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Synthesis, structures and reactions of some metallocene alcohols

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Abstract

E-1-Ferrocenyl-4,4-dimethylpent-2-ene-1-one has been synthesised from the Friedel–Crafts acylation of ferrocene with *E*-3-*tert*-butylacryloylchloride and converted to 1-ferrocenyl-3-chloro-4,4-dimethylpentan-1-one using ethereal hydrogen chloride. This new chloro ketone has been converted into three new ferrocene alcohols: 1-ferrocenyl-3,4-dimethyl-4-hydroxypentan-1-one, 1-ferrocenyl-3-chloro-4,4-dimethylpentan-1-ol, and 2,2,6,6-tetramethyl-3-ferrocenyl-5-chloroheptan-3-ol. A new dinuclear ferrocene derivative, *E,E*-2,2,9,9-tetramethyl-5,6-diferrocenyl-deca-3,7-diene, was isolated after treatment of 1-ferrocenyl-3-chloro-4,4-dimethylpentan-1-ol with acidic alumina; its structure was confirmed by X-ray crystallography, whilst electrochemistry revealed metal–metal interactions of similar magnitude to those seen for other 1,2-bis(ferrocenyl)ethane derivatives. Crystal structures have also been determined for 2,2,6,6-tetramethyl-3-ferrocenyl-5-chloroheptan-3-ol, *rac*-1-hydroxy[3]ferrocenophane, *rac*-1S,3S-1,3-diphenyl-1-hydroxy[3]ferrocenophane, and of *rac*-1,1′-diphenyl-1,1′-(1,1′-ruthenocenediyl)dimethanol and show an intramolecular Cl···H–O hydrogen bond, a tetramer based on O···H–O hydrogen bonds, no hydrogen bonding, and a dimer with inter- and intramolecular O···H–O hydrogen bonds, respectively.
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1. Introduction

α-Hydroxy derivatives of the group 8 metallocenes have attracted interest for a variety of reasons. Many have been synthesised as precursors to metallocene-stablised carbocations, which can be described as (η^5-cyclopentadienyl-η^6-fulvene)metal(II) and whose structures and bonding have been extensively studied [1–12], and which have themselves served as synthetic intermediates [12–17]. Metallocenyl alcohols have also been used as intermediates in the synthesis of chiral ligands for asymmetric catalysis [18,19]. The alcohols themselves have also attracted attention as redox-active probes of micelles [20]. The structures adopted by the alcohols have been much studied; these species show a rich variety of hydrogen bonding motifs, with hydrogen bonds from OH to the metal, to other OH groups, to π-

systems, and to other substituents all possible, and with the conformational flexibility of the species often allowing competition between intra- and intermolecular effects. Many investigations have employed X-ray crystallography [21–34]; others have used computational techniques [35–37] and infra-red spectroscopy [22,32,36].

We were interested in both [3]metallocenophanes – as potential strained precursors to organometallic polymers [38] – and in (η^5-cyclopentadienyl)(η^5-hydropenta-lene)iron complexes – as precursors to pentalene-bridged bi- and trimetallic species [39]. In principle, ketone precursors to both these types of compounds can be obtained through reaction of metallocenes with acryloyl chloride derivatives. This paper presents new metallocene chemistry that we encountered in the course of this work, specifically:

(i) the results of the Friedel–Crafts reaction of ruthenocene with acryloyl chloride and 3-chloropropionyl chloride, and of ferrocene with *E*-3-*tert*-butylacryloylchloride;

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(ii) the use of one of these products, E-1-ferrocenyl-4,4-dimethylpent-2-ene-1-one, in the synthesis of new ferrocene derivatives, including three new α-ferrocenyl alcohols;

(iii) the formation, structure, and electrochemistry of an unusual bimetallic species from one of these alcohols;

(iv) determination of the crystal structures of several new and previously known α-metallocenyl alcohols, and comparison of these structures with those of other metallocene alcohol structures in the zliterature.

2. Experimental details

2.1. 1-Ruthenocenylprop-2-ene-1-one, 1

A solution of ruthenocene (0.25 g, 1 mmol) and AlCl$_3$ (0.16 g, 1 mmol) in dry CH$_2$Cl$_2$ (50 mL) was stirred under dinitrogen at 40 °C for 30 min. Into the mixture was added acryloyl chloride (0.09 mL, 1 mmol) via syringe and the reaction mixture was refluxed for one hour. The mixture was then cooled to ambient temperature and the reaction was quenched with water (5 mL). The organic portion was separated, washed with water (3 × 50 mL) and dried over MgSO$_4$. Purification using column chromatrography on silica gel, eluting with hexane, gave a small amount of ruthenocene as the first band (ca. 2%) and the yellow product as the second band. Yield: 82% (0.23 g, 0.8 mmol) ^{1}H NMR (CDCl$_3$) δ 6.63 (1H, dd, $J = 10.0$ Hz, 17.8 Hz, COCH), 6.62 (1H, dd, $J = 4.0$ Hz, 10.0 Hz, =CH$_2$), 6.35 (1H, dd, $J = 4.0$ Hz, 17.8 Hz, =CH$_2$), 5.11 (2H, t, $J = 1.8$ Hz, sub Cp), 4.81 (2H, t, $J = 1.8$ Hz, sub Cp), 4.55 (5H, s, unsub Cp). ^{13}C{^{1}H} NMR δ 191.4, 133.3, 126.9, 84.9, 74.3, 73.0, 71.8. Anal. Calc.: C, 54.73; H, 4.24. Found: C, 54.12; H, 4.01%. MS (EI) m/z: 296.1 (M$^+$, 100%).

2.2. 1,1′-Ruthenocene-1,1′-diylbis(3-chloropropan-1-one), 2

A mixture of ruthenocene (0.25 g, 1 mmol) and AlCl$_3$ (0.32 g, 2 mmol) in dry CH$_2$Cl$_2$ (50 mL) was stirred under dinitrogen at 40 °C for 30 min. Then to the mixture was added a solution of ClCH$_2$CH$_2$COCl (0.1 mL, 1 mmol) via syringe and the reaction mixture was refluxed for one hour. The mixture was then cooled to ambient temperature and the reaction was quenched with water (5 mL). The organic portion was separated, washed with water (3 × 50 mL) and dried over MgSO$_4$. Purification using column chromatrography on silica gel, eluting with ethyl acetate/hexane (1:4), gave ruthenocene as the first band (45%) and the yellow product as the second band. However, the cyclisation product analogous to the product of the same reaction using ferrocene was not observed. Yield: 48% (0.24 g, 0.5 mmol). ^{1}H NMR (CDCl$_3$) δ 5.23 (4H, t, $J = 1.8$ Hz, Cp), 4.93 (4H, t, $J = 1.8$ Hz, Cp), 3.91 (4H, t, $J = 6.3$ Hz, CH$_2$Cl), 3.05 (4H, t, $J = 6.3$ Hz, COCH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 197.3, 84.7, 75.8, 72.5, 41.4, 38.6. Anal. Calc.: C, 46.61; H, 3.91; Cl, 17.20. Found: C, 46.68; H, 4.03; Cl, 17.18%. MS (EI) m/z: 411.9 (M$^+$, 23%), 375.9 (M$^+$−Cl, 35%), 340.0 (M$^+$−2Cl, 100%).

2.3. E-1-Ferrocenyl-4,4-dimethylpent-2-ene-1-one, 3

Ferrocene (10.66 g, 57.3 mmol) and AlCl$_3$ (7.64 g, 57.3 mmol) were placed under nitrogen in a round-bottomed flask, and CH$_2$Cl$_2$ (250 mL) was added with stirring. The solution was then cooled to −78 °C and a solution of E-3-tert-butylacryloylchloride [40] (8.40 g, 57.3 mmol) in CH$_2$Cl$_2$ (20 mL) added dropwise over 30 min. During the addition the solution became deep purple in colour. The reaction mixture was warmed slowly to room temperature over a period of 20 h after which time it was quenched carefully by the dropwise addition of a saturated aqueous solution of Na$_2$S$_2$O$_4$ (150 mL, deoxygenated for 30 min with dry nitrogen) under nitrogen. The deep red organic layer and aqueous layer were transferred to a separating funnel (from this point the mixture was handled in air) along with a further portion of water (100 mL), and the organic layer separated. This layer was then washed with water (2 × 100 mL) and saturated aqueous NaCl (1 × 100 mL) and dried over MgSO$_4$. The solution was filtered and all volatiles removed in vacuo to yield an essentially NMR-pure brick-red air-stable solid (16.93 g, 57.1 mmol, 99%). Recrystallisation from a saturated solution in hexane/diethyl ether, cooled to −30 °C, gave an analytically pure sample. ^{1}H NMR (CDCl$_3$): δ 7.03 (1H, d, $J = 15.6$ Hz, alk$H$), 6.41 (1H, d, $J = 15.6$ Hz, alk$H$), 4.81 (2H, m, sub Cp), 4.52 (2H, m, sub Cp), 4.16 (5H, s, Cp), 1.15 (9H, s, t-BuH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 193.7, 155.3, 121.6, 80.4, 72.4, 70.0, 69.7, 33.7, 28.9. Anal. Calc.: C, 68.94; H, 6.81. Found: C, 69.12; H, 6.89%. Selected IR data (thin film): v 1657 (C=O), 1606 (C=C) cm^{-1}. MS (EI) m/z: 296.1 (M$^+$, 100%), 213.0 (FcCO$^+$, 17%), 186.0 (FcH$^+$, 54%).

2.4. 1-Ferrocenyl-3-chloro-4,4-dimethylpentan-1-one, 4

Hydrogen chloride (300 mL, 2 M solution in Et$_2$O) was added in one portion to a solution of 3 (18.30 g, 61.80 mmol) in dry diethyl ether (300 mL). The reaction mixture was stirred under nitrogen at room temperature for 4 h, during which the solution lightened considerably in colour. The reaction mixture was then quenched by slow addition to saturated aqueous NaHCO$_3$ (500 mL) in air. The aqueous layer was separated and washed with Et$_2$O (2 × 100 mL), the organic extracts were then combined and washed with sat. NaCl (aq.) (2 × 150 mL)

before drying over MgSO$_4$. The solution was filtered and the solvent removed in vacuo to leave an orange–brown air-stable solid essentially pure by ^{1}H NMR (18.90 g, 56.82 mmol, 92%). Recrystallisation from hexane/CH$_2$Cl$_2$ yielded analytically pure **4**. ^{1}H NMR (CDCl$_3$): δ 4.85 (1H, m, sub Cp), 4.72 (1H, m, sub Cp), 4.52 (1H, m, sub Cp), 4.47 (1H, dd, J = 9 Hz, J = 1.8 Hz, C(t-Bu)H), 4.25 (5H, s, Cp), 3.19 (1H, dd, $^2J_{H-H}$ = 17.1 Hz, $^3J_{H-H}$ = 9 Hz, CHH), 2.93 (1H, dd, $^2J_{H-H}$ = 17.1 Hz, $^3J_{H-H}$ = 1.8 Hz, CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 200.7, 78.9, 72.44, 72.37, 69.9, 69.4, 69.2, 67.4, 43.5, 35.6, 26.7. Anal. Calc.: C, 61.38; H, 6.36. Found: C, 61.08; H, 5.96%. Selected IR data (thin film): ν 1669 (C=O) cm^{-1}. MS (EI) m/z: 332.0 (M$^+$, 72%), 296.1 (M$^+$−HCl, 100%), 213.0 (FcCO$^+$, 35%), 186.0 (FcH$^+$, 45%).

2.5. 1-Ferrocenyl-3,4-dimethyl-4-hydroxypentan-1-one, 5

A stirred suspension of AlCl$_3$ (0.80 g, 6.00 mmol) in dry CH$_2$Cl$_2$ (15 mL) was cooled to 0 °C in an ice-bath, and a solution of **4** (1.00 g, 3.00 mmol) in dry CH$_2$Cl$_2$ (30 mL) was added dropwise, forming a deep purple solution. The cooling bath was removed and the solution stirred for a further 4 h, after which time the reaction was complete according to TLC. The reaction mixture was quenched by pouring into water (50 mL) containing a small amount of Na$_2$S$_2$O$_4$, and the layers separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (50 mL), and the combined organics washed with H$_2$O (3 × 100 mL) and saturated aqueous NaCl (100 mL). The organics were then dried over MgSO$_4$, and all volatiles removed in vacuo to yield a red brown oil. Recrystallisation from diethyl ether gave pure **5** as an air-stable orange–brown solid (0.72 g, 2.30 mmol, 77%). ^{1}H NMR (CDCl$_3$): δ 4.80 (2H, m, CpH), 4.49 (2H, m, CpH), 4.20 (5H, s, unsub. CpH), 3.10 (1H, dd, J = 16.5 Hz, J = 4.1 Hz, CHH), 2.52 (1H, dd, J = 16.5 Hz, J = 7.8 Hz, CHH), 2.24 (1H, m, CMeH), 1.28 (3H, s, Me), 1.17 (3H, s, Me), 0.98 (3H, d, J = 6.9 Hz, CMeH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 205.42, 79.15, 72.61, 72.22, 72.19, 69.78, 69.38, 42.22, 39.85, 29.13, 24.50, 16.42. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 203.87, 80.23, 72.24, 72.04, 72.01, 70.00, 69.79, 69.75, 42.57, 40.07, 29.35, 24.55, 16.64. Anal. Calc.: C, 64.98; H, 7.06. Found: C, 64.62; H, 6.89%. Selected IR data (KBr disk): ν 3413 (O–H), 1646 (C=O) cm^{-1}.

2.6. 1-Ferrocenyl-3-chloro-4,4-dimethylpentan-1-ol, 6

A solution of **4** (5.00 g, 16.90 mmol) in dry diethyl ether (80 mL) and cooled to 0 °C in an ice-bath. A suspension of LiAlH$_4$ (0.32 g, 8.5 mmol) in dry diethyl ether (20 mL) was then added dropwise to this solution and stirred at 0 °C for 2 h. The ice-bath was then removed and the mixture stirred for a further 2 h. The

reaction was then quenched by dropwise addition of diethyl ether saturated with H$_2$O, which was accompanied by the precipitation of a green/white solid. The orange–yellow solution was filtered off and the solid washed with diethyl ether (10 mL). The organic extracts were washed with water (2 × 100 mL), and then saturated NaCl solution (100 mL), and dried over anhydrous K$_2$CO$_3$. The solution was filtered and pumped to dryness in vacuo to yield a sticky yellow solid. Addition of dry pentane (20 mL) with vigorous stirring gave a yellow powdery solid and an orange solution. The solid was isolated by filtration and shown by ^{1}H NMR spectroscopy (CDCl$_3$) to be a pure mixture of isomers, **6a** and **6b** (4.50 g, 13.40 mmol, 80%). Cooling of the supernatant to −30 °C over a period of 24 h yielded a mixture of yellow powder and orange microcrystalline lumps. Manual separation of the orange crystalline material and recrystallisation from dry pentane gave pure **6b**. Both isomers are yellow solids which decompose slowly in both the solid state and in solution.

2.6.1. Isomer: 6a
^{1}H NMR (CDCl$_3$): δ 4.60 (1H, ddd, CHOH), 4.31 (1H, m, sub Cp), 4.23 (5H, s, Cp), 4.20 (2H, m, sub Cp), 3.36 (1H, dd, J_{2H} = 11.9 Hz, J_{2H} = 1.8 Hz, CCl(t-Bu)H), 2.20 (1H, m, CHH), 2.21 (1H, d, 1.8 Hz), 1.85 (1H, m, CHH), 0.91 (9H, s, t-BuH). ^{13}C{^{1}H} NMR (CDCl$_3$): 93.17, 71.21, 68.65, 68.50, 68.26, 67.83, 66.67, 63.86, 41.35, 35.77, 26.56.

2.6.2. Isomer: 6b
^{1}H NMR (CDCl$_3$): δ 4.70 (1H, ddd, CHOH), 4.25 (1H, m, sub Cp), 4.20 (5H, s, Cp), 4.18 (2H, m, sub Cp), 4.13 (1H, dd, J_{2H} = 11.7 Hz, J_{2H} = 1.8 Hz, CCl(t-Bu)H), 1.91 (1H, d, J = 2.9 Hz, –OH), 2.07–1.83 (2H, m, CH$_2$), 1.04 (9H, s, t-BuH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 93.49, 71.36, 68.35, 68.02, 67.98, 66.81, 66.67, 65.62, 41.89, 35.69, 26.73. Anal. Calc.: C, 61.01; H, 6.93. Found: C, 61.13; H, 6.76%. MS (EI) m/z: 334.1 (M$^+$, 85%), 298.1(M$^+$−HCl, 60%), 280.1 (M$^+$−HCl–H$_2$O, 66%), 265.0 (M$^+$−HCl–H$_2$O–Me, 23%), 214.0 (FcCOH$^+$, 68%), 186.0 (FcH$^+$, 100%).

2.7. 1-Ferrocenyl-3-chloro-4,4-dimethylpentane, 7

A suspension of LiAlH$_4$ (0.13 g, 3.40 mmol) in dry diethyl ether (10 mL) and cooled to 0 °C. AlCl$_3$ (0.45 g, 3.40 mmol) was added in one portion as a solid. A solution of **4** (1.00 g, 3.4 mmol) in diethyl ether (25 mL) was then added dropwise over 20 min. The mixture was then allowed to warm to room temperature and stirred for 2 h, after which the reaction was quenched by cautious, dropwise addition of water. The yellow solution was then filtered and the residues washed with diethyl ether (2 × 10 mL). The combined diethyl ether extracts were washed with water (20 mL), saturated aqueous

NaCl (20 mL) and dried over anhydrous K_2CO_3. After filtration, all volatiles were removed in vacuo to leave an air-stable NMR-pure pungent yellow solid (0.75 g, 2.35 mmol, 69%). An analytical sample was recrystallised from hot pentane by cooling to −30 °C. ^{1}H NMR (CDCl$_3$): δ 4.11 (5H, s, Cp), 4.05 (3H, m, sub Cp), 3.65 (1H, dd, $J_{2H} = 11.5$ Hz, $J_{2H} = 1.9$ Hz, CCl(t-Bu)H), 2.74 (1H, m, FcCHH), 2.36 (1H, m, FcCHH), 1.94 (1H, m, CHH), 1.98 (1H, m, CHH), 1.00 (9H, s, t-BuH). ^{13}C NMR (CDCl$_3$): δ 88.13, 74.68, 68.58, 68.49, 67.81, 67.35, 67.21, 36.01, 34.75, 27.80, 26.78. Anal. Calc.: C, 64.08; H, 7.27. Found: C, 64.20; H, 7.01%. MS (EI) m/z: 318.1 (M$^+$, 45%), 282.1 (M$^+$−HCl, 100%) 225.0 (M$^+$−HCl−C$_4$H$_9$, 23%) 212.0 (FcCHCH$_2^+$, 35%), 199.0 (FcCH$_2^+$, 75%), 186.0 (FcH$^+$, 10%).

2.8. 2,2,6,6-Tetramethyl-3-ferrocenyl-5-chloroheptan-3-ol, 8

A solution of **4** (1.00 g, 3.38 mmol) in pentane/Et$_2$O (35 mL/35 mL) was cooled to −78 °C and *tert*-butyllithium (1.98 mL, 1.7 M in pentane) was added dropwise. After stirring at −78 °C for 30 min the solution was allowed to warm to room temperature and stirred for an additional 2 h, during which time it became cloudy. The reaction mixture was then quenched by addition of saturated aqueous NH$_4$Cl (10 mL), filtered and the organic layer washed with aqueous NaHCO$_3$ (2 × 30 mL) and saturated aqueous NaCl (30 mL). The organic layer was then dried over K$_2$CO$_3$, filtered and all volatiles removed in vacuo. The sticky orange solid was recrystallised from a pentane/diethyl ether mixture at −30 °C to give pure **8** as an air stable orange solid (0.61 g, 1.56 mmol, 46%). Crystals suitable for single crystal X-ray diffraction were grown by slow cooling of a concentrated MeOH solution to −30 °C. ^{1}H NMR (CDCl$_3$): δ 4.42 (1H, t, $J = 5.5$ Hz, –CHCl–), 4.31 (1H, m, sub CpH), 4.26 (5H, s, Cp), 4.14 (1H, m, sub CpH), 4.09 (1H, m, sub CpH), 3.82 (1H, m, sub CpH), 2.70 (2H, d, $J = 5.1$ Hz, –CH$_2$–), 2.65 (1H, s, –OH), 1.13 (9H, s, t-BuH), 0.83 (9H, s, t-BuH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 99.94, 75.66, 72.39, 68.67, 68.30, 67.42, 67.37, 65.89, 40.16, 39.25, 37.33, 26.94, 26.34. Anal. Calc.: C, 64.55; H, 8.00. Found: C, 64.13; H, 7.67%. MS (EI) m/z: 390.1 (M$^+$, 15%), 354.1 (M$^+$−HCl, 27%), 336.1 (M$^+$−HCl–H$_2$O, 27%), 297.1 (M$^+$−HCl–C$_4$H$_9$, 75%), 279.1 (M$^+$−HCl–H$_2$O–C$_4$H$_9$, 15%), 264.0 (M$^+$−HCl–H$_2$O–C$_4$H$_9$-Me, 52%), 213.0 (FcCO$^+$, 91%), 186.0 (FcH$^+$, 100%). Selected IR data (Nujol): v 3400 (O–H), 1466 (s), 1366 (s), 996 (s) cm^{-1}.

2.9. 2,2,9,9-Tetramethyl-5,6-diferrocenyl-deca-3,7-diene, 9

Acidic Al$_2$O$_3$ (4 g, Brockmann grade 1) was added to a solution of **6** (3.64 g, 10.90 mmol) in benzene (100 mL)

under an atmosphere of N$_2$ and the mixture was refluxed vigorously, using a Dean–Stark apparatus to remove water. After 1 h the solution had become dark green, and was allowed to cool. The mixture was filtered under air and the solids washed with pentane until the extracts were clear. All volatiles were removed in vacuo to leave a dark green solid shown by TLC to contain 4 mobile components (silica, eluting with hexane/dichloromethane (9:1)). These were separated by column chromatography on silica: the first two bands were eluted with hexane/dichloromethane (9:1), but ^{1}H NMR spectroscopy of the residues after removal of volatiles revealed both these fractions to still contain a mixture of products which was not investigated further. The third band was eluted with hexane/dichloromethane (1:1). Removal of solvent from this fraction in vacuo gave an air-stable yellow–orange solid, shown by ^{1}H NMR spectroscopy to be a mixture of isomers of **9** (0.50 g, 1.78 mmol, 16%). Crystals suitable for single-crystal X-ray diffraction were grown by slow cooling of a saturated pentane solution to −30 °C. ^{1}H NMR (CDCl$_3$): δ 5.47–5.29 (4H, m, vinylic H), 4.01 (5H, s, CpH), 3.99 (5H, s, CpH), 3.95 (4H, m, sub Cp), 3.88 (1H, m, sub Cp), 3.78 (1H, m, sub Cp), 3.75 (1H, m, sub Cp), 3.71 (1H, m, sub Cp), 2.97 (2H, m, allylic H), 1.06 (9H, s, t-BuH), 1.03 (9H, s, t-BuH). ^{13}C NMR (CDCl$_3$): δ 141.33, 141.16, 125.51, 125.31, 90.56, 89.92, 68.77, 68.27, 67.34, 66.99, 66.65, 66.25, 66.20, 51.64, 51.50, 33.01, 32.94, 29.89, 29.83. Anal. Calc.: C, 72.61; H, 7.53. Found: C, 72.54; H, 7.50%. MS (EI) m/z: 560.2 (M$^+$−2H, 12%), 281.1 ([FcCHCH=CH$'$Bu]$^+$, 100%). Selected IR data (KBr disk): v 2958 (s), 2890 (s), 1106 (s), 996 (s), 817 (s), 486(s) cm^{-1}.

The following compounds were prepared according to literature procedures: **10** [41,42], **11** [43,44], and **12** (omitting the chiral auxiliary used in the literature) [45].

2.10. Crystallography

Crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N$_2$ using an Oxford Cryosystems CRYO-STREAM unit. Diffraction data were measured at 150 K using graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). DIP 2000 intensity data were processed using the programs DENZO and SCALEPACK [46]; and Kappa CCD data with DENZO-SMN [46]. Structures were solved using SIR92 [46], with additional non-hydrogen atoms being located, where necessary, from difference Fourier maps. Full-matrix least square refinements were carried out against F (on all data for **8** and **9**; on data with $I > 2\sigma(I)$ for (**10–12**) using CRYSTALS [47]. Chebychev polynomial weighting schemes (five-term for **8**; three-term for (**9–12**) were applied [48]. Details of the data acquisition and refinements are summarised in Table 1; complete crystallographic data

Table 1
Details of crystal structure determinations

	8	9	10	11	12
Formula	$C_{21}H_{31}ClFeO$	$C_{34}H_{42}Fe_2$	$C_{13}H_{14}FeO$	$C_{25}H_{22}FeO$	$C_{24}H_{22}O_2Ru$
Formula weight	392.77	562.40	242.10	394.10	443.51
Crystal growth	MeOH, −30 °C	Pentane, −30 °C	Et_2O, −30 °C	Et_2O, −30 °C	Et_2O, −30 °C
Crystal appearance	Orange prism	Orange prism	Orange–brown fragment	Orange rhombohedron	Colourless block
Crystal size (mm^3)	$0.5 \times 0.4 \times 0.4$	$0.3 \times 0.2 \times 0.15$	$0.5 \times 0.5 \times 0.5$	$0.4 \times 0.4 \times 0.6$	$0.08 \times 0.2 \times 0.35$
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
Diffractometer	DIP2000	DIP2000	DIP2000	DIP2000	KappaCCD
a (Å)	11.8290(2)	5.930(12)	7.592(1)	11.703(1)	29.2157(3)
b (Å)	21.1790(6)	14.70(4)	11.803(1)	11.961(1)	5.9026(1)
c (Å)	15.4910(4)	16.59(4)	12.302(1)	13.246(1)	25.2696(3)
α (°)	90	92.70(3)	113.621(3)	90	90
β (°)	91.361(2)°	96.86(4)	92.141(5)	106.548(4)	120.4456(7)
γ (°)	90	97.60(3)	93.572(5)	90	90
V ($Å^3$)	3879.8(5)	1420.8(5)	1005.7	1777.4	3756.8
Z	8	2	4	4	8
D_{calc} (g cm^{-3})	1.34	1.31	1.59	1.47	1.568
μ (mm^{-1})	0.92	1.04	1.46	0.86	0.851
$F(000)$	1664	596	504	824	1744
θ_{max} (°)	26.6	26.6	26.7	26.6	27.5
Number of reflections	31740	15328	5320	8875	20524
Independent reflections	7501	4788	3828	3429	4664
R_{int}	0.04	0.06	0.036	0.026	0.038
Data	6213 ($I > 6\sigma(I)$)	2435 ($I > 3\sigma(I)$)	3296 ($I > 3\sigma(I)$)	3146 ($I > 3\sigma(I)$)	3641 ($I > 3\sigma(I)$)
Number of parameters	434	352	272	247	332
R	0.0534 (all data)	0.0593 (all data)	0.0444 ($I > 3\sigma(I)$)	0.0438 ($I > 3\sigma(I)$)	0.0288 ($I > 3\sigma(I)$)
wR	0.0354 (all data)	0.0602 (all data)	0.0428 ($I > 3\sigma(I)$)	0.0482 ($I > 3\sigma(I)$)	0.0246 ($I > 3\sigma(I)$)
Final GOF	1.0446	0.8708	1.1566	1.0946	1.0319
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.70, −0.57	0.62, −0.62	−0.75, 1.10	−0.35, 0.80	−0.62, 0.50

for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 210126-210130 for compound **8–12**.

In the structure of **9** the half-molecule containing the atom Fe(2) was modelled with a disordered *tert*-butyl group [C(32), C(34) and C(36) with 33% occupancy; C(33), C(35) and C(37) 67% occupancy]. A number of atoms in both half-molecules are highly correlated with each; their anisotropic thermal parameters were restrained to be similar.

2.11. Electrochemical data

Electrochemical data were acquired at 298 K using a BAS potentiostat, a glassy-carbon working electrode (circular, 3 mm radius), a platinum-wire auxiliary electrode, and a silver wire (coated with AgCl by anodising in KCl solution) pseudo-reference electrode. The cell data were acquired in deoxygenated dry dichloromethane solutions 0.1 M in $[^nBu_4N]^+[PF_6]^-$ and ca. 10^{-4} to 10^{-3} M in analyte. Scan rates employed for cyclic voltammetry (CV) were varied in 50 mVs^{-1} steps from 50 to 400 mVs^{-1} (three examples are shown in Fig. 3); the currents observed showed the expected dependence on the square root of the scan rate [49]. Potentials were referenced to the ferrocenium/ferrocene couple by running ferrocene under the same conditions as the analyte; the error in the reported potentials is estimated from comparison of successive scans to be ca. ±10 mV. Differential pulse (10 mVs^{-1}, pulse height 50 mV) and square-wave (Oster-young, 60 mVs^{-1}) voltammograms were acquired on the same solution of **9** that was used for CV.

3. Results and discussion

3.1. Some reactions of metallocenes and acryloyl chloride derivatives

As discussed in the introduction, ketone precursors to both [3]metallocenophanes and (η^5-cyclopentadie-nyl)(η^5-hydropentalene)iron can, in principle, be obtained through reaction of metallocenes with acryloyl chloride derivatives (Fig. 1). Indeed, reaction of ferrocene with acryloyl chloride under low temperature Friedel–Crafts conditions yields 1-keto[3]ferrocenophane in reasonable yield [50]. Mixtures of unbridged and homo-annularly bridged ferrocenes have been reported as the products of Friedel–Crafts reactions with various acryloyl chlorides and β-chloro acyl chlorides [51,52].
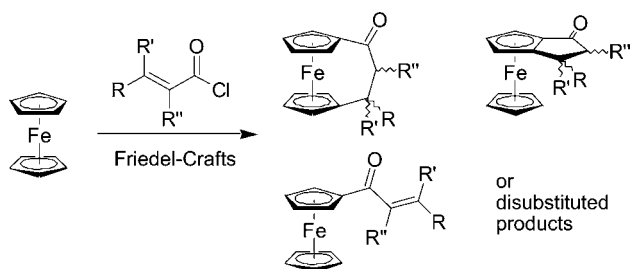
Fig. 1. Possible outcomes from the Friedel–Crafts reaction of ferrocene with substituted acryloyl chlorides.

Reaction of ruthenocene and acryloyl chloride using the same conditions reported for the preparation of 1-keto[3]ferrocenophane has previously been reported to give the α,β-unsaturated ketone, **1**, (Scheme 1) as the major product with no evidence of any cyclisation. We have confirmed this result and characterised **1** for the first time; the same result was also obtained using a variety of reaction temperatures and concentrations. Presumably inter-ring cyclisation to 1-keto[3]ruthenocenophane is disfavoured by the greater distance between the two rings sandwiching the larger ruthenium atom, although it has been reported that 3-ruthenocenyl-propanoate can be cyclised to this product using trifluoroacetic anhydride [53]. Attempts to perform a double Friedel–Crafts reaction (i.e., simultaneous acylation and alkylation) on ruthenocene using 3-chloropropionyl
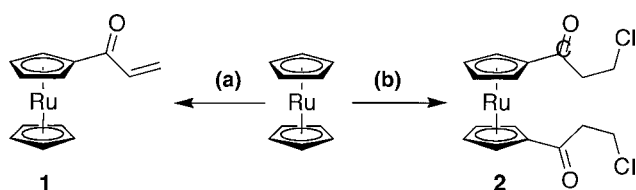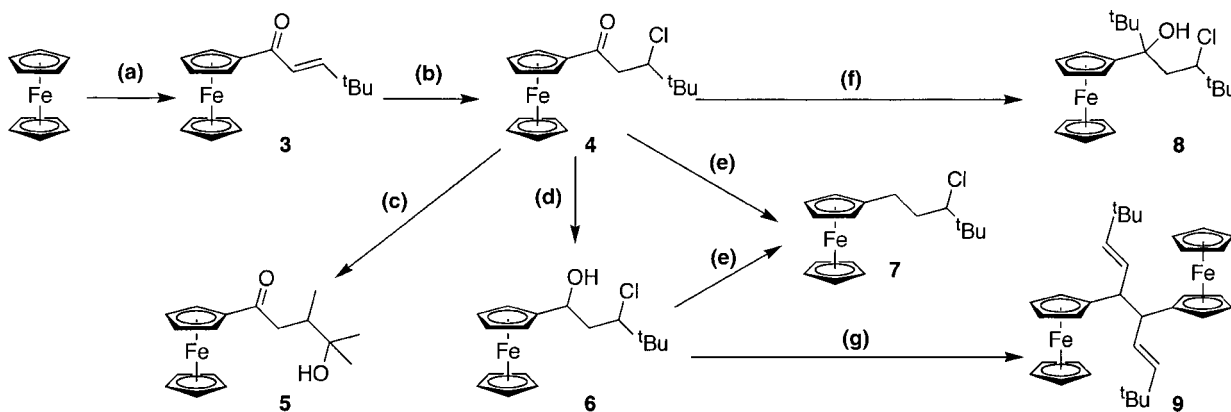
chloride and two equivalents of AlCl$_3$ also gave no cyclised products; in this case the diacylation product 1,1′-ruthenocene-1,1′-diylbis(3-chloropropan-1-one), **2**, was obtained (Scheme 1).

In an attempt to synthesise highly soluble cyclised ferrocene species, we investigated the use of 3-*tert*-butyl-acryloylchloride [40] in AlCl$_3$-catalysed Friedel–Crafts reactions. The reaction of this reagent with an equimolar quantity ferrocene at −78 °C gave, after work-up, an almost quantitative yield of the α,β-unsaturated ketone, **3** (Scheme 2). According to ^{1}H NMR spectroscopy, neither cyclised products nor any disubstituted ferrocene were formed. The same reaction gave a mixture of mono- and 1,1′-disubstituted products when run at room temperature. The lack of cyclised products is consistent with the results of Crawford et al. [51] when investigating acryloyl chlorides with β-substituents; however, El Zohry has been successful in cyclising some β-substituted species [52]. Attempts to cyclise the unsaturated ketone, **3**, by treatment with trifluoroacetic acid in dichloromethane, ethereal tetrafluoroboric acid, and ethereal hydrogen chloride were unsuccessful. Unchanged **3** was recovered from the first two reactions, whilst HCl underwent addition to the C–C double bond to give 1-ferrocenyl-3-chloro-4,4-dimethylpentan-1-one, **4**.

3.2. Synthesis of new ferrocene alcohols

We attempted to cyclise **4** (homo- or hetero-annularly) through an intramolecular Friedel–Crafts reaction using two equivalents of AlCl$_3$ (two equivalents of AlCl$_3$ are necessary as the first equivalent coordinates to the ketone) in dichloromethane. After work up, the rearrangement product, 1-ferrocenyl-3,4-dimethyl-4-hydroxypentan-1-one, **5** was isolated; the initially formed secondary carbocation rearranges to a tertiary cation, which is evidently inert with respect to reaction with the

Scheme 1. Reagents and conditions: (a) CH$_2$=CHCOCl, AlCl$_3$, CH$_2$Cl$_2$, reflux; (b) ClCH$_2$CH$_2$COCl, AlCl$_3$, CH$_2$Cl$_2$, reflux.

Scheme 2. *Reagents and conditions*: (a) *E*-[t]BuCH=CHCOCl, AlCl$_3$, CH$_2$Cl$_2$, −78 °C; (b) HCl, Et$_2$O, r.t.; (c) AlCl$_3$, CH$_2$Cl$_2$, 0 °C; (d) LiAlH$_4$, Et$_2$O, 0 °C; (e) LiAlH$_4$, AlCl$_3$, Et$_2$O, 0 °C; (f) [t]BuLi, Et$_2$O, pentane, −78 °C; (g) acidic Al$_2$O$_3$, benzene, reflux.

ferrocenyl cyclopentadienyl rings and which is trapped by water in the work-up.

Reduction of the ketone functionality in **4** with LiAlH$_4$, led to the formation of another new alcohol 1-ferrocenyl-3-chloro-4,4-dimethylpentan-1-ol, **6**. **6** contains two chiral centres; a total of 4 isomers are formed of which there are 2 enantiomeric pairs (R,R S,S and R,S S,R): thus two species are observed in the ^{1}H NMR spectrum corresponding to the diastereomeric pairs. The relative integration of the two *tert*-butyl resonances of the crude mixture is 2:1 (the more abundant isomer has a *tert*-butyl resonance at 0.91 ppm (**6a**) and the less abundant isomer at 1.04 ppm (**6b**)). Partial separation of the diastereomeric pairs can be achieved by their differing solubilities in pentane, and it was found that **6b** was the least soluble component. Careful recrystallisation from pentane allowed the isolation of solely **6b**, and thus unambigious assignment of ^{13}C and ^{1}H NMR data to each isomer. The proton assignments were made by use of gCOSY ^{1}H–^{1}H correlation experiments, and removal of coupling to the hydroxyl proton by addition of D$_2$O. The most significant difference in chemical shift of the same proton between diastereomeric pairs is that of –CCl(^{t}Bu)*H*, which in **6a** is at 3.36 ppm and in **6b** at 4.13 ppm (CDCl$_3$). Both isomers are unstable in solution, decomposition to unidentified products is observed after several days; decomposition also occurs in the solid over ca. one week – this is observed whether or not the complex is stored under an inert atmosphere. Total reduction of the ketone, **4**, to the yellow ferrocenyl-chloroalkane, **7**, is possible using LiAlH$_4$/AlCl$_3$. This complex is also formed on reduction of the alcohol **6** under the same conditions.

The low-temperature reaction of **4** with *tert*-butyllithium gave 2,2,6,6-tetramethyl-3-ferrocenyl-5-chloroheptan-3-ol, **8**. ^{1}H NMR spectroscopy of the crude product revealed a complex mixture of products consistent with the presence of more than one diastereomer and other unidentified addition products. Again the molecule contains two chiral centres and four different isomers are possible: recrystallisation from pentane/Et$_2$O gave pure **8** as a single pair of enantiomers, as revealed by the presence of only two *tert*-butyl resonances in the ^{1}H NMR spectrum. The crystal structure of **8** is described along with those of several known metallocene alcohols in a later section of this paper.

3.3. Synthesis, structure, and electrochemistry of a bis(ferrocenyl)ethane

Attempts were made to dehydrate alcohol **6** to 1-ferrocenyl-3-chloro-4,4-dimethyl-1-pentene. Subjecting **6** to various conditions, including *para*-toluenesulphonic acid in benzene and (PhO)$_3$PMeI in HMPA [54], led to complex mixtures of products, perhaps due to complications arising from the presence of chloro group. An attempt involving reflux of a benzene solution of **6** with acidic alumina gave one major organic-soluble product, **9**, and several minor components, which were readily separated by column chromatography. A single crystal structure determination indicated **9** to be a dinuclear species, *meso-E,E*-2,2,9,9-tetramethyl-5,6-diferrocenyl-dec-3,7-diene, (Fig. 2). The ^{1}H NMR spectrum of the crude material can be assigned to a mixture of *rac* and *meso* diastereomers of this compound, which arise as a result of the new chiral centre at the carbon α to the ferrocenyl group. The main peak in the EI mass spectrum of **9** corresponds to half that of the dinuclear species, presumably reflecting the weakness of the central C–C bond (vide infra) and the stability of the 1-ferrocenyl-3-(*tert*-butyl)allylium cation.

The mechanism for formation of **9** is unclear, as is the identity of the reducing agent required; however, the intermediacy of 1-ferrocenyl-3-(*tert*-butyl)allylium or 1-ferrocenyl-3-chloro-4,4-dimethylpentyl-1-ium cations seems likely. α-Ferrocenylcarbocations are well-known to slowly dimerise to paramagnetic 1,2-bis(ferroceniumyl)ethanes, [16,55–58] which can be reduced to the corresponding neutral species. 1,2-Bis(metallocenyl)ethanes may also be obtained under acidic reducing conditions from α-ferrocenylalcohols [59,60], α-ferrocenylalkoxides [61], or vinylferrocenes [62], or from direct reduction of the α-metallocenylcarbocations [12].

The asymmetric unit contains two half-molecules, each straddling an inversion centre. There are two previous examples of structures of bis(ferrocenyl)ethanes: FcCH$_2$CH$_2$Fc [63] and FcCMe$_2$CMe$_2$Fc [64]. As with the structure of **9**, both molecules sit astride crystallo-
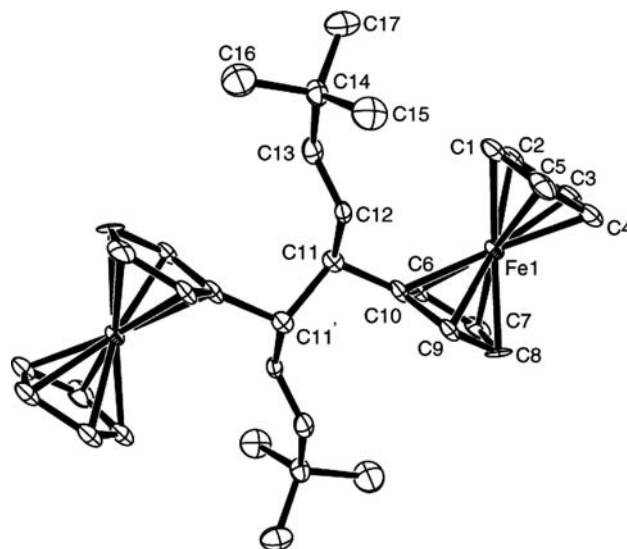

Fig. 2. View of one of the independent molecules of compound **9** in its crystal structure (50% thermal ellipsoids); the molecule sits astride an inversion centre and only the independent atoms are labelled. The second molecule (not shown) adopts a very similar conformation. All H atoms are omitted for clarity.
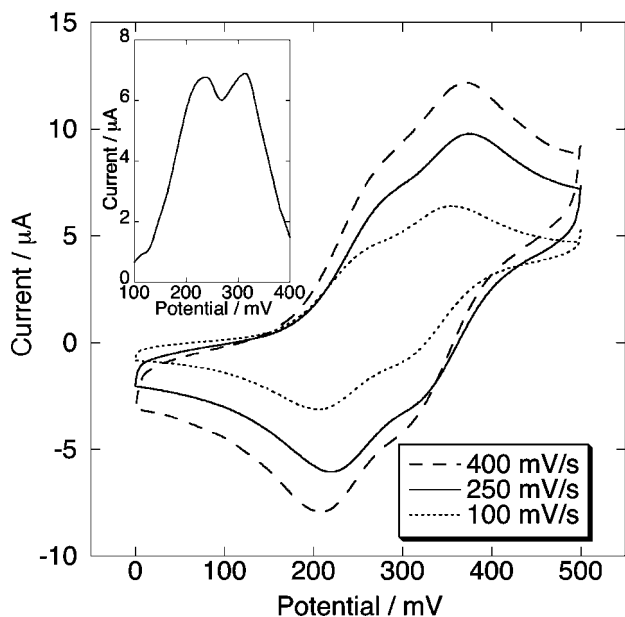
Fig. 3. Cyclic voltammograms of a solution of **9** recorded in dichloromethane, 0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$ at the scan rates indicated; the inset shows a differential pulse voltammogram of the same sample, recorded with a scan rate of 10 mVs^{-1}. The potential scale is relative to the anodised-Ag pseudo-reference electrode; values for the half-wave potentials vs. ferrocenium/ferrocene are given in Table 2.

Table 2
Redox potentials for several ferrocene derivatives (dichloromethane, 0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$)

Compound	$E_{1/2}$ (vs. ferrocenium/ferrocene) (mV)
3	+245
4	+280
9	+100, +180

graphic inversion centres and necessarily adopt perfectly staggered conformations about the central C–C bond. An interesting feature is the rather long central C–C bond in **9** (1.576(12) and 1.579(13) Å for the two independent molecules), significantly longer than the expected value for an unstrained C–C single bond (1.54 Å). The central bond in ethanes is subjected to steric strain on replacement of the H atoms by bulkier alkyl groups [65]: lengthened C–C bonds are observed on the introduction of steric bulk [66], with a bond length as long as 1.634 Å in the highly strained 2,3-di-1-adamantyl-2,3-dimethylbutane [67]. This corresponding bond lengths in FcCH$_2$CH$_2$Fc [63] and FcCMe$_2$C-Me$_2$Fc [64] are 1.528(9) and 1.599(3) Å, respectively. The bond in **9**, where the C–C bond links two secondary centres, is slightly longer than that in FcCH$_2$CH$_2$Fc, where the C–C bond links two primary centres; meaningful comparison with FcCMe$_2$CMe$_2$Fc (two tertiary centres) is precluded by the high esd on the value for **9**. As seen in **8**, there is some bending of the α-C away from the plane of the substituted Cp ring, again as a result of the bulky substituent; there is no significant ring tilt between the Cp planes.

The separation, $\Delta E_{1/2}$, between the redox potentials corresponding to formation of mono- and dications has been often used as a probe of metal–metal interactions in dinuclear ferrocene species [68]. The redox splitting reflects the stability of the Fe^{II}/Fe^{III} mixed-valence monocation with respect to disproportionation, and hence will be affected by any stabilisation arising from

delocalisation between the metal centres, although it should be noted that $\Delta E_{1/2}$ is determined by many factors and cannot be directly equated with the electronic coupling in the mixed valence cation [69]. The cyclic voltammogram of **9** in CH$_2$Cl$_2$ solution is shown in Fig. 3. The redox potentials, along with those for several of the other new ferrocene derivatives, are summarised in Table 2. **9** shows two overlapping redox processes corresponding to successive oxidation of the two iron centres: the separation of these two processes, $\Delta E_{1/2}$, is difficult to accurately determine from the cyclic voltammogram, but differential pulse voltammetry (Fig. 3, inset) and square-wave voltammetry both indicate $\Delta E_{1/2}$ = ca. 77 mV. A value of 80 mV has previously been reported for FcCMe$_2$CMe$_2$Fc in the same solvent [64,70]. Since it has been shown that single carbon-bridged bis(ferrocene) mixed-valence species have been found to belong to Robin and Day's [71] class I (i.e., immeasurable electronic coupling), or towards the weak coupling end of class II [68,72,73], presumably species such as **9** and FcCMe$_2$CMe$_2$Fc are likely to be class I and these separations to be principally determined by through-space electrostatic effects, plus a statistical contribution of (RT/F)ln4, rather than by electronic coupling.

3.4. Crystal structures of metallocene alcohols

We have determined the crystal structure of one of the isomers of **8**, along with those of three other previously reported metallocenes, **10**, **11** and **12** (Scheme 3). These show a variety of hydrogen-bonding motifs, some of which have not previously been observed in metallocene alcohols. Table 3 compares some of the bond lengths and angles pertinent to the hydrogen bonding observed in the structures of **8**, **10** and **12**.
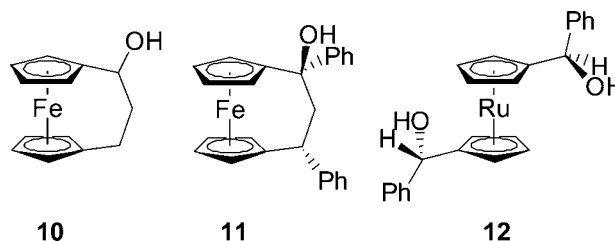
Scheme 3.

Table 3
Bond lengths (Å) and angles (°) pertaining to the hydrogen bonding interactions in the crystal structures of the alcohols **8**, **10** and **12**

8		**12**	
O7–Cl14	3.067(2)	O1–H1	0.91(5)
O30–Cl37	3.102(2)	O2–H2	0.74(5)
		O1–H2′	2.07(5)
		O2–H1	1.89(5)
10			
O1–O2	2.749(3)	O1–O2	2.786(2)
O1–O2′	2.768(3)	O1–O2′	2.805(2)
O2–O1–O2′	88.6(1)	O1–H1–O2	166(5)
O1–O2–O1′	91.4(1)	O1–H2′–O2′	170(5)
		O2–O1–O2′	84.02(6)
		O1–O2–O1′	95.98(6)

Crystallisation of 2,2,6,6-tetramethyl-3-ferrocenyl-5-chloroheptan-3-ol, **8**, afforded one of two possible diastereomers; the crystal structure reveals this to be the 3R,5R/3S,5S enantiomeric pair (the structure is centrosymmetric and contains equal numbers of RR and SS). There are two independent molecules in the asymmetric unit which have similar conformations (Fig. 4). The α *tert*-butyl group points up and away from the Fc moiety as is expected on steric grounds, and as is observed in other bulky FcCRR′OH species [31]. There is no intermolecular hydrogen bonding in the crystal, but both independent molecules show intramolecular O–H···Cl bonds; in terms of Etter's graph set analysis [74,75], the hydrogen bonding pattern can be described as $S_1^1(6)$. The short O–Cl distances (3.067(2) and 3.102(2) Å) are somewhat less than the sum of the van der Waals radii for O and Cl (3.20 Å) and shorter than typical O–Cl distances in O–H···Cl–C bonded systems (e.g., 3.41 Å for the intermolecular O–Cl distance in the structure of 4,4′-dichloro-meso-hydrobenzoin [76]). Presumably the shortness of the O–Cl

distance indicates that this is a rather bent hydrogen bond with a somewhat low O–H···Cl angle; unfortunately the hydrogen position could not be reliably located in the crystal structure. H-bonding partially imposes the observed conformation on the complex: closer inspection of the structures reveal that other non-bonded interactions may also have a bearing on the overall geometry. There are relatively short contacts between the Cl and one of the C atoms on the unsubstituted ring as well as between O and Fe: neither of these contacts is sufficiently short to be considered a H-bond (previous examples of Fe···H–O hydrogen bonds in α-hydroxy ferrocenes, have Fe–O distances of 3.572(2) [21] and 3.466(5) Å [23]). In both molecules, the Fe–C_{ipso} distance is significantly lengthened with respect to the other nine Fe–C distances [Fe1–C5 2.074(2) Å vs Fe1–C(av.) 2.043(2) Å; Fe2–C28 2.072(2) Å vs Fe2–C(av.) 2.052(2) Å], the two cyclopentadienyl rings are non-parallel with small rings tilt of 4.8° and 2.6° for the two molecules, the C_{ipso}–C_α bond is bent away from the plane of the C_5H_4 ring (5.8° and 4.9°). Although similar distortions from regular metallocene geometry are seen in in FcCPh₂OH, where an Fe··· H–O bond has been predicted [21], such distortions are also seen in ferrocenyl complexes with bulky carboranyl side-chains that are not implicated in any interactions with the Fe-centre [77]. Therefore, it appears that the major non-covalent interactions in the structure of **8** are the Cl···H–O hydrogen bond, and steric interactions.

Crystallisation of *rac*-1-hydroxy[3]ferrocenophane [41,42], **10**, gave centrosymmetric crystals containing two molecules in the asymmetric unit. The angles between the two cyclopentadienyl rings are 9.08 and 8.91° for the two independent molecules, similar to those found for other [3]ferrocenophanes with saturated carbon bridging atoms [78,79]. The arrangement of the molecules is dominated by intermolecular O···H–O hydrogen bonds (Fig. 5). The two inequivalent molecules of the asymmetric unit, together with two additional molecules related by the crystallographic inversion centre, form a tetramer composed of enantio-
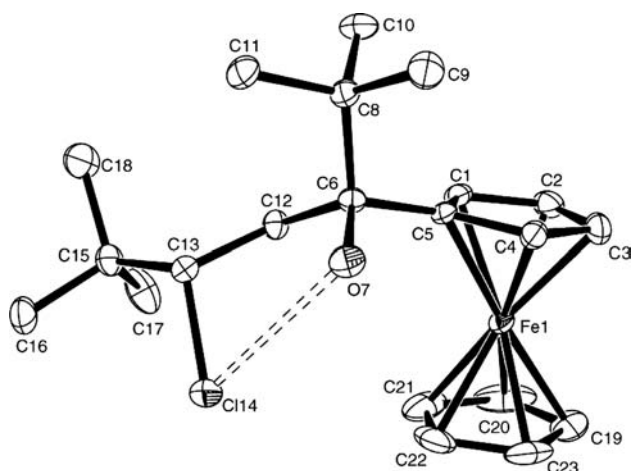

Fig. 4. View of one of the independent molecules of compound **8** in its crystal structure (50% thermal ellipsoids; hydrogen atoms omitted for clarity), illustrating the H-bond (dashed line). The second molecule (not shown) adopts a similar conformation.
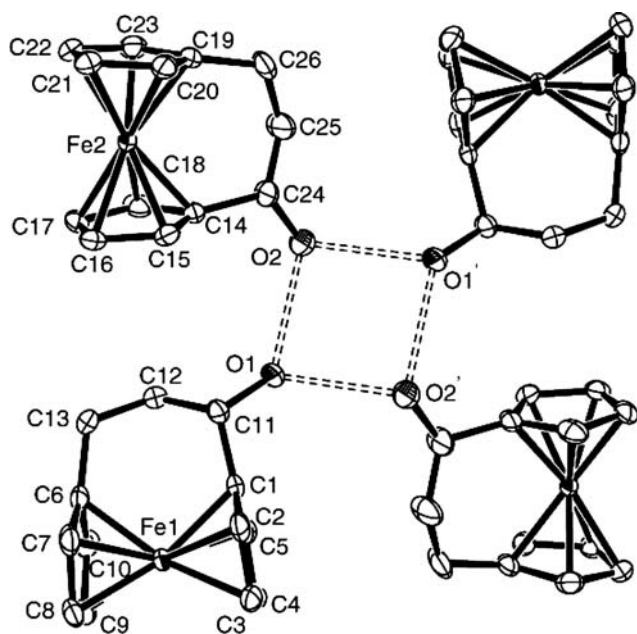
Fig. 5. View of crystal structure of **10** showing both independent molecules and the hydrogen-bonding network (shown as dashed lines) with thermal ellipsoids at 50% probability. The other two molecules are related by a crystallographic inversion centre. All H-atoms are omitted for clarity.
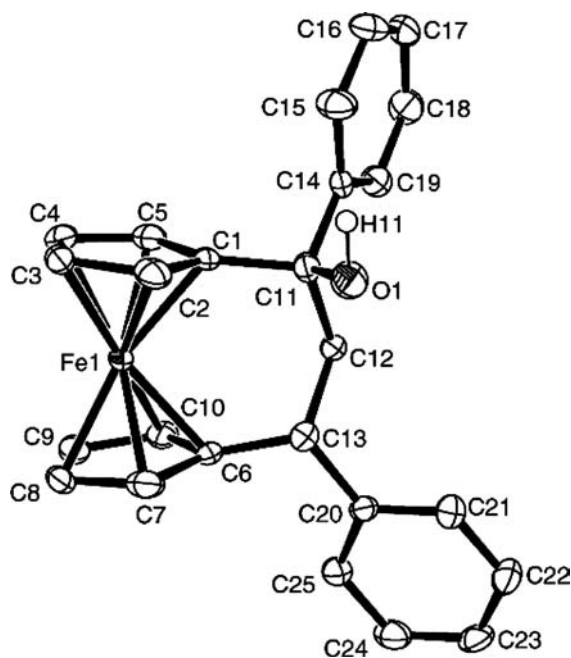

Fig. 6. View of the crystal structure of **11** showing the atom labelling scheme with thermal ellipsoids at 50% probability. All H-atoms, except the hydroxyl H, are omitted for clarity.

mers in the sequence R,R,S,S (i.e., two adjacent metallocenes have the same configuration and the other two have the opposite). The O–O distances are 2.749 and 2.768 Å. This motif can be described by the graph set $R_4^4(8)$. We are not aware of a previous example of a metallocene mono-alcohol adopting this particular hydrogen bonding motif, although it it is quite frequent in organic alcohols [80], as well as being found in bulky hetero-alcohols such as Ph_3SiOH [81], Ph_3GeOH [82].

It has previously been reported that when 1,3-diphenyl-1-hydroxy[3]ferrocenophane, **11**, is synthesised from the reaction of 3-phenyl-1-keto[3]ferrocenophane and PhMgBr, the major product is the 1S,3S/1R,3R pair of enantiomers [43,44]; this is confirmed by the crystal structure of **11** (Fig. 6). The ring tilt of 10.9° induced by the bridge is similar to that seen in **10** and other related species (vide supra). In this species, there is no evidence of any hydrogen bonding, presumably due to steric encumberance around the hydroxyl group (the shortest non-bonded distance between the O atom and another non-hydrogen atom is 3.421(3) Å to a carbon atom of the Cp group in a neighbouring molecule). 1-Ferrocenyl-1-phenylethanol provides another example of a hydrogen-bond-free ferrocene alcohol structure [25]; various others show possible weak Fe···H–O and C···H–O interactions [31]; in **11** these are precluded by the orientation of the OH group enforced by the interannular bridge.

Crystals grown from a solution containing a mixture of the diastereomers of 1,1′-diphenyl-1,1′-(1,1′-ruthe-

nocenediyl)dimethanol [19,45], **12**, were found to contain solely the *meso* (SR) diastereomer (Fig. 7). The Ru–C distances fall in the range 2.175(2)–2.186(2) Å and are typical for ruthenocenes (for example, see [12,83,84]) The two substituents on the two rings almost eclipse one another, as shown by the C1–ring centroid–ring centroid–C13 torsion angle of 7.9°; the molecule has an approximate plane of symmetry passing through the Ru and parallel to the two rings. Two molecules, related to one another by the crystallographic inversion centre, form a dimer containing four hydroxyl groups with two intermolecular (O–O, 2.805(2) Å) and two intramolecular (O–O, 2.786(2) Å) O···H–O hydrogen bonds. The structure can be assigned to graph set $R_4^4(8)$. Interestingly, although the structure of the iron analogue of **12**, *meso*-1,1′-diphenyl-1,1′-(1,1′-ferrocenediyl)dimethanol [30], has also been found to consist of centrosymmetric dimers with graph set $R_4^4(8)$, and with the rings also approximately eclipsed, in the Fe species the two substituents are offset by 1/5 of a turn about the Fe–(Cp centroid) axis. This necessitates rotation about the C_{ipso}–C_α bond of one of the susbtituents, in order that the two OH groups are directed towards one another sufficiently to allow formation of the intramolecular H-bond; the rotation leads to very different orientation of the two phenyl groups and hence to different packing in the two materials (shown schematically in Fig. 8). This subtle conformational preference may result from the increased inter-ring distance in the ruthenium derivative with respect to the ferrocene. The 1/5 turn offset and the
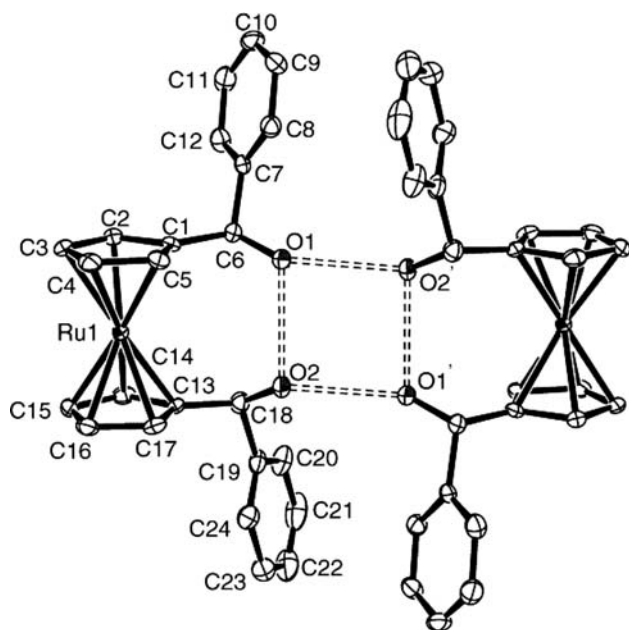
Fig. 7. View of crystal structure of **12** showing the atom labelling scheme and the hydrogen-bonding network (dashed bonds); thermal ellipsoids are shown at 50% probability and all H atoms are omitted for clarity. The second molecule of the dimer is related by a crystallographic inversion centre.
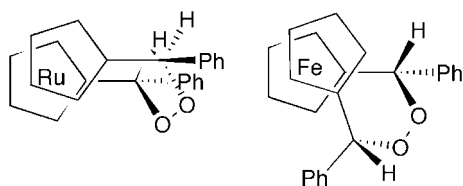

Fig. 8. Schematic showing different conformations adopted by *meso*-**12** and its iron analogue in their crystal structures.

associated arrangement of OH groups seen in *meso*-1,1'-diphenyl-1,1'-(1,1'-ferrocenediyl)dimethanol has also been seen in a number of other ferrocene diol species (all $R_4^4(8)$ dimers, although not necessarily with centrosymmetry): ferrocene-1,1'-diylbis(diphenylmethanol) [25], *rac*-1,1'-diphenyl-1,1'-(1,1'-ferrocenediyl)diethanol [28], *rac*-1,1'-diphenyl-1,1'-(1,1'-ferrocenediyl)diethanol [28], and 2,2'-(1,1'-ferrocenediyl)di(propan-2-ol) [33,85]. To the best of our knowledge, the exact arrangement found in **12** has not previously been seen for metallocene diols.

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