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Preliminary communication

# SYNTHESIS OF α,β-UNSATURATED ACYL LIGANDS BOUND TO THE CHIRAL AUXILIARY $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$

STEPHEN G. DAVIES*, ROBERT J.C. EASTON, JONATHAN C. WALKER and PETER WARNER

*The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY (Great Britain)*

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## Summary

*cis*- and *trans*-α,β-unsaturated acyl complexes of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ can be prepared via Peterson reactions whereas the *trans* complexes can be prepared stereoselectively from the corresponding β-hydroxyacyl complexes either by α-silylation and elimination or more conveniently by treatment with NaH/MeI.

Recently we demonstrated that α,β-unsaturated acyl complexes of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]$ undergo tandem stereoselective Michael additions and subsequent methylations which result in the stereocontrolled synthesis of α- and/or β-substituted acyliron complexes [1]. This work has subsequently been confirmed by Liebeskind et al. [2]. The remarkable stereocontrol exerted by the chiral iron auxiliary prompted us to investigate alternative methods of synthesis of the starting α,β-unsaturated acyliron complexes. We describe here efficient syntheses of such complexes two of which give *trans*-α,β-unsaturated acyl complexes stereoselectively.

We have previously reported that the enolate derived from the α-trimethylsilylacetyl complex 1, reacts with acetaldehyde in a Peterson reaction to generate a 2/1 mixture of the *trans*- and *cis*-α,β-unsaturated acyl complexes 2 and 3 [1]. This methodology is in fact generally applicable to the synthesis of α,β-unsaturated acyl complexes. In each of the cases a—c and e—g the stereoselectivity changes little with complexes 2 and 3 being produced in ratios close to 2/1. In the case of pivalaldehyde however the Peterson reaction is completely stereospecific (>100/1) with only the *trans* complex 2 being produced albeit in a somewhat reduced yield compared with the other cases. In each of these reactions the *trans* and *cis* isomers 2 and 3 are readily and completely separable by column chromatography on activated alumina.

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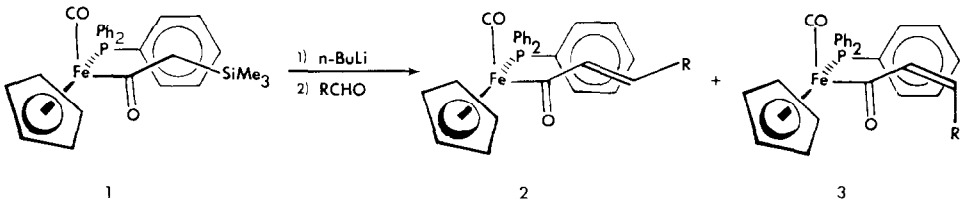
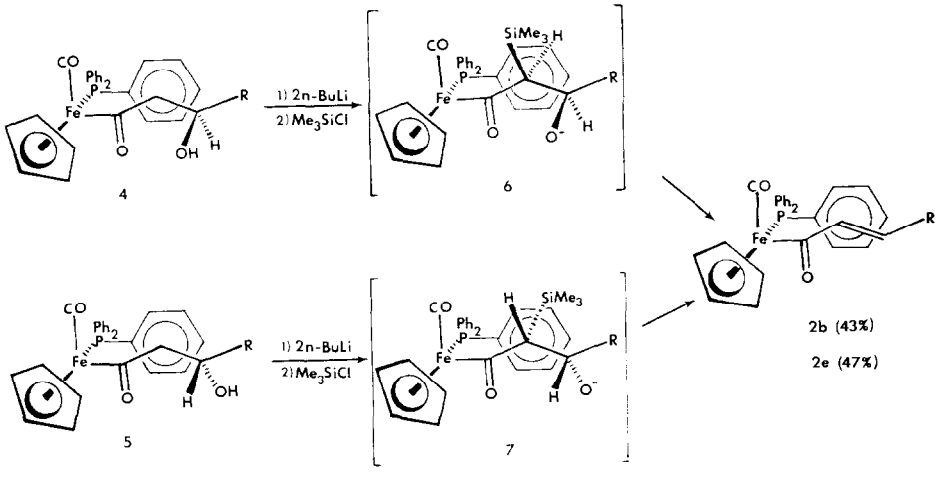



1 2 3

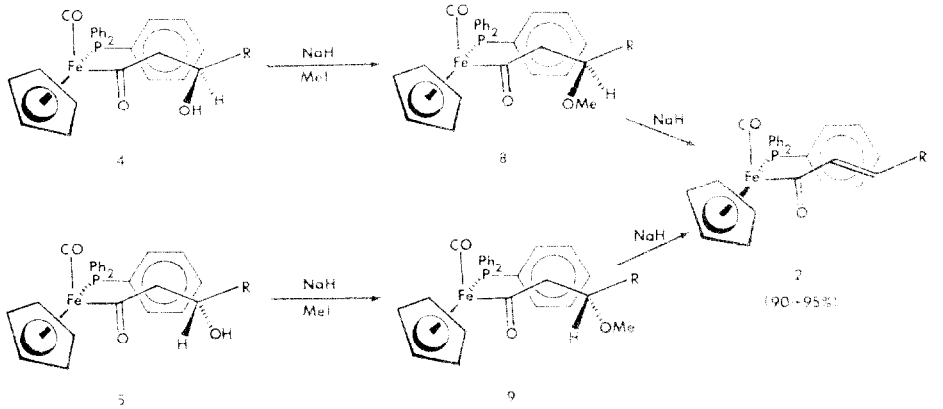
SCHEME 1. Yields: (a) R = Me 88%; (b) R = Et 77%; (c) R = n-Bu 88%; (d) R = t-Bu 63%; (e) R = Ph 80%; (f) R = 2-furyl 78%; (g) R = vinyl 68%. All compounds gave satisfactory elemental analyses and spectroscopic data. Yields correspond to the sum of the yields of pure isolated isomers 2 and 3 after separation.

*General experimental procedure.* n-Butyllithium (3.7 ml; 5.92 mmol) was added to ($\eta^5$-$C_5H_5$)Fe(CO)($PPh_3$)($COCH_2SiMe_3$) (1) (3.04 g; 5.78 mmol) in THF (80 ml) at −78°C to give a deep red solution. After stirring (−78°C; 1 h), valeraldehyde (1.2 ml, 11.3 mmol, dried over anhydrous calcium chloride) was added and the mixture further stirred (−78°C; 2 h). Removal of solvent gave an orange oil which was extracted with $CH_2Cl_2$ (3 × 20 ml) and filtered through deactivated alumina (Grade V). Chromatography on deactivated alumina gave a single orange band eluted with $CH_2Cl_2$ identified as **2c** and **3c** in a 3/2 mixture (88%). Rechromatography on active alumina (Grade I) gave pure **3c** upon elution with 40/60 petrol/$Et_2O$ (1/1) and pure **2c** upon elution with $CH_2Cl_2$.

As an alternative to the above Peterson reactions Liebeskind et al. [3] have recently advocated a non-stereospecific synthesis of mixtures of isomers **2** and **3** from β-hydroxyacyl complexes via acetylation and subsequent base promoted elimination. This methodology exhibits operational problems due to isomerisation of the product α,β-unsaturated complexes to the corresponding β,γ-isomers under the reaction conditions and also to apparent problems in product separation.




SCHEME 2



SCHEME 3

The β-hydroxyacyl complexes 4 and 5 are readily available via aldol additions of iron acetyl enolates to aldehydes [4,5]. Treatment of complex 4 with n-BuLi (2 equiv.) generates the corresponding *E*-enolates [5] which on addition of trimethylsilyl chloride undergo α-silylation to give 6 and subsequent elimination stereoselectively produces 2. Similar deprotonation of 5 gives the corresponding *Z*-enolates [5] which after α-silylation and *syn* elimination also generate 2. These reactions appear to be completely stereoselective with only the *trans* isomers 2 being detected by 300 MHz $^1$H NMR spectroscopy. The advantage of stereoselectivity offered by this route is however somewhat counteracted by the presently low yields (40—50%) although the conditions have not been optimised (Scheme 2).

*O*-Methylation of 4 and 5 can be achieved quantitatively by treatment with NaH in the presence of methyl iodide to give complexes 8 and 9 respectively. Prolonged treatment (24 h) of 8 or 9 with NaH in tetrahydrofuran at room temperature gives the *trans*-α,β-unsaturated acyl complexes 2 presumably via methoxide elimination from the corresponding enolates. When R = Me both the diastereoisomers 4 and 5 either separately or as mixture give a 15/1 mixture of the *trans* and *cis* complexes 2a and 3a. For larger R groups e.g. R = Et only the *trans* isomers 2 could be detected. The use of NaH as base does not cause any double bond isomerisation and consistent yields for 2 of 90—95% after recrystallisation were obtained (Scheme 3).

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