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# CHIRAL DIENOLATES:

## Stereoselective Formation and α-Alkylation of the Lithium Dienolates Derived from (RS)-Z-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH=$CHCH_2R$] (R=Me,Et,n-Pr) and (RS)-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)(COCH=$CMe_2$)].

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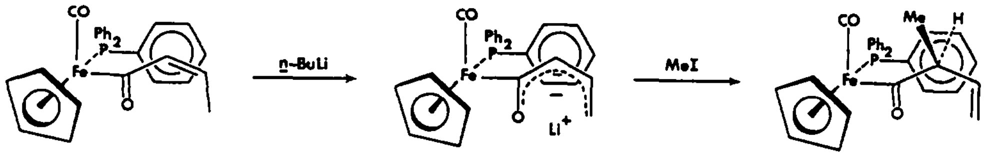
Summary: The acyl ligands Z-(COCH=$CHCH_2R$)(R=Me,Et,n-Pr) and (COCH=$CMe_2$) bound to the chiral auxiliary [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)] undergo exclusive γ-deprotonation to form the corresponding dienolates which react with electrophiles regio- and stereoselectively at the α-position to give in most cases single diastereoisomers of the corresponding α-substituted-βγ-unsaturated acyl complexes, together with in the former cases complete control over the β,γ-double bond geometry (E).

## Introduction

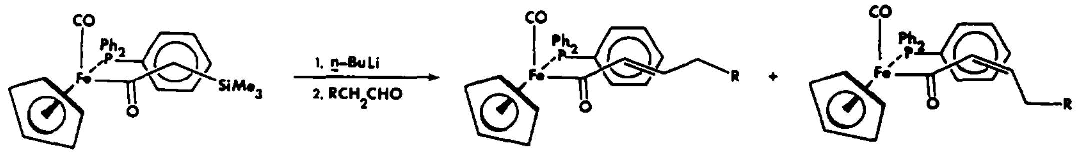
The chiral auxiliary [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)] affords excellent stereochemical control in a variety of carbon-carbon bond forming reactions involving enolates derived from attached acyl ligands. Reactions which have been studied so far include alkylations[1] and aldol-type reactions[2,3,4]. We have recently reported that the Z-crotonyl complex 1 is deprotonated by n-butyllithium to give the corresponding dienolate 2 which undergoes both regio- and stereoselective α-methylation to give the single (RS,SR) diastereoisomer of the β,γ-unsaturated acyl complex 3.[5] This work has been subsequently confirmed independently by Liebeskind et.al[6]. We describe here the formation of dienolates derived from Z-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH=$CHCH_2R$] and their subsequent regio- and stereoselective α-alkylations to give the corresponding α-substituted-E-β,γ-unsaturated acyl complexes.



1 2 3

## Results

α,β-Unsaturated acyl complexes of [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)] can be generated as readily separable mixtures of E and Z isomers by the Peterson olefination reaction between 4 and aldehydes[5,7]. Thus, deprotonation of 4 with n-butyllithium followed by trapping the resultant enolate with butanal gave, after work up, a 2:1 mixture of the E and Z isomers 5 and 6 in 63% yield. The E and Z isomers 5 and 6 were readily separable by chromatography on alumina. The preparation of the Z-α,β-unsaturated acyl complexes 7 and 8 has been described previously[7].

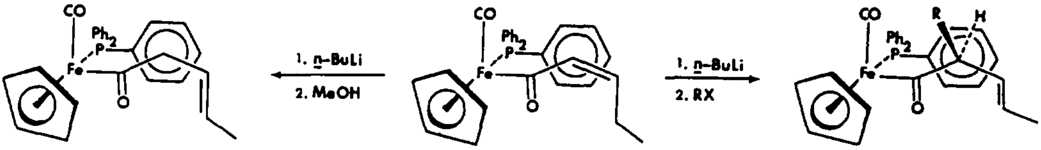


4

5

6 R = Et
7 R = Me
8 R = n-Pr

On addition of n-butyllithium complex 7 underwent exclusive γ-deprotonation to generate the corresponding dienolate which on quenching with methanol gave exclusively the E-β,γ-unsaturated acyl complex 9 as a single diastereoisomer. The β,γ-double bond geometry was established from the $^1$H n.m.r. coupling constant ( J = 15.5 Hz)[††] between the vinyl protons. Addition of methyl iodide to the dienolate derived from 7 generated the α-methyl-β,γ-unsaturated complex 10 as the exclusive product (d.e > 100:1)[†] as shown by 300 MHz $^1$H n.m.r. spectroscopy. The relative configurations of the iron to the α-centre were established from the chemical shift (δ 1.02) of the α-methyl doublet which is characteristic of the RS,SR diastereoisomer[2], while the double bond geometry followed from the trans coupling constant (J = 16 Hz) between the vinylic protons. Similarly, alkylation of the dienolate derived from 7 with ethyl iodide and benzyl bromide gave complexes 11 and 12 respectively as single diastereoisomers by 300 MHz $^1$H n.m.r. spectroscopy.



9 60%

7

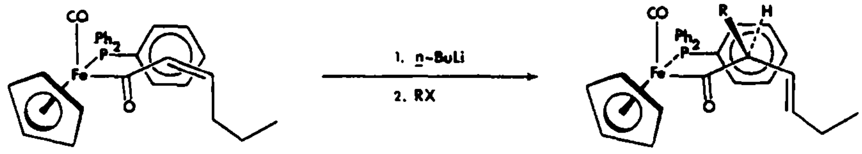
RX = MeI, EtI, PhCH$_2$Br

10 R = Me 86%
11 R = Et 87%
12 R = PhCH$_2$ 90%

Complexes 6 and 8 also undergo exclusive γ-deprotonation with n-butyllithium. Quenching the corresponding dienolates with methanol, methyl iodide or ethyl iodide generated single diastereoisomers by 300 MHz $^1$H n.m.r. spectroscopy of the E-β,γ-unsaturated acyl complexes. The relative configuration of the iron to the α-centre and the double bond geometries were established as before. Trapping the dienolate derived from 8 with benzyl bromide or methyl disulphide to give 19 and 20 respectively resulted in somewhat less stereocontrol at the α-centre (d.e. 90:1 and 18:1 respectively) but still complete control over the double bond geometry. A single crystallisation gave complexes 19 and 20 diastereoisomerically pure (d.e. > 100:1)

[†] Generally, the 300 MHz $^1$H n.m.r. spectra were of sufficient quality that the $^{13}$C satellites due to the major diastereoisomers were clearly visible, thus providing an internal standard for the diastereoisomeric purity.

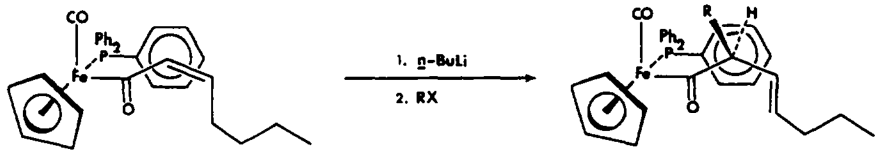
[††] Deduced from computer simulation of the methyl decoupled 500 MHz $^1$H n.m.r. spectrum.



| | | |
|---|---|---|
| 13 | R = H | 95% |
| 14 | R = Me | 92% |
| 15 | R = Et | 90% |

6

RX = MeOH, MeI, EtI

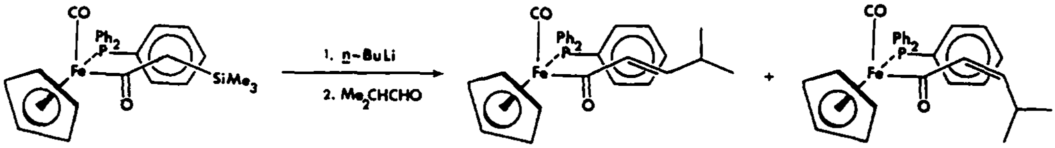


| | | |
|---|---|---|
| 16 | R = H | 80% |
| 17 | R = Me | 94% |
| 18 | R = Et | 90% |
| 19 | R = $PhCH_2$ | 81% |
| 20 | R = SMe | 94% |

8

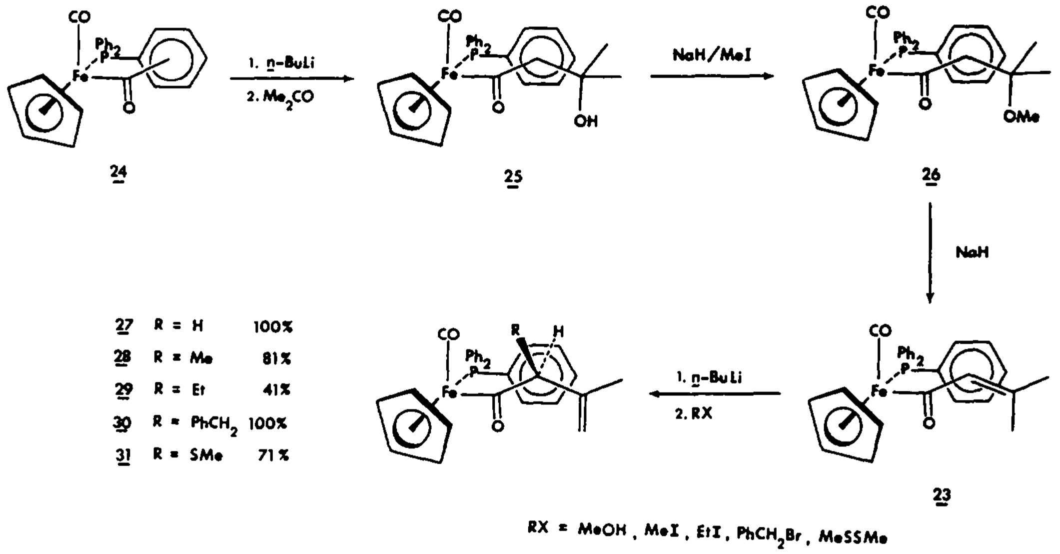
RX = MeOH, MeI, EtI, $PhCH_2Br$, MeSSMe

Treatment of complex 4 with *n*-butyllithium followed by 2-methylpropanal gave, after work up, a readily separable mixture (1 : 1) of the E and Z isomers 21 and 22. Treatment of 22 with *n*-butyllithium followed by attempted trapping with methanol did not however, result in the isolation of any characterisable products.



4 21 22

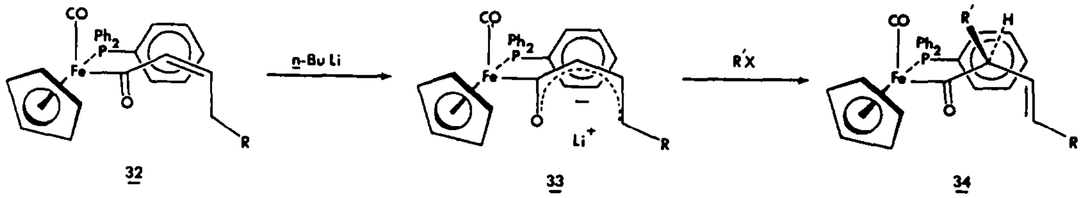
In an attempt to prepare the β,β-dimethyl-α,β-unsaturated acyl complex 23, the enolate derived from complex 4 was treated with acetone. Quantitative recovery of the starting complex 4 indicated that enolisation was occurring in preference to nucleophilic attack. Complex 23 was prepared however, using alternative methodology developed previously[7]. Complex 25, obtained from the reaction between the enolate derived from the parent acetyl complex 24 and acetone [8], was subjected to O-methylation. Sodium hydride-induced elimination of methanol from the resulting complex 26 gave the desired complex 23. Deprotonation of complex 23 generated the corresponding dienolate exclusively as evidenced by the isolation in quantitative yield of the β,γ-unsaturated acyl complex 27 upon addition of methanol. Trapping the dienolate derived from complex 23 with benzyl bromide or methyl disulphide was completely stereoselective giving only the RS,SR diastereoisomers 30 and 31 respectively, whereas trapping with methyl or ethyl iodide was somewhat less stereoselective, the ratios being 14:1 and 17:1 respectively.



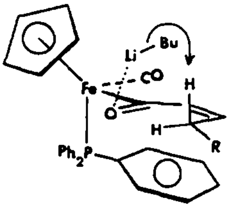
| | | |
|---|---|---|
| 27 | R = H | 100% |
| 28 | R = Me | 81% |
| 29 | R = Et | 41% |
| 30 | R = $PhCH_2$ | 100% |
| 31 | R = SMe | 71% |

## Discussion

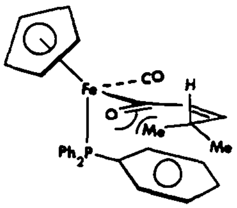
Deprotonation of the Z-α,β-unsaturated acyl complexes 32 generates dienolates 33 which undergo stereoselective alkylations to give the corresponding RS,SR-α-substituted-E-β,γ-unsaturated complexes 34. α-Alkylation from the unhindered face [1,2,9] of 33 and the final β,γ-double bond geometry indicates that complexes 32 are undergoing deprotonation in the cisoid conformation with the R group *exo* to give 33.



The cisoid conformation of 32 is expected to be preferred due to steric interactions between the $CH_2R$ group and the carbon monoxide ligand that would be present in the transoid conformer. An X-ray crystal structure analysis of the Z-crotonyl complex 32 (R=H) shows it to adopt such a conformation in the solid state[4]. Exclusive formation of dienolates from complexes 32 and 23 is consistent with initial coordination of n-butyllithium to the acyl oxygen followed by directed deprotonation of the proximate methylene proton. Coordination to the acyl oxygen is likely to be favoured by the polar nature of the acyl carbonyl group ($\nu_{max}$ 1615-1560 $cm^{-1}$), there being literature precedents for coordination to oxygen directing the deprotonation of adjacent groups.[10] The E-geometry of the product β,γ-double bond is consistent with the $CH_2R$ group being deprotonated in conformation 35 with the bulky R group anti to the acyl group thus producing the dienolate 33 with R in the exo rather than the sterically disfavoured endo position. Complex 22 presumably does not form an enolate because the required conformation for deprotonation of 36 is inaccessible.



35



36

The stereoselective formation of E-β,γ-double bonds has been observed in other systems[11]. Furthermore, there is ample precedent for dienolates undergoing electrophilic additions under kinetic control in the α- rather than the γ-position [11,12].

The availability of resolved iron acyls [13] and methods for their efficient decomplexation to a variety of carbonyl functionalities (e.g. acid, ester, amide)[14] will allow the stereoselectivities described herein to be applied to asymmetric synthesis.

## Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum line and Schlenk tube techniques[15]. Removal of all solvents was carried out under reduced pressure. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled. Dichloromethane was distilled from calcium hydride and hexane refers to that fraction boiling between 67°C and 70°C. n-Butyllithium (1.6M in hexane) was supplied by Aldrich. The complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2SiMe_3)]$ 4, Z-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CHEt)]$ 7 and Z-$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH{=}CH\textit{n}\text{-}Bu)]$ 8 were prepared according to the literature method[7] as was complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)]$ 24.[16] Unless otherwise stated, infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 297 instrument. N.m.r. spectra were recorded in $CDCl_3$ on Bruker WH 300 (300.13 MHz $^1H$) and Bruker AM 250 (62.896 MHz $^{13}C$, 101.26 MHz $^{31}P$) 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 and the Dyson Perrins Analytical Services.

### Peterson reaction between the lithium enolate derived from complex 4 and butyraldehyde

n-Butyllithium (5.3 ml, 8.5 mmol) was added to complex 4 (4.0 g, 7.6 mmol) in THF (100 ml) at -78°C to give a deep red solution. After stirring (-78°C; 1h), freshly distilled butyraldehyde (1.5 ml, 16.7 mmol) in THF (2 ml) was added dropwise and the mixture further stirred (-78°C ; 4h). Methanol (1 ml) was added and the mixture warmed to room temperature. Removal of solvent gave an orange oil which was extracted with dichloromethane (3 x 20 ml) and filtered through celite. Concentration and chromatography on alumina (Grade I) gave complex 6 (0.85 g, 23%) upon elution with diethyl ether and removal of solvent, whilst elution with dichloromethane/ethyl acetate (2:1) gave complex 5 (1.65 g, 44%). Both were obtained as orange needles from dichloromethane/ hexane.

Z-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)(COCH=CH$\underline{n}$-Pr)] $\underline{6}$. (Found: C, 70.9; H, 5.9. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75%); $\nu_{max}$ 1925 vs (C≡O), 1610 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 6.52 (1H, d, $J_{cis}$ 11.2 Hz, COCH), 4.62 (1 H, dt, $J_{cis}$ 11.2 Hz, $J_{1,2}$ 7.0 Hz, C$\underline{H}$CH$_2$), 4.42 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$),1.9-1.6 (2 H, m, CHC$\underline{H}_2$) 1.20 (2 H, m, C$\underline{H}_2$CH$_3$), 0.79 (3 H, t, $J_{1,2}$ 7.4 Hz, CH$_3$); $^{13}C\{^1H\}$ n.m.r. δ 220.5 (d, $J_{PC}$ 31.3 Hz, C≡O), 143.6 (s, CO$\underline{C}$H) 136.7 (d, $J_{PC}$ 43.1 Hz, Ph $C_{ipso}$) 133.4 (d, $J_{PC}$ 9.2 Hz, Ph $C_{ortho}$), 129.6 (s, Ph $C_{para}$), 128.0 (d, $J_{PC}$ 9.4 Hz, Ph $C_{meta}$), 124.9 (s, $\underline{C}$HCH$_2$), 85.5 (s, $C_5H_5$), 30.8 (s, CH$\underline{C}$H$_2$), 23.0 (s, $\underline{C}$H$_2$CH$_3$), 13.8 (s, CH$_3$); $^{31}P\{^1H\}$ n.m.r. δ 73.4; $\underline{m/z}$ 508 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)(CO-CH$\underline{n}$-Pr)] $\underline{5}$. (Found: C, 71.2; H, 6.0. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75%); $\nu_{max}$ 1920 vs (C≡O) 1620 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 6.47 (1H, d, $J_{trans}$ 15.1 Hz, COCH), 5.49 (1 H, dt, $J_{trans}$ 15.1 Hz, $J_{1,2}$ 6.6 Hz, C$\underline{H}$CH$_2$) 4.44 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 1.89 (2H, m, CHC$\underline{H}_2$), 1.37 (2 H, m, C$\underline{H}_2$CH$_3$), 0.88 (3 H, t, $J_{1,2}$ 7.1 Hz, CH$_3$); $^{13}C\{^1H\}$ n.m.r. δ 220.8 (d, $J_{PC}$ 31.2 Hz, C≡O), 145.0 (d, $J_{PC}$ 5.0 Hz, CO$\underline{C}$H), 136.5 (d, $J_{PC}$ 42.5 Hz, Ph $C_{ipso}$), 133.4 (d, $J_{PC}$ 9.5 Hz, Ph $C_{ortho}$), 129.6 (s, Ph $C_{para}$), 129.1 (s, $\underline{C}$HCH$_2$), 127.9 (d, $J_{PC}$ 10.2 Hz, Ph $C_{meta}$), 85.4 (s, $C_5H_5$), 33.3 (s, CH$\underline{C}$H$_2$), 21.8 (s, $\underline{C}$H$_2$CH$_3$), 13.7 (s, CH$_3$); $^{31}P\{^1H\}$ n.m.r. δ 73.4; $\underline{m/z}$ 508 ($M^+$).

### Peterson reaction between the lithium enolate derived from complex 4 and isobutyraldehyde

The procedure used for the preparation of complexes $\underline{5}$ and $\underline{6}$ was repeated using [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)($COCH_2SiMe_3$)] $\underline{4}$ (3.0 g, 5.7 mmol), $\underline{n}$-butyllithium (3.9 ml, 6.2 mmol) and isobutyraldehyde (1.1 ml, 12.0 mmol). Chromatography on alumina (Grade I) gave complex $\underline{22}$ (0.91 g, 31%) upon elution with diethyl ether/dichloromethane (1:1) and removal of solvent, whilst elution with dichloromethane/ethyl acetate (1:1) gave complex $\underline{21}$ (0.96 g, 33%). Both were obtained as orange needles from dichloromethane/hexane.

Z-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)(COCH=CH$\underline{i}$-Pr) $\underline{22}$. (Found: C, 71.1; H, 5.9. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75%); $\nu_{max}$ 1920 vs (C≡O), 1610 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 6.37 (1H, d, $J_{cis}$ 11.3 Hz, COCH), 4.41 (1H, dd, $J_{cis}$ 11.3 Hz, $J_{1,2}$ 9.6 Hz, COCH=C$\underline{H}$), 4.41 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 2.44 (1H, m, C$\underline{H}$(CH$_3$)$_2$), 0.82 (3 H, d, $J_{1,2}$ 6.6 Hz, CH$_3$), 0.72 ( 3 H, d, $J_{1,2}$ 6.6 Hz, CH$_3$); $^{13}C\{^1H\}$ n.m.r. δ 220.5 (d, $J_{PC}$ 31.5 Hz, C≡O), 141.3 (d, $J_{PC}$ 5.4 Hz, CO$\underline{C}$H), 136.7 (d, $J_{PC}$ 42.6 Hz, Ph $C_{ipso}$), 133.4 (d, $J_{PC}$ 9.8 Hz, Ph $C_{ortho}$), 131.7 (s, CH=$\underline{C}$H-CH), 129.6 (s, Ph $C_{para}$) 128.0 (d, $J_{PC}$ 9.8 Hz, Ph $C_{meta}$), 85.4 (s, $C_5H_5$), 27.3 (s, $\underline{C}$H(CH$_3$)$_2$), 23.3 (s, CH$_3$), 23.0 (s, CH$_3$); $^{31}P\{^1H\}$ n.m.r. δ 73.2; $\underline{m/z}$ 508 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)(COCH=CH$\underline{i}$-Pr)] $\underline{21}$. (Found: C, 71.0; H, 5.9. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75%); $\nu_{max}$ 1915 vs (C≡O), 1625 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 6.42 (1H, dd, $J_{trans}$ 15.3 Hz, $J_{1,3}$ 1.3 Hz, COCH), 5.40 (1H, dd, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 6.7 Hz, COCH=C$\underline{H}$), 4.44 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 2.15 (1 H, m, C$\underline{H}$(CH$_3$)$_2$), 0.94 (6 H, d, $J_{1,2}$ 6.7 Hz, CH$_3$); $^{13}C\{^1H\}$ n.m.r. δ 220.8 (d, $J_{PC}$ 31.5 Hz, C≡O), 142.0 (d, $J_{PC}$ 5.4 Hz, CO$\underline{C}$H), 136.5 (d, $J_{PC}$ 42.8 Hz, Ph $C_{ipso}$), 135.2 (s, COCH=$\underline{C}$H), 133.4 (d, $J_{PC}$ 9.4 Hz, Ph $C_{ortho}$), 129.6 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 9.3 Hz, Ph $C_{meta}$), 85.4 (s, $C_5H_5$), 29.8 (s, $\underline{C}$H(CH$_3$)$_2$), 21.9 (s, CH$_3$); $^{31}P\{^1H\}$ n.m.r. δ 73.1; $\underline{m/z}$ 508 ($M^+$).

### General procedure for the reaction between dienolates derived from complexes 6, 7 and 8 and electrophiles

$\underline{n}$-Butyllithium (1.2 equivalents) was added to either complex $\underline{6}$, $\underline{7}$, or $\underline{8}$ (500 mg) in THF (30 ml) at -78°C to give a deep red solution. After stirring (-78°C; 2h), the electrophile (2 equivalents) was added and the mixture further stirred (-78°C; 2h). Warming to room temperature and removal of solvent gave an orange oil which was extracted with dichloromethane (3 x 10 ml) and filtered through alumina (Grade V). The product complexes were purified by chromatography on alumina (Grade I), analysed by $^1H$ n.m.r. spectroscopy to determine diastereoselectivities and obtained as orange needles from dichloromethane/hexane.

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)($COCH_2CH{=}CHCH_3$)] 9. Elution with dichloromethane gave complex 9 (60%). (Found: C, 70.4; H, 5.4; P. 6.3. $C_{29}H_{27}FeO_2P$ requires C, 70.5; H, 5.5; P, 6.3%); $\nu_{max}$ 1908 vs (C≡O), 1592 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.22 (1 H, m, $J_{trans}$ 15.5 Hz, $J_{1,3}$ 0.5 Hz, 0 Hz, $C\underline{H}CH_3$), 5.25 (1 H, m, $J_{trans}$ 15.5 Hz, $J_{1,2}$ 7.1 Hz, 5.8 Hz, $CH_2C\underline{H}$), 4.44 (5 H, d, $J_{PH}$ 1.0 Hz, $C_5H_5$), 3.54 (1 H, m, $J_{1,1}$ 15.4 Hz, $J_{1,2}$ 5.8 Hz, $J_{1,3}$ 0.5 Hz, $COCH_2$), 3.21 (1 H, m, $J_{1,1}$ 15.4 Hz, $J_{1,2}$ 7.1 Hz, $J_{1,3}$ 0Hz, $COCH_2$), 1.59 (3 H, d, $J_{1,2}$ 4.5 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.5 (d, $J_{PC}$ 31.4 Hz, C≡O), 136.5 (d, $J_{PC}$ 43.0 Hz, Ph $C_{ipso}$), 133.4 (d, $J_{PC}$ 10.4 Hz, Ph $C_{ortho}$), 129.6 (s, Ph $C_{para}$) 128.0 (d, $J_{PC}$ 9.7 Hz, Ph $C_{meta}$), 126.8 (s, -CH=), 126.2 (s, -CH=), 85.1 (s, $C_5H_5$), 69.3 (d, $J_{PC}$ 5.3 Hz, $CO\underline{C}H_2$), 17.9 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.8; m/z 494 ($M^+$), 466 ($M^+$-28), 439 ($M^+$-55).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)$COCH(CH_3)CH{=}CHCH_3$] 10. Elution with diethyl ether gave complex 10 (86%) as a 120:1 mixture of diastereoisomers. (Found: C, 70.7; H, 5.7; P, 6.0. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75; P, 6.1%); $\nu_{max}$ 1902 vs (C≡O), 1592 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.3-7.3 (15 H, m, Ph), 5.20 (1 H, dq, $J_{trans}$ 16.0 Hz, $J_{1,2}$ 6.3 Hz, $=C\underline{H}CH_3$), 4.83 (1 H, ddq, $J_{trans}$ 15.2 Hz, $J_{1,2}$ 8.3 Hz, $J_{1,3}$ 1.5 Hz, $CHC\underline{H}{=}$) 4.44 (5 H, d, $J_{PH}$ 1.0 Hz, $C_5H_5$), 3.68 (1 H, quintet, $J_{1,2}$ 7.5 Hz, COCH), 1.52 (3H, dd, $J_{1,2}$ 6.4 Hz, $J_{1,3}$ 1.6 Hz, $=CHC\underline{H}_3$), 1.02 (3 H, d, $J_{1,2}$ 6.9 Hz, $COCHC\underline{H}_3$ major diastereoisomer), 0.38 (3 H, d, $J_{1,2}$ 6.8 Hz, $COCHC\underline{H}_3$ minor diastereoisomer); $^{13}C$ {$^1H$} n.m.r. δ 220.7 (d, $J_{PC}$ 31.5 Hz, C≡O), 136.7 (d, $J_{PC}$ 42.5 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 9.5 Hz, Ph $C_{ortho}$), 132.7 (s, -CH=), 129.5 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 9.5 Hz, Ph $C_{meta}$), 124.2 (s, -CH=), 84.9 (s, $C_5H_5$), 71.5 (d, $J_{PC}$ 5.0 Hz, $CO\underline{C}H$),18.0 (s, $CH_3$), 18.0 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.6; m/z 508 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)$COCH(Et)CH{=}CHCH_3$] 11. Elution with diethyl ether/dichloromethane (1:1) gave complex 11 (87%) as a single diastereoisomer. (Found: C, 71.05; H, 6.1. $C_{31}H_{31}FeO_2P$ requires C, 71.3; H, 6.0%); $\nu_{max}$ 1900 vs (C≡O), 1595 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.17 (1H, dq, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 6,4 Hz, $C\underline{H}CH_3$), 4.75 (1 H, ddd, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 9.5 Hz, $J_{1,3}$ 1.6 Hz, $C\underline{H}{=}CHCH_3$), 4.42 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 3.44 (1 H, dt, $J_{1,2}$ 9.8 Hz, 3.7 Hz, COCH), 1.55 (3 H, dd, $J_{1,2}$ 6.4 Hz, $J_{1,3}$ 1.6 Hz, $CHC\underline{H}_3$),1.72-1.64 (1 H, m, $C\underline{H}_2CH_3$), 1.27-1.15 (1 H, m, $C\underline{H}_2CH_3$), 0.76 (3 H, t, $J_{1,2}$ 7.4 Hz, $CH_2C\underline{H}_3$);$^{13}C$ {$^1H$} n.m.r. δ 220.7 (d, $J_{PC}$ 31.4 Hz, C≡O), 136.8 (d, $J_{PC}$ 42.5 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 9.4 Hz, Ph $C_{ortho}$) 130.7 (s, $\underline{C}H{=}CHMe$), 129.5 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 9.4Hz, Ph $C_{meta}$), 126.3 (s, $CH{=}\underline{C}HMe$), 85.0 (s, $C_5H_5$), 80.3 (d, $J_{PC}$ 5.3 Hz, $CO\underline{C}H$), 24.7 (s, $CH_2$), 18.1 (s, $CH_3$), 11.8 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.8; m/z 522 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)$COCH(CH_2Ph)CH{=}CHCH_3$] 12. Elution with dichloromethane gave complex 12 (90%) as a single diastereoisomer. (Found: C, 73.7; H, 5.65. $C_{36}H_{33}FeO_2P$ requires C, 74.0; H, 5.7%); $\nu_{max}$ 1910 vs (C≡O), 1600 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.1 (20 H, m, Ph), 5.15 (1 H, dq, $J_{trans}$ 15.1 Hz, $J_{1,2}$ 6.4 Hz, $CH{=}C\underline{H}CH_3$), 4.67 (1 H, ddq, $J_{trans}$ 15.1 Hz, $J_{1,2}$ 9.1 Hz, $J_{1,3}$ 1.6 Hz, $CH{=}C\underline{H}CH_3$ ), 4.21 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 3.96 (1 H, m, COCH), 2.33, 2.99 (2 H, ABX system, $J_{AB}$ 13.3 Hz, $C\underline{H}_2Ph$), 1.47 (3 H, dd, $J_{1,2}$ 6.4 Hz, $J_{1,3}$ 1.5 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.6 (d, $J_{PC}$ 31.3 Hz, C≡O), 141.2 (s, $CH_2Ph$ $C_{ipso}$), 136.8 (d, $J_{PC}$ 41.9 Hz, Ph $C_{ipso}$), 133.6 (d, $J_{PC}$ 9.7 Hz, Ph $C_{ortho}$), 129.6 (s, $CH_2Ph$ $C_{meta}$), 129.5 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 9.6 Hz, Ph $C_{meta}$), 127.4 (s, $CH_2Ph$ $C_{ortho}$), 125.5 (s, $CH_2Ph$ $C_{para}$), 85.0 (s, $C_5H_5$), 80.5 (d, $J_{PC}$ 2.5 Hz, $CO\underline{C}H$), 38.9 (s, $\underline{C}H_2Ph$), 18.3 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 73.0; m/z 584 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)($COCH_2CH{=}CHEt$)] 13. Elution with diethyl ether/dichloromethane (1:1) gave complex 13 (95%). (Found: C, 70.9; H, 5.85. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75%); $\nu_{max}$ 1900 vs (C≡O), 1615 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.26 (2 H, m, CH=CH), 4.43 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 3.20, 3.54 (2 H, ABX system, $J_{AB}$ 14.1 Hz, $COCH_2$), 1.96 (2 H, m, $C\underline{H}_2CH_3$), 0.93 (3 H, t, $J_{1,2}$ 7.5 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.6 (d, $J_{PC}$ 31.3 Hz, C≡O), 136.5 (d, $J_{PC}$ 43.0

Hz, Ph $C_{ipso}$), 133.4 (d, $J_{PC}$ 9.8 Hz, Ph $C_{ortho}$), 129.7 (s, Ph C $_{para}$), 128.0 (d, $J_{PC}$ 9.9 Hz, Ph $C_{meta}$), 124.5 (s, $\underline{C}H{=}CH$), 85.1 (s, $C_5H_5$), 69.3 (d, $J_{PC}$ 5.3 Hz. $CO\underline{C}H_2$), 25.6 (s, $\underline{C}H_2CH_3$), 13.8 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.8;$\underline{m/z}$ 508 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH($CH_3$)CH=CHEt] $\underline{14}$. Elution with diethyl ether/dichloromethane (1:1) gave complex $\underline{14}$ (92%) as a single diastereosiomer. (Found: C, 71.2; H, 6.1. $C_{31}H_{31}FeO_2P$ requires C, 71.3; H, 6.0%); $\nu_{max}$ 1900 vs (C≡O), 1590 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.23 (1 H, dt, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 6.3 Hz. $CH{=}C\underline{H}CH_2$), 4.83 (1H, dd, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 8.3 Hz, $C\underline{H}{=}CHCH_2$), 4.44 (5 H, d, $J_{PH}$ 1.1 Hz, $C_5H_5$), 3.67 (1 H, m, COCH), 1.86 (2 H, m, $C\underline{H_2}CH_3$), 1.02 (3 H, d, $J_{1,2}$ 7.1 Hz, $CHC\underline{H_3}$), 0.89 (3 H, t, $J_{1,2}$ 7.4 Hz, $CH_2C\underline{H_3}$); $^{13}C$ {$^1H$} n.m.r. δ 220.8 (d, $J_{PC}$ 31.5 Hz, C≡O), 136.7 (d, $J_{PC}$ 42.6 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 10.6 Hz, Ph $C_{ortho}$), 131.4 (s, $\underline{C}H{=}CHEt$), 130.5 (s, $CH{=}\underline{C}HEt$), 129.6 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 10.5 Hz, Ph $C_{meta}$), 85.0 (s, $C_5H_5$), 71.4 (d, $J_{PC}$ 5.5 Hz, $CO\underline{C}H$ ), 25.7 (s, $\underline{C}H_2CH_3$), 18.2 (s, $CH_3$), 13.7 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.0; $\underline{m/z}$ 522 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH(Et)CH=CHEt] $\underline{15}$. Elution with diethyl ether/dichloromethane (1:1) gave complex $\underline{15}$ (90%) as a single diastereoisomer. (Found: C, 71.7; H, 6.3. $C_{32}H_{33}FeO_2P$ requires C, 71.65; H, 6.2%); $\nu_{max}$ 1900 vs (C≡O), 1600 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.22 (1 H, dt, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 6.4 Hz, $CH{=}C\underline{H}CH_2$), 4.75 (1 H, dd, $J_{trans}$ 15.3 Hz, $J_{1,2}$ 9.5 Hz, $C\underline{H}{=}CHCH_2$), 4.42 (5 H, d, $J_{PH}$1.2 Hz, $C_5H_5$), 3.43 (1 H, dt, $J_{1,2}$ 3.7 Hz, 9.5 Hz, COCH), 1.91 (2 H, dq, $J_{1,2}$ 7.4 Hz, 6.4 Hz, $CH{=}CHC\underline{H_2}$), 1.68-1.64 (1H, m, $COCHC\underline{H_2}$), 1.27-1.18 (1 H, m, $COCHC\underline{H_2}$), 0.91 (3 H, t, $J_{1,2}$ 7.4 Hz, $CH_3$), 0.75 (3 H, t,$J_{1,2}$ 7.4 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.7 (d, $J_{PC}$ 31.4 Hz, C≡O), 136.8 (d, $J_{PC}$ 42.5 Hz, Ph $C_{ipso}$), 133.7 (s, $\underline{C}H{=}CHEt$), 133.5 (d, $J_{PC}$ 10.6 Hz, Ph $C_{ortho}$), 129.5 (s, Ph, $C_{para}$), 128.5 (s, $CH{=}\underline{C}HEt$), 127.9 (d, $J_{PC}$ 10.4 Hz, Ph $C_{meta}$), 85.3 (s, $C_5H_5$), 80.1 (d, $J_{PC}$ 5.3 Hz, $CO\underline{C}H$),25.8 (s, $CH_2$), 24.7 (s, $CH_2$), 13.9 (s, $CH_3$), 11.8 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 73.0; $\underline{m/z}$ 536 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)($COCH_2CH{=}CH\underline{n}$-Pr)] $\underline{16}$. Elution with diethyl ether/dichloromethane (4:1) gave complex $\underline{16}$ (80%). (Found: C, 71.5; H, 6.2; P, 6.1. $C_{31}H_{31}FeO_2P$ requires C, 71.3; H, 5.9; P 5.9%); $\nu_{max}$ ($CHCl_3$) 1915 vs (C≡O), 1595 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.25 (2 H, m, CH=CH), 4.44 (5 H, d, $J_{PH}$ 1.3 Hz, $C_5H_5$) , 3.56 (1 H, m, $COCH_2$), 3.20 (1 H, m, $COCH_2$), 1.92 (2 H, m, $CHC\underline{H_2}$), 1.34 (2 H, m, $C\underline{H_2}CH_3$) 0.87 (3 H, t, $J_{1,2}$ 7.3 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.5 (d, $J_{PC}$ 31.7 Hz, C≡O), 136.5 (d, $J_{PC}$ 42.6 Hz, Ph $C_{ipso}$), 133.3 (d, $J_{PC}$ 9.5 Hz, Ph $C_{ortho}$), 131.8 (s, $\underline{C}H{=}CH$), 129.7 (s, Ph $C_{para}$), 128.0 (d, $J_{PC}$ 9.6 Hz, Ph $C_{meta}$), 125.6 (s, $\underline{C}H{=}CH$), 85.1 (s, $C_5H_5$), 69.3 (d, $J_{PC}$ 5.4 Hz, $CO\underline{C}H_2$), 34.7 (s, $CH_2$), 22.6 (s, $CH_2$), 13.7 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.7; $\underline{m/z}$ 522 ($M^+$), 494 ($M^+$- 28).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH($CH_3$)CH=CH$\underline{n}$-Pr] $\underline{17}$. Elution with 40:60 petrol/diethyl ether (1:5) gave complex $\underline{17}$ (94%) as a 250:1 mixture of diastereoisomers. (Found: C, 71.6; H, 6.1; P. 5.9. $C_{32}H_{33}FeO_2P$ requires C, 71.7; H, 6.2; P, 5.8%); $\nu_{max}$ 1905 vs (C≡O), 1590 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.19 (1 H, m, $C\underline{H}{=}CH$), 4.84 (1 H, m, $C\underline{H}{=}CH$), 4.44 (5 H, d, $J_{PH}$ 1.0 Hz, $C_5H_5$), 3.65 (1 H, m, COCH), 1.83 (2 H, m, $CHC\underline{H_2}$), 1.29 (2 H, m, $C\underline{H_2}CH_3$), 1.03 (3 H, d, $J_{1,2}$ 7.0 Hz, $CHC\underline{H_3}$), 0.85 (3 H, t, $J_{1,2}$ 7.4 Hz, $CH_2C\underline{H_3}$); $^{13}C$ {$^1H$} n.m.r. δ 220.6 (d, $J_{PC}$ 31.4 Hz, C≡O), 136.7 (d, $J_{PC}$ 42.5 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 9.5 Hz, Ph $C_{ortho}$), 131.6 (s, $C\underline{H}{=}CH$), 129.7 (s, CH=CH), 129.5 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 9.3 Hz, Ph $C_{meta}$), 85.0 (s, $C_5H_5$), 71.5 (s, $CO\underline{C}H$), 34.8 (s, $CH_3$) 22.5 (s, $CH_2$), 18.3 (s, $CH_2$), 13.7 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.8; $\underline{m/z}$ 536 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH(Et)CH=CH$\underline{n}$-Pr] $\underline{18}$. Elution with diethyl ether gave complex $\underline{18}$ (90%) as a 250:1 mixture of diastereoisomers. (Found: C, 72.05; H, 6.6. $C_{33}H_{35}FeO_2P$ requires C, 72.0; H, 6.4%); $\nu_{max}$ 1900 vs (C≡O), 1595 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.19 (1 H, m, $C\underline{H}{=}CH$), 4.76 (1 H, m, $C\underline{H}{=}CH$), 4.43 (5 H, d, $J_{PC}$ 1.2 Hz, $C_5H_5$), 3.45 (1 H, dt, $J_{1,2}$ 9.8 Hz, 3.5 Hz, COCH), 1.87 (2 H, m, $CHC\underline{H_2}$), 1.69 (2 H, m, $CH_2$), 1.32 (2 H, m, $CH_2$), 0.87 (3 H, t, $J_{1,2}$ 7.3 Hz, $CH_3$), 0.77 (3 H, t, $J_{1,2}$ 7.3 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.6 (d, $J_{PC}$ 31.0 Hz, C≡O), 136.8 (d,

$J_{PC}$ 42.3 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 9.4 Hz, Ph $C_{ortho}$), 131.9 (s, $\underline{C}$H=CH), 129.7 (s, $\underline{C}$H=CH), 129.5 (s, Ph $C_{para}$), 127.9 (d, $J_{PC}$ 9.3 Hz, Ph $C_{meta}$), 85.0 (s, $C_5H_5$), 80.3 (d, $J_{PC}$ 5.0Hz, CO$\underline{C}$H), 35.0 (s, $CH_2$), 24.8 (S, $CH_2$), 22.6 (s, $CH_2$), 11.8 (s, $CH_3$), 11.8 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 73.0; *m/z* 550 ($M^+$), 522 ($M^+$-20), 439 ($M^+$-111).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH($CH_2$Ph)CH=CH*n*-Pr] 19. Elution with diethyl ether/ dichloromethane (1:1) gave complex 19 (81%) as a 90:1 mixture of diastereoisomers increased to 170:1 upon recrystallisation. (Found: C, 74.5; H, 6.1. $C_{38}H_{37}FeO_2P$ requires C, 74.5; H, 6.05%); $\nu_{max}$ ($CHCl_3$) 1915 vs (C≡O), 1595 s $cm^{-1}$ (C=O); $^1H$ n.m.r.δ 7.8-7.3 (20 H, m, Ph), 5.32 (1 H, m, C$\underline{H}$=CH), 4.91 (1 H, m, C$\underline{H}$=CH), 4.48 (5 H, d, $J_{PH}$ 1.3 Hz, $C_5H_5$), 4.15 (1 H, dt, $J_{1,2}$ 9.2 Hz, 9.2 Hz, COCH), 3.23 (1 H, m, C$\underline{H_2}$Ph), 2.56 (1 H, m, C$\underline{H_2}$Ph), 2.00 (2 H, m, CH=CHC$\underline{H_2}$), 1.42 (2 H, m, C$\underline{H_2}$$CH_3$), 0.97 (3 H, t, $J_{1,2}$ 7.3 Hz, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 220.5 (d, $J_{PC}$ 31.4 Hz, C≡O), 141.1 (s, $CH_2$Ph $C_{ipso}$), 137.1 (d, $J_{PC}$ 42.5 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 10.2 Hz, Ph $C_{ortho}$), 133.1 (s, $\underline{C}$H=CH), 129.5 (s, Ph $C_{para}$), 128.5 (s, $\underline{C}$H=CH), 127.9 (d, $J_{PC}$ 9.2 Hz, Ph $C_{meta}$), 127.9 (s, $CH_2$Ph $C_{meta}$), 125.5 (s, $CH_2$Ph $C_{para}$), 85.0 (s, $C_5H_5$), 80.5 (d, $J_{PC}$ 4.8 Hz, CO$\underline{C}$H), 39.0 (s, $CH_2$), 35.0 (s, $CH_2$), 22.4 (s, $CH_2$), 13.7 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 73.1; *m/z* 612 ($M^+$).

E-[($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH($SCH_3$)CH=CH*n*-Pr] 20. Elution with diethyl ether/dichloromethane (1:4) gave complex 20 (94%) as an 18:1 mixture of diastereoisomers increased to 250:1 upon recrystallisation. (Found: C, 67.45; H, 5.8. $C_{32}H_{33}FeO_2PS$ requires C, 67.6; H, 5.8%); $\nu_{max}$ 1910 vs (C≡O), 1595 s $cm^{-1}$ (C=O); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 5.35 (1 H, m, C$\underline{H}$=CH), 4.81 (1 H, m, C$\underline{H}$=CH), 4.53 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 4.27 (1 H, d, $J_{1,2}$ 9.6 Hz, COCH), 1.91 (2 H, m, $CH_2$), 1.90 (3 H, s, $SCH_3$), 1.34 (2 H, m, $CH_2$), 0.88 (3 H, t, $J_{1,2}$ 7.3 Hz, $CH_2$C$\underline{H_3}$); $^{13}C$ {$^1H$} n.m.r. δ 220.3 (d, $J_{PC}$ 31.2 Hz, C≡O), 136.4 (d, $J_{PC}$ 42.9 Hz, Ph $C_{ipso}$), 133.5 (d, $J_{PC}$ 10.0Hz, Ph $C_{ortho}$), 133.3 (s, CH=CH), 129.6 (s, Ph C $_{para}$), 127.9 (d, $J_{PC}$ 9.5 Hz, Ph $C_{meta}$), 126.4 (s, $\underline{C}$H=CH), 85.1 (s, $C_5H_5$), 78.3 (d, $J_{PC}$ 5.6 Hz, CO$\underline{C}$H), 34.7 (s, $CH_2$), 22.6 ,(s, $CH_2$) 13.7 (s, $CH_3$), 13.5 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 72.7; *m/z* 568 ($M^+$), 540 ($M^+$-28).

## Preparation of [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)COCH=C($CH_3$)$_2$] 23

*n*-Butyllithium (9.0 ml, 14 mmol) was added to [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)($COCH_3$)] 24 in THF (100 ml) at -78°C to give a deep red solution. After stirring (-78°; 3/4 h), acetone (1.4 ml, 19 mmol) was added dropwise. Further stirring (-78°C; 1h), addition of methanol (0.5 ml) and removal of solvents gave an orange oil which was extracted with dichloromethane (3 x 15 ml) and filtered through alumina (Grade V). Concentration and chromatography on alumina (Grade I) gave two orange bands on elution with dichloromethane and dichloromethane/ethyl acetate (1:1) respectively. Removal of solvent from the first fraction gave an orange powder identified as starting material 24 by $^1H$ n.m.r. spectroscopy. Removal of solvents from the second fraction gave [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)$COCH_2$C(OH)($CH_3$)$_2$)] 25[8] (3.39 g, 69%) as an orange powder. $^1H$ N.m.r. δ 7.5-7.3 (15 H, m, Ph), 4.41 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 4.06 (1 H, s, OH), 3.17, 2.84 (2 H, AB system, $J_{AB}$ 18 Hz, $COCH_2$), 1.02 (3 H, s, $CH_3$), 0.69 (3 H, s, $CH_3$). Complex 25 (2.40 g, 4.7 mmol) and sodium hydride (0.33 g, 13.8 mmol) were combined as solids and THF (130 ml) added with stirring. Methyl iodide (3.3 ml, 52 mmol) was added and the stirring continued (20°C; 20h). Removal of solvent, extraction with dichloromethane (3 x 15 ml) and filtration through alumina (Grade V) gave an orange oil which was chromatographed on alumina (Grade I). Elution with dichloromethane/ ethyl acetate (4:1) and removal of solvent gave [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)$COCH_2$C($OCH_3$)($CH_3$)$_2$] 26 (1.0 g, 41%) as an orange powder. $^1H$ N.m.r. δ 7.6-7.3 (15 H, m, Ph), 4.40 (5 H, s, $C_5H_5$), 3.35, 2.78 (2 H, AB system, $J_{AB}$ 20 Hz), 3.03 (3 H, s, $OCH_3$), 1.04 (3 H, s, $CH_3$), 0.73 (3 H, s, $CH_3$). Complex 26 (1.0 g, 1.88 mmol) and sodium hydride (0.9 g, 3.7 mmol) were stirred together (20°C; 60h) in THF (150 ml). Removal of solvent, extraction with dichloromethane (3 x 15 ml) and filtration through alumina (Grade V) was followed by chromatography on alumina (Grade I). Elution with dichloromethane/ ethyl acetate (1:1) and removal of solvents gave [($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)-COCH=C($CH_3$)$_2$] 23 (0.50 g, 53%) as an orange powder. Orange needles of complex 23 were obtained from dichloromethane/hexane. (Found: C, 70.5; H, 5.5. $C_{29}H_{27}FeO_2P$ requires C, 70.5; H, 5.5%); $\nu_{max}$

1915 vs ($C\equiv O$), 1585 s cm$^{-1}$ ($C=O$); $^1H$ n.m.r. δ 7.5-7.3 (15 H, m, Ph), 6.58 (1 H, s, COCH), 4.42 (5 H, d, $J_{PH}$ 1.1 Hz, $C_5H_5$), 1.59 (3 H, s, $CH_3$) 1.56 (3 H, s, $CH_3$); $^{13}C$ {$^1H$} n.m.r. δ 141.7 (d, $J_{PC}$ 5.5 Hz, $CO\underline{C}H$), 136.6 (d, $J_{PC}$ 42.9 Hz, Ph $C_{ipso}$), 133.4 (d, $J_{PC}$ 9.7 Hz, Ph $C_{ortho}$), 129.5 (s, Ph $C_{para}$) 128.0 (d, $J_{PC}$ 9.2 Hz, Ph $C_{meta}$), 85.4 (s, $C_5H_5$), 25.5 (s, $CH_3$), 19.6 (s, $CH_3$); $^{31}P$ {$^1H$} n.m.r. δ 73.5; m/z 494 ($M^+$), 466 ($M^+$-28).

### General procedure for the reaction between the dienolate derived from complex 23 and electrophiles.

An identical procedure to that described for the reaction between dienolates derived from complexes 6, 7, and 8 and electrophiles was followed.

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2C(CH_3)=CH_2]$ 27 Elution with 30:40 petrol/diethyl ether (1:1) gave complex 27 (100%). (Found: C, 70.5; H, 5.5 $C_{29}H_{27}FeO_2P$ requires C, 70.5; H, 5.5%); $\nu_{max}$ 1900 vs ($C\equiv O$), 1610 s cm$^{-1}$ ($C=O$); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 4.68 (1 H, m, $C=CH_2$) 4.43 (5 H, d, $J_{PH}$ 1.3 Hz, $C_5H_5$), 4.38 (1 H, m, $C=CH_2$), 3.72, 3.18 (2 H, AB system, $J_{AB}$ 15.2 Hz, $COCH_2$), 1.39 (3 H, d, $J_{1,3}$ 1.1 Hz, $CH_3$); m/z 494 ($M^+$), 439 ($M^+$-55).

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH(CH_3)C(CH_3)=CH_2]$ 28. Elution with 30:40 petrol/diethyl ether (1:1) gave complex 28 (81%) as a 14:1 mixture of diastereoisomers. (Found: C, 70.4; H, 5.7. $C_{30}H_{29}FeO_2P$ requires C, 70.9; H, 5.75%); $\nu_{max}$ 1910 vs ($C\equiv O$), 1600 s cm$^{-1}$ ($C=O$); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 4.63 (1 H, s, $C=CH_2$), 4.62 (1 H, s, $C=CH_2$), 4.44 (5 H, d, $J_{PC}$ 1.2 Hz, $C_5H_5$ major diastereoisomer), 4.39 (5 H, d, $J_{PH}$ 1.3 Hz, $C_5H_5$ minor diastereoisomer), 3.89 (1 H, q, $J_{1,2}$ 7.2 Hz, COCH), 1.14 (3 H, d, $J_{1,2}$ 7.2 Hz, $CHC\underline{H}_3$ major diastereoisomer), 1.09 (3 H, s, $CCH_3$). 0.28 (3 H, d, $J_{1,2}$ 7.2 Hz, $CHC\underline{H}_3$ minor diastereoisomer); m/z 508 ($M^+$).

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH(Et)C(CH_3)=CH_2]$ 29. Elution with 30:40 petrol/diethyl ether (3:1) gave complex 29 (41%) as a 17:1 mixture of diastereoisomers. (Found: C, 71.4; H, 6.0. $C_{31}H_{31}FeO_2P$ requires C, 71.3; H, 6.0%); $\nu_{max}$ 1905 vs ($C\equiv O$), 1605 s cm$^{-1}$ ($C=O$); $^1H$ n.m.r. δ 7.5-7.3 (15 H, m, Ph), 4.78 (1 H, d, $J_{1,3}$ 2.3 Hz, $C=CH_2$), 4.74 (1 H, d, $J_{1,3}$ 1.3 Hz, $C=CH_2$), 4.43 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$ major diastereoisomer), 4.38 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$ minor diastereoisomer), 3.81 (1 H, dd, $J_{1,2}$ 11.2 Hz, 3.9 Hz, COCH), 1.70-1.36 (2 H, m, $C\underline{H}_2CH_3$), 1.07 (3 H, s, $CCH_3$), 0.73 (3 H, t, $J_{1,2}$ 7.4 Hz, $CH_2C\underline{H}_3$ major diastereoisomer), 0.38 (3 H, t, $J_{1,2}$ 7.4 Hz, $CH_2C\underline{H}_3$ minor diastereoisomer); m/z 522 ($M^+$).

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH(CH_2Ph)C(CH_3)=CH_2]$ 30. Elution with 30:40 petrol/diethyl ether (1:1) gave complex 30 (100%) as a single diastereoisomer. (Found: C, 73.8, H, 6.15. $C_{36}H_{33}FeO_2P$ requires C, 74.0; H, 5.7%); $\nu_{max}$ 1920 vs ($C\equiv O$), 1620 s cm$^{-1}$ ($C=O$); $^1H$ n.m.r. δ 7.6-7.1 (20 H, m, Ph), 4.75 (1 H, d, $J_{1,3}$ 1.7 Hz, $C=CH_2$), 4.67 (1 H, d, $J_{1,3}$ 1.4 Hz, $C=CH_2$), 4.30 (1 H, dd, $J_{1,2}$ 8.1 Hz, 6.6 Hz, COCH), 4.20 (5 H, d, $J_{PH}$ 1.1 Hz, $C_5H_5$), 3.03, 2.51 (2 H, ABX system, $J_{AB}$ 13.5 Hz, $C\underline{H}_2Ph$), 1.09 (3 H, s, $CCH_3$); m/z 584 ($M^+$) 556 ($M^+$-28).

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH(SCH_3)C(CH_3)=CH_2]$ 31. Elution with 40:60 petrol/diethyl ether (1:1) gave complex 31 (71%) as a single diastereoisomer. (Found: C, 66.75; H, 5.5. $C_{30}H_{29}FeO_2PS$ requires C, 66.7; H, 5.4%); $\nu_{max}$ 1905 vs ($C\equiv O$), 1610 s cm$^{-1}$ ($C=O$); $^1H$ n.m.r. δ 7.6-7.3 (15 H, m, Ph), 4.88 (1 H, m, $C=CH_2$), 4.83 (1 H, m, $C=CH_2$), 4.63 (1 H, s, COCH), 4.55 (5 H, d, $J_{PH}$ 1.2 Hz, $C_5H_5$), 1.86 (3 H, s, $SCH_3$), 1.19 (3 H, s, $CCH_3$); m/z 540 ($M^+$).

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