

## Preparation and Reactivity of the Anion $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2)]\text{Li}$

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The elaboration of the acyl ligand in the complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  by addition of electrophiles to the anion  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2)]\text{Li}$  is described.

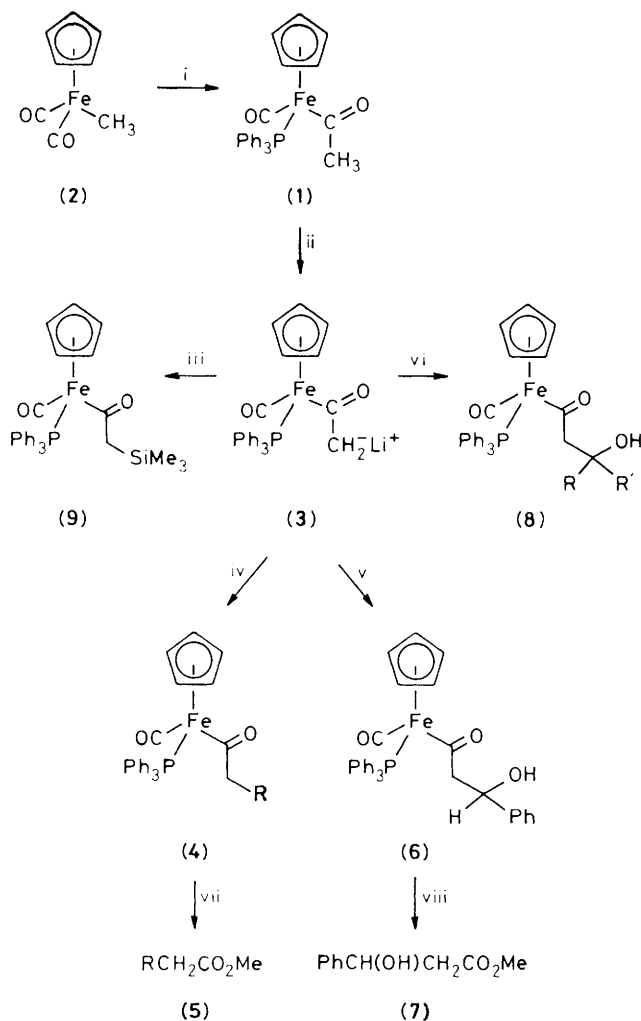
Organotransition metal acyl complexes have found extensive use in organic synthesis both in catalytic and in stoichiometric reactions.<sup>1</sup> The formation of metal acyl complexes is, however, generally limited to insertion of carbon monoxide into a metal-alkyl bond or nucleophilic addition of a carbanion to a carbonyl ligand. Decomplexation of the acyl ligand can lead, depending on the conditions, to a wide variety of carbonyl compounds (*e.g.* aldehyde, ketone, acid, ester, amide, or anhydride). 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. We report here the preparation and reactions of the carbanion  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2)]\text{Li}$  (3) generated from the acetyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  (1) on treatment with base.

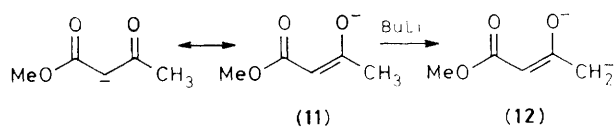
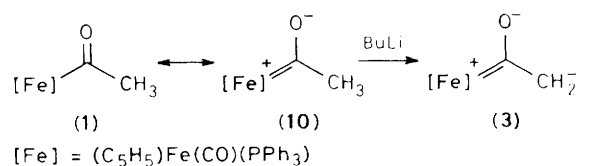
The acetyl complex (1) is readily available from  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  via the methyl complex (2). Treatment of (2) with triphenylphosphine causes migration of methyl from iron to a carbonyl ligand. The acetyl complex (1) reacts with the strong bases *n*-butyl-lithium or lithium di-isopropylamide to generate the anion (3); no reaction is observed with less powerful bases.

Anion (3) reacts at carbon with the alkyl halides methyl iodide, benzyl chloride, allyl bromide, and propargyl bromide to give the elaborated acyl complexes (4). The acyl complexes (1) and (4) can be readily decomposed with bromine in methanol to give the corresponding methyl esters (5). Treatment of (3) with benzaldehyde generates the  $\beta$ -hydroxyacyl compound (6). The two diastereoisomers of (6) are produced in equal proportions; the new chiral centre being formed appears to be too remote from the chiral metal centre for any stereoselective control to operate. Decomplexation as before generates the  $\beta$ -hydroxy-ester (7) making the overall reaction from benzaldehyde equivalent to the Reformatsky reaction. Reaction of (3) with the ketones acetone, cyclohexanone, and benzophenone similarly produces  $\beta$ -hydroxyacyl complexes (8). Methyl vinyl ketone undergoes 1,2- rather than 1,4-addition, again without any stereoselection being observed. Anion (3) does not undergo *O*-silylation with trimethylsilyl chloride; the *C*-trimethylsilyl product (9)<sup>3</sup> is formed in preference (Scheme 1).

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 i.r. absorption assigned<sup>2</sup> to the acetyl carbonyl in (1) is at  $1608\text{ cm}^{-1}$  indicating that there is a significant contribution to its structure of the resonance form (10); strong bases such as *n*-butyl-lithium are necessary to remove a methyl proton from (1); anion (3) undergoes *C*- rather than *O*-silylation. These observations suggest that an appropriate analogy for the acetyl complex (1) is the monoanion from methyl acetoacetate (11) which requires *n*-butyl-lithium to generate the bisanion (12). The



**Scheme 1.** Preparation and reactions of  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}_2)]\text{Li}$ . Reagents and conditions: i,  $\text{PPh}_3$ ,  $110^\circ\text{C}$  (94%); ii,  $\text{BuLi}$  or  $\text{LiN}(\text{Pr})_2$ , tetrahydrofuran,  $-78^\circ\text{C}$ ; iii,  $\text{Me}_3\text{SiCl}$  (50%); iv,  $\text{RX} = \text{MeI}$  (78%);  $\text{PhC}_6\text{H}_4\text{H}_2\text{Cl}$  (63%)  $\text{CH}_2\text{CHCH}_2\text{Br}$  (71%); or  $\text{HC}\equiv\text{CCH}_2\text{Br}$  (80%); v,  $\text{PhCHO}$  (65%); vi,  $\text{R} = \text{R}^1 = \text{Me}$  (33%);  $\text{RR}^1 = [\text{CH}_2]_5$  (37%);  $\text{R} = \text{R}^1 = \text{Ph}$  (50%);  $\text{R} = \text{Me}$ ,  $\text{R}^1 = \text{vinyl}$  (17%); vii,  $\text{Br}_2$ ,  $\text{MeOH}$ ,  $\text{R} = \text{H}$  (40%);  $\text{R} = \text{Me}$ ; viii,  $\text{Br}_2$ ,  $\text{MeOH}$  (45%).



bisanion (**12**) is analogous to (**3**), undergoing silylation on carbon.<sup>4</sup>

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### References

- 1 I. Wender and P. Pino, 'Organic Syntheses via Metal Carbonyls,' Wiley, 1977, Vol. I, 1977, Vol. II.
  - 2 M. L. H. Green and C. R. Hurley, *J. Organomet. Chem.*, 1967, **10**, 188; T. Bodnar, G. Coman, S. Lacroce, C. Lambert, K. Menard, and A. Cutler, *J. Am. Chem. Soc.*, 1981, **103**, 2471.
  - 3 K. H. Pannell, *Chem. Commun.*, 1969, 1346; C. R. Bennett, M. Ishaq, R. B. King, and K. H. Pannell, *J. Organomet. Chem.*, 1969, **19**, 327; K. H. Pannell, *ibid.*, 1970, **21**, P17.
  - 4 K. Yamamoto, S. Susuki, and J. Tsuti, *Chem. Lett.*, 1978, 649.
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