Stereochemical Control and Mechanistic Aspects of the Alkylation of $[(\eta^5\text{-}C_5H_5)Fe(L)(CO)(COCHR)]^-Li^+$ (L = PPh_3, PPh_2NEt_2; R = Me, Et): *X*-Ray Crystal Structure of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)\{COCH(Me)Et\}]$

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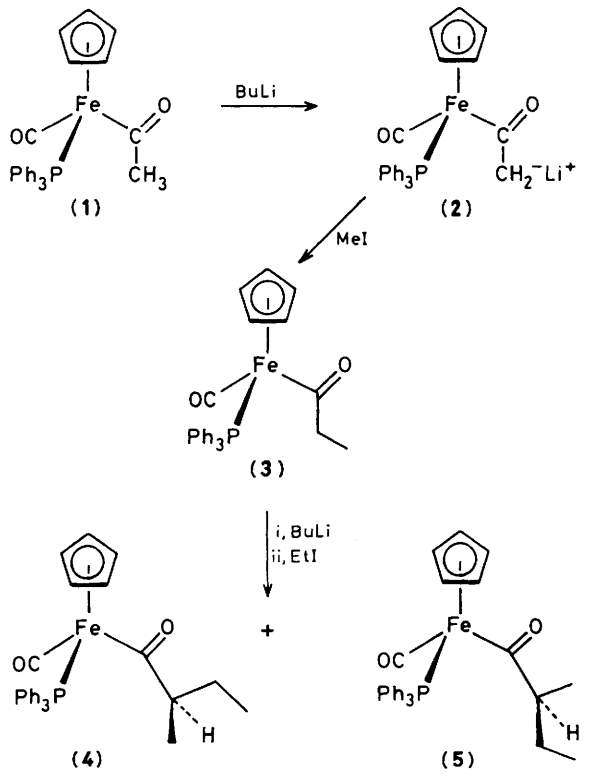
Determination of the molecular structure of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)\{COCH(Me)Et\}]$, formed in the diastereoselective methylation of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)(COCHEt)]^-Li^+$, allows the assignment of the relative configuration of the new chiral centre and indicates the origin of the high diastereoselectivities observed in this type of reaction.

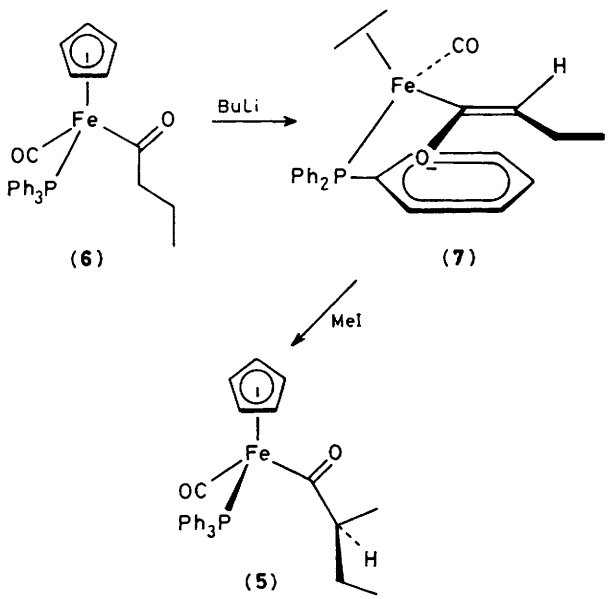
The full potential of transition metal acyl complexes for organic synthesis has not been realised because of limitations in preparative procedures. They are, however, of interest owing to the range of extremely mild decomplexation methods available which lead to a wide variety of carbonyl compounds (*e.g.* aldehyde, ketone, acid, ester, amide, *etc.*). In order to extend the scope of such reactions we[1] and others[2] have recently developed procedures for the elaboration of acyl ligands while they remain bound to the metal. For example, deprotonation of the acetyl complex (**1**) with n-butyl-lithium generates the anion (**2**) which reacts with methyl iodide to give the ethyl acyl complex (**3**). Further elaboration with n-butyl-lithium and ethyl iodide gives the two diastereoisomers (**4**) and (**5**) of the s-butyl acyl complex in the ratio 98:2.[3] Preference for the other diastereoisomer (**5**) is observed when acetyl complex (**1**) is first ethylated to give the propyl acyl complex (**6**) which is then methylated. We describe here the relative configurations of the new chiral centres produced in these reactions and discuss the origins of the diastereoselectivity.

Treatment of the propyl acyl complex (**6**)† in tetrahydrofuran at −78 °C with n-butyl-lithium followed by methyl iodide generates (**5**) as the major diastereoisomer formed in preference to (**4**). Figure 1 shows the *X*-ray crystal structure of (**5**).

Crystal data: $C_{29}H_{29}FeO_2P$, M = 496.37, monoclinic, space group $P2_1/n$, a = 15.561(4), b = 19.188(6), c = 8.050(2) Å, β = 93.66(2)°, U = 2398.6 Å^3, D_c = 1.37 g cm^{-3}, Z = 4, R = 0.032 (R_w = 0.034) for 2712 observed reflections and 4 'soft' constraints, $I > 3\sigma(I)$, λ (Mo-K_α) = 0.71069 Å. Data were collected on an Enraf–Nonius CAD-4F diffractometer to θ = 25°. The crystal structure was solved by Patterson and Fourier methods. Parameters, including those for anisotropic thermal vibration, were obtained by large-block full-matrix refinement. Following location of hydrogen atoms around all carbon atoms except for C(4) in a difference Fourier synthesis, these were included in calculated positions.‡ Carbon atoms C(1)—C(5) were refined with 'soft' Waser constraints on interatomic distances.[4]

The structure (Figure 1) establishes the relative configuration of the new chiral centre. There is no evidence from Fourier syntheses for the alternative isomer. Bond lengths and angles are close to values observed for similar systems[5] for the triphenylphosphine, cyclopentadienyl, and carbon monoxide ligands.





† All compounds described here are racemic but only one enantiomer is shown for clarity.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

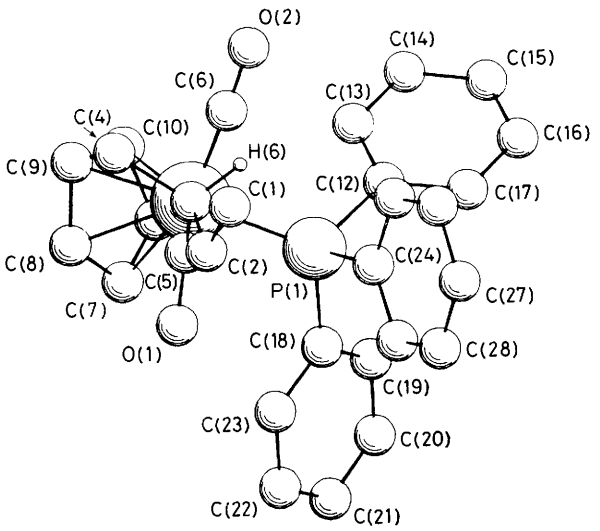


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)Fe(PPh_3)(CO)\{COCH(Me)Et\}]$ (**5**). Selected bond lengths and angles: Fe(1)–P(1) 2.193(1), Fe(1)–C(5) 1.964(3), Fe(1)–C(6) 1.733(3), Fe(1)–C(7) 2.118(3), Fe(1)–C(8) 2.125(3), Fe(1)–C(9) 2.111(4), Fe(1)–C(10) 2.121(4), Fe(1)–C(11) 2.128(4), C(1)–C(2) 1.492(4), C(2)–C(3) 1.533(4), C(3)–C(4) 1.527(5), C(3)–C(5) 1.537(4), C(5)–O(1) 1.207(4), and C(6)–O(2) 1.148(4) Å; C(1)–C(2)–C(3) 114.0(4), C(2)–C(3)–C(4) 108.8(6), C(2)–C(3)–C(5) 112.3(3), C(4)–C(3)–C(5) 110.4(5), C(3)–C(5)–O(1) 117.1(3), C(3)–C(5)–Fe(1) 120.1(3), P(1)–Fe(1)–C(5) 89.33(11), P(1)–Fe(1)–C(6) 92.12(12), C(5)–Fe(1)–C(6) 94.76(15)°.

It can be clearly seen from Figure 1 that the acyl oxygen is *anti* to the carbon monoxide ligand. This preferred conformation is adopted presumably for stereoelectronic reasons and has been observed in other systems of this type.[5,6] Assuming that this *anti* conformation is also preferred in the enolate (**7**) and that the *E* enolate is preferred to the *Z*[7] then one face of the enolate is completely shielded by the triphenylphosphine ligand while the other is open. Approach of the methyl iodide from the unhindered face would then give the observed relative configuration of (**5**).

We are also able to report that replacement of PPh_3 by Ph_2PNEt_2 in these complexes leads to increased stereoselectivity. A further advantage of the Ph_2PNEt_2 system is that the major diastereoisomer is readily separable from small amounts of the other diastereoisomer and from occasional small amounts of unalkylated starting material, whereas this is not possible in the PPh_3 series. These systems have been resolved and their use in asymmetric synthesis is under investigation.

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