Tricarbonylallyliron Cations as Intermediates in the Friedel–Crafts Acylation of Tricarbonylbutadieneiron

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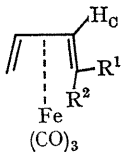
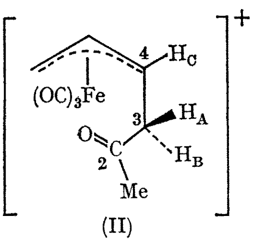
Summary The intermediates $(RCO\cdot CH_2CH\cdots CH\cdots CH_2)$-$Fe(CO)_3^+$ $AlCl_4^-$ (or PF_6^-) probably have the acyl oxygen co-ordinated to iron and lose protons stereoselectively to give *syn*- or *anti*-tricarbonyl-acylbutadieneiron depending on the base used.

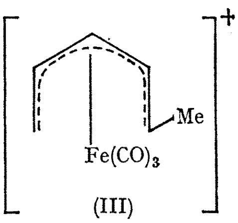
INTEREST in electrophilic substitution reactions of hydrocarbon ligands π-bonded to transition metals has centred on cyclic diene and dienyl complexes. An earlier report[1] that tricarbonylbutadieneiron (Ia) undergoes Friedel–Crafts acylation to give a mixture of 1- and 2-substitution products in the approximate ratio 4 to 1 (estimated after liberation of the free ligand) is the only example of a non-cyclic ligand undergoing substitution. However, the transition state for 2-substitution should be energetically unfavourable compared to that for 1-substitution by a factor greater than that experiment suggested.



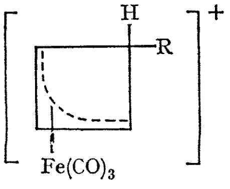
	R^1	R^2
(I) a	H	H
b	H	Ac
c	Ac	H
d	MeCHOH	H
e	H	PhCO
f	PhCO	H



(II)



(III)



(IV)

Using a CH_3COCl–$AlCl_3$ Perrier complex under homogeneous conditions (CH_2Cl_2 solution) we have isolated an insoluble intermediate $[C_4H_6CO\cdot CH_3Fe(CO)_3]^+[AlCl_4]^-$ (II) as the only product (86% yield) before hydrolysis. This diamagnetic yellow crystalline salt and the PF_6^- analogue formed by metathesis, are assigned the *anti*-allyl structure from ^1H n.m.r. spectra (CD_3CN solution). The stereochemistry of the original hydrocarbon ligand is thus retained and the salt corresponds to 1-acylation. No other positional or stereo-isomers are detectable. The iron atom in (II) formally possesses only 16 electrons (like the tricarbonylallyliron cations described by Pettit[2]) but may obtain a closed-shell electronic configuration by intramolecular σ-donation of a lone pair of electrons from the acyl oxygen atom. This effectively lowers the acyl CO bond order (ν_{CO} 1637 cm.$^{-1}$), restricts rotation around C-3–C-4, very significantly increases the value of the geminal coupling constant (J_{AB} -23 Hz.) and causes these protons to be unequally coupled to H_C (J_{AC} 2 Hz.; J_{BC} 6 Hz.).

Displacement of co-ordinated acyl-oxygen by other potential ligands is always accompanied by proton abstraction from the salt. Thus, (II) reacts with water to give a mixture of the *anti*-acetyl complex (Ib) (80%) [ν_{CO} (acyl) 1668 cm.$^{-1}$] and the *syn*-derivative (Ic) (20%) [ν_{CO} (acyl) 1677 cm.$^{-1}$], and a mixed product is also obtained with Ph_3P. That the products are stereo- rather than positional isomers[1] is shown by ^1H n.m.r. spectroscopy. In (Ic) the *anti*-proton (R^2 = H) appears as a doublet at τ 8·75 (J_{H-H_C} 8 Hz.) whilst in (Ib) the *syn*-proton (R^1 = H) appears as a doublet (J_{H-H_C} 8 Hz.) at much lower field (τ 6·91). Dicyclohexylethylamine, a base which is sterically too bulky to act as a ligand, reacts stereospecifically with (II) and removes H_A in the exclusive formation of tricarbonyl-*anti*-1-acetylbutadieneiron (Ib). This is rapidly and completely isomerised to the *syn*-isomer (Ic) by aqueous alkali or acid at room temperature or more slowly thermally without a catalyst, but is unaffected by Ph_3P

or $(C_6H_{11})_2NEt$. The mechanisms of the aqueous-phase isomerisations have not been determined, but deuterium is not incorporated when the reactions are performed in D_2O. These isomerisation reactions are clearly related to those of tricarbonyl-1-acetoxybutadieneiron which have been recently described.[3]

Reduction of (Ic) by borohydride is rapid and yields a single alcohol (Id) (m.p. 61·5°) which is diastereomerically related to the known[4] tricarbonylhexa-3,5-dien-2-oliron, since both give the same tricarbonyl-*syn*-1-methylpentadienyliron cation (III) on treatment with fluoroboric acid and both are oxidised to (Ic) on treatment with MnO_2. Friedel–Crafts benzoylation of (Ia) gives a stable salt analogous to (II) which can be selectively converted into the *anti*-benzoyl derivative (Ie) (m.p. 86—88°) and the *syn*-isomer (If) (m.p. 81—83°).

Tricarbonylbutadieneiron is much less reactive than ferrocene in these Friedel–Crafts acylations and is also less reactive towards other electrophiles.

The allyl cation (II) is the first intermediate isolated and characterised during 'electrophilic substitution' of an organic ligand bonded to a metal atom but corresponds to the type of intermediate commonly postulated, notably cations (IV) postulated by Pettit[5] in the substitution of tricarbonylcyclobutadieneiron.

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