

ACYLATION OF IRON CARBONYL COMPLEXES OF UNSATURATED ALDEHYDES AND KETONES

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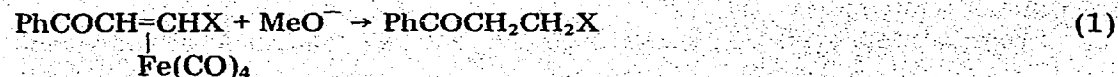
Summary

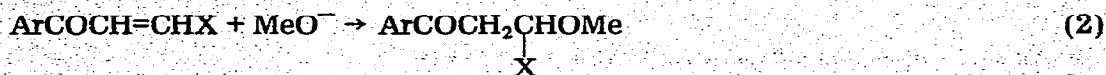
The acylation of some iron carbonyl complexes of α , β -unsaturated aldehydes and ketones by $(\text{MeCO})^+\text{BF}_4^-$ has been investigated and the structure of the salts obtained is discussed on the basis of IR and PMR spectra. Some chemical reactions of the cationic complexes have been studied and they were found to display high reactivity towards nucleophilic reagents.

Introduction

A study of the reactions of complexes of α , β -unsaturated ketones showed a considerable change in the chemical properties of the unsaturated ligand upon coordination. We have found that α , β -unsaturated ketones lose their high reactivity towards nucleophilic reagents when coordinated with an $\text{Fe}(\text{CO})_4$ group. Such changes are obviously due to the strong back donation of electrons from metal to ligand (i.e. to the electron releasing properties of the iron carbonyl group). The electrophilic activity of the double bond and the adjacent ketonic carbonyl group are thus decreased. For example, β -chlorovinyl ketones exhibit high reactivity towards trimethylamine and the thiophenolate anion [1, 2] giving under mild conditions the substitution products quantitatively. However, coordinated β -chlorovinyl ketones do not react, and under more drastic conditions the complexes decompose [3, 4].

The reaction of methoxide or thiophenoxide ions with iron tetracarbonyl complexes of α , β -dibenzoylethylene and methyl β -benzoylacrylate results in metal–ligand π -bond cleavage and reduction of the carbon–carbon double bond [5] while free ligands afforded adducts of the nucleophile to the double bond [6–9]. Such different chemical behaviour of the coordinated and free ligands is illustrated by reactions 1 and 2.



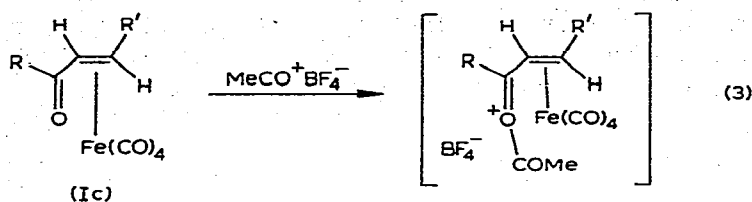


(X = C₆H₅, COOMe)

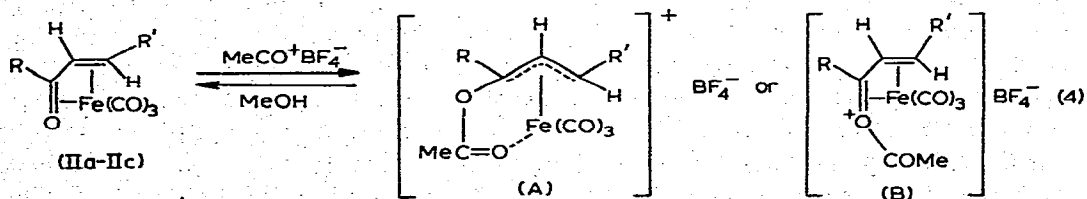
Our attempt at inducing the ketonic carbonyl group in the coordinated α , β -unsaturated ketones to react with nucleophilic reagents (e.g. hydrazines) failed. The attempted cyclization of coordinated *cis*-dibenzoyl ethylene into a heterocycle with hydrazine [10], was also unsuccessful, although the respective non-coordinated compound readily gave 3,6-diphenylpyridazine on treatment with hydrazine [11].

Results and discussion

It may be assumed that β -substituted α , β -unsaturated carbonyl compounds if π -coordinated with zero-valent iron should react with electrophilic reagents; we therefore studied the acylation of iron tetra- and tri-carbonyl complexes of α , β -unsaturated aldehydes and ketones using acetylum tetrafluoroborate $(\text{CH}_3\text{CO})^+ \text{BF}_4^-$ as the acylating agent [12]. The action of $(\text{MeCO})^+ \text{BF}_4^-$ on both iron tetra- and tricarbonyl complexes (I) and (II) yields the same result, the cationic complexes (III) being isolated in both cases.



(Ic)



(IIa-IIc)

(A)

(B)

(IIIa-IIIc)

(IIa, IIIa): R = Me, R' = H;
 IIb, IIIb: R = H, R' = Ph;
 IIc, IIIc: R = R' = Ph)

The compounds which were obtained as yellow crystalline substances, decompose slowly in air. They are well soluble in nitromethane and stable when treated with a strong acid such as trifluoroacetic acid but they decompose very easily on treatment with nucleophilic solvents. For example they will eliminate the acetyl group when dissolved in methanol, to give the iron tricarbonyl complex (II). Such an easy cleavage of the acetyl group may be evidence of bonding through the oxygen in the cation (III).

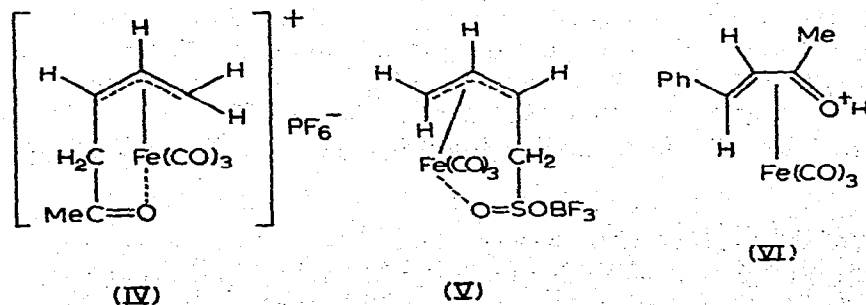
From the data available it is not possible to decide unequivocally between

TABLE I
IR AND PMR SPECTRAL DATA FOR THE COMPLEXES

Complex	IR(cm^{-1})(Nujol)		Chemical shifts (δ ppm) (in CF_3COOH)					Spin-spin coupling constants (Hz)			
	$\nu(\text{C}=\text{O})$	$\nu(\text{C}\equiv\text{O})$	H_A	H_B	H_X	H_Y	CH_3	$J(\text{AX})$	$J(\text{BX})$	$J(\text{AB})$	$J(\text{XY})$
(IIIa)	1630	2140 2080 2065	2.55	5.06	5.50		2.90 2.24	14	9	2.6	
(IIIb)	1640	2120 2080 2050	4.55		5.88	7.95	2.05	15			5
(IIIc)	1630	2120 2080 2055	4.47		6.62		2.32	14.2			

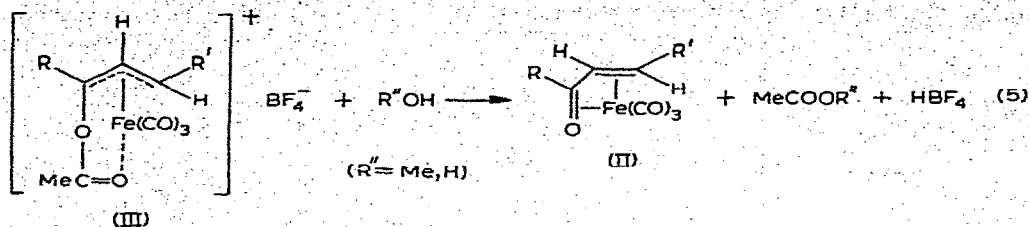
structures (A) and (B) for complex (III), but comparison of the spectra of our salts (Table 1) with those of allylic tricarbonyliron complexes [13, 14] indicates structure (A) to be more plausible. The complete X-ray analysis of adducts (IV) and (V) of butadieneiron tricarbonyl with MeCO^+ or SO_2BF_3 indicates a similar structure [15, 16]. The iron atom in the allyl cation (IV) has been found to fill up its valence electronic shell with electrons from the acyl oxygen [13, 16]. The stretching frequencies of complexes (III) and (IV) are practically coincident and thus one may assume similar release of electrons in our complexes. The assumed positive charge distribution in (III) over the whole allylic system including the metal atom agrees with the short wave shift of $\text{C}\equiv\text{O}$ stretching frequencies ($2140\text{-}2050\text{ cm}^{-1}$).

For the alternative structure (B) the $\text{C}\equiv\text{O}$ absorption would be expected in the region of $2080\text{-}2000\text{ cm}^{-1}$ analogously to cation (VI) which is generated upon protonation of iron tricarbonyl α,β -unsaturated ketone complexes [17].

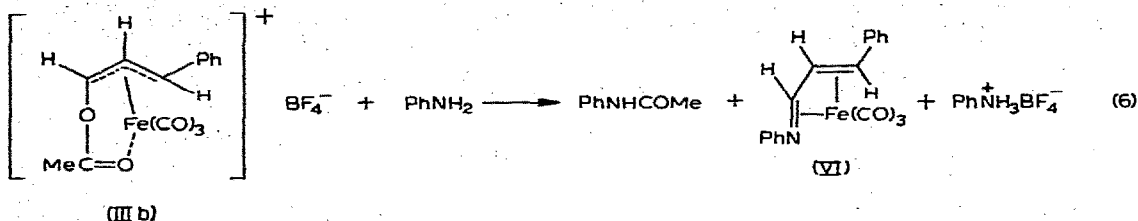


We have studied some chemical reactions of salts (III) and we found that the action of nucleophiles, e.g. alcohols or water, results in rapid cleavage of the acetyl

ium cation and formation of the starting olefinic complexes, (eqn. 5).



In the treatment with aniline of (IIIb) the nucleophile attacks not only the acetyl group but also the terminal carbon of the allyl group bonded to the CH₃COO-substituent to give an iron tricarbonyl complex of cinnamic aldehyde anil (VI) and acetanilide (eqn. 6). It should be pointed out that the iron tricarbonyl



bonyl complex of cinnamic aldehyde (IIb) reacts considerably slower under the same conditions; thus (IIb) probably is not an intermediate in reaction 6.

Experimental

All reactions were carried out under argon and in absolute solvents. IR spectra in Nujol mulls were measured with a UR-10 spectrophotometer. PMR spectra were measured in trifluoroacetic acid using a Hitachi-Perkin-Elmer R-20 spectrometer. The complex (PhCH=CH=NPh)·Fe(CO)₃ was prepared by a previously described method [18], as was the solution of (MeCO)⁺BF₄⁻ in nitromethane [12].

Synthesis of (MeCOCH=CH₂)Fe(CO)₃

Fe₃(CO)₁₂ (5.04 g) and 2 ml of MeCOCH=CH₂ (95% aqueous solution) in benzene (30 ml) were stirred at 70-80° and filtered. On evaporation of the solvent in vacuo 1.05 g of (IIa), melting at room temperature, was obtained. The complex was purified by freezing off from petroleum ether. (Found: C, 40.06; H, 3.16; Fe, 26.70; C₇H₆FeO₄ calcd.: C, 40.04; H, 2.88; Fe, 26.59%.) PMR spectrum (CDCl₃): δ(H_A): 1.30, δ(H_B): 2.00, δ(H_X): 5.50 ppm. J(AX) 9, J(BX) 6.5, J(AB) 1 Hz. IR spectrum: (cyclohexane) ν(C=O): 2069, 2007 and 1983 cm⁻¹.

Reaction of (MeCOCH=CH₂)Fe(CO)₃ with (MeCO)⁺BF₄⁻

A filtered solution of ca. 0.05 mole of (MeCO)⁺BF₄⁻ in 30 ml of nitromethane was added to 5.44 g (0.02 mole) of (IIa) in 20 ml of nitromethane at -78°. The mixture was allowed to remain at room temperature for 1 hour, it was then filtered and the solvent evaporated. The residue was extracted with

hexane and re-filtered. 6.40 g (72%) of (IIIa) was obtained. The product was recrystallized from trifluoroacetic acid by addition of acetic acid. M.p. 130° (dec.). (Found: C, 32.04; H, 2.59; Fe, 16.53. $C_9H_9BF_4FeO_5$ calcd.: C, 31.81; H, 2.67; Fe, 16.43%.)

Reaction of (PhCOCH=CHPh)Fe(CO)₃ with (MeCO)⁺BF₄⁻

The method was similar to that described above. Complex (IIIc) was obtained in 83% yield (3.95 g). The product was recrystallized from acetic anhydride by addition of diethyl ether. M.p. 160° (dec.). (Found: C, 50.10; H, 3.06; Fe, 11.79. $C_{20}H_{15}BF_4FeO_5$ calcd.: C, 50.25; H, 3.16; Fe, 11.68%.)

Reaction of (PhCH=CHCHO)Fe(CO)₃ with (MeCO)⁺BF₄⁻

The reaction was carried out analogously to that described for complex (IIa). (IIIb) was obtained [1.90 g, (48%)]. The product was recrystallized from acetic anhydride by addition of diethyl ether. M.p. 127° (dec.). (Found: C, 41.37; H, 2.70; Fe, 13.91. $C_{14}H_{10}BF_4FeO_5$ calcd.: C, 41.84; H, 2.76; Fe, 13.90%.)

Reaction of (PhCOCH=CHPh)Fe(CO)₄ with (MeCO)⁺BF₄⁻

A filtered solution of 0.05 mole of (MeCO)⁺BF₄⁻ in 30 ml of nitromethane was added to 3.76 g (0.01 mole) of (Ic) in 20 ml of nitromethane at -78°. The reaction mixture was allowed to remain at room temperature for 6 h. The mixture was filtered and the solvent evaporated. The residue was recrystallized from acetic anhydride by addition of diethyl ether. 2.57 g (54%) of (IIIc) was obtained. The product was identified by comparing its IR spectrum with that of the compound prepared from (IIc) and (MeCO)⁺BF₄⁻.

Reaction of (IIIb) with aniline

A solution of 0.09 g of aniline in 3 ml of benzene was added to 0.12 g of (IIIb) in 3 ml of benzene. After 2.5 h the solvent was removed in vacuo. TLC of the residue on alumina in petroleum ether/methylene chloride (4/1) gave 0.08 g (65%) of (PhCH=CH-CH=NPh)Fe(CO)₃ (VII) and 0.03 g (75%) of acetanilide. The products were identified by comparison of their IR spectra with spectra of authentic samples.

A solution of 0.28 g of aniline in 3 ml of benzene was added to 0.27 g of (IIb) in 3 ml of benzene. The reaction was followed by the changes in the IR spectrum of the reaction mixture. The IR spectrum showed practically no vibrations corresponding to the complex (VII) after 6 h. These vibrations appear after ca. 30 h.

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