_2O and methanol respectively. The resulting dark red resin was

repeatedly washed with dichloromethane/*iso*propanol (1:1, 10 ml) at 60°C for 1 hour until no colour was seen in solution, followed by acetone (3 × 10 ml) for 1 hour, filtered and dried overnight in a vacuum oven (0.28 g, 0.77 mmol Rh / g, 0.21 mmol Rh)

Synthesis of 4b

A solution of 2,6-di-tert-butylpyridine (0.39 ml, 1.80 mmol) in dichloromethane (0.84 ml) was added to trifluoromethanesulfonic anhydride (0.15 ml, 0.89 mmol) in dichloromethane (0.92 ml) at -10 °C. A solution of **1b** (0.23 g, 0.23 mmol) in dichloromethane (1 ml) was slowly added over 30 minutes. After stirring for an hour, the solution was evaporated to dryness to remove excess trifluoromethanesulfonic anhydride, leaving a brown residue containing **3b**. The residue was redissolved in 1.07 ml DCM and 0.07 ml was transferred to an ampoule and re-evaporated for an NMR sample. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 4.54 (t,$^{3}J(^{1}H\text{-}^{1}H)$ = 6.5 Hz, 4 H, 2 × CH_2OTf), 2.20 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.6 Hz, 4 H, 2 × CH_2), 1.89-1.75 (m, 4 H, 2 × CH_2), 1.71 (br. s, 12 H, 4 × CH_3), 1.69 (br. s, 12 H, 4 × CH_3), 1.35-1.60 (m, 8 H, 4 × CH_2), 1.20-1.40 (m, 36 H, 18 × CH_2).

The resulting solution containing **3b** was transferred to Wang resin (0.14 g, 0.21 mmol) and agitated. After 22 hours the suspension was filtered and washed with dichloromethane until the filtrate was colourless. The residue was added to H_2O (10 ml) and the slurry filtered. This was repeated with 1M HCl, H_2O and methanol. The resulting dark red resin was repeatedly washed with dichloromethane/*iso*propanol (1:1, 10 ml) at 60°C for 1 hour until no colour was seen in solution, followed by acetone (3 × 10 ml) for 1 hour, filtered and dried overnight in a vacuum oven (0.19 g, 0.64 mmol Rh / g, 0.12 mmol Rh)

Synthesis of 4c (wash regime A)

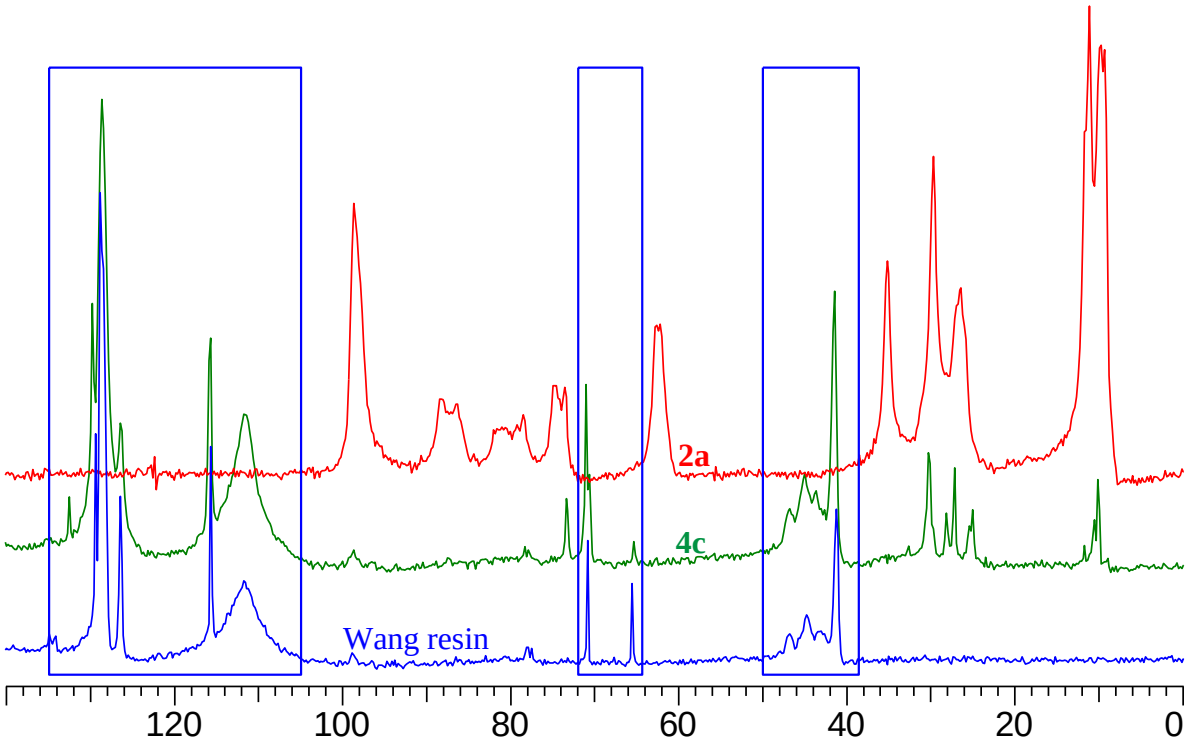
A solution of 2,6-di-tert-butylpyridine (0.37 ml, 0.17 mmol) in dichloromethane (0.78 ml) was added to trifluoromethanesulfonic anhydride (0.14 ml, 0.86 mmol) in dichloromethane (0.86 ml) at -10 °C. A solution of **2a** (0.20 g, 0.21 mmol) in dichloromethane (1.0 ml) was slowly added over 30 minutes. After stirring for 1 hour, a small portion was transferred to an ampoule and the solvent was removed to leave a brown residue containing **3c**. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 4.57 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.1 Hz, 4 H, 2 × CH_2OTf), 2.15 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.2

Hz, 4 H, 2 × CH_2), 1.80-1.96 (m, 4 H, 2 × CH_2), 1.70 (s, 12 H, 4 × CH_3), 1.70 (s, 12 H, 4 × CH_3), 1.45-1.48 (m, 8 H, 2 × CH_2).

The resulting solution of **3c** was evaporated to dryness to remove excess trifluoromethanesulfonic anhydride, The residue was dissolved in dichloromethane (1.0 ml) and transferred to Wang resin, pre-swelled in dichloromethane (0.14 g, 0.21 mmol) and agitated. After 22 hours the suspension was filtered and washed with dichloromethane until the filtrate was colourless. The residue was added to H_2O (10 ml) and the slurry filtered. This was repeated with 1M HCl, H_2O, methanol, and the resulting dark red resin was repeatedly washed with *iso*propanol (10 ml) at 60°C for 1 hour until no colour was seen in solution, filtered and dried overnight in a vacuum oven (0.19 g, 0.65 mmol Ir/g, 0.12 mmol Ir)

A solid state ^{13}C {^1H} NMR spectrum of **4c** shows the functionalised Cp* ligand to be present. The red line (top) is the functionalised Cp* iridium dichloride dimer, **2a**, with a 5 carbon alkyl chain between the hydroxyl and Cp ring. The peaks between 8 and 12 ppm correspond to the methyl peaks, and the peaks between 25 and 36 ppm correspond to the alkyl CH_2 peaks along with the peak at 62 ppm which corresponds to the CH_2OH carbon. The blue line (bottom) is blank Wang resin.

The green line (middle) is the immobilised functionalised Cp* iridium dichloride dimer, **4c**, with a 5 carbon alkyl chain between the oxygen and the Cp ring. The boxes highlight the peaks due to the Wang resin. The peaks between 10 and 12 ppm correspond to the methyl peaks of the immobilised functionalised Cp* ligand, and the peaks between 25 and 31ppm correspond to the alkyl CH_2 peaks along with the peak at 73 ppm which corresponds to the CH_2OR carbon.



Synthesis of 4c (wash regime B)

A solution of 2,6-di-tert-butylpyridine (5.28 ml, 24.8 mmol) in dichloromethane (11.22 ml) was added to trifluoromethanesulfonic anhydride (2.07 ml, 12.3 mmol) in dichloromethane (12.25 ml) at -10 °C. A solution of **2a** (2.90 g, 3.08 mmol) in dichloromethane (14.50 ml) was slowly added over an hour. After stirring for 2 hours, 0.69 ml of the solution was transferred to an ampoule and the solvent was removed to leave a brown residue containing **3c** (see above for NMR)

The resulting solution of **3c** was evaporated to dryness to remove excess trifluoromethanesulfonic anhydride, The residue was dissolved in dichloromethane (15 ml) and transferred to Wang resin (4.0 g, 6.0 mmol) and agitated. After 22 hours the suspension was filtered and washed with dichloromethane until the filtrate was colourless. The residue was added to H_2O (200 ml) and the slurry filtered. This was repeated with 1M HCl, H_2O and methanol. The resulting dark red resin was repeatedly washed with *iso*propanol (200 ml) at 60°C for 1 hour until no colour was seen in solution, filtered and dried overnight in a vacuum oven (5.9 g). 100 mg of the resulting dark red resin was repeatedly washed with dichloromethane/*iso*propanol (1:1, 10 ml) at 60°C for 1 hour until no colour was seen in

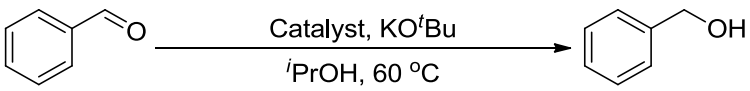
solution, followed by acetone (3 × 10 ml) for 1 hour, filtered and dried overnight in a vacuum oven (0.61 mmol Ir/g).

Synthesis of 4d

A solution of ditertiarybutylpyridine (5.28 ml, 24.8 mmol) in dichloromethane (11.22 ml) was added to trifluoromethanesulfonic anhydride (2.07 ml, 12.3 mmol) in dichloromethane (12.25 ml) at -10 °C. A solution of **2b** (3.81 g, 3.19 mmol) in dichloromethane (14.5 ml) was slowly added over an hour. After stirring for an hour, the solution was evaporated to dryness to remove excess trifluoromethanesulfonic anhydride, leaving a brown residue containing **3d**. The residue was redissolved in 14.5 ml DCM and 0.24 ml was transferred to an ampoule and re-evaporated for an NMR sample. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K) 4.52 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.4 Hz, 4 H, 2 × CH_2OTf), 2.26 (t, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.5 Hz, 4 H, 2 × CH_2), 1.86-1.75 (m, 4 H, 2 × CH_2), 1.69 (s, 12 H, 4 × CH_3), 1.68 (s, 12 H, 4 × CH_3)1.35-1.50 (m,8 H, 4 × CH_2), 1.24 (br. s, 36 H, 18 × CH_2).

The resulting solution containing **3d** was transferred to Wang resin (4.0 g, 6.0 mmol) and agitated. After 22 hours the suspension was filtered and washed with dichloromethane until the filtrate was colourless. The residue was added to H_2O (200 ml) and the slurry filtered. This was repeated with 1M HCl, H_2O and methanol. The resulting dark red resin was repeatedly washed with *iso*propanol (200 ml) at 60°C for 1 hour until no colour was seen in solution, filtered and dried overnight in a vacuum oven (5.6 g, 0.48 mmol Ir/g, 2.7 mmol Ir). A small portion of the resulting dark red resin was repeatedly washed with dichloromethane/*iso*propanol (1:1, 10 ml) at 60°C for 1 hour until no colour was seen in solution, followed by acetone (3 × 10 ml) for 1 hour, filtered and dried overnight in a vacuum oven (0.47 mmol Ir/g)

General catalytic reduction of benzaldehyde



ESI Scheme 2 Catalytic reduction of benzaldehyde to benzyl alcohol

Homogeneous (1a, 1b, 2a, 2b, $[RhCp^*Cl_2]_2$ and $[IrCp^*Cl_2]_2$)

To the selected metal dimer (0.005 mmol) in a carousel tube was added potassium *tert*-butoxide (1.00 mg, 0.01 mmol) and *iso*-propanol (10 ml). The mixture was stirred at 60°C for one hour, then benzaldehyde (0.10 ml, 1.0 mmol) was added. The mixture was stirred at 60°C and the reaction was monitored by GC at intervals of 0, 2, 4, and 24h.

Immobilised (4a-4d)

From ICP results:

0.057 g of **4a** = 0.044 mmol Rh (8.8 mol% Rh)

0.057 g of **4b** = 0.037 mmol Rh (7.3 mol% Rh)

0.057 g of **4c** (wash regime A) = 0.037 mmol Ir (7.4 mol% Ir)

0.057 g of **4c** (wash regime B) = 0.035 mmol Ir (6.9 mol% Ir)

0.057 g of **4d** = 0.027 mmol Ir (5.3 mol% Ir)

To the selected immobilised resin (0.057 g) in a carousel tube was added potassium *tert*-butoxide (0.50 mg, 0.004 mmol) and *iso*-propanol (5 ml). The mixture was stirred at 60°C for one hour, then benzaldehyde (0.05 ml, 0.5 mmol) was added. The mixture was stirred at 60°C and the reaction was monitored by GC at intervals of 0, 2, 4, 24 and 48h. Further runs were conducted by decanting the solution, and recharging the resin with potassium *tert*-butoxide (0.5 mg, 0.004 mmol), *iso*-propanol (5 ml) and benzaldehyde (0.05 ml, 0.5 mmol) immediately. After 35 runs resin **4c** was recovered by filtering, washing with dichloromethane and dried using a vacuum oven (0.035 g, 0.034 mmol Ir).

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