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ELABORATION OF ACYL LIGANDS: PREPARATION AND REACTIVITY OF THE ANION $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2)]^-$

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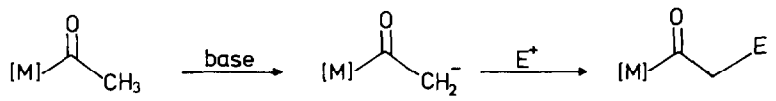
Summary

Addition of electrophiles to the anion $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2)]^-$ Li^+ allows the acyl ligand in the complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_3)$ to be developed. The unstable β-oxo-acyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COCH_2COR)$ (R = H, Me, Ph, OEt) undergo facile carbon–carbon bond cleavage to generate the carbanions $(RCOCH_2)^-$ and the cation $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+$.

Organotransition metal acyl complexes have found extensive use in organic synthesis both in catalytic and in stoicheiometric reactions [1]. The methods generally available for the synthesis of metal acyl complexes involve reaction of a metal nucleophile with acyl chlorides, addition of a carbanion to a metal carbonyl ligand or rearrangement of alkyl metal carbonyl complexes to the corresponding acyl derivatives. A wide variety of decomplexation methods are available for metal acyls allowing the formation, depending on the conditions, of a range of carbonyl compounds (e.g. aldehyde, ketone, acid, ester, amide, etc.). The modification and elaboration of the structure of acyl ligands while they are bonded to the metal would provide a useful extension to the scope of these reactions. In order to achieve such elaboration we have investigated the reaction of a metal acetyl complex with base to produce the corresponding carbanion and its subsequent reactions with electrophiles to generate the modified acyl complexes (Scheme 1).

SCHEME 1. Elaboration strategy.



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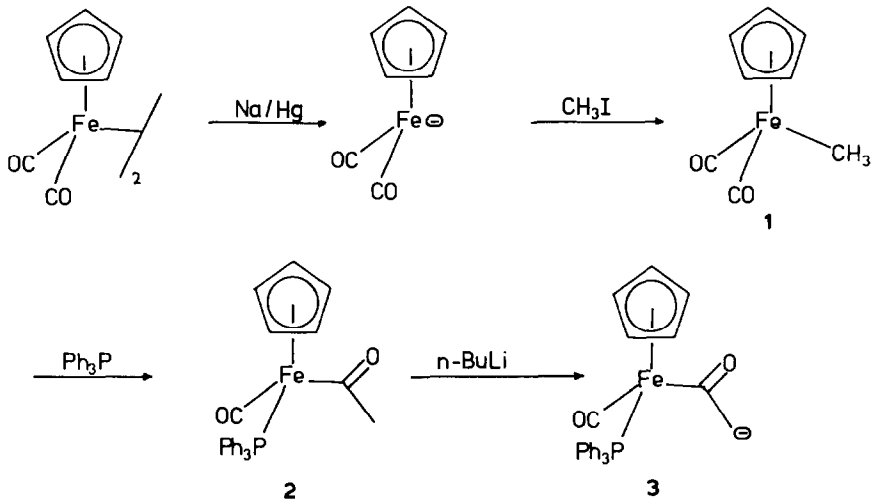
Until very recently no reports of the generation of carbanions from metal acyls had appeared. We describe here the generation from the acetyl complex **2** of the anion **3** and its reactions with electrophiles. Part of this work has been the subject of preliminary communications [2]. Liebeskind and Welker have independently prepared anion **3** and have also described some of its reactions [3]. The elaboration of the acyl ligand in cobaltacyclopentanones via this methodology has recently been described by Bergman et al. [4].

Results

The acetyl complex **2** is readily available on a large scale from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. Cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with sodium amalgam generates the anion $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^- Na^+$ which on addition of methyl iodide produces the methyl complex **1** [5]. Treatment of **1** with triphenylphosphine in acetonitrile at reflux generates the acetyl complex **2** [6]. The acetyl protons of **2** are not as acidic as a normal methyl ketone since no H–D exchange could be observed when **2** was treated with $NaOD/D_2O$ or D_3O^+. The acetyl complex is, however,

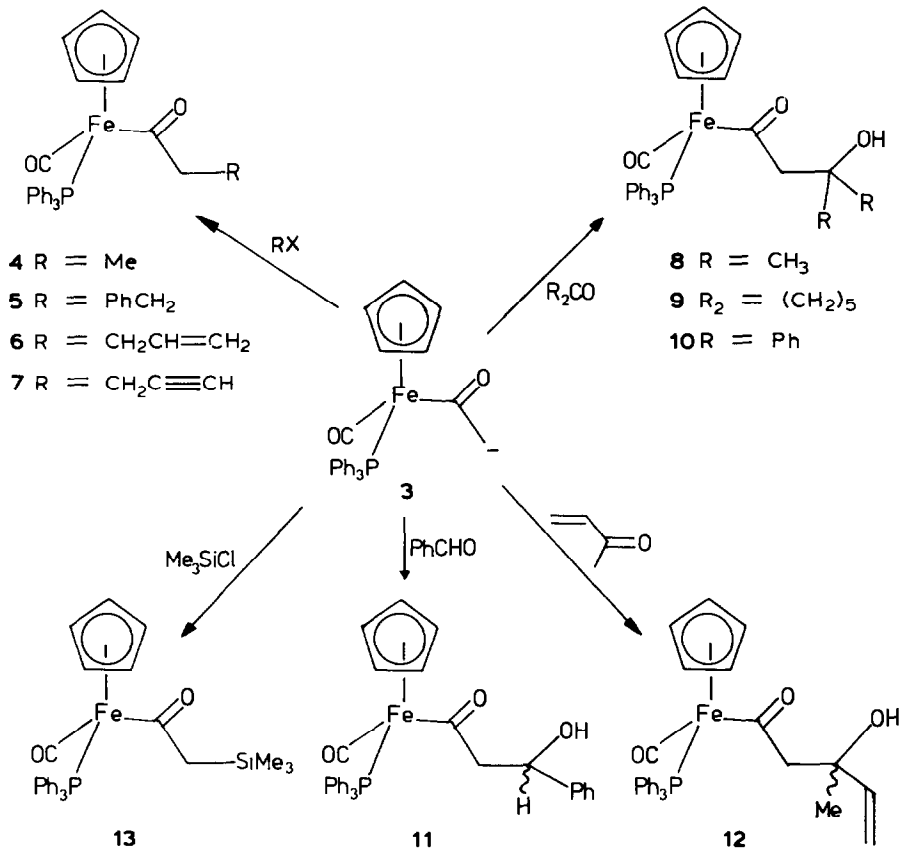


deprotonated by n-butyllithium or lithium di-isopropylamide in tetrahydrofuran at −78°C to generate the anion **3**.

Anion **3** reacts with methyl iodide at −78°C to give the propanoyl complex **4** in 78% yield. Anion **3** is similarly alkylated at carbon by benzyl chloride, allyl bromide and propargyl bromide to give the elaborated acyl complexes **5**, **6** and **7** respectively. Oxidative decomplexation with methanolic bromine [7] releases the elaborated acyl ligands as the corresponding methyl esters.

Treatment of anion **3** with the ketones acetone, cyclohexanone and benzophenone produces the β-hydroxyacyl complexes **8**, **9** and **10** respectively. Reaction of anion **3** with benzaldehyde generates the β-hydroxy acyl complex **11**. Little stereoselectivity was observed in this reaction. Methyl vinyl ketone undergoes 1,2- rather than 1,4-addition to give **12** again without much stereoselection (1.6/1) being observed. Anion **3** does not undergo *O*-silylation with trimethylchlorosilane; the *C*-trimethyl-

silyl product **13** is produced in preference. As before oxidative decomplexation produces the β-hydroxyesters.

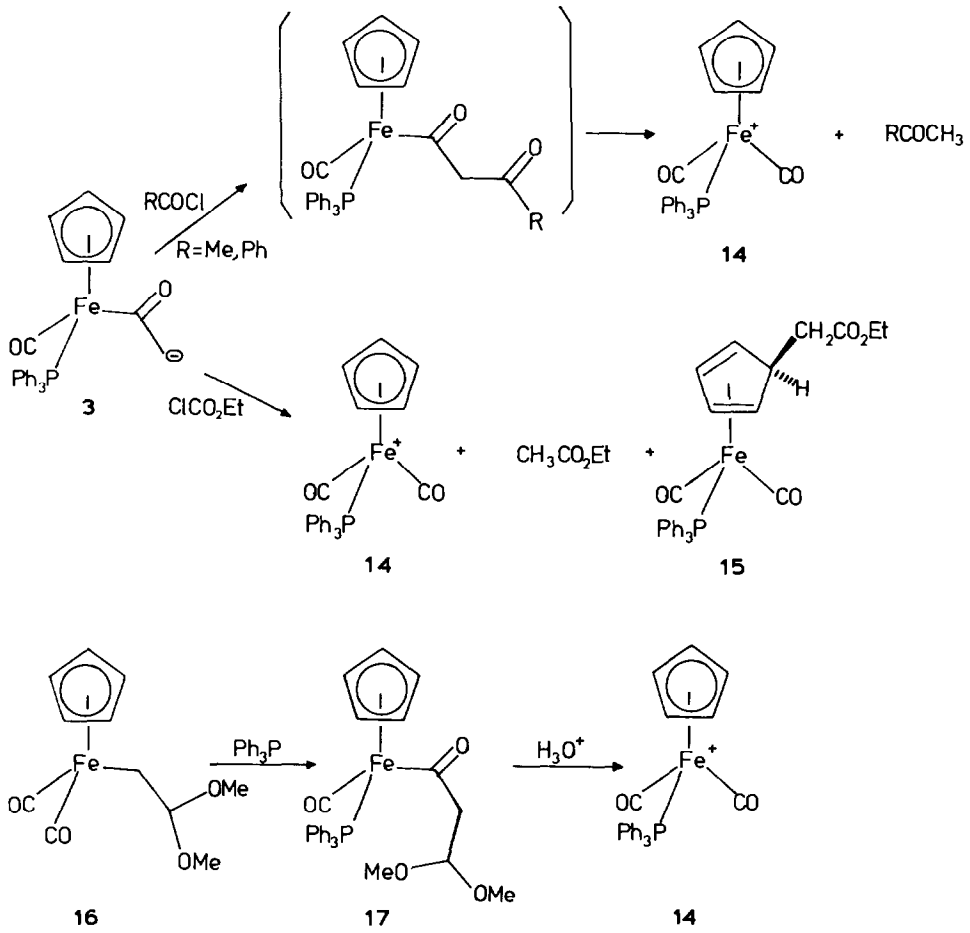


Reaction of anion **3** with acetyl chloride or benzoyl chloride gave after work up the cation **14** [8] together with acetone and acetophenone respectively and not the expected β-ketoacyl complexes. Treatment of **1** with ethyl chloroformate again resulted in formation of cation **14** together with ethyl acetate and the cyclopentadiene complex **15**. Complex **15** can be produced independently from the reaction of cation **14** with the anion derived from ethyl acetate. Cation **14** was, however, inert to the enolates from acetone and acetophenone.

Treatment of chloro acetaldehyde dimethyl acetal with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ generated the alkyl complex **16** [9] which could be readily converted to the corresponding acyl complex **17** on treatment with triphenylphosphine in acetonitrile at reflux [6]. Acid hydrolysis of **17** gave cation **14**.

Discussion

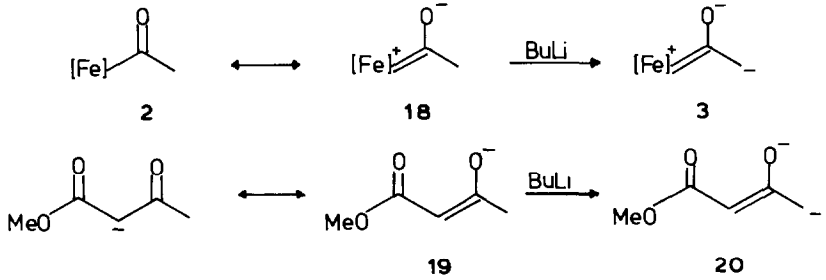
Generation of anion **3** from the acetyl complex **2** followed by treatment with alkyl halides allows the elaboration of the acetyl ligand. Oxidative decomplexation releases the corresponding methyl esters with the overall reactions sequence resulting



in conversion of RX into RCH_2CO_2Me. Addition of anion **3** to ketones and aldehydes non-stereoselectively generates β-hydroxyacyl complexes which after oxidative decomplexation yield the corresponding β-hydroxyesters; the overall reaction being equivalent to the Reformatsky reaction.

Although anion **3** might be regarded at first sight as being equivalent to an enolate several of its properties indicate this analogy to be misleading. The infra-red absorption assigned to the acetyl carbonyl in **2** is at 1608 cm^{-1} indicating that there is a significant contribution to its structure from the carbenealkoxide resonance form **18** [10], strong bases such as n-butyllithium are required to remove a methyl proton from **2** and anion **3** undergoes *C*- rather than *O*-silylation. The *C*-silylated compound appears to be the thermodynamically more favoured since heating **13** in tetrahydrofuran at reflux for 55 h does not lead to the *O*-silylated isomer [11]. These observations suggest that an appropriate analogy for the acetyl complex **2** is the monoanion from methyl acetoacetate **19** which also requires n-butyllithium to generate the bis-anion **20**. The bis-anion **20** is analogous to **3** undergoing silylation on carbon [12] (Scheme 2). Also for bis-trimethylsilyl derivatives of acetoacetic esters the *C*,*O*-bis-silylated product is thermodynamically preferred to the *O*,*O*-bis-silyl derivative [13].

SCHEME 2



β-Oxo-acyl ligands generated either by reaction of anion **3** with acyl chlorides or by hydrolysis of the dimethyl acetal **17**, undergo facile fragmentation to yield the cation **14** and the corresponding stabilised carbanion. In the reaction of anion **3** with ethyl chloroformate the stabilised carbanion produced in the fragmentation attacks the cyclopentadienyl ring of cation **14** to give the *exo*-substituted cyclopentadiene complex **15**. This type of fragmentation is analogous to the decarboxylation of β-keto carboxylates and to the reverse of reactions such as the Claisen condensation. It serves to illustrate that in nucleophilic addition reactions to transition metal cations, attack at a carbonyl ligand by stabilised carbanions should be expected to be readily reversible. The driving force for these fragmentations is presumably the stability of cation **14**. This is consistent with the fact that in polar solvents the metallaester $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COOMe)$ spontaneously ionises with acyl–oxygen bond cleavage to cation **14** and methoxide [14]. This type of fragmentation mechanism would also explain the unexpected formation of $(exo\text{-}\eta^4\text{-}5\text{-}PhCH_2C_5H_5)Fe(CO)_2(PPh_3)$ from $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2Ph)$ on treatment with triphenyl phosphine [15].

Experimental

All reactions and purifications were performed under nitrogen atmosphere using standard vacuum line and Schlenk tube techniques [16]. THF and toluene were dried over sodium benzophenone ketyl and distilled. Diethyl ether was dried over sodium wire and distilled. Dichloromethane and acetonitrile were dried over calcium hydride and distilled. Chromatography was performed on alumina (Grade IV/V) under nitrogen. Infra-red spectra were recorded on Perkin–Elmer 137E, 257 and 297 instruments. Nuclear magnetic resonance spectra were recorded on Perkin–Elmer R12B (60 MHz ^{1}H), Bruker WH90 (90 MHz ^{1}H) and Bruker WH300 (300 MHz ^{1}H) spectrometers. Mass spectra were recorded on an AEIMS50 instrument. Elemental analyses were performed by the Central Microanalytical Service of the C.N.R.S., France and by Dr. F.B. Strauss, Oxford. Gas chromatography was carried out on the following columns; 5% Carbowax 20M on Chromosorb P, 3.5 m and 20% SE30 on Chromosorb HMDS 3.5 m.

n-Butyllithium (1.7 *M* in pentane) was used as supplied by Aldrich. Lithium diisopropylamide and lithium hexamethyldisilazide were prepared according to the literature methods [17,18]. The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ [5], $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$ [6], $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]PF_6$ [8] and

$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH(OMe)_2$ [9] were prepared according to the literature methods.

Preparation of anion 3

n-Butyllithium (1.5 ml, 1.7 *M* in pentane, 2.5 mmol) was added to a stirred solution of acetyl complex **2** (0.5 g, 1.1 mmol) in THF (20 ml) at −78°C.

The initially orange solution immediately became dark red. The solution was stirred at −78°C for a further 30 min before use.

Anion **3** may also be prepared in a similar fashion using a solution of lithium diisopropylamide in THF instead of n-butyllithium.

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COEt$ (4) [6]

Methyl iodide (1.0 ml, 16 mmol) was added to a solution of anion **3**, prepared as described above from acetyl complex **2** (0.5 g, 1.1 mmol), stirred at −78°C. The solution became orange. The cold bath was removed and the solution allowed to warm to r.t. over 30 min. The solvent was removed under reduced pressure, the resultant solid extracted with diethyl ether (2 × 10 ml) and chromatographed (eluant dichloromethane). Evaporation and crystallisation from hexane gave orange crystals of **4** (0.4 g, 78%).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2Ph$ (5)

Benzyl chloride (0.55 ml, 0.48 mmol) was added to a solution of anion **3**, prepared from acetyl complex **2** (0.2 g, 0.44 mmol), stirred at −78°C. The cold bath was removed and the solution allowed to warm to r.t. over 30 min. The solvent was removed under reduced pressure and the resultant orange solid extracted with diethyl ether (2 × 10 ml). Evaporation and crystallisation from heptane gave orange crystals of **5** (0.15 g, 63%) (Found: C, 72.74; H, 5.53; P, 5.94. $C_{33}H_{29}FeO_2P$ calcd.: C, 72.79; H, 5.33; P, 5.70%); ^{1}H NMR ($CDCl_3$) δ 7.8–6.9 (20H, m, aryl-H), 4.4 (5H, s, C_5H_5), and 3.6–2.2 (4H, m, CH_2CH_2); ν_{max} (Nujol) 1910vs (FeCO), 1610vs (FeCOR) cm^{-1}.

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2CHCH_2$ (6) [19]

Allyl bromide (0.2 ml, 2.3 mmol) was added to a solution of anion **3**, prepared from acetyl complex **2** (0.55 g, 1.22 mmol) stirred at −78°C. The cold bath was removed and the solution allowed to warm to r.t. over 30 min. The solvent was removed under reduced pressure and the resulting solid extracted with diethyl ether (2 × 10 ml) and chromatographed (eluant dichloromethane). Evaporation and crystallisation from heptane gave orange crystals of **6** (0.43 g, 71%) (Found: C, 70.19; H, 5.45; P. 6.39. $C_{29}H_{27}FeO_2P$ calcd.: C, 70.44; H, 5.47; P, 6.27%); ν_{max} (Nujol) 1910 vs (FeCO), 1600vs (FeCOR) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (15H, m, aryl-H), 5.46 (1H, ddt, *J* 17.0, 10.2, 6.7, 6.7 Hz, C*H*=CH_2), 4.74 (2H, m, CH=CH_2), 4.32 (5H, d, *J* 1.2 Hz, C_5H_5), 2.85 (1H, ddd, *J* 16.9, 9.2, 6.0 Hz, COC*H*), 2.55 (1H, ddd, *J* 16.9, 9.1, 5.6 Hz, COC*H*), 1.89 (1H, m, $COCH_2CH$), 1.59 (1H, m, $COCH_2CH$); *m/z* 494 (M^+).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH_2CCH$ (7)

Propargyl bromide (0.8 ml, 80% in toluene, 7 mmol) was added to a solution of anion **3** prepared from acetyl complex **2** (0.5 g, 1.1 mmol), stirred at −78°C. The

solution became orange. The cold bath was removed and the solution allowed to warm to r.t. over 30 min. The solvent was removed under reduced pressure, the resultant orange solid extracted with dichloromethane (2 × 10 ml) and chromatographed (eluant dichloromethane). Evaporation and crystallisation from toluene/hexane gave orange crystals of **7** (0.29 g, 54%) (Found: C, 70.62; H, 4.99; P, 6.70. $C_{29}H_{25}FeO_2P$ calcd.: C, 70.75; H, 5.12; P, 6.29%); ν_{max} (Nujol) 3300s (OH), 2105w (C≡C), 1920vs (FeCO), 1585vs (FeCOR) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.3 (15H, m, aryl-H), 4.44 (5H, d, J 1.2 Hz, C_5H_5), 3.1 (1H, m, COC*H*), 2.8 (1H, m, COC*H*), 2.1 (1H, m, $COCH_2CH$), 1.7 (1H, m, $COCH_2CH$) 1.87 (1H, t, J 2.7 Hz, C≡C–H); m/z 492 (M^+).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2C(OH)Me_2$ *(8)*

To a solution of anion **3**, prepared from acetyl complex **2** (0.52 g, 1.1 mmol), was added acetone (0.4 ml, 5.5 mmol) which had been dried over potassium carbonate. After stirring at −78°C for 3 h, 2 drops of water were added to the solution and the cold bath removed. The solution was then allowed to warm to r.t. over 30 min. The solvent was removed under reduced pressure and the resulting solid extracted with dichloromethane (2 × 10 ml). Chromatography (eluant dichloromethane), concentration of the eluate and addition of hexane gave fine orange crystals of **8** (0.28 g, 51%), (Found: C, 68.22; H, 5.67; P. 6.13. $C_{29}H_{29}FeO_3P$ calcd.: C, 67.97; H, 5.66; P, 6.05%); ν_{max}(Nujol) 3500m (OH), 1920vs (FeCO), 1585s (FeCOR) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.3 (15H, m, aryl-H), 4.42 (5H, d, J(PH) 1.1 Hz, C_5H_5), 4.05 (1H, s, OH), 3.18, 2.85 (2H, AB, J 17.7 Hz, CH_2), 1.02 (3H, s, Me), 0.69 (3H, s, Me); m/z 512 (M^+).

Preparation of the compounds $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2C(OH)RR'$ *9–12*

Using a similar procedure to that described above for complex **8** the β-hydroxyacyl complexes **9–12** were prepared:

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2C(OH)(C_5H_{10})$ (**9**) (55%, crystallised from toluene) (Found. C, 69.88; H, 6.11; P, 5.27. $C_{32}H_{33}FeO_3P$ calcd.: C, 69.57; H, 6.02; P, 5.59%); ν_{max}(Nujol) 3500m (OH), 1905vs (FeCO), 1590vs (FeCOR) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.3 (15H, m, aryl-H), 4.40 (5H, d, J 1.3 Hz, C_5H_5), 3.92 (1H, brs, OH), 3.82, 3.18 (2H, AB, J 17.7 Hz, $COCH_2$), 1.6–0.8 (10H, m, CH_2); m/z 496 (M^+).

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2C(OH)Ph_2$ (50%) crystallised from dichloromethane/hexane and containing 0.5 mol dichloromethane (Found: C, 69.72; H, 5.07; P, 4.37; Cl, 4.39. $C_{39.5}H_{34}ClFeO_3P$ calcd.: C, 69.86; H, 5.01; P, 4.57; Cl, 5.20%); ν_{max} (Nujol) 3350m (OH), 1915vs (FeCO), 1570vs (FeCOR), cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (25H, m, aryl-H), 5.3 (1H, s, OH) 5.25 (1H, s, CH_2Cl_2), 4.2 (5H, d, J 1.5 Hz, C_5H_5), 4.3, 2.7 (2H, AB, J 18 Hz, CH_2); m/z 636 (M^+).

$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH(OH)Ph$ (**11**) (67%, crystallised from toluene/hexane) (Found: C, 70.51; H, 5.28; P, 5.44. $C_{33}H_{29}FeO_3P$ calcd.: C, 70.73; H, 5.22; P, 5.53%); ν_{max}(Nujol) 3450m (OH), 1910vs (FeCO), 1560vs (FeCOR) cm^{-1}; ^1H NMR ($CDCl_3$): major diastereoisomer δ 7.6–7.1 (20H, m, aryl-H), 4.42 (5H, d, J(PH) 1.1 Hz, C_5H_5), 4.26 (1H, dd, Ph–C–*H*), 3.99 (1H, brs, OH), 3.06 (2H, m, CH_2); minor diastereoisomer δ 7.6–7.1 (20H, m, aryl-H), 4.83 (1H, dd, J 10.2, 1 Hz, Ph–C–*H*), 4.45 (5H, d, J(PH) 1.1 Hz, C_5H_5), 3.37 (1H, dd, J 17.1, 2Hz, H–C–*H*), 3.15 (1H, s, OH), 2.78 (1H, dd, J 17.1, 10.2 Hz, *H*–C–H), diastereo-

isomers crystallise in ratio 2/1; *m/z* 560 (M^+).

(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2C$(Me)(OH)$CHCH_2$ (**12**) (45%) crystallised from toluene/hexane) (Found: C, 68.85; H, 5.73; P, 6.35. $C_{30}H_{29}FeO_3P$ calcd.: C, 68.71; H, 5.57; P, 5.92%); ν_{max} (Nujol) 3450m, 1910vs, 1595vs cm^{-1}; ^1H NMR ($CDCl_3$) major diastereoisomer δ 7.6–7.3 (15H, m, aryl-H), 5.31 (1H, dd, *J* 16.4, 10.6 Hz, CH_2=C*H*), 5.12 (1H, dd, *J* 16.4, 1.5 Hz, CH=C*H*), 4.67 (1H, dd, *J* 10.6, 1.5 Hz, *cis*-CH=C*H*), 4.42 (5H, d, *J*(PH) 1.3 Hz, C_5H_5) 4.20 (1H, s, OH), 3.20, 2.94 (2H, AB, *J* 17.7 Hz, CH_2), 1.09 (3H, s, Me): minor diastereoisomer δ 7.6–7.3 (15H, m, aryl-H), 5.83 (1H, dd, *J* 17.4, 10.7 Hz, CH_2=C*H*), 4.96 (1H, dd, *J* 10.6, 1.7 Hz, *cis*-CH=C*H*), 4.93 (1H, dd, *J* 17.4, 1.7 Hz, *trans*-CH=C*H*) 4.41 (5H, d, *J*(PH) 1.2 Hz, C_5H_5), 4.31 (1H, s, OH), 3.37, 2.62 (2H, AX, *J* 17.2 Hz, CH_2), 0.82 (3H, s, Me) diastereoisomers formed in ratio 1.6/1, *m/z* 524 (M^+).

Preparation of (η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2SiMe_3$ (13)

Trimethylsilyl chloride (1 ml, 8 mmol) was added to a solution of anion **3**, prepared from acetyl complex **2** (0.51 g, 1.1 mmol), stirred at −78°C. The solution was stirred for 3 h at −78°C then for a further 2 h while warming to r.t. The solvent was removed under reduced pressure and the resulting solid extracted with dichloromethane (2 × 10 ml). After chromatography (eluant dichloromethane), evaporation and crystallisation from hexane gave orange crystals of **13**, (0.50 g, 84%) (Found: C, 65.74; H, 5.83; P, 6.00. $C_{29}H_{31}FeO_2PSi$ calcd.: C, 66.16; H, 5.94; P, 5.89%); ν_{max}(Nujol) 1920vs (FeCO), 1575vs (FeCOR) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6–7.3 (15H, m, aryl-H), 4.43 (5H, d, *J* 1.1 Hz, C_5H_5), 2.76 and 1.73 (2H, AX, *J* 11.4 Hz, CH_2), 0.01 (9H, s, Me); *m/z* 526 (M^+).

Reaction of anion 3 with benzoyl chloride

Benzoyl chloride (0.2 ml, 1.7 mmol) was added to a solution of anion **3**, prepared from acetyl complex **2** (0.2 g, 0.44 mmol), stirred at −78°C. The solution was stirred for 1 h at −78°C and was then allowed to warm to r.t. over 30 min. The solvent was removed under reduced pressure and the resulting solid extracted with diethyl ether (2 × 15 ml). Chromatography, eluting first with diethyl ether/hexane (1/1) in order to remove organic byproducts and then with a solution of ammonium hexafluorophosphate in acetone (0.05 *M*) gave, after crystallisation from acetone/hexane, [(η^5-C_5H_5)Fe$(CO)_2$(PPh_3)]PF_6, (**14**) (0.11 g, 43%) identified by comparison with an authentic sample.

Cation **14** was also obtained as the only isolable product from the reaction of anion **3** with acetyl chloride (32%), ethyl bromoacetate (11%), ethyl chloroacetate (4%) and methyl benzoate (5%).

Preparation of (η^4-C_5H_5)Fe(CH_2CO_2Et)$(CO)_2$(PPh_3) (15) from cation 14

To a solution of lithium hexamethyldisilazide (0.28 g, 1.7 mmol) in THF (35 ml) stirred at −78°C was added ethyl acetate (0.17 ml, 1.74 mmol) which had been dried over calcium chloride. The resulting solution was stirred at −78°C for 20 min. Cation **14** (0.20 g, 0.34 mmol) was added and the solution stirred for a further 1 h at −78°C. Water (0.02 ml, 1.1 mmol) was added, the solution allowed to warm to r.t. over 30 min and the solvent removed under reduced pressure. The resulting oil was extracted with toluene (2 × 10 ml) and the extracts chromatographed (eluant toluene/hexane 1/1) to give, after evaporation and crystallisation from dichloro-

methane/hexane yellow crystals of **15** (0.07 g, 39%) (Found: C, 65.82; H, 5.20; P, 6.11. $C_{29}H_{27}FeO_4P$ calcd.: C, 66.16; H, 5.13; P, 5.89%); ν_{max} (Nujol) 1960vs (FeCO), 1708s (CO_2Et) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.65–7.05 (15H, m, aryl-H), 5.05 (2H, m, H(2,3)), 4.0 (2H, q, CH_2CH_3), 3.0 (1H, m, H_{endo}), 2.45 (2H, m, H(1,4)), 1.6 (2H, d, CH_2CO), 1.20 (3H, t, Me); m/z 526 (M^+).

Reaction of anion 3 with ethyl chloroformate

To a solution of anion **3** prepared from 0.10 g (0.22 mmol) of acetyl complex **2** was added ethyl chloroformate (0.2 ml, 2.1 mmol). The solution was stirred at −78°C for 90 min and was then allowed to warm to r.t. over 30 min. A small amount of solution was removed and the presence of ethyl acetate shown by gas chromatography. The solvent was removed from the remaining solution under reduced pressure and the resulting solid extracted with dichloromethane (20 ml). Chromatography gave two yellow fractions. The first fraction (eluant diethyl ether) gave, after evaporation and crystallisation from dichloromethane/hexane, compound **15** (7 mg, 6%). The second fraction (eluant acetone/ammonium hexafluorophosphate) gave, after crystallisation from acetone/diethyl ether, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]PF_6$ (**14**) (37 mg, 29%).

Decomplexation reactions

Compound **4** (0.20 g, 0.43 mmol) was added to 1 ml of a solution made by addition of bromine (0.6 ml, 23 mmol) to distilled methanol (10 ml). The solution became orange/lemon. After stirring for 2 h at r.t. and distillation, the presence of methyl propionate (b.p. 80°C) was shown by gas chromatography and ^1H NMR.

By a similar procedure β-hydroxy-β-phenyl methylpropionate was prepared from compound **11** in a yield, estimated from ^1H NMR of 45%. The ester was purified by distillation under reduced pressure (b.p. 115°C; 0.1 mmHg); ^1H NMR ($CDCl_3$) δ 7.8–7.5 (5H, m, Ph), 5.2 (1H, m, CH), 3.7 (3H, s, Me), 3.2 (1H, s, OH), 2.75 (2H, d, J 7 Hz, CH_2).

Preparation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COCH_2CH(OMe)_2$ (17)

Alkyl complex **16** (4.83 g, 18.2 mmol) and triphenylphosphine (9.52 g, 36.4 mmol) were dissolved in acetonitrile and the solution heated under reflux, in the absence of light for 5 d. On cooling to r.t. orange needles precipitated from the solution. The supernatant was removed by filtration and the crystals dissolved in dichloromethane (25 ml). Chromatography (eluant dichloromethane), concentration of the eluate and addition of hexane gave orange crystals of **17** (6.0 g, 62%), ν_{max}(Nujol) 1900vs (FeCO), 1605vs (FeCOR) cm^{-1}; ^1H NMR 7.7–6.9 (15H, m, aryl-H), 4.91 (1H, dd, J 7.1, 4.0 Hz, $C(OMe)_2H$), 4.30 (5H, d, J 1.3 Hz, C_5H_5), 3.75 (1H, dd, J 15.9, 7.1 Hz, CHH), 3.25 (3H, s, OMe), 3.12–3.06 (4H, m, CHH + OMe); m/z 528.1149; $C_{29}H_{29}FeO_4P$ calcd.: 528.1153.

Hydrolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2CH(OMe)_2$ (18)

Acetyl complex **17** (0.53 g, 1.0 mmol) was dissolved in hot aqueous ethanol (50 ml, 80% v/v) and the solution heated under reflux for 24 h. After cooling to r.t. the pale yellow solution was filtered and concentrated to 20 ml. Ammonium hexafluorophosphate (0.6 g, 3.7 mmol) was added and the resulting solution stirred at r.t. for 1 h. The solvent was then removed under reduced pressure and the

resulting solid extracted with dichloromethane (3 × 10 ml). The combined extracts were concentrated to 5 ml, and addition of diethyl ether gave pale yellow crystals of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]PF_6$ (**14**) (0.38 g, 65%).

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