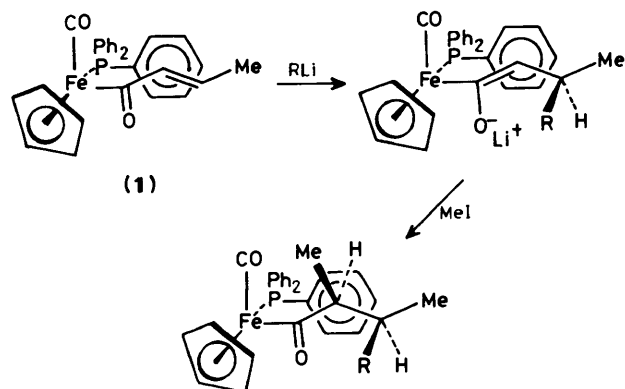


## Chiral Dienolates: Formation and Stereoselective $\alpha$ -Alkylation of the Lithium Dienolate Derived from (*Z*)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCH}=\text{CHMe}]$ . X-Ray Crystal Structure of (*RS*)-(*Z*)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCH}=\text{CHMe}]$

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An X-ray crystal structure analysis of (*RS*)-(*Z*)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCH}=\text{CHMe}]$  (**2**) shows that the crotonoyl group adopts a *cisoid* conformation in the solid state. In solution it is the *cisoid* conformation that is deprotonated by butyl-lithium to give the corresponding dienolate (**3**). Alkylation (MeI, EtI, or PhCH<sub>2</sub>Br) of the lithium dienolate (**3**) occurs regioselectively in the  $\alpha$ -position to give stereoselectively the single diastereoisomers (*RS,SR*)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCHRCH}=\text{CH}_2]$  (R = Me, Et, or PhCH<sub>2</sub>). Protonation of the dienolate (**3**) gives the  $\beta,\gamma$ -unsaturated acyl complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CH}_2]$  exclusively.

Enolates derived from acyl ligands attached to the chiral auxiliary  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)]$  undergo highly stereoselective alkylation reactions.<sup>1,2</sup> The stereochemical control observed in these reactions is consistent with preferential formation of *E*-enolates and their subsequent alkylation in the *anti* conformation (O<sup>-</sup> to CO) from the unhindered face.<sup>2,3</sup> The ready availability of both *E* and *Z* crotonoyl iron acyls<sup>4-6</sup> allowed the possibility of generating either enolates by Michael addition reactions or dienolates by deprotonation to be explored. We have previously reported that the *E*-crotonoyl complex (**1**) undergoes highly stereoselective tandem Michael additions and subsequent methylations which result in the stereocontrolled synthesis of  $\alpha$ - and  $\beta$ -substituted iron acyl complexes.<sup>4</sup> This work has been confirmed subsequently by Liebeskind *et al.*<sup>7</sup>



We describe here in detail the formation of the dienolate derived from the *Z*-crotonoyl iron complex (**2**) and its subsequent stereoselective alkylations. Part of this work has been the subject of a preliminary communication.<sup>4</sup>

### Results and Discussion

The *Z*-crotonoyl complex (**2**)<sup>†</sup> is readily available from the Peterson reaction of acetaldehyde with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCH}_2\text{SiMe}_3]$ .<sup>4,5</sup> Assuming, in common with all

<sup>†</sup> All complexes are racemic but only those with the *R*-configuration at iron are shown for clarity.

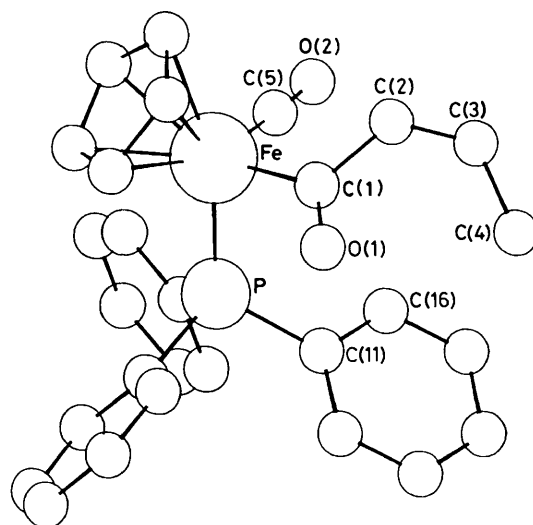


Figure 1. X-Ray crystal structure of (*RS*)-(*Z*)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{COCH}=\text{CHMe}]$  (**2**)

other iron acyls of this type,<sup>3,8</sup> that the acyl oxygen remains *anti* to the CO ligand then molecular models and extended Huckel calculations<sup>9</sup> indicate a clear preference for (**2**) to adopt a *cisoid* conformation. The corresponding *transoid* conformation would be disfavoured by severe steric interactions between the methyl group and the CO ligand.

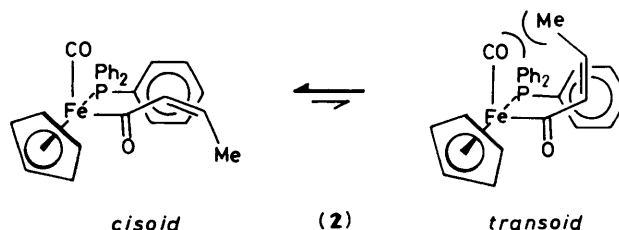


Figure 1 shows the X-ray crystal structure of (**2**). Final atomic positional co-ordinates are listed in Table 1 and selected bond lengths and bond angles are given in Table 2. The geometry around iron is close to octahedral<sup>10</sup> and the acyl oxygen is *anti*

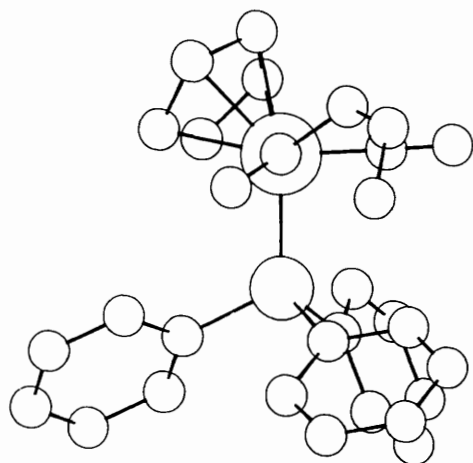


Figure 2. X-Ray crystal structure of (2); C(1)-Fe projection

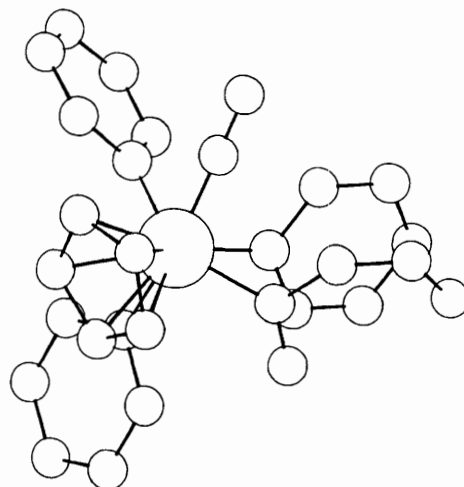


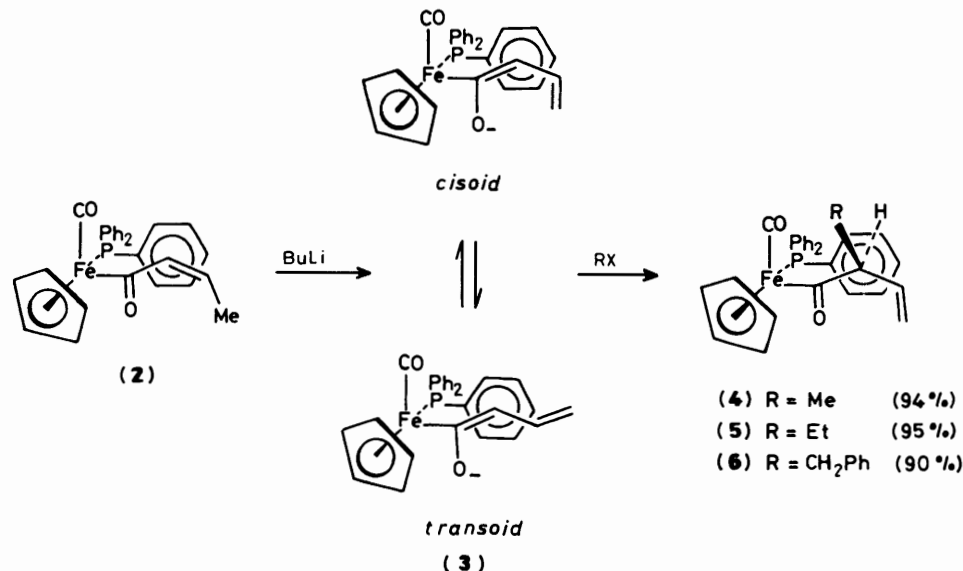
Figure 3. X-Ray crystal structure of (2); Fe-P projection

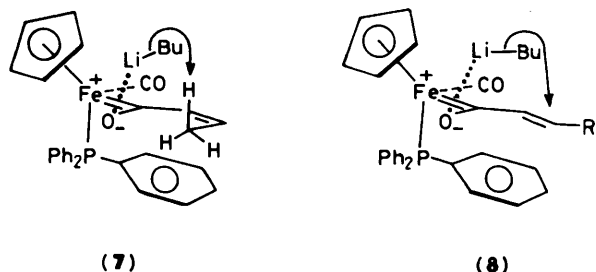
to the CO ligand (Figure 2). The crotonoyl conformation in (2) is *cisoid* with the torsional angle between the C=O and C=C being  $41.2^\circ$ . Figure 3 shows a projection down the Fe-P axis and illustrates the blocking effect of the triphenylphosphine ligand.

On addition of butyl-lithium, the *Z*-crotonoyl complex (2) undergoes exclusive  $\gamma$ -deprotonation to generate the dienolate (3). Addition of methyl iodide to (3) generates the  $\alpha$ -methyl- $\beta,\gamma$ -unsaturated complex (4) as a single diastereoisomer. 300 MHz N.m.r. spectroscopy showed (4) to be the exclusive product (d.e. >100:1).  $\alpha$ -Methylation followed from the presence of three olefinic protons, characteristic of a vinyl group, in the  $^1\text{H}$  n.m.r. spectrum and the relative configurations of the iron to the  $\alpha$ -centre were established from the chemical shift ( $\delta$  1.10) of the  $\alpha$ -methyl doublet which is characteristic of the *RS,SR*-diastereoisomer.<sup>11</sup> Since methylation must have occurred from the unhindered face of (3) the formation of (4) is consistent with (2) undergoing deprotonation in the *cisoid* conformation. This would generate initially the *cisoid* conformation of (3) which may be in equilibrium with the corresponding *transoid* conformation. Such an equilibrium would not however change the geometry about the  $\alpha$ -carbon and both conformations would be expected to undergo methylation stereoselectively from the unhindered face giving (4).

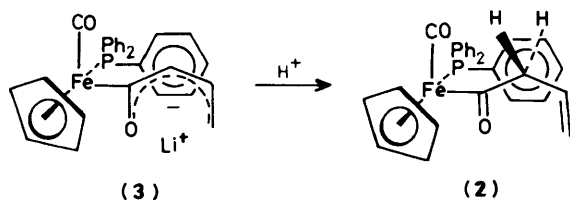
Alkylations of dienolate (3) with ethyl iodide or benzyl bromide also occur exclusively in the  $\alpha$ -position giving the diastereomerically pure (by 300 MHz  $^1\text{H}$  n.m.r. spectroscopy) products (5) and (6) respectively. The relative configurations of (5) and (6) were assigned as *RS,SR* by analogy with the methylation product (4). The exclusive formation of the dienolate (3) from the *Z*-crotonoyl complex (2) contrasts with the exclusive Michael reactions observed for the *E*-crotonoyl complex (1).<sup>4</sup> The difference may be rationalised in terms of initial co-ordination of the butyl-lithium to the acyl oxygen in both cases. This is likely to be extremely favourable given the high polarity of the acyl carbonyl groups as evidenced by their respective i.r. absorptions at  $\nu_{\text{max}}$ . 1 575, 1 565 and 1 615, 1 580  $\text{cm}^{-1}$  for (1) and (2) respectively. Directed deprotonation of the proximate methyl group present in the *Z*-crotonoyl case (7) would then generate the dienolate (3). Although directed deprotonation in the *E*-crotonoyl case (8) is not feasible since the methyl group is held distant from the co-ordinated butyl-lithium, directed Michael addition would be favoured. There is ample precedent for such a directed deprotonation of proximate methyl groups<sup>12</sup> and also for the subsequent alkylations proceeding exclusively in the  $\alpha$ -position.<sup>13</sup>

Protonation of the dienolate (3) at low temperature with trifluoroacetic acid is also completely  $\alpha$ -regioselective giving, in





essentially quantitative yield, the  $\beta,\gamma$ -unsaturated acyl complex (9). Addition of methanol to (3) gives a mixture (70:30) of (9) and the *E*-crotonoyl complex (1). In the latter reaction complex (1) presumably arises from alkoxide-promoted rearrangement of (9) as has been previously observed.<sup>6</sup> Deprotonation (butyllithium) and methylation of (9) generates (4) with a diastereoselectivity of 30:1 indicating that (9) is deprotonated back to (3) with a slightly reduced stereoselectivity compared with that observed in its formation from the *Z*-crotonoyl complex (2).



The methods available for the resolution of iron acyl complexes<sup>14</sup> and for their efficient decomplexation to carboxylic acids, esters and amides<sup>15</sup> will allow the extension of the above stereoselective alkylation reactions to asymmetric synthesis.

### Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum line and Schlenk tube techniques.<sup>16</sup> Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled. Dichloromethane was distilled from calcium hydride and hexane refers to that fraction boiling in the range 67–70 °C. Butyl-lithium (1.6M in hexane) was used as supplied by Aldrich. The complex (*Z*)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH=CHMe] (2) was prepared according to the literature method.<sup>4,5</sup> I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 297 instrument. N.m.r. spectra were recorded in CDCl<sub>3</sub> on Bruker WH 300 (300.13 MHz <sup>1</sup>H) and Bruker AM 250 (62.896 MHz <sup>13</sup>C, 101.26 MHz <sup>31</sup>P) spectrometers. Mass spectra were recorded on a V.G. Micromass ZAB 2F instrument using FD techniques. Elemental analyses were performed by the University of Manchester Analytical Service.

**X-Ray Crystal Structure Analysis of (*RS*)-(*Z*)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH=CHMe] (2).**—Cell parameters and reflection intensities were measured with graphite-monochromated Mo-*K*<sub>α</sub> radiation on an Enraf-Nonius CAD-4 diffractometer operating at room temperature in the  $\omega/2\theta$  scan mode for a crystal having approximate dimensions 0.53 × 0.16 × 0.14 mm. The scan range ( $\omega$ ) was calculated from  $[0.95 + 0.35 \tan \theta]^\circ$ , and the scan speed varied from 1.0 to 5.5° min<sup>-1</sup> depending upon the intensity. Reflections were scanned in the range  $0 < \theta < 25^\circ$ . Three standard reflections measured every hour showed no appreciable variation with time. The data were corrected for Lorentz, polarisation, and absorption effects<sup>17</sup> (relative transmission factors 1.00–1.09) and equivalent

Table 1. Fractional atomic co-ordinates with e.s.d.s in parentheses

| Atom  | <i>x/a</i>  | <i>y/b</i>   | <i>z/c</i>   |
|-------|-------------|--------------|--------------|
| Fe(1) | -0.147 8(1) | -0.146 43(4) | -0.166 49(5) |
| P(1)  | -0.290 4(2) | -0.135 57(7) | -0.292 88(9) |
| C(1)  | -0.141 1(9) | -0.043 8(3)  | -0.151 0(4)  |
| C(2)  | -0.208(1)   | -0.016 6(4)  | -0.067 1(4)  |
| C(3)  | -0.300(1)   | 0.041 1(5)   | -0.057 4(6)  |
| C(4)  | -0.347(1)   | 0.094 6(4)   | -0.123 9(7)  |
| C(5)  | -0.332(1)   | -0.155 3(3)  | -0.108 4(4)  |
| C(6)  | 0.095 9(9)  | -0.168 5(4)  | -0.209 6(4)  |
| C(7)  | 0.111 0(9)  | -0.140 3(4)  | -0.123 2(5)  |
| C(8)  | 0.023(1)    | -0.185 5(4)  | -0.068 4(5)  |
| C(9)  | -0.040 8(9) | -0.242 5(4)  | -0.119 2(5)  |
| C(10) | 0.005 3(9)  | -0.232 2(4)  | -0.206 0(5)  |
| C(11) | -0.424 1(9) | -0.056 9(3)  | -0.308 0(4)  |
| C(12) | -0.405(1)   | -0.007 8(3)  | -0.374 9(4)  |
| C(13) | -0.513(1)   | 0.048 6(3)   | -0.383 8(5)  |
| C(14) | -0.642(1)   | 0.057 3(3)   | -0.327 7(5)  |
| C(15) | -0.665(1)   | 0.008 5(3)   | -0.261 1(4)  |
| C(16) | -0.555(1)   | -0.048 0(3)  | -0.251 3(4)  |
| C(17) | -0.446 7(9) | -0.205 2(3)  | -0.316 5(4)  |
| C(18) | -0.586(1)   | -0.194 9(3)  | -0.374 5(4)  |
| C(19) | -0.701 4(9) | -0.248 0(4)  | -0.391 2(4)  |
| C(20) | -0.678(1)   | -0.313 7(4)  | -0.352 3(5)  |
| C(21) | -0.540(1)   | -0.324 9(3)  | -0.295 1(5)  |
| C(22) | -0.426(1)   | -0.271 4(3)  | -0.277 2(4)  |
| C(23) | -0.163 0(9) | -0.134 8(3)  | -0.390 8(3)  |
| C(24) | -0.192 6(9) | -0.181 3(3)  | -0.461 1(4)  |
| C(25) | -0.093(1)   | -0.177 3(4)  | -0.534 1(4)  |
| C(26) | 0.035(1)    | -0.128 1(4)  | -0.537 0(4)  |
| C(27) | 0.065 6(9)  | -0.082 3(3)  | -0.466 9(4)  |
| C(28) | -0.032 5(9) | -0.085 5(3)  | -0.394 0(4)  |
| O(1)  | -0.083 6(6) | -0.002 7(2)  | -0.202 6(3)  |
| O(2)  | -0.450 6(7) | -0.163 6(3)  | -0.070 1(3)  |

reflections were merged to give 4 014 unique reflections ( $R_m$  0.024) of which 1 398 were considered to be observed [ $I > 3\sigma(I)$ ] and used in the structure analysis.

**Crystal data.** C<sub>28</sub>H<sub>25</sub>O<sub>2</sub>FeP,  $M = 480.3$ , Monoclinic,  $a = 7.935(2)$ ,  $b = 18.972(5)$ ,  $c = 15.218(6)$  Å,  $\beta = 92.64(2)^\circ$ ,  $U = 2 288.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.39$  mg m<sup>-3</sup>,  $\mu$  (Mo-*K*<sub>α</sub> 0.710 69 Å) = 7.7 cm<sup>-1</sup>, space group  $P2_1/n$  (established from systematic absences).

The structure was solved by Patterson and electron density methods. Final full-matrix least squares refinement for 289 parameters included atomic positions, temperature factors (anisotropic for non-hydrogen atoms), and an overall scale factor. All hydrogen atoms were included in calculated positions, being allowed to 'ride' on their respective carbon atoms and were assigned a common overall temperature factor.<sup>18</sup> The refinement was terminated when all shifts were less than 0.1 $\sigma$  with  $R$  0.033 ( $R_w$  0.042), GOF = 1.10. The weight for each reflection was calculated from the Chebyshev series  $w = [24.05 t_0(X) + 28.96 t_1(X) + 9.74 t_2(X) + 1.59 t_3(X)]$  where  $X = F_o/F_{max}$ .<sup>19</sup> Final difference Fourier synthesis showed no significant residual electron density and a detailed analysis failed to reveal any systematic errors. All calculations were performed with the CRYSTALS package on the Chemical Crystallography Laboratory VAX 11/750 computer. Final atomic positional co-ordinates with e.s.d.'s in parentheses are listed in Table 1. Selected bond lengths and bond angles are given in Table 2.\*

\* Full listings of bond lengths and angles together with the hydrogen atomic co-ordinates and thermal parameters are available from the Cambridge Crystallographic Data Centre. [See Instructions for Authors (1987), para. 5.6.3 in *J. Chem. Soc., Perkin Trans. I*, 1987, Issue 1].

**Table 2.** Selected bond lengths (Å) and angles (°) and torsional angles (°) with e.s.d.s in parentheses for (RS)-(Z)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)(COCH=CHCH<sub>3</sub>)] (2)

|                       |          |                       |          |
|-----------------------|----------|-----------------------|----------|
| Fe(1)–P(1)            | 2.196(2) | C(1)–C(2)             | 1.497(9) |
| Fe(1)–C(1)            | 1.962(6) | C(2)–C(3)             | 1.33(1)  |
| Fe(1)–C(5)            | 1.753(9) | C(3)–C(4)             | 1.47(1)  |
| C(1)–O(1)             | 1.210(7) |                       |          |
| C(1)–Fe(1)–C(5)       | 93.0(3)  | Fe(1)–C(1)–C(2)       | 115.8(5) |
| C(1)–Fe(1)–P(1)       | 91.3(2)  | C(1)–C(2)–C(3)        | 126.8(7) |
| P(1)–Fe(1)–C(5)       | 92.4(2)  | C(2)–C(3)–C(4)        | 127.9(8) |
| Fe(1)–C(1)–O(1)       | 124.8(5) | Fe(1)–P(1)–C(11)      | 117.1(2) |
| C(5)–Fe(1)–C(1)–O(1)  | 150      | C(5)–Fe(1)–C(1)–C(2)  | 33       |
| C(1)–Fe(1)–P(1)–C(11) | 28       | C(3)–C(2)–C(1)–O(1)   | 41       |
| C(1)–C(2)–C(3)–C(4)   | 5        | Fe(1)–P(1)–C(1)–C(16) | 62       |

Distances and angles about the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> ligand (Z = Cp-centroid; co-ordinates  $x = 0.0389$ ,  $y = -0.1938$ ,  $z = -0.1453$ )

|             |          |              |        |
|-------------|----------|--------------|--------|
| Fe(1)–C(6)  | 2.112(7) | Fe(1)–Z      | 1.75   |
| Fe(1)–C(7)  | 2.130(7) | Z–Fe(1)–C(5) | 125.3° |
| Fe(1)–C(8)  | 2.106(7) | Z–Fe(1)–C(1) | 118.0° |
| Fe(1)–C(9)  | 2.123(6) | Z–Fe(1)–P(1) | 127.4° |
| Fe(1)–C(10) | 2.134(6) |              |        |

**General Procedure for the Reaction between the Dienolate (3) and Electrophiles.**—Butyl-lithium (0.7 ml, 1.12 mmol) was added to complex (2) (500 mg, 1.04 mmol) in THF (30 ml) at  $-78^\circ\text{C}$  to give a deep red solution. The mixture was stirred at  $-78^\circ\text{C}$  for 2 h after which the electrophile (2 equiv.) was added and the mixture further stirred ( $-78^\circ\text{C}$ ; 2 h). Warming to room temperature and removal of solvent gave an orange oil which was extracted with dichloromethane (3  $\times$  10 ml) and filtered through alumina (Grade V). The product complexes were purified by chromatography on alumina (Grade I), analysed by  $^1\text{H}$  n.m.r. spectroscopy to determine diastereoselectivities and obtained as orange needles from dichloromethane–hexane.

(RS/SR)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH(Me)CH=CH<sub>2</sub>] (4). Elution with diethyl ether–dichloromethane (3:1) gave complex (4) (94%) as a 150:1 mixture of diastereoisomers (Found: C, 70.3; H, 5.4; P, 6.3. C<sub>29</sub>H<sub>27</sub>FeO<sub>2</sub>P requires C, 70.5; H, 5.5; P, 6.3%;  $\nu_{\text{max}}$  1 915 vs (C=O) and 1 592 s cm<sup>-1</sup> (C=O);  $^1\text{H}$  n.m.r.  $\delta$  7.6–7.3 (15 H, m, Ph), 5.21 (1 H, ddd,  $J_{\text{trans}}$  17.8 Hz,  $J_{\text{cis}}$  10.5 Hz,  $J_{1,2}$  7.7 Hz, CH=CH<sub>2</sub>), 4.71 (2 H, m, CH=CH<sub>2</sub>), 4.46 (5 H, d,  $J_{\text{PH}}$  1.1 Hz, C<sub>5</sub>H<sub>5</sub>), 3.64 (1 H, quintet,  $J_{1,2}$  7.3 Hz, COCH), 1.10 (3 H, d,  $J_{1,2}$  7.0 Hz, Me major diastereoisomer), and 0.39 (3 H, d,  $J_{1,2}$  6.3 Hz, Me minor diastereoisomer);  $^{13}\text{C}\{^1\text{H}\}$  n.m.r.  $\delta$  220.7 (d,  $J_{\text{PC}}$  31.6 Hz, C=O), 140.2 (s, CH=CH<sub>2</sub>), 136.5 (d,  $J_{\text{PC}}$  42.6 Hz, Ph C<sub>ipso</sub>), 133.5 (d,  $J_{\text{PC}}$  10.0 Hz, Ph, C<sub>ortho</sub>), 129.6 (s, Ph, C<sub>para</sub>), 128.0 (d,  $J_{\text{PC}}$  9.3 Hz, Ph, C<sub>meta</sub>), 113.0 (s, CH=CH<sub>2</sub>), 85.1 (s, C<sub>5</sub>H<sub>5</sub>), 71.6 (d,  $J_{\text{PC}}$  5.4 Hz, COCH), and 17.1 (s, Me);  $^{31}\text{P}\{^1\text{H}\}$  n.m.r.  $\delta$  71.8;  $m/z$  494 ( $M^+$ ).

(RS/SR)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH(Et)CH=CH<sub>2</sub>] (5). Elution with diethyl ether–dichloromethane (1:1) gave complex (5) (95%) as a single diastereoisomer (Found: C, 70.6; H, 5.9. C<sub>30</sub>H<sub>29</sub>FeO<sub>2</sub>P requires C, 70.9; H, 5.75%;  $\nu_{\text{max}}$  1 910 vs (C=O) and 1 600 s cm<sup>-1</sup> (C=O);  $^1\text{H}$  n.m.r.  $\delta$  7.6–7.3 (15 H, m, Ph), 5.19 (1 H, ddd,  $J_{\text{trans}}$  17.2 Hz,  $J_{\text{cis}}$  10.2 Hz,  $J_{1,2}$  3.6 Hz, CH=CH<sub>2</sub>), 4.72 (2 H, ddd,  $J_{\text{trans}}$  17.2 Hz,  $J_{\text{cis}}$  10.2 Hz,  $J_{\text{gem}}$  2.2 Hz, CH=CH<sub>2</sub>), 4.44 (5 H, d,  $J_{\text{PH}}$  0.9 Hz, C<sub>5</sub>H<sub>5</sub>), 3.43 (1 H, dt,  $J_{1,2}$  9.8 Hz, 3.6 Hz, COCH), 1.85–1.20 (2 H, m, CH<sub>2</sub>Me), and 0.79 (3 H, t,  $J_{1,2}$  7.4 Hz, Me);  $^{13}\text{C}\{^1\text{H}\}$  n.m.r.  $\delta$  220.6 (d,  $J_{\text{PC}}$  30.3 Hz, C=O), 138.3 (s, CH=CH<sub>2</sub>), 136.5 (d,  $J_{\text{PC}}$  42.6 Hz, Ph, C<sub>ipso</sub>), 133.5 (d,  $J_{\text{PC}}$  9.6 Hz, Ph C<sub>ortho</sub>), 129.6 (s, Ph C<sub>para</sub>), 128.0 (d,  $J_{\text{PC}}$  10.0 Hz, Ph, C<sub>meta</sub>), 115.2 (s, CH=CH<sub>2</sub>), 85.1 (s, C<sub>5</sub>H<sub>5</sub>), 80.6 (d,  $J_{\text{PC}}$  4.1 Hz, COCH), 24.2 (s, CH<sub>2</sub>Me), and 11.8 (s, Me);  $^{31}\text{P}\{^1\text{H}\}$  n.m.r.  $\delta$  72.1;  $m/z$  508 ( $M^+$ ).

(RS/SR)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH(CH<sub>2</sub>Ph)CH=CH<sub>2</sub>] (6). Elution with diethyl ether–dichloromethane (1:1) gave complex (6) (90%) as a single diastereoisomer (Found: C, 73.6; H, 5.7. C<sub>35</sub>H<sub>31</sub>FeO<sub>2</sub>P requires C, 73.7; H, 5.5%;  $\nu_{\text{max}}$  1 910 vs (C=O) and 1 600 s cm<sup>-1</sup> (C=O);  $^1\text{H}$  n.m.r.  $\delta$  7.6–7.2 (20 H, m, Ph), 5.10 (1 H, ddd,  $J_{\text{trans}}$  15.7 Hz,  $J_{\text{cis}}$  10.1 Hz,  $J_{1,2}$  3.7 Hz, CH=CH<sub>2</sub>), 4.66 (2 H, ddd,  $J_{\text{trans}}$  15.7 Hz,  $J_{\text{cis}}$  10.1 Hz,  $J_{\text{gem}}$  2.0 Hz, CH=CH<sub>2</sub>), 4.27 (5 H, d,  $J_{\text{PH}}$  1.3 Hz, C<sub>5</sub>H<sub>5</sub>), 3.98 (1 H, m, COCH), and 3.12, 2.35 (2 H, ABX system,  $J_{\text{AB}}$  13.3 Hz, CH<sub>2</sub>Ph);  $^{13}\text{C}\{^1\text{H}\}$  n.m.r.  $\delta$  220.6 (d,  $J_{\text{PC}}$  31.2 Hz, C=O), 140.8 (s, CH<sub>2</sub>Ph C<sub>ipso</sub>), 137.1 (s, CH<sub>2</sub>Ph C<sub>meta</sub>), 136.6 (d,  $J_{\text{PC}}$  43.6 Hz, Ph C<sub>ipso</sub>), 133.6 (d,  $J_{\text{PC}}$  10.4 Hz, Ph C<sub>ortho</sub>), 129.6 (s, Ph C<sub>para</sub>), 129.4 (s, CH<sub>2</sub>Ph C<sub>ortho</sub>), 128.0 (d,  $J_{\text{PC}}$  8.8 Hz, Ph C<sub>meta</sub>), 125.6 (s, CH<sub>2</sub>Ph C<sub>ortho</sub>), 116.4 (s, CH=CH<sub>2</sub>), 85.1 (s, C<sub>5</sub>H<sub>5</sub>), 80.9 (d,  $J_{\text{PC}}$  4.5 Hz, COCH), and 38.4 (s, CH<sub>2</sub>Ph);  $^{31}\text{P}\{^1\text{H}\}$  n.m.r.  $\delta$  72.1;  $m/z$  570 ( $M^+$ ).

(R/S)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH<sub>2</sub>CH=CH<sub>2</sub>] (9). Trifluoroacetic acid (excess) in THF (2 ml) at  $-78^\circ\text{C}$  was added dropwise to a solution of the dienolate (3). The reaction mixture was stirred ( $-78^\circ\text{C}$ ; 15 min) to give a light red solution which was then poured onto saturated aqueous NaHCO<sub>3</sub> (15 ml). Dichloromethane (10 ml) was added and the organic layer separated and chromatographed on alumina (Grade I). Elution with dichloromethane–ethyl acetate (2:1) gave complex (9) (90%) (Found: C, 70.1; H, 5.4; P, 6.5. C<sub>28</sub>H<sub>25</sub>FeO<sub>2</sub>P requires C, 70.0; H, 5.25; P, 6.45%;  $\nu_{\text{max}}$  1 905 vs (C=O), 1 610 s cm<sup>-1</sup> (C=O);  $^1\text{H}$  n.m.r.  $\delta$  7.6–7.3 (15 H, m, Ph), 5.61 (1 H, m, CH=CH<sub>2</sub>), 4.89 (1 H, d,  $J_{\text{cis}}$  10.1 Hz, CH=CH<sub>2</sub>), 4.78 (1 H, d,  $J_{\text{trans}}$  17.1 Hz, CH=CH<sub>2</sub>), 4.45 (5 H, d,  $J_{\text{PH}}$  1.2 Hz, C<sub>5</sub>H<sub>5</sub>), 3.61, 3.25 (2 H, ABX system,  $J_{\text{AB}}$  15.5 Hz, COCH<sub>2</sub>);  $^{13}\text{C}\{^1\text{H}\}$  n.m.r.  $\delta$  220.5 (d,  $J_{\text{PC}}$  31.0 Hz, C=O), 136.4 (d,  $J_{\text{PC}}$  42.7 Hz, Ph C<sub>ipso</sub>), 134.2 (s, CH=CH<sub>2</sub>), 133.3 (d,  $J_{\text{PC}}$  9.5 Hz, Ph C<sub>ortho</sub>), 129.7 (s, Ph C<sub>para</sub>), 128.0 (d,  $J_{\text{PC}}$  9.3 Hz, Ph C<sub>meta</sub>), 115.5 (s, CH=CH<sub>2</sub>), 85.2 (s, C<sub>5</sub>H<sub>5</sub>), and 70.3 (d,  $J_{\text{PC}}$  5.4 Hz, COCH<sub>2</sub>);  $^{31}\text{P}\{^1\text{H}\}$  n.m.r.  $\delta$  72.3;  $m/z$  480 ( $M^+$ ), 439 ( $M^+ - 41$ ).

Quenching of the dienolate (3) with methanol (excess) and following a similar work-up to that described in the general procedure gave, upon elution with dichloromethane, the complex (9) (70%) and, upon elution with dichloromethane–ethyl acetate (1:1), (E)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH=CHMe] (1) (30%) identified by comparison of its spectroscopic data with literature values.<sup>5</sup>

**Preparation of (RS/SR)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH(Me)CH=CH<sub>2</sub>] (4) from (R/S)-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>)COCH<sub>2</sub>CH=CH<sub>2</sub>] (9).**—Butyl-lithium (0.15 ml, 0.24 mmol) was added to complex (9) (65 mg, 0.14 mmol) in THF (10 ml) at  $-78^\circ\text{C}$  to give a deep red solution. The mixture was stirred for 1 h at  $-78^\circ\text{C}$  after which methyl iodide (0.2 ml, 3.2 mmol) was added and the mixture further stirred ( $-78^\circ\text{C}$ ; 2 h). The mixture was then allowed to warm to room temperature when solvent was removed; the residue was extracted with dichloromethane (2  $\times$  10 ml) and the combined extracts evaporated to give an orange oil which was filtered through alumina (Grade V) and chromatographed on alumina (Grade I). Elution with dichloromethane gave complex (4) (55 mg, 81%) as a 30:1 mixture of diastereoisomers.

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