

Efficient regio- and diastereo-controlled synthesis of 1,1'- and 1,1',2,2'-functionalised ferrocenes and the formation of 2-oxa[3]ferrocenophanes

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Michael A. Carroll,^a Andrew J. P. White,^b David A. Widdowson^{*a} and David J. Williams^b

^a Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY. E-mail: d.widdowson@ic.ac.uk

^b Chemical Crystallography Laboratory, Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY

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A synthesis of a C_2 symmetric 1,1',2,2'-tetrasubstituted ferrocene system is described. The route involves the reduction of ferrocenyl carbonyl compounds which give access to a range of alcohols, alkenes, alkanes, ethers and 2-oxa[3]ferrocenophanes depending on the precise conditions used.

Introduction

Since its discovery ferrocene **1** and its derivatives have seen widespread application in a number of areas,¹ most notably in electroactive materials,^{2,3} and asymmetric catalysis. Of particular note are 1,1',2,2'-tetrasubstituted systems (Fig. 1), which may possess C_2 symmetry,⁴⁻¹⁰ as these have been shown to be effective ligands in a range of metal catalysed asymmetric processes such as hydrogenation,¹¹⁻¹⁶ allylic substitution,¹⁷⁻²⁰ and cross-coupling reactions.²¹ It is the preparation and application of the much less common C_2 symmetric ferrocene based ligands, which possess only the elements of planar chirality, that we address here.^{22,23}

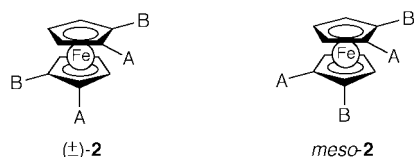
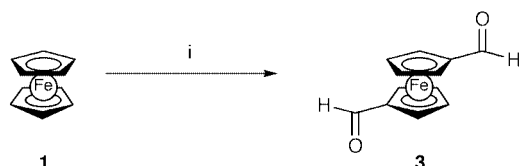


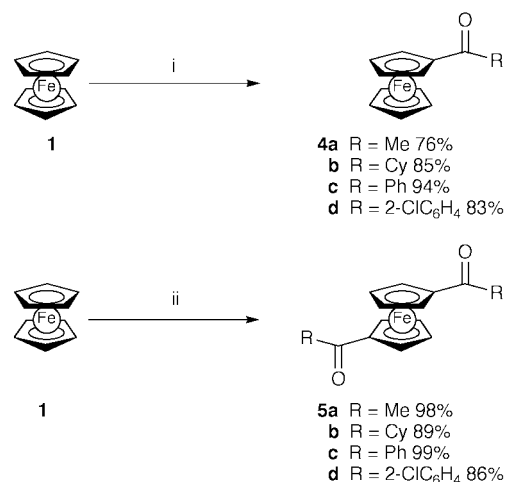
Fig. 1 1,1',2,2'-Tetrasubstituted ferrocenes.

The ability to selectively substitute both of the η^5 -cyclopentadienyl rings in the ferrocene system, rather than disubstitute a single ring, is an important initial step in accessing systems of this type. The desired 1,1'-substitution pattern may be obtained from the dilithiation of ferrocene using butyllithium–TMEDA in hexane or ether²⁴⁻²⁶ and application of this technique is our preferred route to 1,1'-diformylferrocene **3** (Scheme 1).^{22,27}



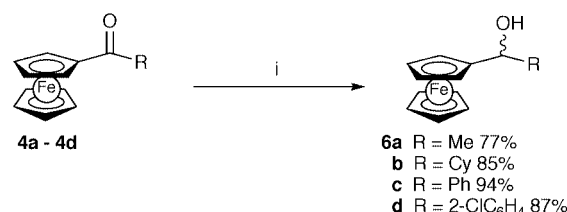
Scheme 1 Reagents and conditions: (i) BuLi, TMEDA, ether, DMF, 77%.

1,1'-Ferrocenyl diketones may also be accessed using this methodology, however Friedel–Crafts chemistry provides a more convenient alternative^{28,29} and we prepared a range of ferrocenyl ketones and diketones in excellent yield (Scheme 2).



Scheme 2 Reagents and conditions: (i) RCOCl (1.1 equiv.), AlCl₃ (1.1 equiv.), DCM, rt, 16 h; (ii) RCOCl (2.2 equiv.), AlCl₃ (2.2 equiv.), DCM, rt, 16 h.

With the 1,1'-functionality established, the next step towards the synthesis of the target 1,1',2,2'-tetrasubstituted system was the conversion of the carbonyl moiety into a group suitable for the directed metallation of the *ortho*-positions of the ferrocene system. An ether substituent, rather than a more conventional tertiary amine, was chosen for this role³⁰ since it may be envisaged as being derived from the carbonyl compounds above. Trial reduction of the monoketones with LiAlH₄ in THF, NaBH₄ or LiBH₄ in methanol gave the target alcohols as expected (Scheme 3). However the isolation of vinylferrocene **7**



Scheme 3 Reagents and conditions: (i) LiAlH₄, THF, rt, 16 h; NaBH₄ or LiBH₄, MeOH, rt, 16 h.

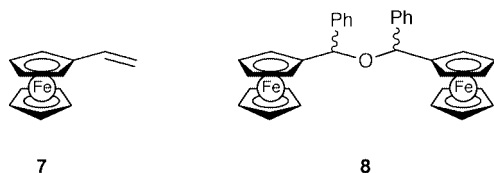
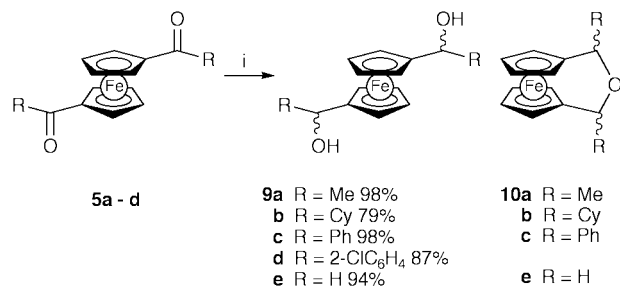


Fig. 2 By-products from reduction of **4a** and **4c**.

(Fig. 2; from the reaction of **4a**) and bis(α -ferrocenylbenzyl) ether **8** (Fig. 2; from the reaction of **4c**) suggests that the stabilised α -carbocation^{31,32} is readily formed during isolation of the products.

The major diol products **9** from the reduction of the diketones **5** were isolated as a mixture of (\pm)- and *meso*-isomers, but the formation of **10** by intramolecular trapping of the α -carbocation by the second hydroxy group occurs readily and in all cases the previously reported, but poorly characterised, 2-oxo[3]ferrocenophane was isolated (Scheme 4). The relative



Scheme 4 Reagents and conditions: (i) LiBH₄, MeOH, rt, 16 h.

amounts of diol and ether were dependent on the nature of the work-up used. Acidic rather than neutral conditions led, predictably, to an increase (up to 35%) in the amount of **10** being detected. The ratio of the (\pm)- to *meso*-isomers of the diols was variable and prolonged treatment with an acid catalyst (e.g. (\pm)-camphor-10-sulfonic acid, silica gel) resulted in a 2:1 mixture being obtained.

The solid state structures of a number of 2-oxo[3]ferrocenophanes have been reported^{5,33–35} and in the case of **10b** the identities of the *rel*-(*S,S*)- and *meso*-isomers were confirmed by single crystal X-ray analysis. The *meso*-isomer (Fig. 3a) has almost perfect non-crystallographic C_s symmetry about a plane passing through the iron and oxygen atoms. The two cyclopentadienyl rings are thus perfectly eclipsed, but due to the constraints of the bridging ligand, they are inclined by *ca.* 12° to each other. Although each Cp ring is planar to within 0.01 Å the geometries at the bridgehead carbons C(1) and C(6) are slightly pyramidalized, C(11) and C(18) each lying more than 0.1 Å out of their associated Cp ring planes (in the direction of the bridging ether oxygen atom). The geometric arrangement observed here mirrors almost exactly that seen in the crystal structure³³ of the simple methylene analogue **10e** where the Cp rings are also perfectly eclipsed and inclined by 12°; the angle at the bridging ether oxygen atom is also essentially the same [115.7(5)° in *meso*-**10b**, *cf.* 114.7° in **10e**]. Inversion of one of the chiral centres to give either the (*S,S*)- or (*R,R*)-stereoisomers (the (*S,S*) is shown in Fig. 3b) produces only a very small perturbation in the conformation of the core structure. Here there is a small (*ca.* 3°) out of register twist of the two Cp rings with respect to each other, though the rings are still inclined by 12°—there are similar out of plane deviations (*ca.* 0.1 Å) of C(11) and C(18). The angle at the ether oxygen atom is slightly enlarged to 118.6(2)°. There are no intermolecular packing interactions of note in either structure.

The loss of optical activity of 1,1'-bis(hydroxymethyl)ferrocenes and 1,1'-bis(hydroxymethyl)ruthenocenes, which had been prepared by asymmetric reduction, has been demon-

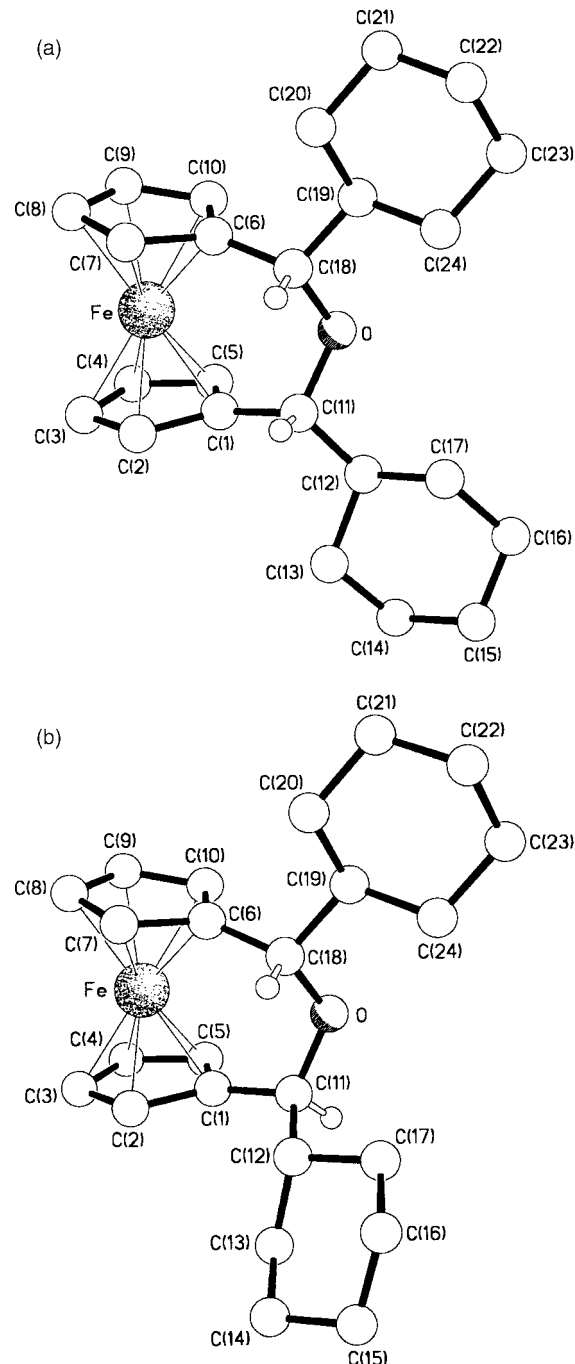
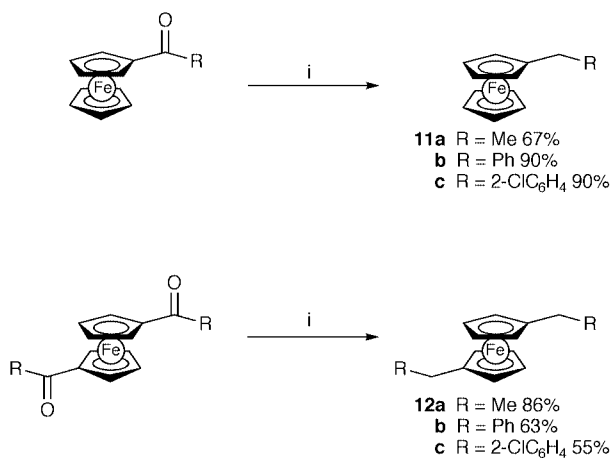


Fig. 3 (a) The molecular structure of *meso*-**10b**; (b) the molecular structure of *rel*-(*S,S*)-**10b**.

strated in an acidic medium by extensive ¹H NMR studies.³⁶ The 2-oxa[3]metalloenophane has been proposed as a vehicle to achieve this epimerisation. These observations concerning the lack of optical stability at the α -position of a 1,1'-substituted ferrocene system are in stark contrast to that reported for monosubstituted ferrocenes.^{37,38} Therefore whilst the configuration at the α -carbon of a monosubstituted ferrocene system can be assumed to be fixed and nucleophilic substitution to proceed with retention, the same assumption cannot be made for 1,1'-substituted systems. This demonstrates that when optically pure materials are required strategies utilising chirality at the α -position should be avoided or used with great caution.

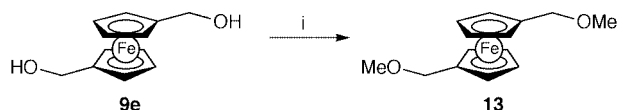
Investigation of alternative reducing agents found that treatment of a range of ferrocenyl ketones, at room temperature, with BH₃·THF resulted in complete deoxygenation of the substrates cleanly generating the corresponding ferrocenyl alkanes (Scheme 5). The 'one-pot' reduction of ferrocenyl



Scheme 5 Reagents and conditions: (i) BH₃·THF, ether, rt, 16 h.

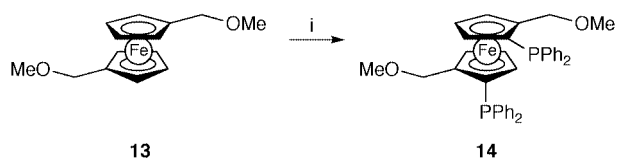
carbonyl compounds to the corresponding alkyl ferrocenes has been achieved in the presence of Lewis acids using zinc borohydride³⁹ and sodium cyanoborohydride.⁴⁰ The latter reagent has also been used in conjunction with Brønsted acids.⁴¹ The use of BH₃·THF as the reducing agent therefore provides an alternative, non-acidic route to these materials.

To obviate the possibility of epimerisation occurring at the α -position of 1,1'-substituted systems, the target 1,1',2,2'-tetrasubstituted systems were approached from the achiral diol **9e**. Conversion of this substrate to the corresponding dimethyl ether, **13** by treatment with a base (NaOH, *tert*-BuOK, Et₃N, pyridine, DMAP, NaH) and a methylating agent (Me₂SO₄, MeI) was unsuccessful although small amounts of the bridged species **10e** were present. However, simply dissolving the alcohol in methanol, in the presence of a catalytic amount of (\pm)-camphor-10-sulfonic acid, provided **13** in excellent yield (Scheme 6).⁴²



Scheme 6 Reagents and conditions: (i) (\pm)-camphor-10-sulfonic acid, MeOH, rt, 16 h, 94%.

Lithiation of **13** using *tert*-BuLi has been reported but multiple products were produced⁴² which suggested that under these conditions the metallation is too facile and uncontrolled. However, our target was finally achieved by di-*ortho*-lithiation of **13** with the use of an excess (6.0 equiv.) of *n*-BuLi in ether at reflux. Dissolution of the precipitated orange solid occurred on addition of chlorodiphenylphosphine. The diphosphine, **14** was isolated in 63% yield as a mixture of the (\pm)-isomers with a trace of the *meso* form being detected (Scheme 7).



Scheme 7 Reagents and conditions: (i) BuLi, ether, 34 °C, 16 h; Ph₂PCl, rt, 16 h, 63%.

In summary we have prepared our target 1,1',2,2'-tetrasubstituted ferrocene system and, *en route*, demonstrated that the reduction of ferrocenyl carbonyl compounds is not trivial. Alcohols, alkenes, alkanes, and ethers including 2-oxa[3]ferrocenophanes can all be obtained. These results demonstrate the highly labile nature of α -hydroxyferrocenes and highlight the lack of optical stability of 1,1'- α -dihydroxyferrocenes which is

contrary to that observed for monosubstituted systems. Thus when optically pure materials are required strategies utilising chirality at the α -position should be avoided or used with great caution. The syntheses of enantiopure materials, taking into account these factors, are in hand.²³

Experimental

General

Reactions requiring anhydrous conditions were performed using oven-dried glassware and conducted under a positive pressure of nitrogen. Anhydrous solvents were prepared in accordance with standard protocols, or alternatively purchased from Aldrich in Sure/SealTM bottles. IR spectra were recorded on a Perkin-Elmer 1710 Infra-red Fourier Transform spectrometer with internal calibration. NMR spectra were recorded on a JEOL GSX 270, a Bruker WH 250 or a Bruker AM 500 spectrometer with residual protic solvent as an internal reference. Melting points were recorded on a Reichert Microscope Hot-Stage Apparatus and are uncorrected. Butyllithium was titrated against diphenylacetic acid⁴³ prior to use. Elemental analysis was carried out on a Perkin-Elmer 2400 CHN elemental analyser or at the University of North London. Mass spectra and accurate masses were recorded on a Micromass-70 E or a Micromass AUTOSPEC-Q instrument or at the EPSRC Mass Spectrometry Centre, University College, Swansea.

1,1'-Diformylferrocene, **3**

Compound **3** was prepared using the reported procedure.^{22,27} Red crystalline solid (1.00 g, 4.13 mmol, 77%); mp 172–174 °C (lit.,²⁵ 179–180 °C); silica gel TLC *R_f* 0.24 (1:3 acetone–hexane) (Found: C, 59.26; H, 4.12. C₁₂H₁₀O₂Fe requires C, 59.50; H, 4.16%); $\nu_{\max}/\text{cm}^{-1}$ (thin film) 1658, 1452, 1370, 1243; δ_{H} (270 MHz; CDCl₃) 9.93 (2H, s), 4.87 (4H, t, *J* 2 Hz), 4.66 (4H, t, *J* 2 Hz); δ_{C} (68 MHz; CDCl₃) 192.83, 80.27, 74.16, 70.86; *m/z* (EI) 242 (M⁺), 214, 186 (Found: M⁺, 242.0019. C₁₂H₁₀O₂Fe requires 242.0030).

Typical procedure for the preparation of ferrocenyl ketones

Ferrocene (1.0 equiv.) was added to a stirred suspension of the acyl chloride (1.1 equiv. for monoketones and 2.2 equiv. for diketones) and aluminium chloride (1.1 equiv. for monoketones and 2.2 equiv. for diketones) in dichloromethane. The resulting mixture was stirred at room temperature overnight and then washed with water. The organic layer was passed through a plug of alumina, which was then washed with chloroform until the washings became colourless. The washings were combined and concentrated *in vacuo* to give the crude product which was purified by flash column chromatography on silica gel to give the ferrocenyl ketone.

Acetylferrocene, 4a. Orange crystalline solid (1.87 g, 8.20 mmol, 76%); mp 79–81 °C (lit.,⁴⁴ 84–86 °C); silica gel TLC *R_f* 0.45 (1:3 acetone–hexane) (Found: C, 63.00; H, 5.23. C₁₂H₁₂OFe requires C, 63.15; H, 5.30%); $\nu_{\max}/\text{cm}^{-1}$ (thin film) 3116, 1645, 1456, 1281; δ_{H} (270 MHz; CDCl₃) 4.77 (2H, t, *J* 2 Hz), 4.50 (2H, t, *J* 2 Hz), 4.20 (5H, s), 2.39 (3H, s); δ_{C} (125 MHz; CDCl₃) 201.84, 79.13, 72.16, 69.69, 69.43, 27.27; *m/z* (EI) 228 (M⁺), 213, 185 (Found: M⁺, 228.0246. C₁₂H₁₂OFe requires 228.0237).

Cyclohexylcarbonylferrocene, 4b. Orange crystalline solid (4.09 g, 13.81 mmol, 85%); mp 79–81 °C; silica gel TLC *R_f* 0.40 (1:3 ether–hexane) (Found: C, 69.10; H, 6.89. C₁₇H₂₀OFe requires C, 68.92; H, 6.76%); $\nu_{\max}/\text{cm}^{-1}$ (thin film) 2929, 2853, 1662, 1451; δ_{H} (270 MHz; CDCl₃) 4.77 (2H, t, *J* 2 Hz), 4.48 (2H, t, *J* 2 Hz), 4.19 (5H, s), 2.80 (1H, m), 1.88–1.66 (10H, m); δ_{C} (125 MHz; CDCl₃) 206.44, 77.32, 71.12, 68.55, 68.40, 46.59,

28.73, 24.90; m/z (EI) 296 (M^+), 213, 185 (Found: M^+ , 296.0870. $C_{17}H_{20}OFe$ requires 296.0863).

Benzoylferrocene, 4c. Red crystalline solid (4.38 g, 15.10 mmol, 94%); mp 106–107 °C (lit.,⁴⁵ 108.1–108.3 °C); silica gel TLC R_f 0.34 (1:3 ether–hexane) (Found: C, 70.12; H, 4.74. $C_{17}H_{14}OFe$ requires C, 70.35; H, 4.83%); ν_{max}/cm^{-1} (thin film) 3100, 1640, 1450, 1290; δ_H (270 MHz; $CDCl_3$) 7.88 (2H, m), 7.48 (3H, m), 4.90 (2H, t, J 2 Hz), 4.58 (2H, t, J 2 Hz), 4.19 (5H, s); δ_C (125 MHz; $CDCl_3$) 199.24, 139.85, 131.53, 128.35, 128.26, 128.10, 78.20, 72.63, 71.58, 70.27; m/z (EI) 290 (M^+), 197, 185 (Found: M^+ , 290.0393. $C_{17}H_{14}OFe$ requires 290.0394).

(2-Chlorobenzoyl)ferrocene, 4d. Red crystalline solid (4.32 g, 13.33 mmol, 83%); mp 97–99 °C (lit.,⁴⁶ 99–100 °C); silica gel TLC R_f 0.30 (1:3 ether–hexane) (Found: C, 62.78; H, 3.83. $C_{17}H_{13}ClOFe$ requires C, 62.96; H, 4.04%); ν_{max}/cm^{-1} (thin film) 3098, 1652, 1590, 1477; δ_H (270 MHz; $CDCl_3$) 7.51–7.32 (4H, m), 4.73 (2H, t, J 2 Hz), 4.58 (2H, t, J 2 Hz), 4.26 (5H, s); δ_C (125 MHz; $CDCl_3$) 198.73, 139.47, 131.04, 130.72, 130.29, 128.64, 126.21, 78.49, 72.92, 71.10, 70.15; m/z (EI) 326 (M^+ , ^{37}Cl), 324 (M^+ , ^{35}Cl), 288, 273 (Found: M^+ , 323.9996. $C_{17}H_{13}ClOFe$ requires 324.0004).

1,1'-Diacetylferrocene, 5a. Red crystalline solid (4.23 g, 15.66 mmol, 98%); mp 127–128 °C (lit.,²⁸ 127–127.5 °C); silica gel TLC R_f 0.24 (1:3 acetone–hexane) (Found: C, 62.08; H, 5.18. $C_{14}H_{14}O_2Fe$ requires C, 62.22; H, 5.18%); ν_{max}/cm^{-1} (thin film) 3093, 1657, 1456; δ_H (270 MHz; $CDCl_3$) 4.74 (4H, t, J 2 Hz), 4.48 (4H, t, J 2 Hz), 2.33 (6H, s); δ_C (125 MHz; $CDCl_3$) 200.88, 80.55, 73.41, 70.78, 27.45 (CH_3); m/z (EI) 270 (M^+), 255, 228 (Found: M^+ , 270.0316. $C_{14}H_{14}O_2Fe$ requires 270.0343).

1,1'-Bis(cyclohexylcarbonyl)ferrocene, 5b. Orange crystalline solid (2.48 g, 6.11 mmol, 89%); mp 135–136 °C; silica gel TLC R_f 0.20 (1:3 ether–hexane) (Found: C, 70.73; H, 7.45. $C_{24}H_{30}O_2Fe$ requires C, 70.91; H, 7.44%); ν_{max}/cm^{-1} (thin film) 2932, 2845, 1662, 1450; δ_H (270 MHz; $CDCl_3$) 4.61 (4H, t, J 2 Hz), 4.34 (4H, t, J 2 Hz), 2.60 (2H, m), 1.76–1.07 (20H, m); δ_C (125 MHz; $CDCl_3$) 206.33, 79.10, 72.95, 71.71, 47.34, 29.29, 25.53, 25.46; m/z (EI) 406 (M^+), 323, 296, 241 (Found: M^+ , 406.1598. $C_{24}H_{30}O_2Fe$ requires 406.1595).

1,1'-Dibenzoylferrocene, 5c. Red crystalline solid (6.26 g, 15.88 mmol, 99%); mp 103–105 °C (lit.,⁴⁵ 106.5–106.7 °C); silica gel TLC R_f 0.26 (1:1 ether–hexane) (Found: C, 72.98; H, 4.61. $C_{24}H_{18}O_2Fe$ requires C, 73.09; H, 4.57%); ν_{max}/cm^{-1} (thin film) 1771, 1733, 1654, 1580; δ_H (270 MHz; $CDCl_3$) 7.72–7.32 (10H, m), 4.82 (4H, t, J 2 Hz), 4.46 (4H, t, J 2 Hz); δ_C (125 MHz; $CDCl_3$) 197.0, 131.5, 130.9, 127.9, 127.7, 79.1, 74.1, 72.7; m/z (EI) 394 (M^+), 289, 260 (Found: M^+ , 394.0649. $C_{24}H_{18}O_2Fe$ requires 394.0656).

1,1'-Bis(2-chlorobenzoyl)ferrocene, 5d. Red crystalline solid (6.41 g, 13.84 mmol, 86%); mp 148–150 °C; silica gel TLC R_f 0.32 (1:3 acetone–hexane) (Found: C, 61.95; H, 3.54. $C_{24}H_{16}Cl_2O_2Fe$ requires C, 62.24; H, 3.48%); ν_{max}/cm^{-1} 3100, 1652, 1471, 1446; δ_H (270 MHz; $CDCl_3$) 7.46–7.33 (8H, m), 4.81 (4H, t, J 2 Hz), 4.69 (4H, t, J 2 Hz); δ_C (125 MHz; $CDCl_3$) 197.46, 138.62, 131.14, 131.04, 130.41, 128.77, 126.40, 79.77, 74.74, 72.45; m/z (EI) 464 (M^+ , $2 \times ^{37}Cl$), 462 (M^+ , ^{35}Cl , ^{37}Cl), 460 (M^+ , $2 \times ^{35}Cl$), 259, 195 (Found: M^+ , 461.9877. $C_{24}H_{16}Cl_2O_2Fe$ requires 461.9877).

Typical procedure for the reduction of ferrocenyl ketones using lithium borohydride

Lithium borohydride (5.0 equiv.) was added to a solution of the ferrocenyl ketone (1.0 equiv.) in methanol. The mixture was allowed to stir at room temperature overnight when water was

added. The mixture was extracted with ether, dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product which was purified by flash column chromatography on silica gel to give the ferrocenylmethyl alcohol.

(±)- α -Hydroxyethylferrocene, 6a. Orange crystalline solid (932 mg, 4.05 mmol, 77%); mp 65–67 °C (lit.,⁴⁷ 70–72 °C); silica gel TLC R_f 0.66 (1:3 acetone–hexane) (Found: C, 62.64; H, 5.93. $C_{12}H_{14}OFe$ requires C, 62.60; H, 6.13%); ν_{max}/cm^{-1} (thin film) 3926, 3392, 3094, 2974, 2930, 2869, 1651; δ_H (270 MHz; $CDCl_3$) 4.53 (1H, q, J 7 Hz), 4.27–4.10 (9H, m), 1.99 (1H, s), 1.44 (3H, d, J 7 Hz); δ_C (68 MHz; $CDCl_3$) 94.73, 68.23, 67.86, 67.81, 66.06, 65.52, 23.66; m/z (EI) 230 (M^+), 212 (Found: M^+ , 230.0380. $C_{12}H_{14}OFe$ requires 230.0380).

Vinylferrocene, 7. Orange crystalline solid (25 mg, 0.12 mmol, 2%); mp 50–52 °C (lit.,⁴⁸ 49–52 °C); silica gel TLC R_f 0.43 (hexane) (Found: C, 67.84; H, 5.68. $C_{12}H_{12}Fe$ requires C, 67.96; H, 5.70%); ν_{max}/cm^{-1} (thin film) 3085, 1629, 1105, 894, 818; δ_H (270 MHz; $CDCl_3$) 6.44 (1H, dd, J 11, 17 Hz), 5.33 (1H, dd, J 2, 17 Hz), 5.01 (1H, dd, J 2, 11 Hz), 4.34 (2H, t, J 2 Hz), 4.20 (2H, t, J 2 Hz), 4.09 (5H, s); δ_C (68 MHz; $CDCl_3$) 134.73, 111.13, 83.55, 69.29, 68.74, 66.73; m/z (EI) 212 (M^+), 121, 56 (Found: M^+ , 212.0290. $C_{12}H_{12}Fe$ requires 212.0288).

(±)- α -Hydroxy(cyclohexylmethyl)ferrocene, 6b. Yellow crystalline solid (217 mg, 0.73 mmol, 85%); mp 77–78 °C; silica gel TLC R_f 0.47 (1:3 ether–hexane) (Found: C, 68.55; H, 7.67. $C_{17}H_{22}OFe$ requires C, 68.43; H, 7.44%); ν_{max}/cm^{-1} (thin film) 3566, 3093, 2926, 1651, 1450; δ_H (270 MHz; $CDCl_3$) 4.26–4.12 (9H, m), 4.04 (1H, dd, J 2, 7 Hz), 2.14 (1H, d, J 2 Hz), 1.92–0.84 (11H, m); δ_C (68 MHz; $CDCl_3$) 93.29, 74.24, 68.67, 68.08, 67.62, 67.29, 64.51, 44.48, 29.15, 28.80, 26.35, 25.95; m/z (EI) 298 (M^+), 280, 215, 211 (Found: M^+ , 298.1015. $C_{17}H_{22}OFe$ requires 298.1019).

(±)- α -Hydroxybenzylferrocene, 6c. Yellow crystalline solid (5.60 g, 19.17 mmol, 94%); mp 69–70 °C (lit.,³² 80 °C); silica gel TLC R_f 0.50 (1:1 ether–hexane) (Found: C, 69.66; H, 5.40. $C_{17}H_{16}OFe$ requires C, 69.85; H, 5.52%); ν_{max}/cm^{-1} (thin film) 3555, 3429, 2855, 1493; δ_H (270 MHz; $CDCl_3$) 7.41–7.27 (5H, m), 5.48 (1H, d, J 3 Hz), 4.23–4.19 (9H, m), 2.50 (1H, d, J 3 Hz); δ_C (68 MHz; $CDCl_3$) 143.20, 128.15, 127.37, 126.17, 94.17, 71.95, 68.44, 68.10, 68.04, 67.36, 65.96; m/z (EI) 292 (M^+), 275, 227, 209 (Found: M^+ , 292.0544. $C_{17}H_{16}OFe$ requires 292.0550).

(±)-Bis(α -ferrocenylbenzyl) ether, 8. Yellow crystalline solid (193 mg, 0.34 mmol, 3%); mp 98–102 °C (lit.,⁴⁹ 59–61 °C); silica gel TLC R_f 0.32 (hexane) (Found: C, 72.34; H, 5.15. $C_{34}H_{30}OFe_2$ requires C, 72.11; H, 5.34%); ν_{max}/cm^{-1} (thin film) 3092, 2873, 1492, 1455, 1107, 1079, 818, 702; δ_H (270 MHz; $CDCl_3$) 7.45–7.33 (10H, m), 5.05 (2H, s), 4.23–3.90 (18H, m); δ_C (68 MHz; $CDCl_3$) 142.64, 141.73, 128.36, 128.12, 127.95, 127.39, 91.10, 90.32, 68.83, 68.39, 68.05, 67.84, 67.45, 66.85; m/z (EI) 566 (M^+), 275, 153, 121 (Found: M^+ , 566.0992. $C_{34}H_{30}OFe_2$ requires 566.0995).

(±)- α -Hydroxy(2-chlorobenzyl)ferrocene, 6d. Yellow crystalline solid (419 mg, 1.28 mmol, 87%); mp 109–112 °C; silica gel TLC R_f 0.56 (1:1 ether–hexane) (Found: C, 62.51; H, 4.51. $C_{17}H_{15}ClOFe$ requires C, 62.57; H, 4.64%); ν_{max}/cm^{-1} (thin film) 3445, 3094, 1470, 1440; δ_H (270 MHz; $CDCl_3$) 7.64–7.18 (4H, m), 5.85 (1H, d, J 3 Hz), 4.38–4.06 (9H, m), 2.62 (1H, d, J 3 Hz); δ_C (68 MHz; $CDCl_3$) 140.86, 132.22, 129.28, 128.49, 127.49, 126.88, 93.72, 68.95, 68.54, 68.23, 68.04, 67.93, 67.65, 66.22; m/z (EI) 328 (M^+ , ^{37}Cl), 326 (M^+ , ^{35}Cl), 309, 290, 273 (Found: M^+ , 326.0163. $C_{17}H_{15}ClOFe$ requires 326.0161).

(±), *meso*-1,1'-Bis(α -hydroxyethyl)ferrocene, **9a**. Orange crystalline solid (504 mg, 1.84 mmol, 98%); mp 73–74 °C (lit.,⁵⁰ 69–70 °C); silica gel TLC R_f 0.33 (1:3 acetone–hexane) (Found: C, 61.13; H, 6.61. $C_{14}H_{18}O_2Fe$ requires C, 61.30; H, 6.62%); ν_{max}/cm^{-1} (thin film) 3326, 2971, 1394, 1368; δ_H (270 MHz; $CDCl_3$) 5.03 (2H, s), 4.65 (2H, m), 4.29–4.13 (8H, m), 1.39 (6H, m); δ_C (68 MHz; $CDCl_3$) 95.08, 67.64, 67.47, 67.38, 67.21, 66.41, 66.04, 65.81, 65.40, 65.37, 65.02, 25.57, 25.16; m/z (EI) 274 (M^+), 256, 242 (Found: M^+ , 274.0663. $C_{14}H_{18}O_2Fe$ requires 274.0656).

(±), *meso*-1,1'-Bis[α -hydroxy(cyclohexylmethyl)]ferrocene, **9b**. Yellow crystalline solid (258 mg, 0.63 mmol, 79%); mp 93–96 °C; silica gel TLC R_f 0.50 (1:1 ether–hexane) (Found: C, 70.18; H, 8.52. $C_{24}H_{34}O_2Fe$ requires C, 70.21; H, 8.35%); ν_{max}/cm^{-1} (thin film) 3262, 2921, 2851, 1448; δ_H (270 MHz; $CDCl_3$) 4.27 (10H, m), 3.73 (2H, s), 1.81–0.82 (20H, m); δ_C (68 MHz; $CDCl_3$) 92.91, 91.83, 74.83, 74.03, 67.73, 67.33, 67.26, 67.14, 67.10, 66.87, 65.44, 45.65, 45.35, 28.92, 28.79, 28.71, 28.50, 26.40, 26.11; m/z (EI) 410 (M^+), 392, 374 (Found: M^+ , 410.1908. $C_{24}H_{34}O_2Fe$ requires 410.1908).

(±), *meso*-1,1'-Bis(α -hydroxybenzyl)ferrocene, **9c**. Yellow crystalline solid (5.07 g, 12.74 mmol, 98%); mp 132–133 °C (lit.,⁴⁵ 136–137 °C); silica gel TLC R_f 0.29 (1:1 ether–hexane) (Found: C, 72.35; H, 5.36. $C_{24}H_{22}O_2Fe$ requires C, 72.34; H, 5.57%); ν_{max}/cm^{-1} (thin film) 3319, 3029, 1493, 1452; δ_H (270 MHz; $CDCl_3$) 7.35–7.21 (10H, m), 5.55 (2H, s), 5.48 (2H, s), 4.86 (2H, s), 4.43–4.08 (8H, m); δ_C (68 MHz; $CDCl_3$) 144.25, 143.80, 128.33, 128.23, 127.41, 126.25, 126.22, 94.00, 93.52, 72.76, 71.87, 68.29, 68.17, 67.93, 67.71, 67.21, 66.73, 66.43; m/z (EI) 398 (M^+), 380, 364, 153 (Found: M^+ , 398.0968. $C_{24}H_{22}O_2Fe$ requires 398.0969).

(±), *meso*-1,1'-Bis[α -hydroxy(2-chlorobenzyl)]ferrocene, **9d**. Yellow crystalline solid (491 mg, 1.05 mmol, 87%); mp 149–151 °C; silica gel TLC R_f 0.44 (1:1 ether–hexane) (Found: C, 61.70; H, 4.28. $C_{24}H_{20}Cl_2O_2Fe$ requires C, 61.70; H, 4.32%); ν_{max}/cm^{-1} (thin film) 3277, 1470, 1440, 1046; δ_H (270 MHz; $CDCl_3$) 7.58–7.14 (8H, m), 6.04 (1H, s), 5.96 (1H, s), 4.44–4.09 (8H, m); δ_C (68 MHz; $CDCl_3$) 141.44, 141.24, 132.06, 129.27, 129.24, 128.61, 128.58, 127.76, 127.71, 127.08, 126.99, 92.84, 92.61, 68.76, 68.39, 68.28, 68.09, 67.99, 67.66, 67.43, 66.96, 66.84, 66.60; m/z (EI) 468 (M^+ , $2 \times ^{37}Cl$), 466 (M^+ , $^{35}Cl, ^{37}Cl$), 464 (M^+ , $2 \times ^{35}Cl$), 448, 212, 153 (Found: M^+ , 466.0190. $C_{24}H_{20}Cl_2O_2Fe$ requires 466.0190).

1,1'-Bis(α -hydroxymethyl)ferrocene, **9e**.⁵¹ Yellow crystalline solid (606 mg, 2.46 mmol, 94%); mp 106–108 °C; silica gel TLC R_f 0.47 (1:1 acetone–hexane) (Found: C, 58.52; H, 5.49. $C_{12}H_{14}O_2Fe$ requires C, 58.53; H, 5.73%); ν_{max}/cm^{-1} (thin film) 3089, 2929, 2857, 1457; δ_H (270 MHz; $CDCl_3$) 4.39 (4H, s), 4.21 (4H, m), 4.17 (4H, m), 3.39 (2H, s); δ_C (68 MHz; $CDCl_3$) 89.30, 68.00, 66.99, 60.28; m/z (EI) 246 (M^+), 228, 134, 78 (Found: M^+ , 246.0335. $C_{12}H_{14}O_2Fe$ requires 246.0343).

rel-(*S,S*), *meso*-1,3-Dimethyl-2-oxa[3]ferrocenophane, **10a**.⁵² Orange crystalline solid (153 mg, 0.60 mmol, 5%); mp 96–98 °C; silica gel TLC R_f 0.56 (1:3 ether–hexane) (Found: C, 65.79; H, 6.52. $C_{14}H_{16}OFe$ requires C, 65.65; H, 6.30%); ν_{max}/cm^{-1} (thin film) 3082, 2974, 1448, 1369, 1304, 1069, 1012, 808; δ_H (270 MHz; $CDCl_3$) 4.31 (2H, q, J 7 Hz), 4.24–4.00 (8H, m), 3.80 (2H, q, J 7 Hz), 1.50 (6H, d, J 7 Hz), 1.45 (6H, d, J 7 Hz); δ_C (68 MHz; $CDCl_3$) 90.56, 88.78, 72.11, 71.27, 70.15, 69.95, 69.35, 68.28, 67.41, 65.21, 62.73, 22.33, 19.30; m/z (EI) 256 (M^+), 213, 164 (Found: M^+ , 256.0558. $C_{14}H_{16}OFe$ requires 256.0551).

rel-(*S,S*), *meso*-1,3-Dicyclohexyl-2-oxa[3]ferrocenophane, **10b**. Orange crystalline solid (25 mg, 0.06 mmol, 8%); mp 106–

108 °C; silica gel TLC R_f 0.73 (1:3 ether–hexane) (Found: C, 73.52; H, 8.10. $C_{24}H_{32}OFe$ requires C, 73.47; H, 8.22%); ν_{max}/cm^{-1} (thin film) 2921, 2851, 1449, 1040; δ_H (270 MHz; $CDCl_3$) 4.19–4.02 (8H, m), 3.65 (2H, d, J 9 Hz), 3.20 (2H, d, J 9 Hz), 2.20 (2H, d, J 12 Hz), 2.15 (2H, d, J 12 Hz), 1.82–0.83 (20H, m); δ_C (68 MHz; $CDCl_3$) 88.92, 87.25, 82.46, 72.95, 71.99, 71.15, 69.90, 69.21, 69.06, 68.17, 67.18, 65.08, 42.83, 39.94, 31.37, 30.87, 30.64, 30.23, 26.53, 26.07, 25.98, 25.74; m/z (EI) 392 (M^+), 374, 309 (Found: M^+ , 392.1802. $C_{24}H_{32}OFe$ requires 392.1802). Crystal data for *rel*-(*S,S*)-**10b** $C_{24}H_{32}OFe$, $M = 392.4$, triclinic, $P\bar{1}$ (no. 2), $a = 6.010(1)$, $b = 11.636(2)$, $c = 14.551(3)$ Å, $a = 80.22(2)$, $\beta = 81.78(2)$, $\gamma = 88.12(2)^\circ$, $V = 992.5(3)$ Å³, $Z = 2$, $D_c = 1.313$ g cm⁻³, $\mu(Cu-K\alpha) = 61.4$ cm⁻¹, $F(000) = 420$, $T = 293$ K; yellow platy needles, $0.33 \times 0.08 \times 0.04$ mm, Siemens P4/RA diffractometer, ω -scans, 2774 independent reflections. The structure was solved by the heavy atom method and all of the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.038$, $wR_2 = 0.085$ for 2337 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 116^\circ$] and 236 parameters. Crystal data for *meso*-**10b** $C_{24}H_{32}OFe$, $M = 392.4$, monoclinic, $P2_1/c$ (no. 14), $a = 5.864(2)$, $b = 28.331(11)$, $c = 12.241(3)$ Å, $\beta = 98.36(3)^\circ$, $V = 2012(1)$ Å³, $Z = 4$, $D_c = 1.295$ g cm⁻³, $\mu(Cu-K\alpha) = 60.6$ cm⁻¹, $F(000) = 840$, $T = 293$ K; thin yellow platy needles, $0.47 \times 0.05 \times 0.02$ mm, Siemens P4/RA diffractometer, ω -scans, 2805 independent reflections. The structure was solved by the heavy atom method and all of the non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.074$, $wR_2 = 0.143$ for 1759 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 116^\circ$] and 235 parameters. For both structures, CCDC reference number 207/417. See <http://www.rsc.org/suppdata/p1/b0/b000833h/> for crystallographic files in .cif format.

rel-(*S,S*), *meso*-1,3-Diphenyl-2-oxa[3]ferrocenophane, **10c**.³⁶ Orange crystalline solid (65 mg, 0.17 mmol, 70%); mp 186–188 °C; silica gel TLC R_f 0.54 (1:9 ether–hexane) (Found: C, 75.71; H, 5.14. $C_{24}H_{20}OFe$ requires C, 75.81; H, 5.30%); ν_{max}/cm^{-1} (thin film) 2925, 1600, 1494, 1446; δ_H (270 MHz; $CDCl_3$) 7.54 (4H, m), 7.32 (4H, m), 7.25 (2H, m), 5.05 (2H, s), 4.53 (2H, m), 4.23 (2H, m), 4.20 (2H, m), 4.16 (2H, m); δ_C (68 MHz; $CDCl_3$) 141.71, 128.06, 127.09, 126.61, 89.06, 78.57, 72.29, 70.78, 68.83, 66.74; m/z (EI) 380 (M^+), 299, 287, 275, 226 (Found: M^+ , 380.0863. $C_{24}H_{20}OFe$ requires 380.0863).

2-Oxa[3]ferrocenophane, **10e**. Orange crystalline solid (5 mg, 0.02 mmol, 8%); mp 91–93 °C (lit.,³³ 145–146 °C); silica gel TLC R_f 0.44 (1:3 ether–hexane) (Found: C, 62.96; H, 5.01. $C_{12}H_{12}OFe$ requires C, 63.15; H, 5.30%); ν_{max}/cm^{-1} (thin film) 3086, 2980, 1226, 1060; δ_H (270 MHz; $CDCl_3$) 4.18 (4H, t, J 2 Hz), 4.15 (4H, t, J 2 Hz), 3.90 (4H, s); δ_C (68 MHz; $CDCl_3$) 83.19, 70.12, 69.95, 64.54; m/z (EI) 228 (M^+), 199, 134 (Found: M^+ , 228.0237. $C_{12}H_{12}OFe$ requires 228.0237).

Typical procedure for the reduction of ferrocenyl ketones using $BH_3 \cdot THF$

$BH_3 \cdot THF$ (1.1 equiv. of a 0.8 M solution in THF) was added, at room temperature, to a solution of the ferrocenyl ketone (1.0 equiv.) also in THF. The mixture was allowed to stir at room temperature overnight when water was added. The mixture was extracted with chloroform, dried ($MgSO_4$) and concentrated *in vacuo* to give the crude product which was purified by flash column chromatography on silica gel to give the alkylferrocene.

Ethylferrocene, **11a**.⁴⁸ Orange oil (339 mg, 1.58 mmol, 67%); silica gel TLC R_f 0.56 (hexane) (Found: C, 66.99; H, 6.60. $C_{12}H_{14}Fe$ requires C, 67.28; H, 6.59%); ν_{max}/cm^{-1} (neat) 3094, 2964, 2925; δ_H (270 MHz; $CDCl_3$) 4.14–4.05 (9H, m), 2.35 (2H, q, J 7 Hz), 1.17 (3H, t, J 7 Hz); δ_C (68 MHz; $CDCl_3$) 91.14,

68.37, 67.43, 66.93, 22.21, 14.61; m/z (EI) 214 (M^+), 199, 148 (Found: M^+ , 214.0437. $C_{12}H_{14}Fe$ requires 214.0445).

Benzylferrocene, 11b. Yellow crystalline solid (485 mg, 1.76 mmol, 90%); mp 66–68 °C (lit.,⁵³ 75–76 °C); silica gel TLC R_f 0.35 (hexane) (Found: C, 73.96; H, 5.87. $C_{17}H_{16}Fe$ requires C, 73.90; H, 5.84%); ν_{max}/cm^{-1} (thin film) 3085, 3027, 1678, 1495, 1452; δ_H (270 MHz; $CDCl_3$) 7.33–7.23 (5H, m), 4.17 (2H, m), 4.14 (7H, m), 3.75 (2H, s); δ_C (68 MHz; $CDCl_3$) 141.53, 128.33, 128.19, 125.84, 87.95, 68.61, 67.50, 36.00; m/z (EI) 276 (M^+), 208, 153 (Found: M^+ , 276.0614. $C_{17}H_{16}Fe$ requires 276.0601).

(2-Chlorobenzyl)ferrocene, 11c. Yellow crystalline solid (262 mg, 0.65 mmol, 90%); mp 72–74 °C; silica gel TLC R_f 0.40 (hexane); ν_{max}/cm^{-1} (thin film) 3091, 2925, 1472, 1442, 1106, 1038, 819, 745; δ_H (270 MHz; $CDCl_3$) 7.32 (1H, m), 7.12 (3H, m), 4.15 (7H, m), 4.10 (2H, t, J 2 Hz), 3.81 (2H, s); δ_C (68 MHz; $CDCl_3$) 139.61, 133.54, 130.26, 129.27, 127.41, 126.76, 86.35, 69.09, 68.80, 67.68, 33.50; m/z (EI) 312 (M^+ , ^{37}Cl), 310 (M^+ , ^{35}Cl), 208, 153, 152 (Found: M^+ , 310.0208. $C_{17}H_{15}ClFe$ requires 310.0211).

1,1'-Diethylferrocene, 12a.⁵⁴ Orange oil (408 mg, 1.68 mmol, 86%); silica gel TLC R_f 0.56 (hexane) (Found: C, 69.08; H, 7.49. $C_{14}H_{18}Fe$ requires C, 69.40; H, 7.49%); ν_{max}/cm^{-1} (neat) 3089, 2985, 2929, 1456; δ_H (270 MHz; $CDCl_3$) 4.03 (8H, s), 2.36 (4H, q, J 7 Hz), 1.19 (6H, t, J 7 Hz); δ_C (68 MHz; $CDCl_3$) 90.95, 67.92, 67.54, 22.10, 14.84; m/z (EI) 242 (M^+), 227, 212 (Found: M^+ , 242.0753. $C_{14}H_{18}Fe$ requires 242.0758).

1,1'-Dibenzylferrocene, 12b. Yellow crystalline solid (381 mg, 1.04 mmol, 63%); mp 97–99 °C (lit.,⁵⁵ 100–102 °C); silica gel TLC R_f 0.30 (hexane) (Found: C, 78.39; H, 6.23. $C_{24}H_{22}Fe$ requires C, 78.67; H, 6.06%); ν_{max}/cm^{-1} (thin film) 2918, 1494, 1452; δ_H (270 MHz; $CDCl_3$) 7.37–7.17 (10H, m), 4.06 (8H, m), 3.67 (4H, s); δ_C (68 MHz; $CDCl_3$) 141.60, 128.34, 128.21, 125.87, 88.14, 69.45, 68.44, 35.83; m/z (EI) 366 (M^+), 275, 208, 153 (Found: M^+ , 366.1057. $C_{24}H_{22}Fe$ requires 366.1071).

1,1'-Bis(2-chlorobenzyl)ferrocene, 12c. Yellow crystalline solid (294 mg, 0.68 mmol, 55%); mp 115–117 °C; silica gel TLC R_f 0.44 (hexane) (Found: C, 66.42; H, 4.50. $C_{24}H_{20}Cl_2Fe$ requires C, 66.24; H, 4.63%); ν_{max}/cm^{-1} (thin film) 3067, 2903, 1466, 1440; δ_H (270 MHz; $CDCl_3$) 7.35–7.15 (8H, m), 4.14 (8H, m), 3.85 (4H, s); δ_C (68 MHz; $CDCl_3$) 139.49, 133.46, 130.11, 129.17, 127.31, 126.60, 86.42, 69.75, 68.67, 68.48, 33.17; m/z (EI) 436 (M^+ , $2 \times ^{37}Cl$), 434 (M^+ , ^{35}Cl , ^{37}Cl), 432 (M^+ , $2 \times ^{35}Cl$), 400, 310 (Found: M^+ , 434.0291. $C_{24}H_{20}Cl_2Fe$ requires 434.0291).

1,1'-Bis(methoxymethyl)ferrocene, 13

Compound **13** was prepared using the reported procedure.⁴² Orange oil (857 mg, 3.13 mmol, 94%); silica gel TLC R_f 0.50 (1:3 acetone–hexane) (Found: C, 61.52; H, 6.35. $C_{14}H_{18}O_2Fe$ requires C, 61.30; H, 6.35%); ν_{max}/cm^{-1} (neat) 3088, 2817, 1466, 1450; δ_H (270 MHz; $CDCl_3$) 4.20 (4H, s), 4.18 (4H, t, J 2 Hz), 4.13 (4H, t, J 2 Hz), 3.32 (6H, s); δ_C (68 MHz; $CDCl_3$) 83.35, 70.63, 69.89, 69.10, 57.71; m/z (EI) 274 (M^+), 243, 228, 213 (Found: M^+ , 274.0636. $C_{14}H_{18}O_2Fe$ requires 274.0656).

(*R,S*)-1,1'-Bis(diphenylphosphino)-2,2'-bis(methoxymethyl)ferrocene, 14

Compound **14** was prepared using the reported procedure.²² Yellow crystalline solid (768 mg, 1.20 mmol, 63%); mp 182–185 °C; silica gel TLC R_f 0.24 (1:3 ether–hexane); ν_{max}/cm^{-1} (thin film) 1378, 1093, 1066, 943; δ_H (270 MHz; $CDCl_3$) 7.61–7.08 (20H, m), 4.31 (2H, m), 4.21 (2H, m), 4.13 (2H, dd, J 2, 11 Hz), 3.82 (2H, m), 3.48 (2H, d, J 11 Hz), 2.97 (6H, s); δ_C (68 MHz; $CDCl_3$) 139.79, 137.02, 134.88, 132.05, 129.12, 128.06, 127.84, 127.59, 90.45, 77.08, 72.51, 69.14, 69.06, 74.87, 58.00; δ_P (101 MHz; $CDCl_3$) –22.91; m/z (EI) 642 (M^+), 595,

262, 217, 201 (Found: M^+ , 642.1540. $C_{38}H_{36}O_2P_2Fe$ requires 642.1540).

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References

- 1 T. Hayashi and A. Togni, *Ferrocenes*, VCH, Weinheim, 1995.
- 2 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.
- 3 G. G. A. Balavoine, J.-C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton, K. Nakatani and S. D. Bella, *Organometallics*, 1999, **18**, 21.
- 4 D. Enders and R. Lochtmann, *Eur. J. Org. Chem.*, 1998, 689.
- 5 G. Iftime, J.-C. Daran, E. Manoury and G. G. A. Balavoine, *Angew. Chem., Int. Ed.*, 1998, **37**, 1698.
- 6 L. Schwink and P. Knochel, *Tetrahedron Lett.*, 1996, **37**, 25.
- 7 Y. Imai, W. Zhang, T. Kida, Y. Nakatsuji and I. Ikeda, *Chem. Lett.*, 1999, 243.
- 8 T. Hayashi, A. Yamamoto, M. Hojo, K. Kishi, Y. Ito, E. Nishioka, H. Miura and K. Yanagi, *J. Organomet. Chem.*, 1989, **370**, 129.
- 9 H. Jendrala and E. Paulus, *Synlett*, 1997, 471.
- 10 W. Zhang, Y. Adachi, T. Hirao and I. Ikeda, *Tetrahedron: Asymmetry*, 1996, **7**, 451.
- 11 M. Lotz, T. Ireland, J. J. A. Perea and P. Knochel, *Tetrahedron: Asymmetry*, 1999, **10**, 1839.
- 12 J. Kang, J. H. Lee, S. H. Ahn and J. S. Choi, *Tetrahedron Lett.*, 1998, **39**, 5523.
- 13 J. J. A. Perea, A. Borner and P. Knochel, *Tetrahedron Lett.*, 1998, **39**, 8073.
- 14 J. J. A. Perea, M. Lotz and P. Knochel, *Tetrahedron: Asymmetry*, 1999, **10**, 375.
- 15 M. T. Reetz, E. W. Beuttenmuller, R. Goddard and M. Pasto, *Tetrahedron Lett.*, 1999, **40**, 4977.
- 16 L. Schwink, T. Ireland, K. Püntener and P. Knochel, *Tetrahedron: Asymmetry*, 1998, **9**, 1143.
- 17 W. Zhang, T. Hirao and I. Ikeda, *Tetrahedron Lett.*, 1996, **37**, 4545.
- 18 W. Zhang, T. Kida, Y. Nakatsuji and I. Ikeda, *Tetrahedron Lett.*, 1996, **37**, 7995.
- 19 K. H. Ahn, C. W. Cho, J. Park and S. Lee, *Tetrahedron: Asymmetry*, 1997, **8**, 1179.
- 20 W. Zhang, T. Shimanuki, T. Kida, Y. Nakatsuji and I. Ikeda, *J. Org. Chem.*, 1999, **64**, 6247.
- 21 T. Hayashi, A. Yamamoto, M. Hojo and Y. Ito, *J. Chem. Soc., Chem. Commun.*, 1989, 495.
- 22 M. A. Carroll, D. A. Widdowson and D. J. Williams, *Synlett*, 1994, 1025.
- 23 Y.-J. Cho, M. A. Carroll, A. J. P. White, D. A. Widdowson and D. J. Williams, *Tetrahedron Lett.*, 1999, **40**, 8265.
- 24 D. W. Slocum, T. R. Engelmann, C. Ernst, C. A. Jennings, W. Jones, B. Koonvitsky, J. Lewis and P. Shenkin, *J. Chem. Ed.*, 1969, **46**, 144.
- 25 U. T. Mueller-Westerhoff, Z. Yang and G. Ingram, *J. Organomet. Chem.*, 1993, **463**, 163.
- 26 M. D. Rausch and D. J. Ciappenelli, *J. Organomet. Chem.*, 1967, **10**, 127.
- 27 G. G. A. Balavoine, G. Doisneau and T. Fillebeen-Khan, *J. Organomet. Chem.*, 1991, **412**, 381.
- 28 M. Vogel, M. Rausch and H. Rosenberg, *J. Org. Chem.*, 1957, **22**, 1016.
- 29 R. B. Woodward, M. Rosenblum and M. C. Whiting, *J. Am. Chem. Soc.*, 1952, **74**, 3458.
- 30 D. W. Slocum and B. P. Koonvitsky, *J. Org. Chem.*, 1976, **41**, 3664.
- 31 C. Zou and M. S. Wrighton, *J. Am. Chem. Soc.*, 1990, **112**, 7578.
- 32 G. L. Sterzo and G. Ortaggi, *Gazz. Chim. Ital.*, 1983, **113**, 721.
- 33 M. Hillman and J. D. Austin, *Organometallics*, 1987, **6**, 1737.
- 34 G. Iftime, J.-C. Daran, E. Manoury and G. G. A. Balavoine, *Organometallics*, 1996, **15**, 4808.
- 35 H. Schottenberger, M. Buchmeiser, C. Rieker, P. Jainter and K. Wurst, *J. Organomet. Chem.*, 1997, **541**, 249.
- 36 M. N. Nefedova, I. A. Mamedyarova, P. P. Petrovski and V. I. Sokolov, *J. Organomet. Chem.*, 1992, **425**, 125.
- 37 G. W. Gokel, D. Marquarding and I. K. Ugi, *J. Org. Chem.*, 1972, **37**, 3052.
- 38 T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1138.
- 39 S. Bhattacharyya, *Organometallics*, 1996, **15**, 1065.
- 40 S. Bhattacharyya, *Synlett*, 1995, 971.

- 41 S. Bhattacharyya, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1381.
42 R. C. Petter and C. I. Milberg, *Tetrahedron Lett.*, 1989, **30**, 5085.
43 W. G. Kofron and L. M. Baclawski, *J. Org. Chem.*, 1976, **41**, 1879.
44 C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, 1957, **22**, 482.
45 M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, 1957, **22**, 903.
46 P. C. Reeves, J. J. Mrowca, M. M. Borecki and W. A. Sheppard, *Org. Synth.*, 1976, **56**, 28.
47 S. Kovac and V. Ropic, *J. Organomet. Chem.*, 1990, **384**, 147.
48 A. Sonoda, I. Moritani, T. Saraie and T. Wada, *Tetrahedron Lett.*, 1969, 2943.
49 D. Bankston, *J. Organomet. Chem.*, 1989, **379**, 129.
50 J. F. Gallagher, G. Ferguson, C. Gildewell and C. M. Zakaria, *Acta Crystallogr., Sect. C*, 1994, **C50**, 18.
51 K. Gonsalves, L. Zhan-ru and M. D. Rausch, *J. Am. Chem. Soc.*, 1984, **106**, 3862.
52 A. Harada, Y. Hu, S. Yamamoto and S. Takahashi, *J. Chem. Soc., Dalton Trans.*, 1988, 729.
53 T. Akiyama, Y. Hoshi, S. Goto and A. Sugimori, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1851.
54 B. V. Zhuk, G. A. Domrachev, N. M. Semenov, E. I. Mysov, R. B. Materikova and N. S. Kochetkova, *J. Organomet. Chem.*, 1980, **184**, 231.
55 P. Singh, M. D. Rausch and T. E. Bitterwolf, *J. Organomet. Chem.*, 1988, **352**, 273.