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Synthesis and reactivity of the pentamethylcyclopentadienyl iron acetyl complex [(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe]

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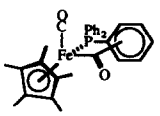
Abstract

(*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe] (**1**) was synthesised from [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$ (**3**) in three steps with an overall yield of 28%. The lithium enolate from **1** was alkylated with methyl iodide and benzyl bromide to give **11** and **12** in 94 and 97% yields respectively. The corresponding diethylaluminium enolate derived from **1** reacted with high stereoselectivity with benzaldehyde whereas no selectivity was observed with the lithium enolate. A single crystal X-ray structure analysis of (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)$COCH_2CH_2Ph$] (**12**) is reported.

1. Introduction

The [(η^5-C_5H_5)Fe(CO)(PPh_3)] moiety has been established [1] as a versatile chiral auxiliary for asymmetric synthesis. In particular, reactions of enolates derived from acyl ligands attached to this chiral auxiliary proceed with high stereoselectivity. A crucial feature of the origin of this stereocontrol derives from the cyclopentadienyl ligand and, in order to investigate this, studies on substituted derivatives are warranted [2]. To this end we describe here the synthesis of the pentamethylcyclopentadienyl iron acetyl complex (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe] (**1**) and compare its reactivity with that of the cyclopentadienyl equivalent (*RS*)-[(η^5-C_5H_5)Fe(CO)(PPh_3)COMe] (**2**). Among other advantages, permethylation of the cyclopentadienyl ligand might be expected to enhance the stability of the enolate derived from the complex (at temperatures above −40°C) by preventing rearrangement reactions involving deprotonation of the cyclopentadienyl ligand [3]. Furthermore the stereoselectivities of the reactions of the enolates in the pentamethylcyclopentadienyl series should be improved, since the formation of the minor diastereoisomer in this process requires the incoming electrophile E^+ to pass very close to (if not actually through) the space occupied by the cyclopentadienyl ligand. However, the severe steric crowding resulting from the simultaneous presence of two ligands as bulky as triphenylphosphine and pentamethylcyclopentadienyl in the co-ordination sphere of a single metal atom was expected to complicate the synthesis of (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe] (**1**) and to lower the reactivity of its enolate by blocking the approach of the electrophile. In addition to this problem it should be pointed out that, due to its better electron-releasing properties, co-ordination of a pentamethylcyclopentadienyl ligand to the iron atom should also lead to increased electron density at the metal centre and a subsequent decrease in the thermodynamic acidity of the C_α-protons of the acetyl ligand in **1** compared to **2**.



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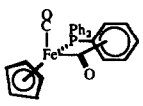

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2. Results and discussion

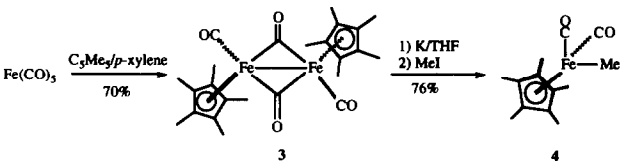
The first problem to be addressed was the actual synthesis of the desired, but unknown, iron acetyl complex **1**. The first attempts followed lines previously established for the cyclopentadienyl analogue **2**. Thermolysis of iron pentacarbonyl with pentamethylcyclopentadiene [4] in refluxing *p*-xylene gave the red crystalline [(η^5-C_5Me_5)Fe$(CO)_2]_2$, **3**, in 70% yield (Scheme 1) [5]. Whereas reductive cleavage of the dimer **3** with a sodium/mercury amalgam proved to be very slow and incomplete, presumably due to the electron-donating properties of the pentamethylcyclopentadienyl ligands, a rapid reaction occurred when **3** was treated with finely divided potassium metal. Alkylation of the resulting potassium salt of the [(η^5-C_5Me_5)Fe-$(CO_2]$ anion with methyl iodide yielded the yellow iron methyl complex **4**.

Although, as reported by others [6*], the methyl complex **4** reacted with trimethylphosphine to provide the acetyl complex **5** in modest yield, no such carbonyl insertion into the iron–carbon bond was observed when the less nucleophilic and sterically more demanding triphenylphosphine was used (Scheme 2).

Another possible precursor to the required iron acetyl complex was the bromide **7**, which was prepared from [(η^5-C_5Me_5)Fe$(CO)_2]_2$ (**1**) in two steps with an overall yield of 62% (Scheme 3) [7]. It was expected that the synthesis of the acetyl complex **1** could be achieved by displacement of the bromide in **7** with lithium acetylide, followed by acid-catalysed addition to water to the resulting ethynyl complex. Unfortunately, reaction of **7** with both lithium acetylide and lithium phenylacetylide did not yield the expected alkynyl complexes, but resulted only in extensive decomposition. All attempts to generate an iron anion from **7** by a bromine/metal exchange failed as well.

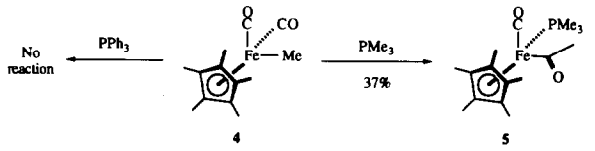
Since the photolytic replacement of a carbonyl ligand by triphenylphosphine on an iron atom already bearing a pentamethylcyclopentadienyl ligand had been established (Scheme 3, **6** → **7**), the same reaction on the iron acyl complex **8** [8,9a] was attempted. Complex **8** was obtained in low yield by treatment of the potassium salt of the [(η^5-C_5Me_5)Fe$(CO)_2$] anion with propionyl chloride (Scheme 4). However, UV irradiation of a solution of **8** and triphenylphosphine gave exclusively the dimer **3**, perhaps via a homolytic cleavage of the iron–acyl bond, this process apparently being favoured over the expected ligand exchange reaction.

The synthesis of [(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe] (**1**) was finally achieved by adopting the route shown in



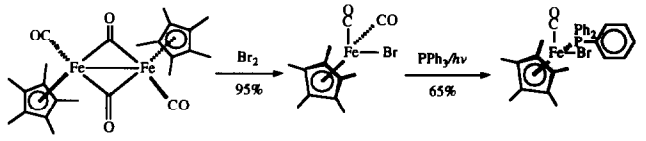
3 4

Scheme 1.



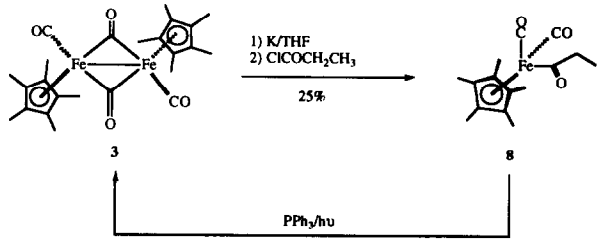
4 5

Scheme 2.



3 6 7

Scheme 3.



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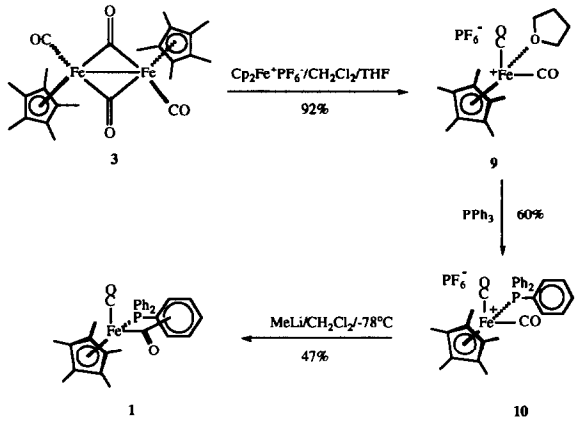
Scheme 4.



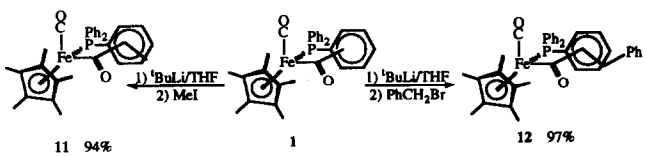
3 9 1 10

Scheme 5.

* Reference number with an asterisk indicates a note in the list of references.

Scheme 5. Oxidation of [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$ (**3**) with ferricinium hexafluorophosphate [9] in a dichloromethane/THF mixture produced the salt **9**, which, after repeated washing in ether to remove ferrocene, was converted without further purification into **10** [5a] in 55% overall yield from **3** after crystallisation. Addition of methyllithium to the hexafluorophosphate salt **10** afforded the iron acetyl complex **1** (47%) as well as some dimer **3** (22%) and the iron methyl complex **4** (9%). Despite the obvious possibility of an acid/base reaction with methyllithium, the choice of dichloromethane as a solvent was dictated by the very low solubility of the salt **10** in ether, THF or hexane. Fortunately, nucleophilic addition to the cationic iron complex proved to be rapid enough to prevent any side-reactions, although it must be stressed that the "scaling-up" of this process gave very variable yields, usually much lower than those observed for small scale reactions. For example, on a 10 g scale the yield of the acetyl complex **1** dropped to 27% whereas the isolated amount of [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$ (**3**) increased to 40%. The complex [(η^5-C_5Me_5)Fe(CO)(PPh$_3$)COMe] (**1**) crystallised from hexane/diethyl ether as orange-red needles which gave microanalytical data consistent with the expected molecular formula. This compound showed two carbonyl stretches in its infrared spectrum at 1900 and 1585 cm^{-1}, and showed two upfield resonances in the ^{1}H NMR spectrum at δ 1.50 and 2.00 ppm which integrated for 15 and 3 hydrogens respectively, and were assigned to C_5Me_5 and CO*Me*. Two carbonyl resonances were observed, at δ 222.45 (d, *J* 28.3 Hz) and 288.01 (d, *J* 23.8 Hz), in the ^{13}C NMR spectrum, both showing the expected P–C coupling.

In contrast to the cyclopentadienyl analogue **2**, deprotonation of the iron acetyl complex **1** proved difficult since no alkylation was observed when **1** was treated successively with butyllithium and methyl iodide in THF at −78°C (86% recovery of starting material). Deprotonation of the acetyl ligand in **1** was however readily achieved using t-butyllithium at −78°C or −42°C, and subsequent alkylation of the resultant enolate with methyl iodide generated the propanoyl complex **11** in excellent yield (63 and 94% respectively) (Scheme 6).



Scheme 6.

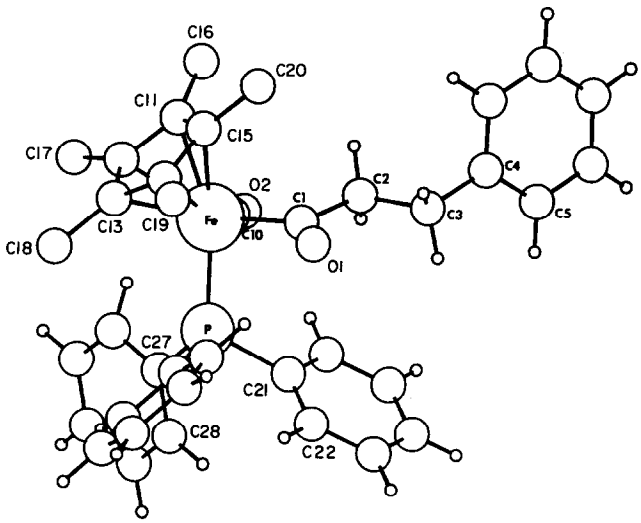


Fig. 1. Molecular structure of (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh$_3$)CO-CH_2CH_2Ph] (**12**).

Relative to that derived from [(η^5-C_5H_5)Fe(CO)-(PPh$_3$)COMe] (**2**) the lithium enolate derived from **1** showed enhanced stability at ambient temperature, the propanoyl complex **11** being isolated in 56% yield after t-butyllithium deprotonation of **1** at −78°C followed by stirring at room temperature for 20 min and quenching with methyl iodide.

Treatment of **1** at −42°C with t-butyllithium followed by quenching with benzyl bromide afforded complex **12** in 97% yield. The X-ray crystal structure of racemic (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh$_3$)$COCH_2CH_2$-Ph] **12** is shown in Fig. 1. Fractional atomic coordinates are listed in Table 1 and selected bond angles are given in Table 2. The fragment [(η^5-C_5Me_5)Fe(CO)(PPh$_3$)-$COCH_2$–] of the crystal structure of complex **12** is essentially superimposable on the crystal structure of the cyclopentadienyl acetyl complex **2**, indicating that permethylation of the cyclopentadienyl ring in **2** merely increases the bulk of that ligand without perturbing the rest of the structure.

The iron propanoyl complex **11** proved to resist further alkylation, with only starting material being recovered in good yield (83 to 88%) on successive treatment of a THF solution of **11** with an alkyllithium base (methyllithium, s-butyllithium, or t-butyllithium) and methyl iodide at −78°C, −42°C or ambient temperature. Similarly, no reaction occured when sodium hexamethyldisilazide was used as base and complex **11** even survived one hour of reflux in THF in the presence of excess sodium or potassium hydride. A stereoselective partial incorporation of deuterium (30% yield from ^{1}H-NMR data) was observed when LDA and d^4-methanol were sequentially added at −15°C to a

TABLE 1. Fractional atomic coordinates and isotropic temperature factors for (*RS*)-**12**

	x	*y*	*z*	U_{eq} / U_{iso}
Fe(1)	0.8053(1)	0.7752(1)	0.89128(7)	0.0537
P(1)	0.8006(2)	0.7671(3)	0.7873(1)	0.0586
O(1)	0.8808(6)	0.5480(6)	0.8845(4)	0.0718
O(2)	0.5899(7)	0.8036(7)	0.8697(4)	0.0872
C(1)	0.8056(8)	0.6038(9)	0.8929(5)	0.0610
C(2)	0.7170(9)	0.5349(8)	0.9095(6)	0.0756
C(3)	0.733(1)	0.4013(8)	0.9033(8)	0.0987
C(4)	0.6593(9)	0.329(1)	0.9318(6)	0.0866
C(5)	0.579(1)	0.264(1)	0.8946(6)	0.1055
C(6)	0.517(1)	0.194(1)	0.9236(7)	0.1187
C(7)	0.538(1)	0.189(1)	0.9898(7)	0.1190
C(8)	0.618(1)	0.252(1)	1.0267(6)	0.1114
C(9)	0.678(1)	0.323(1)	0.9982(6)	0.0980
C(10)	0.6776(9)	0.788(1)	0.8774(5)	0.0650
C(11)	0.821(1)	0.843(1)	0.9838(6)	0.0995
C(12)	0.835(1)	0.936(1)	0.9433(6)	0.0990
C(13)	0.920(1)	0.909(1)	0.9186(6)	0.0951
C(14)	0.9591(9)	0.802(1)	0.9449(6)	0.0973
C(15)	0.899(1)	0.760(1)	0.9851(6)	0.0995
C(16)	0.742(1)	0.837(2)	1.0255(6)	0.1165
C(17)	0.772(1)	1.050(1)	0.9341(8)	0.1209
C(18)	0.972(1)	0.991(1)	0.8789(6)	0.1080
C(19)	1.0594(9)	0.742(1)	0.9408(7)	0.1151
C(20)	0.923(1)	0.655(1)	1.0312(7)	0.1176
C(21)	0.7379(5)	0.6358(5)	0.7445(3)	0.059(3)
C(22)	0.7843(4)	0.5663(6)	0.7064(3)	0.071(3)
C(23)	0.7339(6)	0.4689(6)	0.6756(3)	0.080(3)
C(24)	0.6371(6)	0.4410(6)	0.6829(4)	0.085(4)
C(25)	0.5906(5)	0.5105(7)	0.7209(4)	0.096(4)
C(26)	0.6410(5)	0.6080(6)	0.7517(3)	0.077(3)
C(27)	0.7271(5)	0.8837(6)	0.7381(4)	0.065(3)
C(28)	0.6914(7)	0.8702(6)	0.6724(4)	0.093(4)
C(29)	0.6324(7)	0.9574(8)	0.6366(3)	0.109(5)
C(30)	0.6092(6)	1.0580(7)	0.6667(4)	0.100(4)
C(31)	0.6449(6)	1.0715(5)	0.7324(4)	0.088(4)
C(32)	0.7039(6)	0.9844(7)	0.7681(3)	0.071(3)
C(33)	0.9224(4)	0.7689(6)	0.7635(3)	0.056(2)
C(34)	0.9938(6)	0.6840(5)	0.7894(3)	0.071(3)
C(35)	1.0874(5)	0.6817(6)	0.7730(4)	0.092(4)
C(36)	1.1097(4)	0.7642(7)	0.7306(4)	0.087(4)
C(37)	1.0383(5)	0.8491(6)	0.7047(3)	0.079(4)
C(38)	0.9446(5)	0.8514(5)	0.7212(3)	0.068(3)

THF/HMPA solution of **11**, but no 2-methylpropanoyl complex was isolated when methyl iodide was used as the electrophile. Presumably in this substituted enolate the approach of the electrophile is too hindered for reaction to occur.

TABLE 2. Selected bond and torsional angles (°) for (*RS*)-**12**

C(1)–Fe(1)–P(1)	88.7(3)	P(1)–Fe(1)–C(1)–O(1)	−67.7
C(10)–Fe(1)–P(1)	92.2(4)	Fe(1)–C(1)–C(2)–C(3)	−176.9
C(10)–Fe(1)–C(1)	94.9(5)	C(1)–C(2)–C(3)–C(4)	−170.3
		C(2)–C(3)–C(4)–C(5)	−109.4

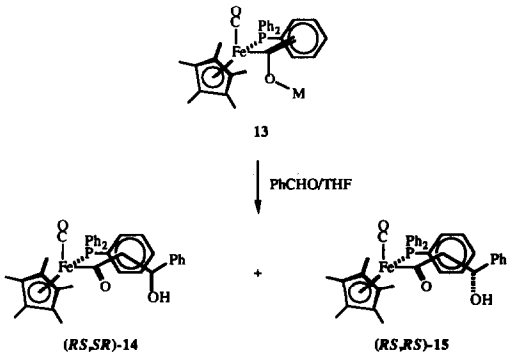
TABLE 3. Aldol reaction of the enolate **13** with benzaldehyde

Metal M **13**	Reaction temp. (°C)	Recovered **1** [%]	Yield **14**+**15** [%]	Ratio **14**/**15**
Li	−42	24	55	1:1
$AlEt_2$	−100	23	48	18:1

Whereas the lithium enolate **13** (M = Li) derived from **1** reacted without selectivity with benzaldehyde, an 18:1 ratio of diastereoisomers was observed when the diethylaluminium counterpart **13** (M = Et_2Al) was used (Scheme 7, Table 3). A similar relationship between the counterion of the enolate and the stereoselectivity of the aldol reaction had been previously reported in the cyclopentadienyl series [10]. The stereochemistries of the aldol products from the aluminium enolate reaction were assigned using the characteristic NMR chemical shift data obtained for the same aldol reaction with the enolate of [(η^5-C_5H_5)Fe(CO)(PPh_3)COMe] (**2**) [10] where the structure of the major diastereoisomer was established by X-ray crystallographic analysis as (*RS, RS*).

3. Conclusion

The first synthesis of the acetyl complex (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe] (**1**) has been achieved in 28% overall yield from the [(η^5-C_5Me_5)Fe(CO)$_2$]$_2$ (**3**). This new organometallic compound is an air-stable orange solid which has been fully characterised. The lithium enolate derived from [(η^5-C_5Me_5)Fe(CO)(PPh_3)COMe] (**1**) can be cleanly monoalkylated with methyl iodide and benzyl bromide, and the corresponding diethylaluminium enolate reacts highly stereoselectively with benzaldehyde. Unfortunately, the propanoyl complex (*RS*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)$COCH_2$Me] (**11**) proved very resistant to deprotonation and no C_α-disubstituted complexes could be prepared.



Scheme 7.

4. Experimental section

All reactions and purifications were performed under nitrogen by use of standard vacuum line and Schlenk tube techniques [11]. All solvents were deoxygenated before use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Acetonitrile and dichloromethane were distilled from calcium hydride. Toluene and *p*-xylene were dried over sodium wire. Reagent grade cyclohexane (BDH) and acetone (FSA) were used without purification. The petroleum ether used for column chromatography was the redistilled hydrocarbon fraction boiling at 40–60°C. Unless otherwise indicated, all commercially available reagents were used as received. Iron pentacarbonyl was added to reaction systems via a plug of glass wool. Column chromatography was performed on grade I (activated) basic alumina or on silica gel (Merck Kieselgel 60). For organometallic complexes all chromatography was carried out under nitrogen. Elemental analyses were carried out by Mrs. V. Lamburn of the Dyson Perrins Laboratory. n-Butyllithium (1.5 M in hexane), s-butyllithium (1.3 M in cyclohexane), t-butyllithium (1.7 M in pentane), and diethylaluminium chloride (1.8 M in toluene) were used as supplied by Aldrich. Infrared spectra were recorded on either a Perkin-Elmer 781 or on a Perkin-Elmer 1750 Fourier Transform spectrophotometer as solutions in chloroform using 1 mm NaCl cells unless otherwise stated. NMR spectra were recorded on either a Varian-Gemini 200 (200 MHz) or a Bruker AM500 (500.13 MHz) spectrometer in $CDCl_3$ solutions unless otherwise stated. ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AM250 spectrometer (at 62.90 and 125.76 MHz respectively) in $CDCl_3$ solutions. ^1H and ^{13}C NMR spectra were referenced to tetramethylsilane using internal solvent peaks. In the Experimental section, ^{13}C and ^{31}P NMR data are given in terms of the proton decoupled (broad band) spectra. Abbreviations used: b, broad signal; d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet. Mass spectra were recorded on V.G. Micromass ZAB1F or MM30F instruments using FAB techniques for organometallic compounds.

4.1. Preparations

4.1.1. Preparation of [(η^5-C_5Me_5)$Fe(CO)_2$]$_2$ (3)

A solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene [4] (4.85 ml, 30 mmol) and iron pentacarbonyl (12 ml, 90 mmol) in dry *p*-xylene (60 ml) was thoroughly deoxygenated and refluxed under nitrogen for 68 h. The solution was cooled to −15°C (ice/NaCl bath) and the dark red precipitate was collected on a Büchner funnel. The solid was adsorbed on to activated alumina and eluted with dichloromethane (1.5 l). Concentration of the red solution to a volume of 40 ml, followed by cooling to −15°C and filtration on a Büchner funnel, gave pure **3** (5.22 g, 10.6 mmol, 70%). ν_{max} 1925 (CO), 1742 (bridged CO); δ_H 1.69 (30H, s, $2 \times C_5(CH_3)_5$). See reference 5.

4.1.2. Preparation of [(η^5-C_5Me_5)$Fe(CO)_2Me$] (4)

Potassium metal (0.92 g, 23.6 mmol) was covered with dry *p*-xylene (10 ml) and heated under nitrogen until it melted completely. The molten metal was vigorously stirred with a magnetic stirrer bar and the suspension was rapidly cooled to room temperature. Removal of the solvent and drying *in vacuo* left a potassium sand, which was suspended in dry THF (60 ml). Solid **3** (5.83 g, 11.8 mmol) was added in one portion and the resulting brown solution was stirred at room temperature for 4 h. Addition of methyl iodide (3.7 ml, 59 mmol) followed 30 min later by removal of the solvents, extraction of the residue with pentane (4×30 ml), filtration of the yellow solution through deactivated (10% water) alumina under nitrogen, and sublimation (70°C, 1 mmHg) of the crude solid provided the yellow air-sensitive methyl complex **4** (4.71 g, 18 mmol, 76%). ν_{max} 2040 and 1985 (CO); δ_H 1.75 (15H, s, $C_5(CH_3)_5$), −0.20 (3H, s, CH_3). See reference 7.

4.1.3. Preparation of (RS)-[(η^5-C_5Me_5)Fe(CO)(PMe_3)COMe] (5)

A 1 M solution of trimethylphosphine in toluene (4 ml, 4 mmol) was added to a solution of **4** (524 mg, 2 mmol) in acetonitrile (20 ml). The solution was thoroughly deoxygenated, refluxed under nitrogen for 20 h, transferred into a sealed tube and heated at 100°C for a further 48 h. Removal of the solvents followed by column chromatography of the residue (activated alumina, petroleum ether/diethyl ether/ethyl acetate) gave the yellow-orange acetyl complex **5** (250 mg, 0.74 mmol, 37%). ν_{max} 1890 (Fe–CO), 1587 (C=O); δ_H 2.45 (3H, d, J(PH) 1 Hz, $COCH_3$), 1.71 (15H, d, J(PH) 1 Hz, $C_5(CH_3)_5$), 1.24 (9H, d, J(PH) 9 Hz, $P(CH_3)_3$). See reference 6.

4.1.4. Preparation of [(η^5-C_5Me_5)$Fe(CO)_2Br$] (6)

A solution **3** (7.41 g, 15 mmol) in chloroform (160 ml) and dichloromethane (80 ml) was cooled to 0°C and a solution of bromine (0.9 ml, 17.3 mmol) in chloroform (80 ml) was added dropwise during 40 min. The mixture was stirred at room temperature for a further 3 h and was washed with aq. sat. $Na_2S_2O_3$ (3×40 ml) and H_2O (2×30 ml). Drying over magnesium sulphate followed by removal of the solvents gave the bromide as an crystalline orange solid **6** (9.35 g,

28.6 mmol, 95%). ν_{max} 2008 and 1957 (CO); δ_H 1.86 (15H, s, $C_5(CH_3)_5$). See reference 7.

4.1.5. Preparation of (RS)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)Br] (7)

A solution of **6** (1.47 g, 4.5 mmol) and triphenylphosphine (2.1 g, 8.1 mmol) in cyclohexane (235 ml) and THF (15 ml) was thoroughly deoxygenated and irradiated for 3 h (Hanovia medium pressure mercury lamp, quartz thimble). Removal of the solvents left a solid residue from which unchanged triphenylphosphine was removed by column chromatography (silica gel, hexane/ethyl) acetate 9:1). Recrystallisation from dichloromethane/hexane gave analytically pure **7** (1.65 g, 2.9 mmol, 65%) as green needles, m.p. 135–137°C (Found: C, 61.56; H, 5.65; P, 5.78. $C_{29}H_{30}BrOP$ requires: C, 61.26; H, 5.51; P, 5.64%). ν_{max} 1928 (Fe–CO); δ_H 7.80–7.60 (6H, m, PPh_3), 7.45–7.30 (9H, m, PPh_3), 1.44 (15H, s, C_5Me_5); δ_C 9.58 (s, C_5Me_5), 91.60 (s, C_5Me_5), 127.70 (d, J(PC) 9.0 Hz, C_{meta}, PPh_3), 128.89 (bs, C_{ipso}, PPh_3), 129.62 (s, C_{para}, PPh_3), 134.27 (d, J(PC) 8.7 Hz, C_{ortho}, PPh_3), 221.88 (bs, Fe–CO); δ_P 59.48; m/z 534/532 (M^+–CO, 33/34), 481(M–Br, 16), 453(534/532–Br, 100), 344(18), 295(30), 279(28), 270(26), 263(35), 183(35), 133(20), 85(30).

4.1.6. Preparation of [(η^5-C_5Me_5)Fe(CO)$_2$COEt] (8)

A solution of the potassium salt of [(η^5-C_5Me_5)Fe(CO)$_2$]$^-$ was generated as described for the preparation of **4** by addition of **3** (1.48 g, 3 mmol) to a suspension of finely divided potassium (235 mg, 6 mmol) in THF (25 ml). After 4 h propionyl chloride (0.8 ml, 18 mmol) was added to the solution and after a further 30 min the solvent was removed, the resulting sticky semi-solid was extracted with pentane (4 × 10 ml) and the solution was filtered through deactivated alumina. Concentration of the solution *in vacuo* followed by column chromatography activated alumina, petroleum ether/dichloromethane, 9:1) gave the iron acyl complex **8** (0.45 g, 1.48 mmol, 25%). ν_{max} 1988 and 1936 (Fe–CO); δ_H 2.84 (2H, q, J(1,3) 7.5 Hz, $COCH_2CH_3$), 1.79 (15H, s, $C_5(CH_3)_5$), 0.93 (3H, t, J(1,3) 7.5 Hz, $COCH_2CH_3$). See references 8, 9a.

4.1.7. Preparation of [Fe(η^5-C_5H_5)$_2$]$^+PF_6^-$

Ferrocene (25 g, 134 mmol) was added in portions to concentrated sulphuric acid (250 ml) and the resulting blue solution was stirred at room temperature for 1 h. Water (400 ml) was carefully added with cooling (ice/water) and the solution was filtered through Celite to remove precipitated sulphur. Addition of ammonium hexafluorophosphate (50 g, 0.31 mol) gave a blue precipitate, which was collected on a Celite bed (in a 5 cm frit) and washed with H_2O (3 × 60 ml), ethanol (2 × 60 ml) and ether (2 × 60 ml). The solid was dried on the frit for 3 h and washed off the Celite with acetone (400 ml) into a flask containing deoxygenated ether (1 l). The microcrystals thus obtained were collected on a frit and dried overnight (28.2 g, 64%). See reference 7.

4.1.8. Preparation of [(η^5-C_5Me_5)Fe(CO)$_2$(PPh_3)]$^+$ PF_6^- (10)

A solution of **3** (11.27 g, 23 mmol) and ferricinium hexafluorophosphate (15.1 g, 45 mmol) in dichloromethane (160 ml) and THF (80 ml) was stirred at room temperature for 20 h under nitrogen. After removal of the solvents the solid residue was transferred to a 5 cm frit and was repeatedly washed with deoxygenated ether (5 × 20 ml) to remove ferrocene; the [(η^5-C_5Me_5)Fe(CO)$_2$(THF)]$^+PF_6^-$ (**9**) thus obtained was dried and used without further purification in the next step (19.5 g, 92%). See reference 5a.

A solution of **9** (2.1 g, 4.5 mmol) and triphenylphosphine (2.4 g, 9.1 mmol) in dichloromethane (25 ml) was stirred at room temperature for 12 h under a nitrogen. The solvent was removed and the brown solid was washed with hot toluene (3 × 15 ml) to remove excess triphenylphosphine. Recrystallisation of the crude salt from acetone/diethyl ether gave [(η^5-C_5Me_5)Fe(CO)$_2$-(PPh_3)]$^+PF_6^-$ (**10**) as pale yellow microneedles (1.66 g, 2.7 mmol, 55% from **3**). ν_{max} 2025 (Fe–CO), 1985 (Fe–CO); δ_H (CD_3COCD_3) 7.80–7.45 (15H, m, PPh_3), 1.80 (15H, d, J(PH) 2.2 Hz, $C_5(CH_3)_5$); m/z 509(M^++H), 453(M^+ – 56).

4.1.9. Preparation of (RS)-[(η^5-C_5Me_5)Fe(CO)-(PPh_3)COMe] (1)

A solution of **10** (3.55 g, 5.7 mmol) in dichloromethane (10 ml) was cooled to −42°C and a solution of methyllithium in ether (0.95 M, 18 ml, 17.1 mmol) was added dropwise during 5 min. After a further 5 min stirring methanol (4 ml) was added to quench the reaction and the solvents were removed *in vacuo*. The residue was extracted with dichloromethane (3 × 10 ml) and the solution was filtered through deactivated alumina. Column chromatography (activated alumina, hexane/diethyl ether 4:1 diethyl ether) yielded the acetyl complex (*RS*)-**1** (1.40 g, 2.7 mmol, 47%) as well as the less polar iron compounds **3** (0.31 g, 22%) and **4** (0.13 g, 9%). (*RS*)-**1** was recrystallised from hexane/diethyl ether as orange-red needles, m.p. 142–144°C (Found: C, 70.82; H, 6.44. $C_{31}H_{33}FeO_2P$ requires: C, 71.00; H, 6.35%). ν_{max} 1900 (Fe–CO), 1585 (C=O); δ_H 7.75–7.20 (15H, m, PPh_3), 2.00 (3H, s, $COCH_3$), 1.50 (15H, s, $C_5(CH_3)_5$); δ_C 238.21 (d, J(PC) 23.8 Hz, C=O), 222.43 (d, J(PC) 28.3 Hz, CO), 134.06 (*b*s, PPh_3, C_{ipso} and C_{ortho}), 129.34 (s, PPh_3, C_{para}),

127.64 (d, J(PC) 8.8 Hz, PPh_3, C_{meta}), 93.70 (s, C_5Me_5), 49.82 (d, J(PC) 6.0 Hz, COMe), 9.61 (C_5Me_5); m/z 525(M^+ + H, 8), 509(M − CH_3, 10), 496(M − CO, 11), 468(M^+ − 2CO, 22), 481(M − $COCH_3$, 2), 453(496 − COMe, 100), 263(50), 234(37) 206(30).

4.1.10. Preparation of (RS)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)COEt] (11)

A solution of (*RS*)-**1** (1.17 g, 2.2 mmol) in THF (20 ml) was cooled to −42°C and a solution of t-butyllithium in pentane (1.24 M, 2.3 ml, 2.9 mmol) was added dropwise. After 35 min, methyl iodide (0.69 ml, 11.2 mmol) was added to the deep red solution, the mixture was allowed to warm to room temperature during 15 min, and methanol (1.5 ml) was added to quench the reaction. The solvents were removed and the solid residue was extracted with hexane/dichloromethane 2:1. Filtration of the solution through deactivated alumina followed by concentration and column chromatography (activated alumina, hexane/diethyl ether) gave (*RS*)-**11** (1.13 g, 2.1 mmol, 94%), which was recrystallised from acetone-methanol/water as red globular crystals, m.p. 135–137°C (Found: C, 71.11; H, 6.76. $C_{32}H_{35}FeO_2P$ requires: C, 71.38; H, 6.56%). ν_{max} (CCl_4) 1898 (Fe–CO), 1602 (C=O); δ_H 7.80–7.20 (15H, m, PPh_3), 2.62 (1H, dq, J(1,2) 17.5 Hz, J(1,3) 7.5 Hz, $COCH_2CH_3$), 2.17 (1H, dq, J(1,2) 17.5 Hz, J(1,3) 7.5 Hz, $COCH_2CH_3$), 1.50 (15H, s, $C_5(CH_3)_5$), 0.40 (3H, t, J(1,3) 7.5 Hz, $COCH_2CH_3$); δ_C 283.7 (d, J(PC) 23.73 Hz, C=O), 222.5 (d, J(PC) 28.2 Hz, CO), 134.0 (bs, PPh_3, C_{ipso} and C_{ortho}), 129.2 (s, PPh_3, C_{para}), 127.6 (d, J(PC) 8.6 Hz, PPh_3, C_{meta}), 93.7 (s, C_5Me_5), 57.6 (s, $COCH_2CH_3$), 9.95 (s, $COCH_2CH_3$), 9.58 (C_5Me_5); δ_P 69.12; m/z 539(M^+ + H, 20), 509(M − CH_2CH_3, 52), 453(509 − 2CO, 100), 439(8), 376(7), 318(9), 263(65), 248(62), 239(14), 190(45), 133(145).

4.1.11. Preparation of (RS)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)$COCH_2CH_2Ph$] (12)

A solution of **1** (0.19 g, 0.36 mmol) in THF (5 ml) was cooled to −42°C and a solution of t-butyllithium in pentane (1.24 M, 0.28 ml, 0.47 mmol) was added dropwise. After 35 min benzyl bromide (0.22 ml, 1.81 mmol) was added to the deep red solution, the mixture was allowed to warm to room temperature during 15 min, and methanol (1.5 ml) was added to quench the reaction. The solvents were removed and the solid residue was extracted with hexane/dichloromethane 2:1. Filtration of the solution through deactivated alumina followed by concentration and column chromatography (silica gel, hexane/diethyl ether) gave the ethyl acyl complex (*RS*)-**12** (0.22 g, 0.34 mmol, 97%), which was recrystallised from pentane/diethyl ether as red-orange prisms, m.p. 150–151°C (Found: C, 74.30; H, 6.56; P, 5.04. $C_{38}H_{39}FeO_2P$ requires: C, 74.27; H, 6.40; P, 5.01%). ν_{max} (CH_2Cl_2) 1894 (Fe–CO), 1595 (C=O); δ_H 7.60–7.50 (6H, m, PPh_3), 7.40–7.30 (9H, m, PPh_3), 7.19 (2H, bt, J 7.2 Hz, $COCH_2CH_2Ph$, H_{meta}), 7.10 (1H, bt, J 7.4 Hz, $COCH_2CH_2Ph$, H_{para}), 6.89 (2H, bd, J 7.1 Hz, $COCH_2CH_2Ph$, H_{ortho}), 2.85 (1H, ddd, J 17.2 Hz, 11.8, 4.6 Hz, $COCH_2CH_2Ph$), 2.52 (1H, ddd, J 17.1, 11.7, 4.6 Hz, $COCH_2CH_2Ph$), 2.38 (1H, ddd, J 13.6, 11.6, 4.6 Hz, $COCH_2CH_2Ph$), 1.97 (1H, ddd, J 13.5, 11.6, 4.5 Hz, $COCH_2CH_2Ph$), 1.50 (15H, s, $C_5(CH_3)_5$); δ_C 282.23 (d, J(PC) 24.2 Hz, C=O), 222.18 (d, J(PC) 28.3 Hz, CO), 143.28 (CH_2CH_2Ph, C_{ipso}), 134.23 (bs, PPh_3, C_{ortho}), 132.72 (d, J(PC) 43.2 Hz, PPh_3, C_{ipso}), 129.29 (s, CH_2CH_2Ph, C_{ortho}), 128.28 (s, PPh_3, C_{para}), 128.0 (s, CH_2CH_2Ph, C_{para}), 127.67 (d, J(PC) 8.3 Hz, PPh_3, C_{meta}), 125.05 (s, CH_2CH_2Ph, C_{meta}), 93.73 (s, C_5Me_5), 66.42 (s, $COCH_2CH_2Ph$), 31.93 (s, CH_2CH_2Ph), 9.54 (s, C_5Me_5); δ_P 68.90; m/z 615(M^+ + H, 10), 509(M − CH_2CH_2Ph, 33), 453(509 − 2CO, 85), 296(100), 281(21), 263(37), 190(20), 183(17), 133(14).

Crystal data: $C_{38}H_{29}FeO_2P$, M = 614.5, monoclinic, a = 13.511(4), b = 11.433(4), c = 21.464(8) Å, β = 103.42(3)°, U = 3225 Å^3 (by least squares refinement of the diffractometer angles for 25 accurately centred reflections, λ = 1.5418 Å), spacegroup $P2_1/c$ (No. 14), Z = 4, D_x = 1.27 gcm^{-3}. Dark orange, air sensitive rectangular prisms. Crystal dimensions: 1.0 × 1.0 × 1.0 mm, μ(Cu Kα) = 44.66 cm^{-1}.

Data collection and processing: Enraf-Nonius CAD4 diffractometer, $\omega/2\theta$ mode with, graphite-monochromated Cu Kα radiation; 9416 reflections measured ($0 < \theta \leq 75°$, $-14 \leq h \leq 14$, $-1 \leq k \leq 16$, $-26 \leq l \leq 26$), 3824 unique [merging R = 0.058, after an empirical absorption correction [12] (min., max. corrections = 0.715, 1.310)], giving 1637 with $I > 3\sigma(I)$. Three standard reflections measured every hour showed no appreciable decay.

Structure analysis and refinement: the structure was solved by Patterson methods [13], which yielded coordinates for all non-hydrogen atoms [14]. Refinement of the model was hampered by the weakly diffracting nature of the crystal which yielded only 1637 observed reflections. Further, the apparent electron density in the vicinity of the pentamethylcyclopentadienyl and acyl ligands was highly diffuse and stable refinement could only be achieved by means of restraints. The phenyl rings in the PPh_3 group were regularised (*i.e.* C–C distances of 1.390 Å and angles of 120°) and group refined, all aliphatic C–C bonds in the pentamethylcyclopentadienyl ring and acyl chain were restrained to 1.54(1) Å, C–C bonds within the cyclopentadienyl ring were restrained to the mean distance for

the pentamethylcyclopentadienyl ring and all C–C bonds in structure were restrained to have equal amplitudes of vibration. Final refinement cycles included positional and anisotropic thermal parameters for all non-hydrogen atoms except the phenyl rings of the PPh_3 group for which isotropic thermal parameters were used. Hydrogen atoms were included in the model at geometrically idealised positions on the PPh_3 and acyl ligands. A four term Chebychev polynomial weighting scheme [15] was employed and yielded a satisfactory agreement analysis. At convergence $R = 0.070$, $R_w = 0.080$, min. and max. residual electron density -0.26 and 0.39 e Å^{-3}. All calculations were performed on a Microvax 3800 computer. Supplementary data have been deposited at the Cambridge Crystallographic Data Centre.

4.2. Aldol reaction of the lithium enolate derived from (RS)-1 with benzaldehyde

The lithium enolate of **1** was generated as reported for the preparation of **11** by treating the acetyl complex (0.12 g, 0.23 mmol) with t-butyllithium (0.3 mmol) in THF (3 ml) at −42°C. A solution of freshly distilled benzaldehyde (70 μl, 0.68 mmol) in THF (1 ml) was added dropwise to the enolate and after 1 h the reaction was quenched with methanol (0.2 ml). The solvents were removed and the residue was extracted with dichloromethane (4 × 10 ml). Filtration of the solution through deactivated alumina followed by concentration and column chromatography (activated alumina, hexane, diethyl ether, ethyl acetate) gave (*RS,RS*) and (*RS,SR*)-[(η^5-C_5Me_5)Fe(CO)(PPh_3)$COCH_2CH$(OH)Ph] (*RS,SR*)-**14** and (*RS,RS*)-**15** as a 1:1 mixture of diastereomers (78 mg, 0.12 mmol, 55%) and recovered starting material **1** (29 mg, 24%), recrystallisation from diethyl ether/pentane afforded orange-red plates, m.p. 147–159°C (dec) (Found: C, 72.12; H, 5.99; P, 5.07. $C_{38}H_{39}FeO_3P$ requires: C, 72.38; H, 6.24; P, 4.91%), ν_{max} 3400 (OH), 1889 (Fe–CO), 1559 (C=O); *m/z* 631 (M^+ + H, 57), 601(M − CO − H, 13), 509(29), 453(M − C_5Me_5 − CO, 95), 263(34), 208(100), 190(35), 183(24), 133(19). (*RS,SR*)-**14** δ_H 7.70–7.30 (15H, m, PPh_3), 7.30–7.12 (3H, m, $COCH_2CH$(OH)*Ph*), 7.03 (2H, d, *J* 7.6 Hz, $COCH_2CH$(OH)*Ph*), 4.16 (1H, d, *J*(1,3), 1.3 Hz, $COCH_2$(O*H*)Ph), 4.00 (1H, bd, *J*(1,3) 9.9 Hz, $COCH_2C$*H*(OH)Ph), 2.76 (1H, bd, *J*(1,2) 16.3 Hz, $COCH_2$CH(OH)Ph), 2.67 (1H, dd, *J*(1,2) 17.8, *J*(1,3) 10.1 Hz, $COCH_2$CH(OH)Ph, 1.53 (15H, s, $C_5(CH_3)_5$); (*RS,SR*)-**15** δ_H 7.70–7.30 (15H, m, PPh_3), 7.30–7.12 (3H, m, $COCH_2CH$(OH)*Ph*), 7.09 (2H, d, *J* 7.6 Hz, $COCH_2CH$(OH)*Ph*), 4.74 (1H, d, *J*(1,3) 10.3 Hz, $COCH_2C$*H*(OH)Ph), 3.26 (1H, s, $COCH_2$-CH(O*H*)Ph), 3.13 (1H, d, *J*(1,2) 17.8 Hz, $COCH_2$-CH(OH)Ph), 2.34 (1H, dd, *J*(1,2) 17.9, *J*(1,3) 10.5 Hz, $COCH_2CH$(OH)Ph), 1.50 (15H, s, $C_5(CH_3)_5$).

4.3. Aldol reaction of the aluminium enolate derived from (RS)-1 with benzaldehyde

The lithium enolate of **1** was generated as reported in the preparation of **11** by treating the acetyl complex (0.12 g, 0.24 mmol) with t-butyllithium (0.47 mmol) in THF (5 ml) at −42°C. A 2 M solution of diethyl aluminium chloride in toluene (0.62 ml, 1.24 mmol) was added and after stirring at −42°C for 45 min, the mixture was cooled to −98°C. A solution of freshly distilled benzaldehyde (0.36 ml, 3.52 mmol) in THF (4 ml) was added dropwise to the enolate. After 2 h the mixture was quenched with methanol (0.5 ml). The solvents were removed *in vacuo* and the residue was extracted with dichloromethane (4 × 10 ml). Filtration of the solution through deactivated alumina followed by concentration and column chromatography (activated alumina, hexane/diethyl ether/ethyl acetate) gave (*RS, SR*) and (*RS, RS*)-[(η^5-C_5Me_5)Fe(CO)-(PPh_3)$COCH_2CH$(OH)Ph] (*RS,SR*)-**14** and (*RS,RS*)-**15** as an 18:1 mixture of diastereoisomers (71 mg, 0.11 mmol, 48%) and recovered **1** (28 mg, 23%). The major diastereoisomer was crystallised out of this mixture using diethyl ether/pentane to give (*RS,SR*)-**14** as red-orange plates, m.p. 148–150°C (dec) (Found: C, 72.62; H, 6.39; P, 4.72. $C_{38}H_{39}FeO_3P$ requires: C, 72.38; H, 6.24; P, 4.91%), ν_{max} 3400 (OH), 1889 (Fe–CO), 1559 (C=O); δ_H 7.70–7.30 (15H, m, PPh_3), 7.30–7.12 (3H, m, $COCH_2CH$(OH)*Ph*), 7.03 (2H, d, *J* 7.6 Hz, $COCH_2CH$(OH)*Ph*), 4.16 (1H, d, *J*(1,3) 1.3 Hz, $COCH_2$(O*H*)Ph), 4.00 (1H, bd, *J*(1,3) 9.9 Hz, $COCH_2C$*H*(OH)Ph), 2.76 (1H, bd, *J*(1,2) 16.3 Hz, $COCH_2$CH(OH)Ph), 2.67 (1H, dd, *J*(1,2) 17.8, *J*(1,3) 10.1 Hz, $COCH_2$CH(OH)Ph, 1.53 (15H, s, $C_5(CH_3)_5$); δ_C 9.52 (s, C_5*Me*$_5$), 70.56 (s, $COCH_2$*C*H(OH)Ph), 72.50 (s, *C*H_2CH(OH)Ph), 93.95 (s, *C*$_5$Me$_5$), 125.55 (s, Ph, C_{ortho}), 126.40 (s, Ph, C_{para}), 127.85 (d, *J* 9.4 Hz, PPh_3, C_{meta}), 127.88 (s, Ph, C_{meta}), 134.03 (bs, C_{ipso} and C_{ortho}), 143.55 (s, C_{ipso}), 221.90 (d, *J* 27.8 Hz, Fe–CO), 291.43 (d, 25.1 Hz, Fe*C*OCH_2CH(OH)Ph); δ_P 68.12; *m/z* 631(M^+ + H, 51), 601(M − CO − H, 19), 509(33), 453(M − C_5Me_5 − CO, 97), 263(39), 208(100), 190(32), 183(29), 133(29).

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