SYNTHESIS AND PROPERTIES OF π-ALLYLCARBONYL COMPLEXES OF IRON

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Abstract

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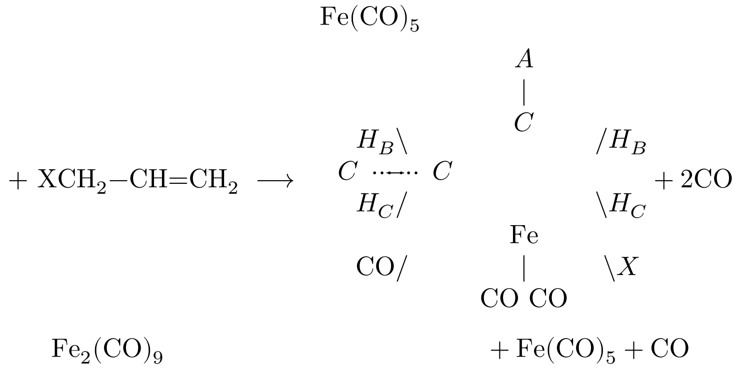
SYNTHESIS AND PROPERTIES OF π-ALLYLCARBONYL COMPLEXES OF IRON

In the course of our investigations we obtained, as intermediates for further syntheses, π-allylcarbonyl complexes of iron of type I, where $A = H_a, \mathrm{Br}$, $X = \mathrm{I}, \mathrm{Br}, \mathrm{Cl}, \mathrm{NO_3}$. The first information on 6-coordinate complexes of iron containing a π-allyl ligand was published almost simultaneously by two groups of researchers in 1962 (^{1,2}). Subsequently this area was developed in further work by Murdoch (^{3}) and, in addition, a third group of researchers was involved —Heck and co-workers (^{4}). Complexes of type I are formed by the interaction of allyl halides with iron carbonyls. Iron pentacarbonyl is the least active in these syntheses; reaction in satisfactory yield occurs only with allyl iodide. To obtain the chloro and bromo complexes, higher carbonyls are used. We obtained allyliron tricarbonyliodide in 85-87% yield, doubling, in comparison with the stoichiometric amount, the amount of allyl iodide in the reaction mixture.



$$\begin{array}{llll} \mathrm{Fe(CO)_5} & & & \\ & & \begin{array}{c} A \\ | \\ C \end{array} & \\ + \mathrm{XCH_2{-}CH{=}CH_2} \longrightarrow & \begin{array}{c} H_B\backslash \\ C \cdots\cdots C \\ H_C/ \end{array} & & \begin{array}{c} /H_B \\ \\ \backslash H_C \end{array} + 2\mathrm{CO} \\ & \mathrm{CO}/ & \begin{array}{c} \mathrm{Fe} \\ | \\ \mathrm{CO\ CO} \end{array} & \backslash X \\ \mathrm{Fe_2(CO)_9} & & + \mathrm{Fe(CO)_5} + \mathrm{CO} & \end{array}$$

(I)

The reaction was carried out at 40–44° for 12 h without solvent in an inert-gas atmosphere. The excess reagents were distilled off in vacuo; the reaction product was extracted from the solid residue with hexane and then crystallized out at −80°. Allyliron tricarbonyl bromide and chloride were obtained by us by an exchange reaction from the iodide and the corresponding ammonium salts at room temperature. The former with $(C_2H_5)_4NBr$ in $CHCl_3$, yield 35%; the latter with $(CH_3)_4NCl$ in CH_3OH, yield 20%. The low yields of these complexes are apparently connected with decomposition during isolation. The physical properties of the substances obtained and analytical data are given in Table 1. Substituted

Table 1

Physical properties of the substances obtained

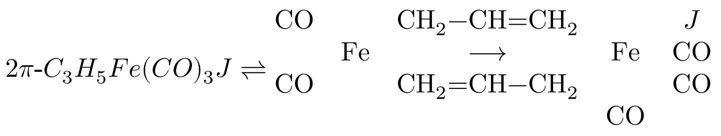
Substance	Color	Decomp. temp., °C	Found, % C	Found, % H	Found, % Fe	Found, % X	Calculated, % C	Calculated, % H	Calculated, % Fe	Calculated, % X	Mol. wt. found	Mol. wt. calc.
$C_3H_5Fe(CO)_3J$	dark-brown	97–98	23.26	1.63	17.89	41.62	23.41	1.63	18.13	41.21	288	307.8
$C_3H_5Fe(CO)_3J$	dark-brown	97–98	23.21	1.59	18.11	41.36	23.41	1.63	18.13	41.21	288	307.8
$C_3H_5Fe(CO)_3Br$	light-brown	91	27.82	2.09	21.43	30.46	27.62	1.93	21.40	30.63	258	260.8
$C_3H_5Fe(CO)_3Br$	light-brown	91	27.60	1.98	21.11	30.87	27.62	1.93	21.40	30.63	258	260.8
$C_3H_5Fe(CO)_3Cl$	yellow	82–85	32.86	2.42	25.30	16.42	33.05	2.31	25.77	16.36	190	216
$C_3H_5Fe(CO)_3Cl$	yellow	82–85	33.05	2.48	25.20	16.46	33.05	2.31	25.77	16.36	190	216
2-$BrC_3H_4Fe(CO)_3Br$	light-brown	84	21.26	1.22	16.69	46.69	21.19	1.18	16.44	47.07	338	340
2-$BrC_3H_4Fe(CO)_3Br$	light-brown	84	21.15	1.23	16.37	46.80	21.19	1.18	16.44	47.07	338	340
$C_3H_5Fe(CO)_2P(C_6H_5)_3J$	dark-red	121–122	50.63	3.59	10.43	23.44	50.94	3.72	10.30	23.42	–	–
$C_3H_5Fe(CO)_2P(C_6H_5)_3J$	dark-red	121–122	50.80	3.79	10.48	23.07	50.94	3.72	10.30	23.42	–	–
$C_3H_5Fe(CO)_3NO_3$	yellow	83–85	30.01	2.21	22.49	5.51	29.66	2.07	22.98	5.76	–	–
$C_3H_5Fe(CO)_3NO_3$	yellow	83–85	30.13	2.06	22.44	5.49	29.66	2.07	22.98	5.76	–	–

in the allylic ligand, 2-bromoallyliron tricarbonyl bromide was obtained in 30% yield from $Fe_2(CO)_9$ and 2,3-dibromopropene-1 in hexane on heating for 2 h to 35–45° in an inert-gas atmosphere. The iodide was isolated analogously. In the solid state all the substances obtained are comparatively stable at room temperature; in air they gradually oxidize, forming ferric hydroxide. In solutions they decompose very rapidly. Solubility in nonpolar solvents decreases markedly on going from the iodide to the chloride. The molecular weights were determined cryoscopically in benzene and, as is seen from the data of Table

1, are always somewhat low, which contradicts some literature data (1). With time the molecular weight of one and the same sample steadily decreases; this decrease is accompanied by precipitation of decomposition products.

The proton magnetic resonance spectra, recorded in CCl_4 immediately after dissolution, differ from the usual spectra for π-allyl complexes by the appearance of a symmetrical doublet in the region of ~2.5 δ, the intensity of which varies somewhat depending on the substance but never exceeds the intensity of the signals H and H . In the case of 2-bromoallyliron tricarbonyl bromide these additional signals are entirely absent, and in the case of allyliron tricarbonyl chloride they are shifted to higher field, to 1.2 δ.

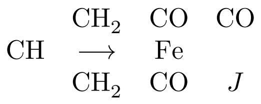
Plowman and Stone also noted the appearance of additional lines in the spectrum of $C_3H_5Fe(CO)_3J$, but of a different position and different intensity than in our case (1). The complication of the spectrum and the considerable increase in the molecular weight of the iodide, which they observed, were attributed to the establishment in solution of an equilibrium in the sense of equation I:



$$2\pi\text{-}C_3H_5Fe(CO)_3J \rightleftharpoons \begin{array}{c}CO\\ \\ CO\end{array} \; Fe \; \begin{array}{c}CH_2{-}CH{=}CH_2\\ \longrightarrow \\ CH_2{=}CH{-}CH_2\end{array} \; \begin{array}{c} \\ Fe \\ \\ CO\end{array} \; \begin{array}{c}J\\ CO\\ CO\\ \\ \end{array} \qquad (I)$$

The principal argument in favor of formation of the dimer—the increase in molecular weight—is not confirmed by us. We did not observe an increase in molecular weights for any of the substances obtained. Such a disruption of the π-allyl structure without a sufficiently strong external influence seems improbable, owing to the special character of the metal bond with the π-allyl ligand. The only precedent—the rearrangement of $(\pi\text{-}C_3H_5PdCl)_2$ into $\sigma\text{-}C_3H_5PdCl$ on dissolution in dimethyl sulfoxide or under the action of an excess of triphenylphosphine, confirmed only by NMR data—is explained by the action of strong donor complex-forming agents, dimethyl sulfoxide and triphenylphosphine (5, 6).

We suppose that the deviations in the NMR spectra may be connected with a greater or lesser distortion of delocalization in the π-allyl ligand and an approach to structure II. A detailed analysis of the spectra and further substantiation of this assumption will be presented subsequently.



$$\begin{array}{ccccc} & CH_2 & CO & CO \\ CH & \longrightarrow & Fe & \\ & CH_2 & CO & J \end{array} \qquad (II)$$

The shifts of the H protons of the allylic ligand depend strongly on the electronegativity of the halide present in the molecule. On going from iodide to chloride, the position of the H signals shifts toward higher field by almost 1δ. In parallel with them there occurs a shift of the H signals, whereas the H_B lines shift in the opposite direction. The somewhat exceptional value of the H_A shift for $C_3H_5Fe(CO)_3Br$ has as yet no satisfactory explanation.

An analogous dependence of the shifts for the protons of the cyclopentadienyl ring on the electronegativity of the σ-bonded group was observed by King and Bisnette in the series $C_5H_5Fe(CO)_2R$ (^{7}). There, however, these shifts are considerably smaller in absolute magnitude. It must be emphasized that the opposite sign of the change in the chemical shifts of the H_B and H_C protons with increasing electronegativity of substituents X at the iron atom cannot be explained purely by an inductive effect. Both hydrogen atoms are separated from the substituent by the same number of chemical bonds, and the differences in the behavior of the corresponding chemical shifts can be correlated only with the fact that the protons under consideration are at different distances from the iron atom. The observed differences can be explained by jointly taking into account both the transmission of inductive effects through the iron atom and the change in the anisotropy of its electron shell upon substitution. A correct treatment of the magnetic anisotropy will be possible after accurate information on the structure of the molecule has been obtained. These facts are also of interest for comparison with data on chemical shifts in cyclopentadienyl (CPD) titanium compounds (^{8}). The arrangement of the protons of the CPD ring, symmetric with respect to the Ti atom, made it possible, in a first approximation, not to take into account the influence of magnetic anisotropy (which, moreover, according to NMR data, is considerably smaller for the Ti atom than for the Fe atom).

Thus, an interesting possibility arises: by a joint study of the chemical shifts of π-allyl and π-CPD derivatives of one and the same element, to separate the contributions to the chemical shift caused by the inductive effect and by the effects of magnetic anisotropy.

In the carbonyl region of the IR spectra, recorded by N. A. Chumaevskii, all four substances have three bands of valence CO vibrations.

π-Allyliron tricarbonyliodide is diamagnetic, and since mutual transformations by simple substitution of X have been shown, all the remaining complexes apparently are also diamagnetic.

Allyliron tricarbonyliodide very readily replaces one of the carbonyl groups by a triphenylphosphine molecule even at room temperature. If this reaction is carried out in tetrahydrofuran, then, along with the phosphine complex, poorly soluble triphenylallylphosphonium iodide is formed in tetrahydrofuran, yield 31%, m.p. 225–229° (decomp.; recrystallized from a solution in CH_2Cl_2 with tetrahydrofuran).

Found, %: C 58.80; 58.76; H 4.76; 4.67; P 7.05; 7.11; I 29.23; 29.12
$C_{21}H_{20}PJ$. Calculated, %: C 58.60; H 4.65; P 7.20; I 29.46

Attempts to replace more than one carbonyl group, using a large excess of phosphine, heating to 45°, and UV initiation for 3 hours, gave no positive result.

As follows from the communication of Murdoch and Lunken (^{9}), removal of halide from allyliron tricarbonyliodide in the presence of certain complex anions, as well as electrolytic reduction, proceeds with formation of the dimer of allyliron tricarbonyl, which is readily cleaved at the Fe—Fe bond, giving the paramagnetic particle $C_3H_5Fe(CO)_3$. We removed iodine from $C_3H_5Fe(CO)_3J$ by the action of $AgNO_3$ in nitromethane with the addition of a minimal amount of methyl alcohol in an inert atmosphere. The reaction proceeds instantaneously at room temperature. After separation of AgJ, the filtrate was evaporated at 50 mm, the residue was rapidly washed with a small amount of water and dried in vacuum. In this way allyliron tricarbonyl nitrate was obtained, yield 50%. It is a yellow crystalline substance, resistant to oxidation, soluble in nitromethane and liquid SO_2, less soluble in acetone, $CHCl_3$, and ether. Hydroxyl-containing solvents rapidly decompose it. The mechanism and prod-

decomposition in solutions are being studied by us. The nitrate is thermally unstable; it decomposes and burns with an explosion. Under the action of KI, the starting iodide complex is readily obtained from it. The nitrate is diamagnetic; in the carbonyl region of the IR spectrum it has only two bands, which indicates a high symmetry of the molecule in comparison with the starting iodide and, apparently, the ionic character of the bond with the nitrate group. The NMR spectrum of the nitrate has no additional lines in the high-field region, but in

Table 2

IR and NMR spectra and magnetic susceptibility

Substance	IR, cm^{-1}*	IR, cm^{-1}*	IR, cm^{-1}*	NMR, δ** H_A	NMR, δ** H_B	NMR, δ** H_C	$\chi_{sp} \cdot 10^{-6}$****
$C_3H_5Fe(CO)_3J$	2012	2033	2083	6.0	4.2	3.76	−0.4 (22°), −0.2 (−195°)
$C_3H_5Fe(CO)_3Br$	2016	2047	2090	4.85	4.3	3.4	—
$C_3H_5Fe(CO)_3Cl$	2012	2048	2095	5.1	4.57	3.19	—
2-$BrC_3H_4Fe(CO)_3Br$	2020	2049	2092	—	4.6	3.9	—
$C_3H_5Fe(CO)_3NO_3$***	—	2030	2100	5.63	4.81	2.68	−0.3 (22°)

* IKS-14, vaseline oil; ** TsLA-5535, 40 MHz, CCl_4, $(CH_3)_4Si$; *** $CHCl_3$, $(CH_3)_4Si$; **** χ does not depend on field strength in the interval 2000–4500 Oe; there are no EPR signals. The magnetic susceptibility was measured by A. A. Slinkin, to whom the authors express their gratitude.

the remaining respects it is quite analogous to the spectra of the other complexes obtained.

Our attempts to carry out certain electrophilic substitution reactions in the π-allyl ligand ended in failure. Thus, acylation in the presence of various catalysts and nitration with acetyl nitrate did not proceed. In these experiments, the starting substance was recovered to a greater or lesser extent. On an attempt at mercuration with mercury acetate, complete decomposition occurred and iron acetate and allylmercury iodide, m.p. 114-116° (decomp.), were obtained.

Found, %: C 10.19; 9.84; H 1.49; 1.39; Hg 54.10; 54.84; J 34.12; 34.6
C_3H_5HgJ. Calculated, %: C 9.78; H 1.40; Hg 54.46; J 34.45

It remains an open question what accounts for the inertness of the π-allyl ligand in electrophilic substitution reactions: whether this is a consequence of the deactivating influence of electronegative neighbors or of the inability of the noncyclic delocalized system to undergo aromatic substitution.

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Note: Figure translations are in progress. See original paper for figures.