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Preliminary communication

FRAGMENTATION OF (η^5-C_5H_5)Fe(CO)(PPh_3)($COCH_2COR$) COMPLEXES TO THE CATION [(η^5-C_5H_5)Fe$(CO)_2$(PPh_3)]$^+$

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Summary

The unstable iron complexes (η^5-C_5H_5)Fe(CO)(PPh_3)($COCH_2COR$) (R = H, Me, Ph, OEt) undergo facile fragmentation with carbon—carbon bond cleavage to generate the iron carbonyl cation [(η^5-C_5H_5)Fe$(CO)_2$(PPh_3)]$^+$ and the corresponding carbanion $RCOCH_2^-$.

Nucleophilic addition to unsaturated hydrocarbon species which are activated by coordination to a transition metal cation is becoming increasingly useful for organic synthesis [1]. Mechanistic details for many of these reactions have still to be elucidated, but general guidelines, which allow prediction of the regioselectivity, are available [2]. For cations possessing both a dienyl and a carbonyl ligand addition of heteratomic nucleophiles to carbonyl is kinetically favoured. This may be a reversible process, however, allowing formation of the thermodynamically most favourable product from *exo*-addition to dienyl [3]. For carbon nucleophiles products from *exo*-addition to dienyl are generally the only ones observed [2]. We demonstrate here that certain neutral β-oxoiron acyl complexes can only be formed as unstable intermediates and undergo facile fragmentation to the corresponding metal carbonyl cations and carbanions, which indicates that carbon nucleophiles may also reversibly attack metal carbonyl ligands.

The acetyl ligand in (η^5-C_5H_5)Fe(CO)(PPh_3)($COCH_3$) can be readily elaborated via treatment of the anion **1** with alkyl halides [4]. Treatment of anion **1** with the acid chlorides RCOCl (R = Me, Ph), however, gives after work-up the cation **3** (isolated as a PF_6^- salt) and the methyl ketones **4**.

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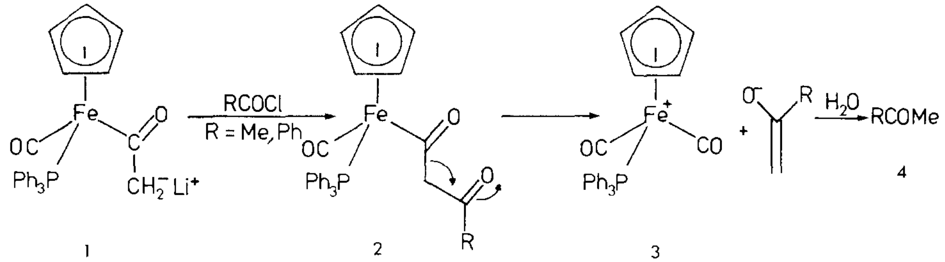
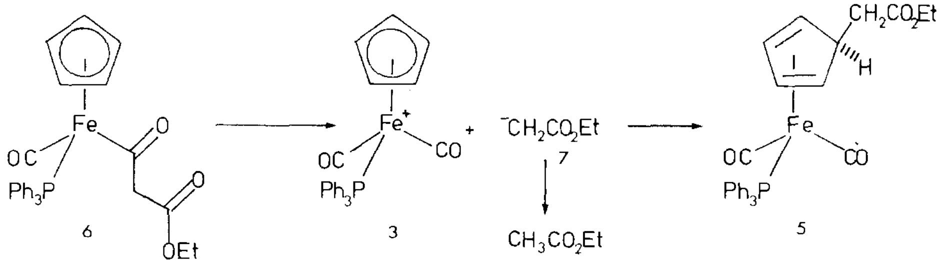
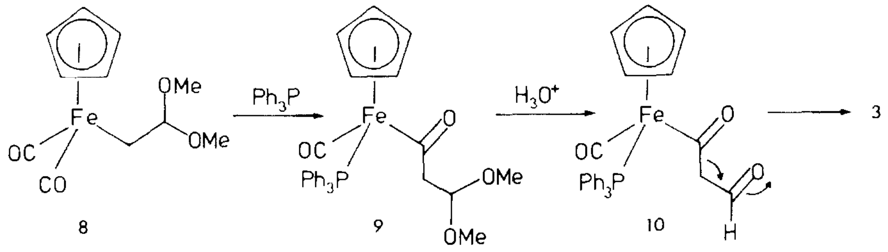


Treatment of **1** with ethyl chloroformate again results in cation **3** together with ethyl acetate and the cyclopentadiene complex **5**.



Facile fragmentation of the intermediate β-oxoacyl complexes **2** and **6** would give cation **3** and the corresponding stabilised carbanions. In the latter reaction *exo*-nucleophilic attack of carbanion **7** onto the cyclopentadienyl ligand of cation **3** would then give **5**. We have verified that treatment of **3** with **7** does indeed generate **5** whereas the corresponding cyclopentadienes are not formed from **3** with acetone or acetophenone enolates.

Treatment of chloroacetaldehyde dimethyl acetal with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]Na$ generates the alkyl complex **8** [5] which can be readily converted [6] to the acyl complex **9** on treatment with Ph_3P in refluxing acetonitrile. Acid hydrolysis ($TsOH/EtOH/H_2O$) of **9** gives cation **3**, again presumably via fragmentation of the intermediate β-oxoacyl complex **10**.



This type of fragmentation is analogous to the decarboxylation of β-keto-acid salts and to the reverse of reactions such as the Claisen condensation. It serves to illustrate that in nucleophilic addition reactions to transition metal cations, attack at a carbonyl ligand by stabilised carbanions should be expected to be readily reversible. The driving force for the fragmentations is presumably the stability of cation **3**. This is consistent with the fact that in polar solvents the metalla-ester (η^5-C_5H_5)Fe(CO)(PPh_3)(CO_2Me) spontaneously ionises with acyl—oxygen bond cleavage to cation **3** and methoxide [7]. This type of fragmentation mechanism would also explain the unexpected formation of (*exo*-η^4-5-$PhCH_2C_5H_5$)Fe$(CO)_2$(PPh_3) from (η^5-C_5H_5)Fe$(CO)_2$(CH_2Ph) on treatment with PPh_3 [8]. In the above reactions anion **1** is behaving as a source of $CH_2{}^{2-}$ and the possibilities this presents for synthesis are being explored.

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