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SYNTHESIS OF π-(β-CHLOROVINYL KETONE) TETRACARBONYLIRON COMPLEXES*

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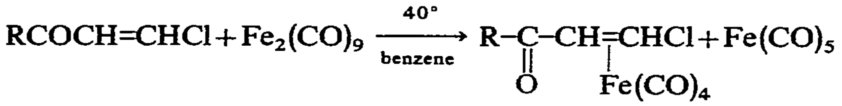
The ideas developed by Dewar[1] and Chatt and Dunkanson[2] regarding the stabilization of the olefin–transition-metal bond in the presence of electron-acceptor groups that facilitate the "back-donation" of electrons from the metal to the π^*-molecular orbitals of the olefins, have been confirmed experimentally in a number of cases. It was found that fairly stable π-complexes with the transition-metal carbonyls, and in particular with iron carbonyl are formed when maleic[3-5], fumaric[3-5], acrylic[5], methacrylic[4-6] and cinnamic[5] acids and their derivatives, as well as acrylonitrile[7,8], acrolein[6] and cinnamaldehyde[5,9], are used as ligands. But the π-complexes of carbonyliron with α,β-unsaturated ketones have not yet been reported.

In the present work, we report the synthesis of the π-complexes of tetracarbonyliron with alkyl and aryl β-chlorovinyl ketones. The reaction proceeds according to the following equation:



$$RCOCH{=}CHCl + Fe_2(CO)_9 \xrightarrow[\text{benzene}]{40^\circ} \underset{\displaystyle O}{\underset{\|}{R{-}C}}{-}\underset{\displaystyle Fe(CO)_4}{\underset{|}{CH{=}CHCl}} + Fe(CO)_5$$

$$(R = CH_3, C_6H_5, p\text{-}CH_3C_6H_4, p\text{-}CH_3OC_6H_4, p\text{-}BrC_6H_4)$$

These complexes are readily formed on heating equimolecular mixtures of β-chlorovinyl ketone and nonecarbonyldiiron in benzene in an inert gas atmosphere.

It is worth noting that the photochemical method of Schenk *et al.*[3] using pentacarbonyliron did not give satisfactory results in our studies.

From the analytical data, the complexes obtained have the composition $(RCOCH{=}CHCl)Fe(CO)_4$ and are monomeric as is shown by the molecular weight determination of $(C_6H_5COCH{=}CHCl)Fe(CO)_4$ (mol. wt. determined cryoscopically in benzene, 314; calcd. for the monomer, 334.5). All the complexes are light-yellow crystalline substances and, like the analogous tetracarbonyliron complexes with other ligands[3-10], are quite stable in the crystalline state but sensitive to oxygen in solution. They dissolve readily even in non-polar solvents, *e.g.* petroleum ether, and may be recrystallised from this solvent by cooling.

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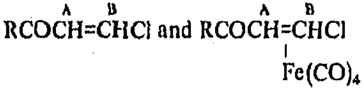
TABLE 1

IR[a] AND NMR SPECTRAL DATA



$$\mathrm{RCO}\overset{A}{\mathrm{C}}\mathrm{H{=}}\overset{B}{\mathrm{C}}\mathrm{HCl} \text{ and } \mathrm{RCO}\overset{A}{\mathrm{C}}\mathrm{H{=}}\underset{\underset{\mathrm{Fe(CO)_4}}{|}}{\overset{B}{\mathrm{C}}}\mathrm{HCl}$$

No.	Compound	C=O (cm^{-1})	C=C (cm^{-1})	C≡O (cm^{-1})	A (ppm)	B (ppm)	J(AB) (cps)
1	$CH_3COCH{=}CHCl$	1678	1584		6.16	7.02	13
2	π-($CH_3COCH{=}CHCl$)$Fe(CO)_4$	1675	1425	2110, 2030, 2000	3.69	5.07	8.6
3	$C_6H_5COCH{=}CHCl$	1660	1580[b] 1595		7.12	7.29	13.5
4	π-($C_6H_5COCH{=}CHCl$)$Fe(CO)_4$	1645	1410	2115, 2060–1980 (band)	4.43	5.35	8.0
5	p-$CH_3C_6H_4COCH{=}CHCl$	1640	1560[b] 1580		7.01	7.21	13.7
6	π-(p-$CH_3C_6H_4COCH{=}CHCl$)$Fe(CO)_4$	1640 (1650)[a]	1425 (1420)	2115, 2035 2015 (2120, 2045, 2020)	4.42	5.31	8.5
7	p-$CH_3OC_6H_4COCH{=}CHCl$	1670	1595[b] 1610		7.11	7.28	13.7
8	π-(p-$CH_3OC_6H_4COCH{=}CHCl$)$Fe(CO)_4$	1640	1415	2110, 2030, 2000	4.41	5.31	8.0
9	p-$BrC_6H_4COCH{=}CHCl$	1675	1595[b] 1605		7.08	7.31	13.0
10	π-(p-$BrC_6H_4COCH{=}CHCl$)$Fe(CO)_4$	1650	1420	2115, 2050–2000 (band)	4.35	5.32	8.0

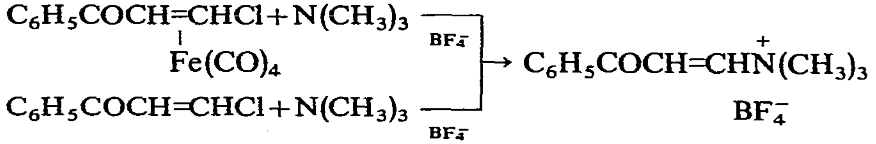
[a] IR spectra of π-complexes were taken in KBr tablets as they easily decompose in solution. The data cited in brackets R = p-$CH_3C_6H_4$) refer to the spectrum taken in $CHCl_3$ solution and it can be seen that it differs very slightly from the spectrum taken in KBr. [b] For aryl β-chlorovinylketones, both absorption bands of the C=C band (ethylene and aromatic) appearing adjacent to each other, are cited.

The IR and NMR data indicate that the metal ligand is attached to the carbon–carbon double bond and that the ketone carbonyl group practically does not take part in the reaction. In fact, by comparing the IR spectra of the complexes with the spectra of the free ligands, distinct changes in the C=C absorption and slight changes in the ketone carbonyl band are observed (see Table 1). This can best be seen in the example of methyl-β-chlorovinyl ketone in which $\nu(C{=}O) = 1678$ and $\nu(C{=}C) = 1587\ cm^{-1}$ (ref. 11), and when complexed, $\nu(C{=}O) = 1675$ and $\nu(C{=}C) = 1425\ cm^{-1}$ (*i.e.* $\Delta\nu(C{=}C) = 162\ cm^{-1}$). An analogous picture is also given by aryl-β-chlorovinyl ketones and their complexes. Such large shifts in the complexed double-bond absorption bands are in accordance with the data reported in the literature for other ethylenic complexes[5,6].

Studies of the IR spectra in the C≡O stretching region and comparison of this data with the data reported for other complexes (π-L-$Fe(CO)_4$ where L stands for other ethylenic ligands) indicates that in this case also, the β-chlorovinyl ketone ligand substitutes the carbonyl group in $Fe(CO)_5$ in the equatorial position[5,8].

In the NMR spectra of the complexes obtained, the shift of the olefinic proton signals, increasing to high field, is observed to the extent of 2.5–2.7 ppm for the proton neighbouring the ketone carbonyl group, and to the extent of approximately 2 ppm for the proton situated near the chlorine atom. These changes are typical of the complex-bonded olefins. They were observed earlier by Schenk and Gustorf[3] and also by Weiss *et al.*[5] for the complexes of iron carbonyls with maleic and fumaric acids and their derivatives. It is important to note that the coupling constants, $J(AB)$, when passing from free β-chlorovinyl ketone to the complex, decrease sharply (from 13 to 8 cps). These facts and the IR data point to the substantial reduction of the C=C bond order in the complexes.

During a study of the chemical properties of the complexes obtained, it was of interest to consider first of all how far the complexating of the olefin double bond affects the capacity of the chlorine to interact in nucleophilic substitution as shown by us for the starting β-chlorovinyl ketones, which readily undergo these substitutions[12,13]. Preliminary investigations in the case of π-$(C_6H_5COCH{=}CHCl)Fe(CO)_4$ with trimethylamine used as a nucleophilic reagent (which readily gives the quarternary salts with β-chlorovinyl ketones) has shown that the interaction proceeds very slowly under mild conditions (current of $(CH_3)_3N$, room temperature) but under stronger conditions (heating for many hours in a sealed tube) the same quarternary salt is formed that is obtained from the initial β-chlorovinyl ketone. Thus ligand splitting takes place and this probably proceeds more quickly than the nucleophilic substitution of the halogen in the complex.



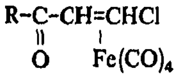
$$\left.\begin{array}{l} C_6H_5CO\underset{\displaystyle Fe(CO)_4}{\underset{|}{C}}H{=}CHCl + N(CH_3)_3 \xrightarrow[BF_4^-]{} \\ C_6H_5COCH{=}CHCl + N(CH_3)_3 \xrightarrow[BF_4^-]{} \end{array}\right] \rightarrow C_6H_5COCH{=}CH\overset{+}{N}(CH_3)_3\ BF_4^-$$

Investigations in this direction are being continued.

EXPERIMENTAL

β-Chlorovinyl ketones were obtained by the methods already reported[14,15]

TABLE 2



$R{-}\underset{\underset{O}{\|}}{C}{-}CH{=}\underset{\underset{Fe(CO)_4}{|}}{CHCl}$

No.	R	Yield (%)	M.p. (°C)	Formula	Analytical values							
					Found				Calcd.			
					C	H	Hal.	Fe	C	H	Hal.	Fe
1	CH_3	67	49	$C_8H_8ClO_5Fe$	35,37	1.92	12,70	20.50	35.26	1,84	13,01	20,50
2	C_6H_5	90	68	$C_{13}H_7ClO_5Fe$	47,17	2.40	10,59	16,04	46,68	2,11	10,60	16,69
3	p-$CH_3C_6H_4$	78	98	$C_{14}H_9ClO_5Fe$	48,38	3.16	9,86	16,01	48,25	2,89	10,17	16,03
4	p-$CH_3OC_6H_4$	57	71	$C_{14}H_9ClO_6Fe$	46,40	2.40		15,07	46,13	2,47		15,32
5	p-BrC_6H_4	70	99	$C_{13}H_6ClBrO_5Fe$	37,97	1,37	28,09	13,34	37.73	1,45	27,90	13,54

IR spectra were taken with the spectrophotometer UR-10. NMR spectra were recorded on an INM-100 instrument with a working frequency of 100 Mc, in carbon tetrachloride solution (concentration approximately 8%) with hexamethyldisiloxane as internal standard. The accuracy of the chemical shift determination was ±0.5 cps.

Synthesis of π-complexes of β-chlorovinyl ketones with tetracarbonyliron

To a suspension of 0.015 mole of $Fe_2(CO)_9$ in 60 ml of dry benzene was added 0.015 mole of the corresponding β-chlorovinyl ketone in benzene (10 ml) with stirring. The mixture was stirred for 2 h at room temperature in a current of inert gas and then heated for 6 h at 40°. After standing overnight, the solution was filtered in an inert gas atmosphere and then evaporated to dryness *in vacuo*. The dry substance was extracted with three small portions of petroleum ether until the soluble part was completely extracted. The petroleum ether solution on cooling to −70° yielded light-yellow crystals of the π-complex. In the case of methyl- and phenyl-β-chlorovinyl ketones the products may be purified by vacuum sublimation at 40–50° ($4 \cdot 10^{-2}$ mm). Purification of the other complexes was carried out by repeatedly dissolving in petroleum ether and cooling the solution to −70°. The yields, melting points and other analytical data are given in Table 2.

Interaction of π-(C_6H_5CH=$CHCl$)$Fe(CO)_4$ with trimethylamine

A solution of 1 g of π-(C_6H_5COC=$CHCl$)$Fe(CO)_4$ and 2 ml of liquid trimethylamine in 20 ml of benzene was heated at 40° in a sealed tube in an argon atmosphere for 20 h. The precipitate formed was filtered and washed with benzene. The yield of β-benzoylvinyltrimethylammonium chloride was 0.1 g. It was identified as the tetrafluoroborate melting at 246° (lit.[16] m.p., 245–246°) and by comparison of the IR spectra with that of a known sample.

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SUMMARY

New π-complexes of tetracarbonyliron with alkyl and aryl β-chlorovinyl ketones have been prepared. The IR and NMR spectra of the newly-prepared complexes have been recorded and compared with the spectra of the original ketones. The changes in the C=C and C=O frequencies of the β-chlorovinyl ketones on complexation have been discussed. Preliminary investigations of the chemical properties of the complexes have been made.

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