

Preliminary communication

STEREOSELECTIVE ELABORATION OF THE ACYL LIGAND IN $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2\text{R})$ VIA THE ALKYLATION OF THE ANIONS $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCHR})]\text{Li}$ (R = Me, Et)

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Summary

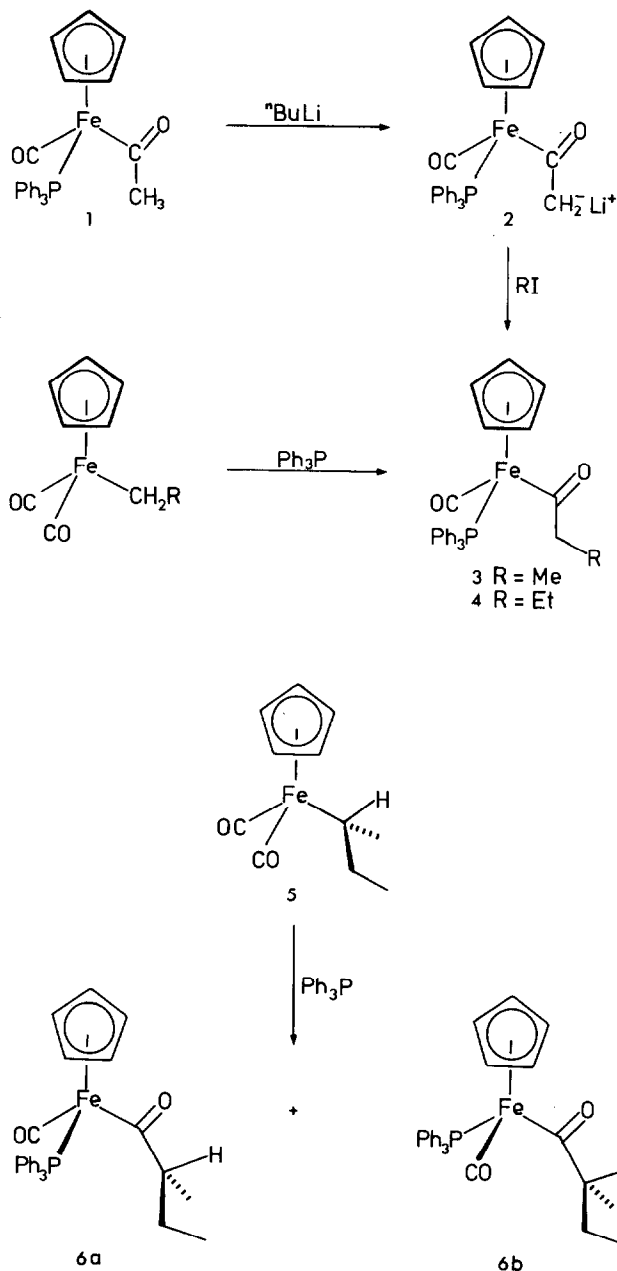
The stereoselective elaboration of the acyl ligand in the complexes $(\eta^5\text{-C}_5\text{H}_5)\text{-Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2\text{R})$ by addition of electrophiles to the anions $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCHR})]\text{Li}$ is described (R = Me, Et).

We have previously reported that the acetyl ligand of complex 1 can be elaborated via alkylation of the anion 2 with a variety of electrophiles [1]. Recently some of these results have received independent confirmation [2] and a similar reactivity has been reported for cobaltacyclopentanones [3]. We describe here that the acyl complexes 3 and 4 may be further elaborated by successive treatment with base and another electrophile, the new chiral centre being formed stereoselectively.

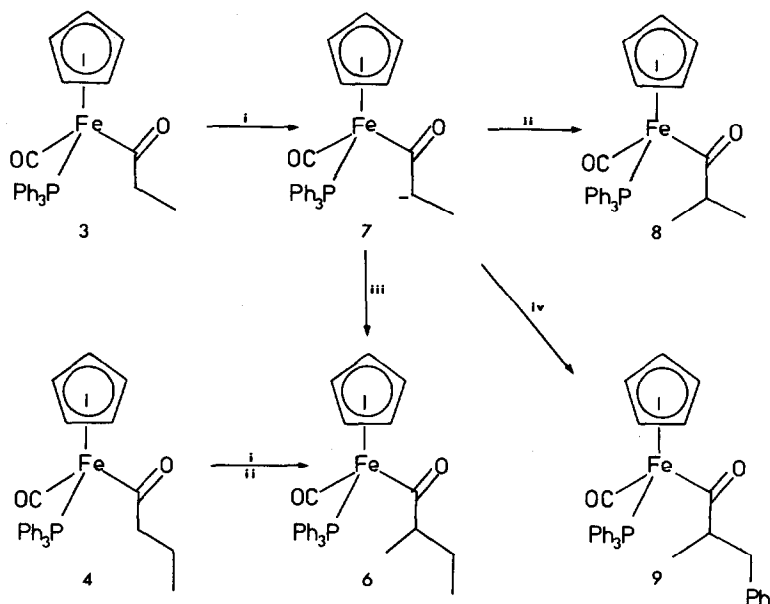
Acyl complexes 3 and 4 are readily prepared either from anion 2 or from $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ via treatment of the corresponding alkyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2\text{R})$ with triphenylphosphine. Similarly treatment of the racemic 2-butyliron complex 5* with triphenylphosphine generates the acyl complex 6 [4]. No stereoselectivity is observed in this reaction; the two diastereoisomers 6a and 6b* being formed in equal proportions. The diastereoisomers 6a and 6b are readily distinguishable by ^1H and ^{13}C NMR spectroscopy.

Treatment of the acyl complex 3 with n-butyllithium in tetrahydrofuran at -78°C generates anion 7. Anion 7 reacts with methyl iodide to produce 8 which is readily identifiable by the two doublets in the ^1H NMR spectrum corresponding to the diastereotopic methyl groups [5]. Alkylation of anion 7 at -78°C with ethyl iodide generates the acyl complex 6. Good stereoselectivity is observed with the diastereoisomers of 6 being produced in the ratio 98/2. Acyl complex 6 may

*Compounds 5, 6a and 6b are racemic but only one enantiomer is shown for clarity.



also be prepared by alkylation with methyl iodide at -78°C of the anion generated from 4. In this reaction slightly lower diastereoselectivity 4/96 was observed with the smaller electrophile. In this latter case, however, it is the other diastereoisomer to that formed from anion 7 which is produced. At higher reaction temperatures stereoselectivity diminishes. Similar diastereoselectivity is observed in the reaction of anion 7 with benzyl bromide to generate 9.



(i) *n*-BuLi, THF, -78°C ; (ii) MeI, -78°C ; (iii) EtI, -78°C ; (iv) PhCH₂Br, -78°C .

This stereoselective elaboration of acyl ligands combined with known procedures for the resolution of **1** [6] and the decomplexation of acyl ligands without racemisation [4] will allow the development of efficient asymmetric syntheses.

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References

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