Iridium complexes of chiral diamines containing carbon and nitrogen stereocentres: synthesis, structure and evaluation as transfer hydrogenation catalysts†

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Received (in Durham, UK) 24th July 2008, Accepted 7th November 2008
First published as an Advance Article on the web 24th November 2008
DOI: 10.1039/b812699b

Novel Rh(III) and Ir(III) complexes of a chiral diamine ligand have been synthesised and structurally characterised. Both complexes were formed as a single diastereomeric species with a single configuration at nitrogen. Ir complexes of the chiral diamine were found to be active in the asymmetric transfer hydrogenation of bulky ketones. Excellent conversions (up to 100%) and moderate enantioselectivities (up to 60%) were obtained in the asymmetric reduction of 2,2-dimethylpropiophenone.

Introduction

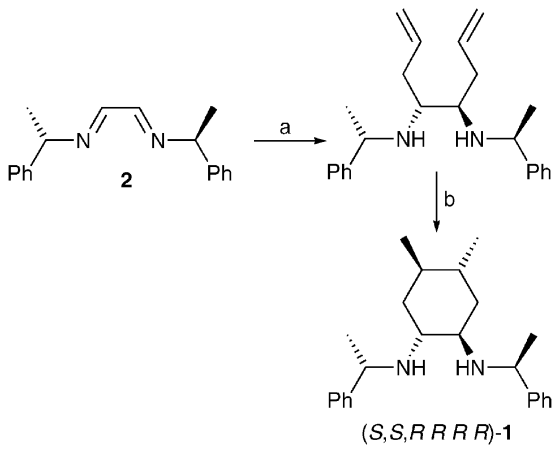
Chiral nitrogen ligands have many important applications in asymmetric catalysis.[1] A less studied class of nitrogen ligands are those that have stereogenic nitrogen centres.[2] Nitrogen stereocentres are normally configurationally unstable, but upon complexation to a metal, this rapid stereochemical inversion process can be frozen. In the case of metal complexes that contain other non-labile stereocentres, one configuration at nitrogen can be favoured over the other. Thus chiral diamines containing C stereocentres and N stereocentres can form transition metal complexes with a single defined and stable nitrogen stereochemistry. There is even an example where the enantiomers of a complex containing only nitrogen stereocentres were resolved and studied.[3] If the nitrogen stereocentres freeze to a single configuration on co-ordination to the metal centre and present a C_2 symmetric or *pseudo* C_2 symmetric environment, it can be envisaged that such metal complexes would be capable of high levels of enantiocontrol reminiscent of the high stereocontrol possible with C_2 symmetric P-chiral diphosphines.[4] The most readily available bidentate nitrogen ligands that might display these characteristics are bis-secondary amines derived from chiral diimines. One potential ligand that attracted our attention was the known compound **1**.[5,6] Compound **1** has been reported as an intermediate *en route* to the corresponding bis-primary amine but has not, to the best of our knowledge, ever been used as a ligand. In this paper we report the synthesis and structure of a rhodium and an iridium complex of this ligand and present encouraging results demonstrating the potential of this ligand class in asymmetric transfer hydrogenation of some bulky ketones that are generally considered to be challenging substrates.

Results and discussion

Synthesis of complexes of ligand 1

Ligand **1** was prepared by addition of allyl magnesium bromide to diimine **2** followed by reductive cyclisation with *n*-butyl magnesium bromide and Cp_2ZrCl_2 (Scheme 1), as described previously.[6]

The ligand forms complexes with rhodium and iridium precursors. Reaction with $[Ir(COD)Cl]_2$ or $[Rh(COD)Cl]_2$ leads to a species active for the transfer hydrogenation of ketones (see below); however, a stable complex could not be isolated cleanly, even when the complex was first treated with $AgBF_4$ prior to addition of the ligand. On the other hand, treatment of **1** with $[RhCp^*Cl_2]_2$ followed by $AgBF_4$ led to clean formation of complex **3**, isolated as a red solid in 87% yield (Scheme 2).



Scheme 1 *Conditions:* (a) allylMgBr, THF, −78 °C to r.t.; (b) *n*-BuMgBr (5 equiv.), Cp_2ZrCl_2 (20 mol%) Et_2O, r.t.

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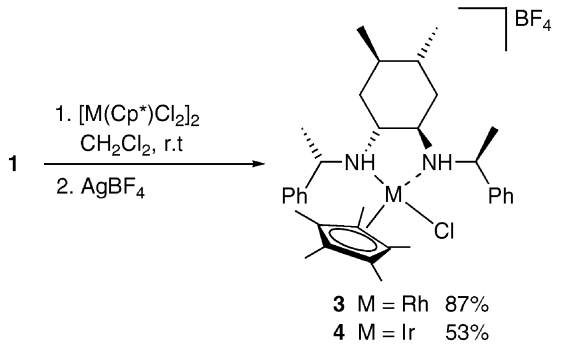
† Electronic supplementary information (ESI) available: PDF file containing bond lengths and distances for the X-ray structure determination. CCDC reference number 708595. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b812699b



Scheme 2 Synthesis of bidentate Rh and Ir complexes of ligand **1**.

Similarly, $[IrCp^*Cl_2]_2$ was converted into complex **4**, which was recrystallised by slow diffusion of hexane into a solution of **4** in $CHCl_3$ to give a 53% yield of pure yellow–orange needles. Both complexes were characterised by optical rotation, IR, ^1H, ^{13}C, ^{19}F NMR spectroscopy and mass spectrometry. The X-ray crystal structure determination unambiguously confirmed the structure of **4** in Scheme 2 (Fig. 1). Upon complexation only a single stereoisomer was observed in the solid state, and there are no signs of diastereomers in solution. The nitrogen stereocentres are thus frozen into a single *S* configuration upon co-ordination to the metal centre. This homochirality at the N centres is in contrast with the heterochirality observed in similar complexes. Jones recently described two Rh(I) complexes of *N*,*N*-dibenzyl-(1*R*,2*R*)-diaminocyclohexane and *N*,*N*-diferrocenyl-(1*R*,2*R*)-diaminocyclohexane where the N atoms in both examples acquired opposite absolute configurations and a *syn* relationship between the nitrogen substituents.[7] Relatively strong heteronuclear hydrogen bonding interactions N(1)H···F between the amine group and the BF_4^- anion are also observed, with an H···F distance of 2.09 Å. X-Ray analysis of Rh complex **3** gave a structure similar to that of Ir complex **4**.[8]

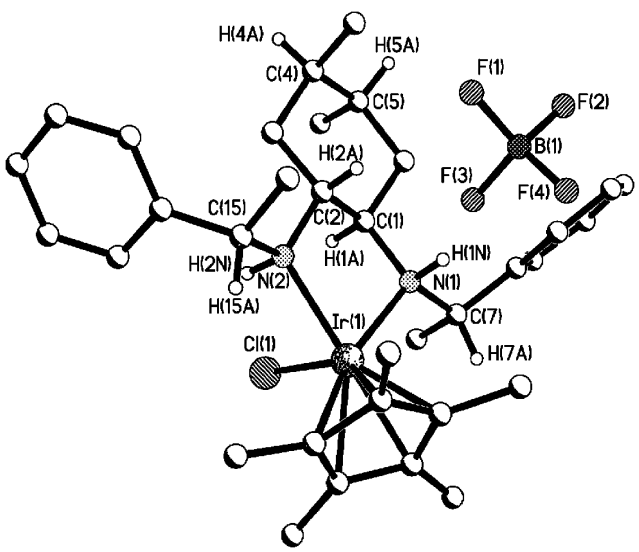


Fig. 1 X-Ray structure of Ir complex **4**. Key bond lengths (Å): Ir(1)–N(1) = 2.179(3); Ir(1)–N(2) = 2.199(4); Ir(1)–Cl(1) = 2.4187(11).

Transfer hydrogenation with complexes of ligand 1

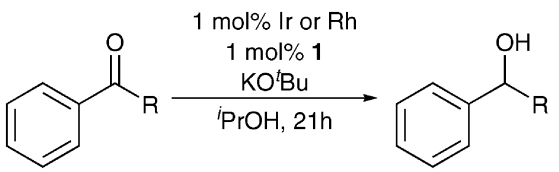
Transfer hydrogenation of ketones is an extremely widely studied reaction.[9] Although pressure hydrogenation is preferred at large scale, transfer hydrogenation can have a niche for certain types of substrates that are incompatible with hydrogen gas. In addition, at laboratory scale, the greater convenience of transfer hydrogenation makes it the preferred reaction. Many transfer hydrogenation catalysts are based on ruthenium complexes,[9,10] although there are also notable examples of rhodium and iridium catalysts.[9,11] We elected to compare Ru, Rh and Ir precursors with ligand **1**, with the aim of understanding more about the ideal metal–ligand system for the reaction and to discover a catalyst that could hydrogenate challenging ketones such as bulky substrate 2,2-dimethyl-propiophenone.[12,13] The results obtained for the transfer hydrogenation of acetophenone by various catalysts and reaction conditions are shown in Table 1 (Scheme 3, R = Me).

When Rh was used with ligand **1**, only traces of product were obtained (entries 1 and 2). On the other hand, when $[Ru(C_6H_6)Cl_2]_2$ was used as metal precursor, the desired 1-phenyl-ethanol was formed, but with low enantioselectivity (32%) (entry 3). Increasing the temperature to 55 °C produced an increase in the reaction rate to almost full conversion with no detrimental effect on the ee (34%) (entry 4). The species prepared *in situ* from **1** and $[IrCp^*Cl_2]_2$ showed the same level of enantioselectivity (entries 5 and 6), while the related isolated complex **4** gave lower ee's, although essentially full conversion was obtained (entries 7 and 8). $[Ir(COD)Cl]_2$ gave the best ee (53%) and the highest conversion (92%) (entries 9–11) of the metal precursors employed with ligand **1**. Therefore, iridium was the metal of choice to use in reactions with other more challenging substrates.

Table 1 Transfer hydrogenation of acetophenone using various catalyst precursors and ligand **1**

Entry	Metal complex	KO^{t}Bu/ mol%	*T*/°C	Conv./%[a]	e.e./%[b]
1	$[RhCp^*Cl_2]_2$	2.5	RT	N/A	1
2	$[Rh(COD)Cl]_2$	2.5	RT	N/A	2
3	$[Ru(C_6H_6)Cl_2]_2$	2.5	RT	32	32 ((*S*)-(−))
4	$[Ru(C_6H_6)Cl_2]_2$	5	55	92	34 ((*S*)-(−))
5	$[IrCp^*Cl_2]_2$	2.5	55	70	31 ((*R*)-(+))
6	$[IrCp^*Cl_2]_2$	5	55	67	29 ((*R*)-(+))
7	**4**	2.5	55	97	6 ((*R*)-(+))
8	**4**	5	55	97	14 ((*S*)-(−))
9	$[Ir(COD)Cl]_2$	2.5	RT	33	53 ((*S*)-(−))
10	$[Ir(COD)Cl]_2$	2.5	55	92 (81)	49 ((*S*)-(−))
11	$[Ir(COD)Cl]_2$	5	55	92	33 ((*S*)-(−))

[a] % Conversion, determined by ^1H NMR (% isolated yield following chromatography on silica gel). [b] Determined by HPLC on ChiralPak AD or OD-H column. Absolute configuration and direction of optical rotation are shown in parentheses.



Scheme 3 Transfer hydrogenation of ketones using ligand **1**.

Table 2 Transfer hydrogenation of various ketones using iridium complexes of ligand **1**[a]

Entry	R	Metal complex	KO^{t}Bu/mol%	Conv./%[b]	Yield/%[c]	e.e./%[d]
1	*i*-Pr	$[IrCp^*Cl_2]_2$	2.5	19		17 ((*S*)-(−))
2	*i*-Pr	$[IrCp^*Cl_2]_2$	5	22		31 ((*S*)-(−))
3	*i*-Pr	$[Ir(COD)Cl]_2$	2.5	61	34	53 ((*S*)-(−))
4	*i*-Pr	$[Ir(COD)Cl]_2$	5	53		40 ((*S*)-(−))
5	Cy	$[IrCp^*Cl_2]_2$	2.5	17		26 ((*S*)-(−))
6	Cy	$[IrCp^*Cl_2]_2$	5	15		22 ((*S*)-(−))
7	Cy	$[Ir(COD)Cl]_2$	2.5	80	54	58 ((*S*)-(−))
8	Cy	$[Ir(COD)Cl]_2$	5	78	57	49 ((*S*)-(−))
9	*t*-Bu	$[IrCp^*Cl_2]_2$	2.5	18		26 ((*S*)-(−))
10	*t*-Bu	$[IrCp^*Cl_2]_2$	5	22		26 ((*S*)-(−))
11	*t*-Bu	$[Ir(COD)Cl]_2$	2.5	100	81	60 ((*S*)-(−))
12	*t*-Bu	$[Ir(COD)Cl]_2$	5	100	74	47 ((*S*)-(−))

[a] All reactions were carried out at 55 °C. [b] % Conversion, determined by ^{1}H NMR. [c] % Isolated yield following chromatography on silica gel, eluting with CH_2Cl_2. [d] Determined by HPLC on ChiralPak AD or OD-H column. Absolute configuration and direction of optical rotation are shown in parentheses.

In the case of acetophenone, changing the metal precursor from $[Ir(COD)Cl]_2$ to $[IrCp^*Cl_2]_2$ resulted in a change of the configuration of the alcohol product from *S* to *R*, even though the same ligand configuration was used (entries 5 and 10, 6 and 11). Such a reversal in the sense of asymmetric induction, confirmed by both optical rotation and HPLC, was not observed for other substrates (Table 2). Although this is relatively unusual, the pseudo-octahedral Ir(III) complex presents a very different structure to the square planar Ir complex. Such a phenomenon has been observed in other systems.[14] Surprisingly, with complex **4**, different configurations of the product were obtained at different concentrations of KO^{t}Bu; however, in these cases the enantioselectivity was low. In any case, the effect of different catalyst systems on the absolute configuration remains to be explored further with other substrates.

The $[Ir(COD)Cl]_2$–**1** catalyst system (Scheme 3) was screened with additional substrates at 55 °C, as shown in Table 2. The lower concentration of base generally seems to give higher enantioselectivities while having only a relatively minor effect on the conversion. Interestingly, the challenging substrates with bulkier substituents (R = Cy, *t*-Bu) gave the highest enantioselectivities, with moderate to excellent conversion and ee's up to 60% (entry 11). The species prepared *in situ* from **1** with $[IrCp^*Cl_2]_2$, which is related to isolated complex **4**, was less effective than the species prepared from **1** with $[Ir(COD)Cl]_2$ (Table 2). While a stable species could not be isolated from ligand **1** and $[Ir(COD)Cl]_2$, the reasonably high enantioselectivities obtained suggest that the active complex presents a single well defined chiral environment.

Conclusions

In conclusion, a new iridium complex of a C_2 symmetric chiral diamine has been synthesised. The complex formed was homochiral at the N centres and was formed as a single diastereomer. The complex exhibits good activity and moderate enantioselectivity for the transfer hydrogenation of some bulky ketones.

Experimental

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and degassed prior to use. Other reagents were purchased commercially and used as received. Ligand **1** was prepared as described previously.[6] Solvents were removed by rotary evaporation on a Heidolph labrota 4000. Flash column chromatography was performed on Davisil silica gel Fluorochem 60 Å, particle size 35–70 μm. HPLC analysis was determined on a Varian Prostar operated by Galaxie workstation software equipped with ChiralPak AD or OD-H columns. NMR spectra were recorded on Bruker Avance 300 and 400 instruments. Proton chemical shifts are referenced to internal residual solvent protons. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of the above. All spectra were recorded at room temperature and the solvent for a particular spectrum is given in parentheses. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Fluorine chemical shifts are reported relative to $CFCl_3$. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 Spectrum GX FT-IR system. Mass spectrometry was performed on a Waters Micromass GCT (time of flight) fitted with lockspray for accurate mass (ESI) or GCT (CI). Optical rotations were measured on a Perkin Elmer 341 polarimeter using a 1 ml cell with a 1 dm path length at 20 °C using the sodium D-line.

Complex 3

A solution of ligand **1** (145 mg, 0.41 mmol) in methylene chloride (2 mL) was added to a solution of $[Rh(Cp^*)Cl_2]_2$ (127 mg, 0.20 mmol) in methylene chloride (2 mL) in a Schlenk flask under a nitrogen atmosphere. The reaction mixture was stirred at ambient temperature for 45 min, after which $AgBF_4$ (79 mg, 0.41 mmol) and methylene chloride (1 mL) were added, and the reaction mixture was stirred for an additional 30 min. The reaction mixture was filtered to remove AgCl, and the filtrate was concentrated under vaccuum to give complex **3** as a red solid (253 mg, 87%). Mp 110–112 °C (decomp.); $[\alpha]_D^{20}$ −131.3 (*c* 0.16, $CHCl_3$); IR ($CDCl_3$, cm^{-1}) 3250, 3214, 3063, 2961, 1602, 1471, 1448, 1381, 1201 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.63 (3H, d, *J* 7.1 Hz, CH_3), 0.70–1.37 (6H, m, $CH_2CHCHCH_2$), 0.89 (3H, d, *J* 7.2 Hz, CH_3), 1.59 (15H, s, $C_5(CH_3)_5$), 1.78 (3H, d, *J* 7.2 Hz, CH_3), 1.85 (3H, d, *J* 7.2 Hz,

CH_3), 2.69–2.80 (1H, m, C*H*), 3.23–3.45 (1H, m, C*H*), 4.63 (1H, d, *J* 10.9 Hz, N*H*), 4.73–4.81 (2H, m, 2×C*H*), 5.77 (1H, d, *J* 10.7 Hz, N*H*), 7.16–7.45 (8H, m, Ar *H*), 7.57–7.60 (2H, m, Ar *H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 9.5 ($C_5(CH_3)_5$), 13.9 (CH_3), 16.7 (CH_3), 19.5 (CH_3), 19.6 (CH_3), 34.2 (*C*H), 34.5 (*C*H), 35.2 (CH_2), 37.5 (CH_2), 57.3 (*C*H), 58.3 (*C*H), 59.6 (*C*H), 62.4 (*C*H), 96.5 (d, $^1J_{C,Rh}$ 8.3 Hz, 5×C_5Me_5), 126.3 (Ar *C*), 126.5 (Ar *C*), 128.0 (Ar *C*), 128.4 (Ar *C*), 129.6 (Ar *C*), 129.7 (Ar *C*), 143.9 (Ar *C*), 144.4 (Ar *C*); ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ = −149.6 (s); MS (FAB) *m*/*z*: 623.3 (43%), 588.3 (5), 547.0 (4), 351.2 (100), 272.8 (14), 230.0 (15); found (FAB) 623.2631 ([M − BF_4]$^+$), $C_{34}H_{49}ClN_2Rh$ requires 623.2634. X-Ray quality crystals were grown by slow diffusion of hexane into a $CHCl_3$ solution of **3**.

Complex 4

A Schlenk flask under a nitrogen atmosphere was charged with ligand **1** (40 mg, 0.114 mmol) and [Ir(Cp*)Cl_2]$_2$ (43 mg, 0.05 mmol). Methylene chloride (2 mL) was added, and the reaction mixture was stirred at ambient temperature for 90 min. $AgBF_4$ (26 mg, 0.13 mmol) was added, and the reaction mixture was stirred for an additional 15 min. The reaction mixture was filtered to remove AgCl, and the filtrate was concentrated under vacuum to give complex **4** as a yellow solid, which was recrystallised by slow diffusion of hexane into a $CHCl_3$ solution to yield X-ray quality crystals (46 mg, 53%). $[\alpha]_D^{20}$ −42.8 (*c* 0.025, $CHCl_3$); IR (KBr, cm^{-1}) 3232, 3199, 3058, 3025, 2957, 2918, 1625, 1499, 1471, 1448, 1379, 1311, 1284 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.68 (3H, d, *J* 7.3 Hz, CH_3), 0.77–1.33 (6H, m, $CH_2CHCHCH_2$), 0.92 (3H, d, *J* 7.3 Hz, CH_3), 1.53 (15H, s, $C_5(CH_3)_5$), 1.79 (3H, d, *J* 7.4 Hz, CH_3), 1.80 (3H, d, *J* 7.6 Hz, CH_3), 3.02–3.12 (1H, m, C*H*), 3.31–3.40 (1H, m, C*H*), 4.77–4.87 (2H, m, 2×C*H*), 4.98 (1H, d, *J* 11.2 Hz, N*H*), 6.22 (1H, d, *J* 10.8 Hz, N*H*), 7.23–7.58 (10H, m, Ar *H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 8.8 ($C_5(CH_3)_5$), 13.2 (CH_3), 16.3 (CH_3), 19.1 (CH_3), 19.2 (CH_3), 34.1 (*C*H), 34.3 (CH_2), 34.3 (*C*H), 36.8 (CH_2), 57.9 (*C*H), 59.5 (*C*H), 67.7 (*C*H), 63.8 (*C*H), 87.8 (5×C_5Me_5), 125.9 (Ar *C*), 126.2 (Ar *C*), 127.8 (Ar *C*), 128.2 (Ar *C*), 129.3 (Ar *C*), 129.4 (Ar *C*), 142.8 (Ar *C*), 143.7 (Ar *C*); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = −149.4 (s); MS (ES) *m*/*z*: 713.3 (10%), 711.3 (5), 677.4 (100), 675.4 (50), 351.4 (40), 113.0 (5), 59.2 (4); found (ES) 711.3178 ([M − BF_4]$^+$), $C_{34}H_{49}Cl^{191}IrN_2$ requires 711.3185.

X-Ray crystallography of (*S*$_{N1}$,*S*$_{N2}$,*R*$_{C1}$,*R*$_{C2}$,*R*$_{C4}$,*R*$_{C5}$, *S*$_{C7}$,*S*$_{C15}$)-(−)-4. $C_{36}H_{51}BCl_7F_4N_2Ir$, *M* = 1038.95, orthorhombic, space group *P*2(1)2(1)2(1), *Z* = 4, *a* = 13.5451(7), *b* = 17.3548(10), *c* = 18.4163(10) Å, α = 90°, β = 90°, γ = 90°, *V* = 4329.2(4) Å^3, ρ_{calcd} 1.594 mg m^{-3}, μ(Mo*K*α) = 3.561 mm^{-1} (max./min. transmission 1.0000/0.7678), *T* = 93(2) K. Of 28 479 measured data, 7939 were unique (R_{int} = 0.0423) and 7663 observed [$I > 2\sigma(I)$] to give *R* = 0.0290, w*R*2 = 0.0570. Data were collected using a Rigaku MM007 High brilliance RA generator (Mo*K*α radiation, confocal optics) and Saturn 70 CCD system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. Hydrogen atoms bound to carbon were idealised. Structural refinements were performed with full-matrix least-squares based on F^2 by using SHELXTL.[15] (Chloroform molecules are omitted in Fig. 1 for clarity.)

Typical transfer hydrogenation procedure

A Schlenk tube was charged with the metal complex (0.005 mmol complex, corresponding to 0.01 mmol Ir or Rh) and put under nitrogen atmosphere. Isopropanol (1 mL) and a solution of ligand **1** in isopropanol (0.066 M; 0.150 mL, 0.01 mmol) were added *via* syringe. The reaction mixture was stirred at 80 °C for 30 min. After cooling to 55 °C, additional isopropanol (3.3 or 3.1 mL) and a solution of KO^{t}Bu (0.10 M; 0.25 mL, 0.025 mmol or 0.5 mL, 0.05 mmol) were added followed by ketone (1 mmol). The reaction mixture was stirred at 55 °C for 21 hours. After cooling to room temperature, a small aliquot of the reaction mixture was filtered through a plug of alumina, eluting with 30% isopropanol–70% hexane and analysed by HPLC. The remaining reaction mixture was diluted with HCl (aq), extracted three times with CH_2Cl_2, dried over $MgSO_4$ and concentrated to a yellow oil, which was chromatographed on silica gel eluting with CH_2Cl_2.

1-Phenyl-ethanol

^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.43 (3H, d, *J* 6.5 Hz, CH_3), 1.63 (1H, broad s, O*H*), 4.84 (1H, q, *J* 6.4, C*H*OH), 7.18–7.33 (5H, m, Ar *H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 25.19 (CH_3), 70.46 (*C*HOH), 125.41 (Ar *C*), 127.51 (Ar *C*), 128.54 (Ar *C*), 145.83 (Ar *C*). Enantioselectivity determined by HPLC, ChiralPak OD-H, 0.5 mL min^{-1}, 95 : 5 hexane–2-propanol. Retention times: 17.4 min (*R*)-(+)-enantiomer and 21.2 min (*S*)-(−)-enantiomer.

2-Methyl-1-phenylpropan-1-ol

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.73 (3H, d, *J* 6.8 Hz, diastereotopic CH_3), 0.93 (3H, d, *J* 6.6 Hz, diastereotopic CH_3), 1.63 (1H, broad s, O*H*), 1.89 (1H, octet, *J* 6.7, C*H*Me$_2$), 4.30 (1H, d, *J* 6.9, C*H*OH), 7.16–7.21 (5H, m, Ar *H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.25 (CH_3), 19.03 (CH_3), 35.29 (*C*HMe$_2$), 80.09 (*C*HOH), 126.58 (Ar *C*), 127.45 (Ar *C*), 128.22 (Ar *C*), 143.70 (Ar *C*). Enantioselectivity determined by HPLC, ChiralPak OD-H, 0.5 mL min^{-1}, 98 : 2 hexane–2-propanol. Retention times: 27.6 min (*S*)-(−)-enantiomer and 30.4 min (*R*)-(+)-enantiomer.

2,2-Dimethyl-1-phenylpropan-1-ol

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.83 (9H, s, 3×CH_3), 1.97 (1H, broad s, O*H*), 4.28 (1H, s, C*H*OH), 7.19 (5H, m, Ar *H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.93 (CH_3), 35.64 (*C*Me$_3$), 82.42 (*C*HOH), 127.30 (Ar *C*), 127.57 (Ar *C*), 127.61 (Ar *C*), 142.20 (Ar *C*). Enantioselectivity determined by HPLC, ChiralPak OD-H, 1 mL min^{-1}, 99.5 : 0.5 hexane–2-propanol. Retention times: 10.5 min (*S*)-(−)-enantiomer and 13.6 min (*R*)-(+)-enantiomer.

Cyclohexyl(phenyl)methanol

^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.8–1.9 (11H, m, C_6H_{11}), 1.91 (1H, broad s, O*H*), 4.34 (1H, d, *J* 7.5, C*H*OH), 7.2–7.3 (5H, m, Ar *H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 26.02

(CH_2), 26.10 (CH_2), 26.43 (CH_2), 28.83 (CH_2), 29.32 (CH_2), 44.97 (*C*H), 79.42 (*C*HOH), 126.64 (Ar *C*), 127.43 (Ar *C*), 128.20 (Ar *C*), 143.63 (Ar *C*). Enantioselectivity determined by HPLC, ChiralPak AD, 0.5 mL min^{-1}, 98 : 2 hexane–2-propanol. Retention times: 23.5 min (*S*)-(−)-enantiomer and 26.5 min (*R*)-(+)-enantiomer.

Acknowledgements

The authors thank the EPSRC for an equipment grant, and for the use of the National mass spectrometry service. Mrs C. Horsborough and Mrs M. Smith are also thanked for technical assistance. The authors thank the Donors of the American Chemical Society Petroleum Research Fund and Washington and Lee University (Glenn Grant) for support of this work. The authors also wish to thank Johnson Matthey for the loan of precious metal salts.

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