Stereospecificity of the Rearrangement of the α-Alkoxy Iron Acyl [(η^5-C_5H_5)Fe(CO)(PPh_3)$COCH_2OCH_2Ph$] to the α-Metalla-ester [(η^5-C_5H_5)Fe(CO)(PPh_3)$CH_2CO_2CH_2Ph$]

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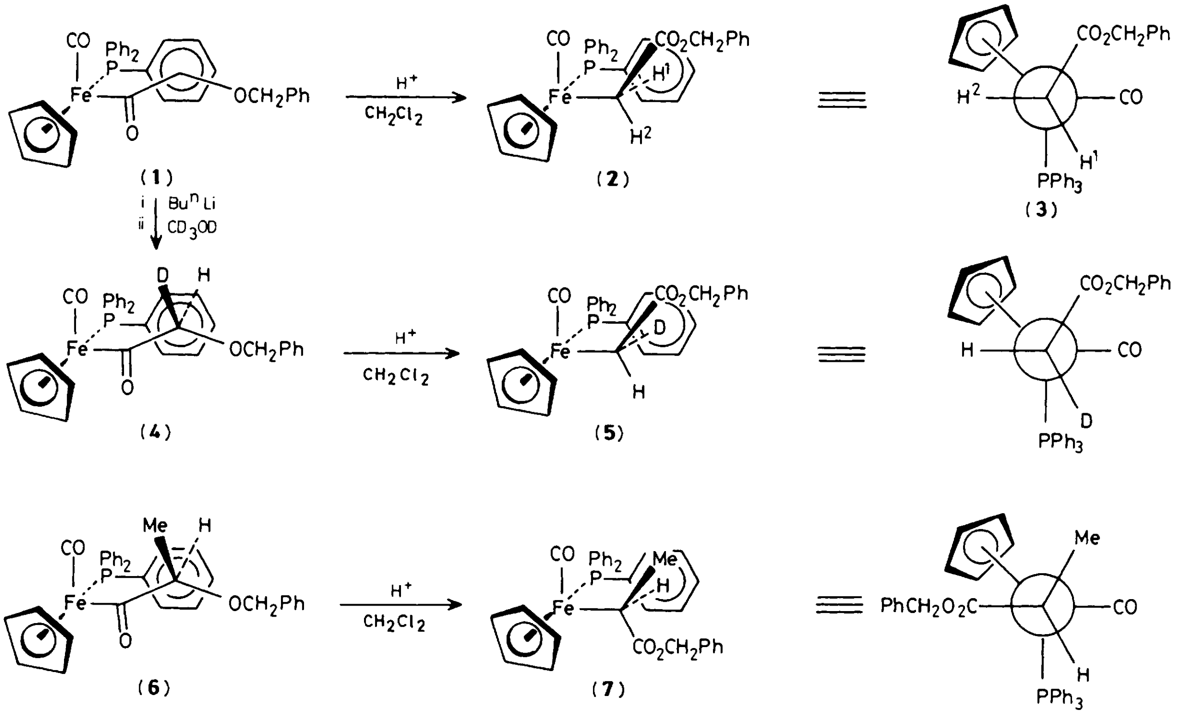
The acid catalysed rearrangement of [(η^5-C_5H_5)Fe(CO)(PPh_3)COCH(R)OCH_2Ph] (R = H, D, Me) to [(η^5-C_5H_5)Fe(CO)(PPh_3)CH(R)CO_2CH_2Ph] occurs stereospecifically with inversion of configuration at carbon.

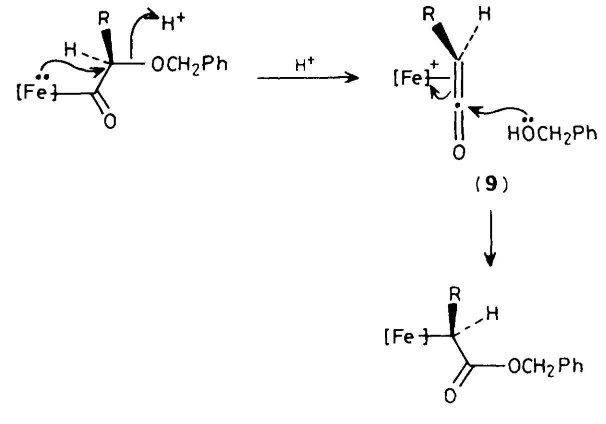
The acid catalysed rearrangement of α-alkoxy iron acyls to α-metalla-esters has been implicated in the reductive polymerisation of carbon monoxide[1] and has potential for organic synthesis. We describe herein that the rearrangements are stereospecific and thus potentially applicable to asymmetric synthesis.

Treatment of the α-benzyloxy iron acyl (**1**)[2] with CF_3SO_3H generated the α-metalla benzyl ester (**2**) in 84% yield. The diastereotopic α-protons can be assigned in the 300 MHz n.m.r. spectrum of (**2**) on the basis of the Karplus equation and chemical shift arguments. The preferred conformation of (**2**) places the CO_2CH_2Ph group staggered between the cyclopentadienyl and carbon monoxide ligands as depicted in Newman projection (**3**).[3] Proton H^1 is deshielded by the proximate phenyl of the triphenylphosphine ligand and appears upfield (δ 0.75) with respect to H^2 (δ 1.30). The $^3J_{PH}$ coupling constants for H^1 and H^2 of 10.6 and 2.9 Hz respectively are consistent with this structure, the respective H–C^α–Fe–P torsional angles being *ca.* 30 and −90°.

Deprotonation of (**1**) with butyl-lithium and quenching the derived enolate with CD_3OD gave the monodeuteriated analogue (**4**) stereoselectively as a 10:1 mixture of the (*RR*,*SS*) and (*RS*,*SR*) diastereoisomers.[2] Acid catalysed rearrangement of (**4**) gave (**5**) as a 10:1 mixture of diastereoisomers (88%). The stereochemistry of the major diastereoisomer could be assigned as (*RS*,*SR*) owing to the absence of the signal at δ 0.75 in the n.m.r. spectrum. These results indicate that the rearrangement of (**1**) to (**2**) is occurring stereospecifically with inversion of configuration at carbon. To confirm this the diastereoisomerically pure (*RR*,*SS*) complex (**6**) obtained by methylation of the enolate derived from (**1**)[2] was treated with acid. A single diastereoisomer of the α-metalla propionate ester (**7**) was obtained (80%). The stereochemistry of (**7**) could be deduced as (*RS*,*SR*) from analysis of the 300 MHz n.m.r. spectrum. The characteristic[4] long range $^4J_{PH}$ coupling of 1.6 Hz between the phosphorus and the methyl protons place the methyl group between the cyclopentadienyl and carbon monoxide ligands while the chemical shift δ 1.62 and $^3J_{PH}$ coupling constant of 8.1 Hz places the α-proton between the carbon monoxide and the triphenylphosphine. These results are only consistent with the assigned (*RS*,*SR*)-stereochemistry in the expected conformation[3] depicted in the Newman projection (**8**).

The inversion of configuration at carbon observed in these rearrangements is consistent with the mechanism shown in Scheme 1 where the intermediate cationic ketene complex (**9**) is formed stereospecifically and subsequently trapped by benzyl alcohol from the unco-ordinated face.





Scheme 1

Oxidative decomplexation (Br_2–Ph_2CH_2OH) of (**7**) gave α-methyl dibenzyl malonate (58%).

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