ON THE   α-CARBENIUM CENTRE STABILIZATION IN OLEFIN IRON   CARBONYL COMPLEXES. REALIZATION OF OLEFIN AND ALLYL STRUCTURES

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Abstract - For ironcarbonyl complexes with cationic allyl ligands($>C=C-\overset{+}{C}-R$), it has been shown that the relative contributions of olefin and allyl structures depend on the nature of the substituent R. A new case of tautomerism and a $\pi \rightarrow \sigma$ (N) rearrangement were detected during this investigation. The problem of realization of olefin and allyl structures was also studied by means of the reaction between $Fe_2(CO)_9$ and vinyl derivatives of heteroelement compounds ($RCH=CHELnLm$).

INTRODUCTION

The problem concerning the mechanism by which the carbenium centre located in the α-position relative to the π-bonding of organometallic fragment is stabilized, arose as a consequence of the "anomalously" high solvolysis rate measured for methylferrocenylcarbinyl acetate (Ref. 1).

This gave rise to a lengthy discussion among researchers working in this area, and two general concepts were formulated. One group of investigators considers that the stabilization of the carbenium centre achieved by its direct interaction with a metal forming a $M-C_\alpha$ bond is most important. The other group adheres to the opinion that the principal role in this stabilization is played by the organometallic fragments as a whole and by electrons being supplied to the carbenium centre from the metal via a ligand (i.e., insignificant direct interaction).

These problems also proved to be pertinent to α-carbenium ions bonded with other π-complex systems (Refs.3-10), illustrated below together with the ferrocenyl systems (1)-(4):

(1)   (2)   (3)   (4)
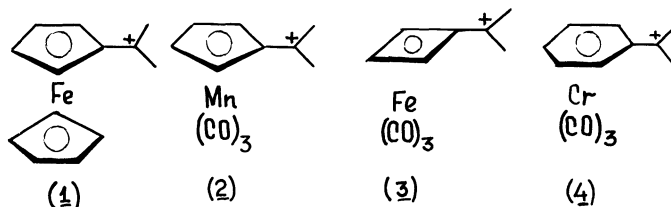
The mechanism of carbenium centre stabilization in these systems has been studied with the help of various spectral methods, which, since they are indirect methods, could not produce an unambiguous answer. At the same time, the direct method of X-ray analysis has been successfully applied only in the case of a few examples. Consequently, there is no unanimous point of view at present on the mechanism of carbenium centre stabilization in such systems.

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TECTION OF A NEW CASE OF TAUTOMERISM AND $\pi \rightarrow \sigma$ REARRANGEMENT.

This problem is also significant today with reference to more simple systems such as
as monoolefin complexes. In this case it is natural   to pose the question:
under what conditions can olefin and allyl structures of types (5) and (6),
differing from each other by the presence of a metal-C_α valent interaction,
be realized?

In order to provide an answer to this question we studied the α-carbenium
centre stabilization of the π-olefin iron carbonyl complexes, Ref. 11.
                    From the literature data (Refs.I2-I5) it was known
that cationic allyl complexes of type (6) were obtained by protonating the
corresponding 1,2- and 1,3-diene iron carbonyl complexes. Their structures ha-
ve been assigned by IR and NMR spectra. Since the cationic olefin compounds of
(5) were unknown, it was of interest to study the synthesis of such
compounds.   Analyzing the causes that could account for the exis-
tence of structures (5) and (6), one would naturally assume that the mechanism
of stabilization of the carbenium centre must depend on the nature of the sub-
stituents R at C_α in particular, on their electron donating capability.
From (Refs.I2-I5) it follows that the presence of alkyl and aryl substituents
 at this centre leads to the formation of allyl structure (6). To arrive at
olefin structures of type (5), it was necessary to use more electron donating
groups, such as amino-groups. In order to synthesize the model compounds we
used the irontetracarbonyl π -complexes of α,β -unsaturated amides. By al-
kylating the complexes with triethyloxonium tetrafluoroborate, we obtained
stable cations (7). By reacting complexes (7) with equimolecular quantities of
amines it was possible to transform them into stable cations (8) (Refs.II,I6):

The observed
pKa of =7.49 for the cation $PhCH=CH-C\begin{smallmatrix}OEt\\+\\NH_2\end{smallmatrix}$ (H_2O + I% CH_3CN, 25°C) (Ref. I7)
$Fe(CO)_4$

can be indicative of this type of cation stability.

The resulting cations (7) and (8) were confirmed to be of olefin structures
on the basis of IR and NMR (^{1}H,^{13}C) spectra (Ref. I8). The most informative ^{13}C
NMR spectra (Table I) will be discussed later.   While both our data on ca-
tionic olefin complexes and those from the literature on allyl cations (Refs.
I2-I5) were not corroborated by direct X-ray analysis, we did obtain an X-ray
of a subsequent reaction product. Investigating the possibility of preparing
amidines (9), we used a considerable excess of amine in reaction with 8 and
instead of the expected compound (9) we obtained a chelate complex (10), which
can be formed as a result of an intramolecular attack of the imine-group of the
intermediate (9) on the carbonyl ligand, (Refs. 16, 18).

$$R'CH{=}CH{-}C\underset{OEt}{\overset{R}{\lessgtr}}{+} \xrightarrow{\ NH_2R''\ } R'CH{=}CH{-}\underset{(CO)_4Fe\ (8)\ NHR''}{C{=}R}{+}\xrightarrow{\ NH_2R''\ }$$

$$\xrightarrow{\quad} \underset{(CO)_3Fe\diagdown_{CO}}{R'{-}CH{=}CH{-}C{-}R}\ \underset{NR''}{\overset{\|}{}}\ (\underline{9}) \xrightarrow{\quad} (CO)_3Fe\diagdown_{C}^{R'{-}CH{=}CH{-}C{=}R}\underset{O}{\overset{NR''}{+}}(\underline{10})$$

$$R = NMe_2,\ N\bigcirc\ ;\ \ R' = H, Ph;\ \ R'' = H, Me$$

The structure of the resultant compound as a chelate π-olefin complexes is consistent with the spectral data (see ^{13}C NMR spectra, Table I) and was supported by X-ray analysis of compound (<u>IO</u>, R=R"=Me, R'=H). According to these data (Fig.1) the distance from the iron atom to $C\alpha$ is 2.73Å, which is significantly greater than the sum of iron and carbon covalent radii (2.04Å) (Refs. I9,20), whereas the Fe-$C_{(I)}$ and Fe-$C_{(2)}$ distances are 2.05 and 2.02Å, respectively.

Fig.1. Molecular structure of complex (<u>1O</u>, R=R"=Me, R'=H).

The zwitterionic character of these compounds is in accordance with their facility for alkylation, forming cationic   chelate carbene complexes (<u>11</u>) (Ref.I6)   which, according to X-ray analysis data (Fig.2)   also reveal an olefin structure   (Ref.2I):

$$R'-CH=CH-C \rightleftharpoons R$$

(CO)$_3$Fe, N-R" (10)

$$\xrightarrow{Et_3\overset{+}{O}BF_4^-}$$

$$R'-CH=CH-C \rightleftharpoons R$$

(CO)$_3$Fe—C, N-R"

OEt (11)

From among the spectral data, the ^{13}C NMR assignments (Ref.18) (Table 1) were found to be the most informative with respect to the structure of complexes (7),(8),(10) and (11). The Cα atom signal ($\delta \approx$ 170-180 p.p.m.) is markedly shifted downfield as compared to the C$_{(1)}$ and C$_{(2)}$ atom signals ($\delta \approx$ 30-40

p.p.m.) and is located in the region characteristic of carbenium ions (Ref. 22). The validity of the assignment of structures (7) and (8) to π-olefin complexes is confirmed by the similarity of their ^{13}C NMR spectra to those of chelate complexes (10) and (11), whose olefinic structure has been unambiguously proved by X-ray analysis. For comparison we can note that the signals for the allyl carbon atoms in cationic complexes of type (6) are located in the region of $\delta \approx$ 50-100 p.p.m. (Table 2), which is in good agreement with literature data (Ref.23). Thus, the dialkylamine groups contribute to the stability of the olefin structure not only in the case of non-ring systems, but also for chelate complexes where, one would think the cyclic structure must promote the formation of the valence bond Fe-C$_\alpha$.

Fig.2. Molecural structure of complex (11, R$_2$=N(CH$_2$)$_5$,R'=H,R"=Me)

It would be appropriate to mention here, that in accordance with the calculations of cations A and B made by HET and CNDO/2 methods (by D.A.Bochvar, E.G.Galpern and N.P.Gambaryan) the positive charge is localized almost equally at the carbon and nitrogen atoms.   Thus, it is believed that the olefin

$$CH_2=CH-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-NH_2 \quad (A) \qquad\qquad CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-NH_2 \quad (B)$$

structure is realized when one half of the positive charge is approximately localized at the C_α atom.

TABLE I. ^{13}C NMR spectra data of olefin complexes.

Complex	R	R'	R"	δ (CH$_2$Cl$_2$), p.p.m.		
				C$_{(1)}$	C$_{(2)}$	C$_\alpha$
(10)	Me	H	Me	31.80	34.13	178.83
	(CH$_2$)$_5$	H	Me	31.80	34.07	176.56
(11)	Me	H	Me	34.66	36.22	167.79
	(CH$_2$)$_5$	H	Me	34.72	36.02	165.13
(7)	Me	H	–	31.21	37.65	180.66
(8)	(CH$_2$)$_5$	H	Me	–*	–*	173.64
	**	–	–	36.41	36.41	180.33

*) The C$_{(1)}$ and C$_{(2)}$ signals overlap with carbon signals of the piperidine group.

**) In MeNO$_2$

The investigation of the chelate complexes was further carried on with the aim of   preparing   allyl compounds. This can be anticipated when less electrondonating substituents than those of the NAlk$_2$ groups, (e.g. Ph,H and Alk) are used.To prepare such chelate compounds we used BF$_3$-adducts of irontetra-carbonyl 𝜋-complexes of α,β -unsaturated ketones and cinnamaldehyde (Refs.24-26). In fact, the chalcone BF$_3$-adduct in reaction with an excess of primary amines afforded chelate compounds (12) having a 𝜋-allyl structure (12 R=R'=Ph) (Ref.24). The same result was obtained for a trans-dibenzoylethylene BF$_3$-adduct.

$$R'\!-CH\!=\!CH\!-\!\underset{\underset{O\,\underline{B}F_3}{||+}}{C}\!-\!R \quad \xrightarrow{2\,H_2NR''} \quad R' \diagup\!\!\!\diagdown\! R$$

R = R' = Ph ; R" = Me, i-Pr, C$_6$H$_{11}$;

R = Ph, R' = COPh ; R" = Me, i-Pr, C$_6$H$_{11}$

The structure of these compounds was confirmed by X-ray analysis of complex
(I2, R=R'=Ph, R"=C_6H_{11}) (Ref.24).

Fig.3. Molecular structure of complex (I2, R=R'=Ph, R"=C_6H_{11})

From X-ray data (Fig.3) it can be seen that a greater contribution of the al-
lyl structure is present in complex (I2, R=R'=Ph, R"=C_6H_{11}), because the dis-

tance Fe-Cα is equal to 2.235Å, and those of Fe-C$_{(I)}$ and Fe-C$_{(2)}$ to 2.180 and

2.089Å, respectively. The allyl structure of (I2) is also in agreement with

^{13}C NMR spectra data (Table 2). It was interesting to study the models with
substuents having intermediate electron donating properties,such as the hydro-
gen and alkyl groups. With this aim in view we used the BF_3-adduct of the
cinnamaldehyde-iron tetracarbonyl complex. But the results were

unexpected, and instead of the chelate complex (<u>10</u>) or (<u>12</u>) we obtained the N-donor ligand complexes (<u>13</u>), (Ref. 26):

$$R'-CH=CH-C\overset{R}{\underset{O\bar{B}F_3}{<_+^{\nwarrow}}} \quad + \; 2\,NH_2R'' \longrightarrow \quad R'-CH=CH-C\overset{R}{\underset{NR''}{<^{\nwarrow}}}$$

$$(CO)_4Fe \qquad\qquad\qquad\qquad\qquad (\underline{13}) \qquad \underset{Fe\,(CO)_4}{|}$$

$$R = H, \; R' = Ph, \; R'' = Me, \; i\text{-}Pr, \; C_6H_{11}, \; Ph$$
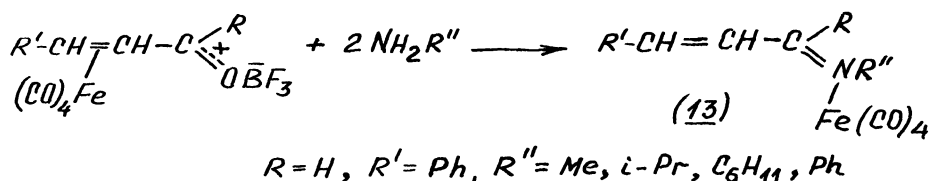
Their structure was confirmed by X-ray analysis of complex (<u>13</u>, R=H, R'=Ph, R"=Me) (Ref.26). The result of the X-ray analysis will be discussed below.

The behaviour of the cinnamaldehyde   complex in this reaction became much clearer after we studied the properties of the chelate complexes (<u>12</u>) which were obtained from BF_3-adducts of benzilidenacetone and benzilidenmethylethyl ketone irontetracarbonyl complexes using methylenechloride as the solvent (Ref.27). It turned out that this chelate allyl compounds (<u>12</u>, R=Me or Et, R'=Ph and R"=Me or Et) in solution underwent a rearrangement into N-donor ligand complexes (<u>13</u>). The rearrangement proceeded with great ease in hydrocarbon solvents (Ref. 27).

$$R'\overset{\displaystyle\frown}{\underset{\underset{\underset{O}{\parallel}}{(CO)_3Fe-C}}{\diagup}}\!\!R \quad\xrightarrow{\quad hexane \quad}\quad R'-CH=CH-C\overset{R}{\underset{NR''}{<^{\nwarrow}}}$$

$$(\underline{12}) \quad R=Me,Et; R'=Ph; \qquad (\underline{13}) \quad \underset{Fe\,(CO)_4}{|}$$
$$R''=Me, Et$$
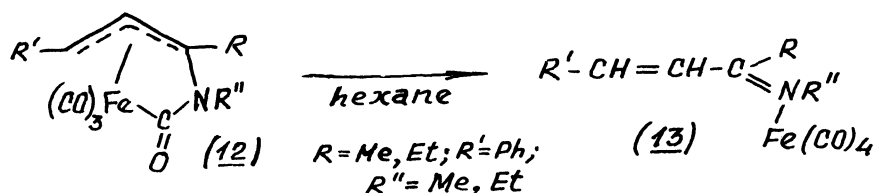
TABLE 2. ^{13}C NMR spectra data of allyl complexes.

Complex	R	R'	R"	δ^v (CH$_2$Cl$_2$), p.p.m.		
				$C_{(1)}$	$C_{(2)}$	C_α
	Me	Ph	Me	62.66	88.07	I03.62
	Me	Ph	C_6H_{11}	64.09	89.82	98.46
	Me	Ph	i-Pr	63.77	84.69	95.I5 *)
	Ph	Ph	Me	64.48	85.27	-**)
	Ph	Ph	C_6H_{11}	65,52	87.03	99.24
	H	H	H	56.80	99.24	56.80
	H	H	Me	56.5I	94.30	82.4I
	Me	H	Me	47.64	93.72	II5.68

*) At -70°C
**) The C_α signal is not seen because of the low concentration
***) In CF_3COOH (Ref,I5).

     The investigation of this phenonenon in hydrocarbon solvents (hexane,
cyclohexane) using IR spectra in the 2000 cm^{-1} region has shown the π → σ
rearrangement to proceed via intermediate olefin complexes (9), which exist
in equilibrium with the chelate allyl compounds (12). It should be noted
that the equilibrium was established very quickly whereas the π → σ (N)
rearrangement (9) → (13) occurred slowly. As a result we have discovered
a hitherto unknown ring-chain tautomerism* between the chelate π-allyl
complexes (12) and the noncyclic π-olefin complexes (9) and a new π → σ
rearrangement (9) → (13) with the migration of a Fe(CO)$_4$ fragment from the
C=C bond to the nitrogen atom.

The π→σ (N) rearrangement was prevented by using bulky alkyl substituents
R" at the nitrogen atom (Ref,27). This allowed us to establish the two tauto-
meric forms (12) and (9) in equilibrium (see Table 2) and to study the equi-
librium dependence on the nature of the solvent and the electronic and ste-
ric effects of substituents R,R' and R".

     As follows from Table 3, structure 12 has three absorption bands and
structure 9 has four bands (in hexane), one of which (ν = 2008 cm-1) is the
same for both structures. In the polar solvents (CH$_2$Cl$_2$, CHCl$_3$) not all the
bands are split. The quantitative relations of the tautomeric forms were
determined for complex (12, R=Me, R'=Ph, R"=C$_6$H$_{11}$), containing bulky cyclo-
hexyl substituents R" at the nitrogen atom, by optical density measurements
of the solutions at 2068 cm^{-1} for form 12 and at 2085 cm^{-1} for form 9 at 25°C.
The calculation was carried out according to (Ref. 31). It turned out that
when dissolved in hexane this complex (possessing a chelate allyl structure
in the solid state) produced tautomeric forms, consisting of 30% 12 and 70%
9. The addition of CH$_2$Cl$_2$ to the solution shifts the equilibrium towards 12,
which predominates over 9 in pure CH$_2$Cl$_2$ or CHCl$_3$ (90% 12 and 10% 9). It is
of interest to note that all attempts to isolate 9 yielded only crystals of
12. The IR control for the equilibrium state does not detect absorption
bands of ν ⋏ 2050,1970,1960,1940 cm^{-1} characteristic of σ (N) complex, Ref. 26.
Complexes 12 with R=Me, R'=H, R" = i-Pr and R'=Cl, R" = i-Pr, prepared from
methylvinylketone and methyl-β-chlorovinylketone complexes, proved to be less
stable; because of their poor stability we could not make a quantitative
study of the equilibrium. However, it was shown qualitatively that the non-
cyclic olefin forms 9 were predominant in these cases.
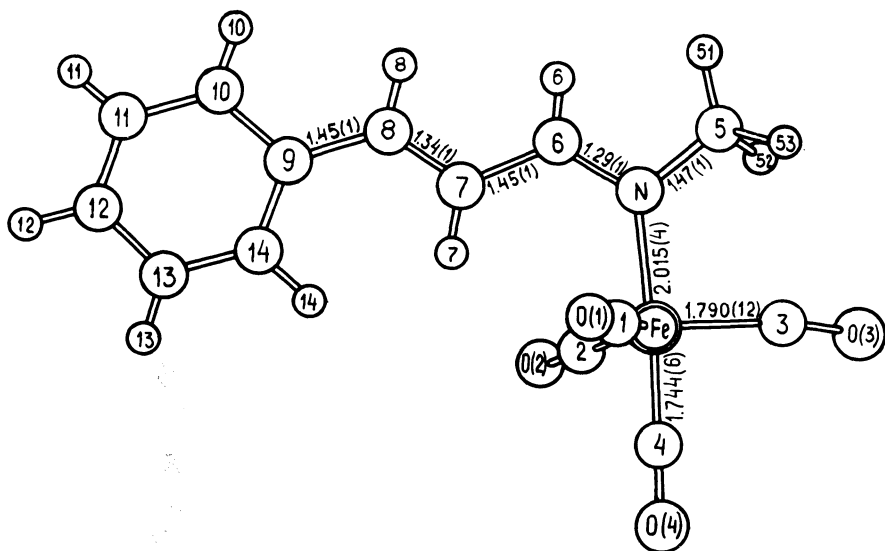
Fig.4. Molecular structure of complex (13, R=H,R'=Ph, R"=Me)

*) Here tautomerism denotes dynamic isomerization (Refs.28-30).

The $\pi \rightarrow \sigma$ (N) rearrangement in the case of the reaction of the cinnamalde-
hyde complex was also prevented by using t-butylamine. The isolated crystalli-
ne product (12, R=H, R'=Ph, R"=t-Bu) revealed a chelate allyl structure (in
the IR spectra in KBr the first band $\nu_{C \equiv O}$ is observed at 2070 cm^{-1} as well
as for all other chelate allyl compounds in crystals(see Table 3). But it is
interesting to note that the noncyclic form (9) prevails in solution not only
in hexane, but also in polar solvents (CH$_2$Cl$_2$ or CHCl$_3$). This may be due to
the steric hindrances of the t-Bu-substituent at the imine group.

We did not attempt to investigate the mechanism of the $\pi \rightarrow \sigma$ (N)
rearrangement, but one cannot exclude the possibility that this process is
intramolecular. This is consistent with the cis position of Fe(CO)$_4$ and
the PhCH=CH-groups, relative to the C=N bond as follows from the X-ray
analysis of the $\pi \rightarrow \sigma$ (N) rearrangement product (13, R=H, R'=Ph, R"=Me).

All the processes studies by us can be presented by the following general
scheme I.

<div align="center">Scheme I.</div>

TABLE 3.

$$\text{\textbackslash}C{=}O \qquad {(CO)_3}Fe{<}\!\!\genfrac{}{}{0}{}{R'\,R}{\,NR''}\!\!{>}_C^{} \ (12) \qquad and \qquad R'{-}CH{=}CH{-}C{<}_{NR''}^{R}\ (9)$$

$(CO)_4 Fe$
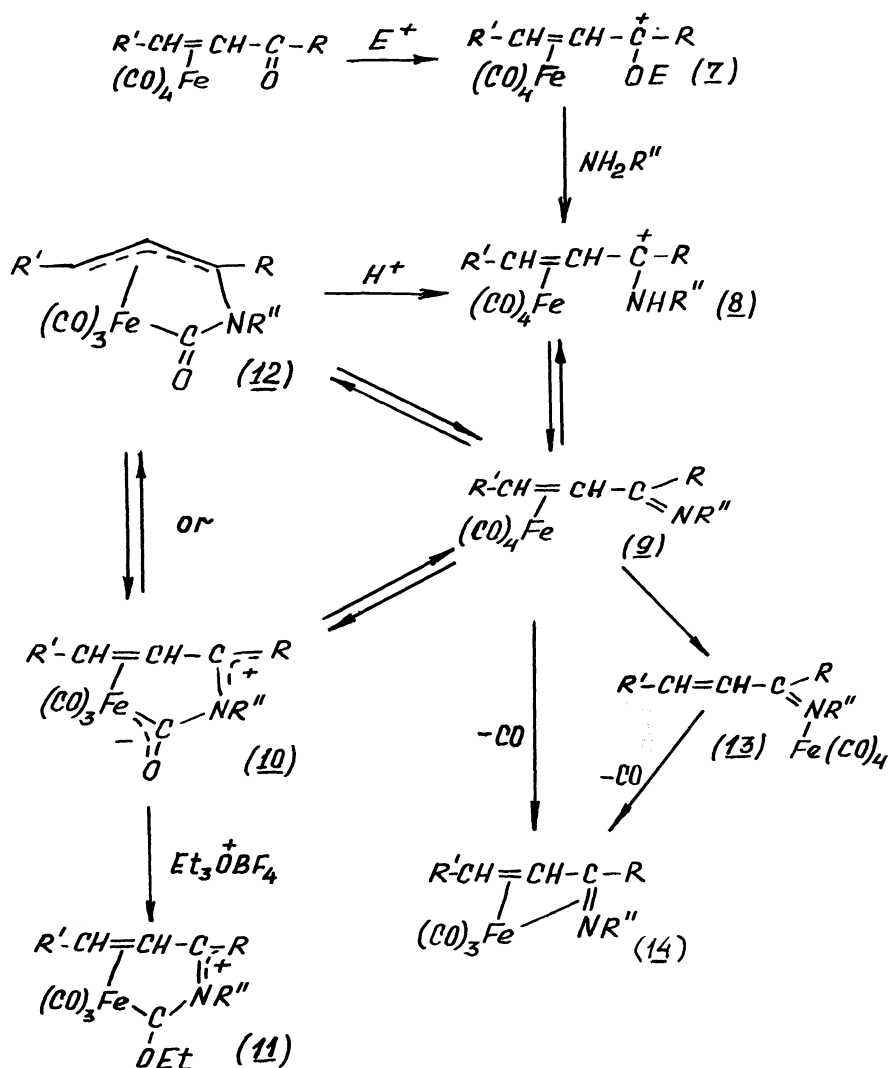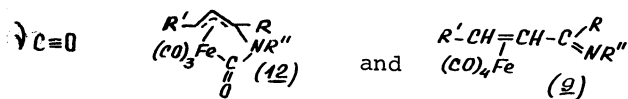
in solution and KBr.

R	R'	R''	Solvent (KBr)	ν C≡O cm^{-1} (12)	ν C≡O cm^{-1} (9)
Me	Ph	Me	hexane (KBr)	2068,2008,1991 2060,1990,(broad)	2085,2017,2008,1980
Me	Ph	C_6H_{11}	hexane (KBr)	2068,2008,1992 2065,1990,(broad)	2085,2017,2008,1980
Me	Ph	$PhCH_2$	hexane (KBr)	2068,2008,1992 2060,2010,1985	2085,2017,2008,1980
Me	Ph	i-Pr	hexane (KBr)	2068,2008,1993 2070,1990 (broad)	2085,2017,2008,1980
Me	Cl	i-Pr	hexane CH_2Cl_2	2078[*] 2078,1995 (broad)	2098,2028,2008,1995 2098[*]
Me	H	i-Pr	hexane CH_2Cl_2	2071[*] 2071,2010 (broad)	2088,2018,2009,1985 2088[*]
H	Ph	t-Bu	hexane CH_2Cl_2 (KBr)	2071[*] 2071[**] 2070,2000(broad)	2087,2018,2008,1987 2087[**]

[*] The other bands are overlapped by considerably more intensive bands of the other form.

[**] In the 2020-1980 cm^{-1} region there are unsplit bands with max. at 2008 cm^{-1}.

The possibility of a back transformation of σ (N) complexes (13) in the π-olefin iron tetracarbonyl complexes (9) (Refs.11,26) by consecutive treatment with a protonic acid (formation of cations 8) and bases was also included in scheme I. In addition, we included in this scheme the transformation of (13) and (9) into iron tricarbonyl complexes (14), which proceeded slower than the π σ (N) rearrangement (Ref.26). However, this process significantly complicated our investigation. It is important to note also that the chelate rings open quite easily after acid treatment. Therefore this method was used for the preparation of analytically pure cation salts (8). Summarizing the results of the investigation on α-carbenium centre stabilization, one can say that the structures of this type form something of a kind of continuum, the border positions of which are occupied by the allyl and olefin complexes; between them there are structures with different degrees of metal and C_α interactions (Ref.11). In the case of chelate complexes the olefin complexes 10, R=NAlk$_2$) and the allyl complexes (12, R=Ph) are related to the border compounds. The intermediate compounds with R=H and Alk possessing comparatively weak C-N and Fe-C$_\alpha$ bonds show tautomeric properties in solu-
O
tions. It is important to note, that in the case of chelate compounds the tautomerism phenomenon observed by spectral methods is connected with the formation and cleavage of the C-N bond. These processes go on considerably
O
slower than the formation and cleavage of the Fe-C$_\alpha$ bond, otherwise the tautomerism would be also fixed for noncyclic systems, but this was not the case (Ref.15). Therefore the former process should be related to the ring-chain tautomerism, the latter - to valence tautomerism.

REALIZATION OF OLEFIN AND HETEROALLYL STRUCTURES BY REACTION

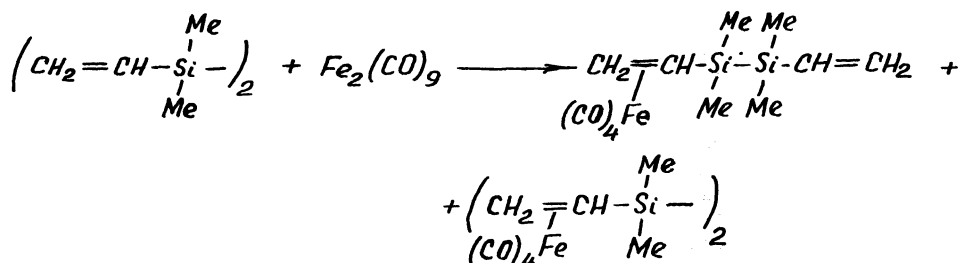OF CERTAIN VINYL-DERIVATIVES WITH $Fe_2(CO)_9$

The investigation of olefin and allyl structure realization was continued by us using heteroanalogs of allyl compounds as the ligands, such as RCH=CHELnLm. It was especially interesting to study the behaviour of a silicon-con taining analog of allyl chloride towards $Fe_2(CO)_9$.   It appeared that vinyldimethylchlorosilane as distinct from allyl chloride does not form a π-allyl, but a usual π-olefin irontetracarbonyl complex. Trimethyl- and trimethoxyvinylsilanes reveal the same behaviour in the analogous reactions, Ref. 32.

$$CH_2=CH-SiR_2R' + Fe_2(CO)_9 \longrightarrow \underset{\underset{Fe(CO)_4}{|}}{CH_2 = CH-SiR_2R'}$$

$$R=Me, R'=Ce \ ; \ R=R'=Me, OMe$$
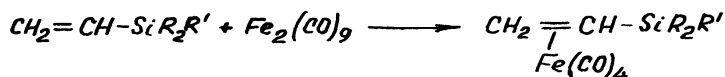
Tetravinylsilane along with its monoiron tetracarbonyl derivative forms a number of products containing $Fe(CO)_4$ and $Fe(CO)_3$ groups, the most interesting complex is $(CH_2=CH)_4Si(Fe(CO)_3)_2$, Ref. 32 which contains an unconjugated 1,4-diene ligand.   This compound is formed as a single product upon UV-irradiation of the monotetracarbonyl π-olefin complex in the presence of $Fe(CO)_5$. Its structure was confirmed by X-ray analysis (Ref.33).

$$(CH_2=CH)_3 \underset{(CO)_4Fe}{Si} CH=CH_2 \xrightarrow[h\nu]{Fe(CO)_5} \ \ (CO)_3Fe\underset{CH_2=CH}{\overset{CH_2=CH}{<}} Si \underset{CH=CH_2}{\overset{CH=CH_2}{>}} Fe(CO)_3$$
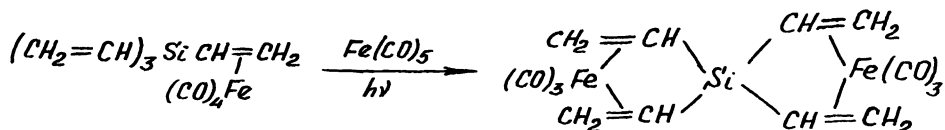
In connection with the fact that vinyldimethylchlorosilane did not yield a π-silaallyl complex even in the presence of anion chloride coordinating agents, we repeated the work of japanese investigators who studied the inter-action of vinyldisilanes with $Fe_2(CO)_9$ (Refs.34,35). We arrived at the conclu-sion, simultaneously with US scientists (Ref.36) that in this case ordinary π-olefin irontetracarbonyl rather than π-silaallyl complexes are formed, Ref. 37:

$$\left(CH_2=CH-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}- \right)_2 + Fe_2(CO)_9 \longrightarrow \underset{(CO)_4Fe}{\overset{}{CH_2}}=CH-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}-CH=CH_2 +$$

$$+ \left(\underset{(CO)_4Fe}{CH_2}=CH-\underset{Me}{\overset{Me}{\underset{|}{\overset{|}{Si}}}}- \right)_2$$

Thus, unlike its carbon neighbour the silicon did not form a π-silaallyl li-gand in any of the cases studied by us.

At the same time when studying the problem of σ-vinyl complexes of transition metals, we were able to show that the complexes of both π-ole-fin and π-heteroallyl structures can be realized, depending on the nature of the metal (Ref.38). Thus, in the case of σ'-RCOCH=CHRe(CO)$_5$ compounds only π-olefin complexes are formed (Ref.39):
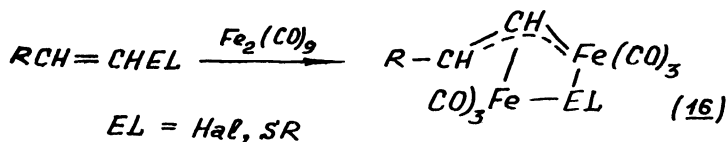
$$RCOCH=CHRe(CO)_5 + Fe_2(CO)_9 \longrightarrow \underset{\underset{Fe(CO)_4}{|}}{RCOCH = CHRe(CO)_5}$$
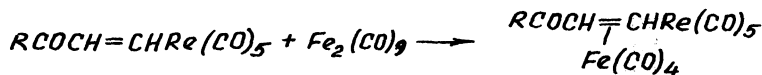
whereas in the case of $RCOCH=CHW(CO)_3C_5H_5$ compounds, π-complexes of both types as well as irontricarbonyl compounds (15) are formed (Refs.40,4I):

$$RCOCH=CH-W(CO)_3\,C_5H_5 \xrightarrow{\ Fe_2(CO)_9\ } RCOCH\!=\!CH-W(CO)_3\,C_5H_5\ +$$
$$\underset{Fe(CO)_4}{\big|}$$

$$+\ RCO-CH\overset{CH}{\diagdown}\!\!\!\!\diagdown W(CO)_2\,C_5H_5 \qquad\qquad RC-CH\!=\!CH-W(CO)_3C_5H_5$$
$$(CO)_3Fe-C\!\approx\!O \qquad +\quad \overset{\parallel}{O}\!\!-\!\!Fe(CO)_3 \qquad (\underline{15})$$
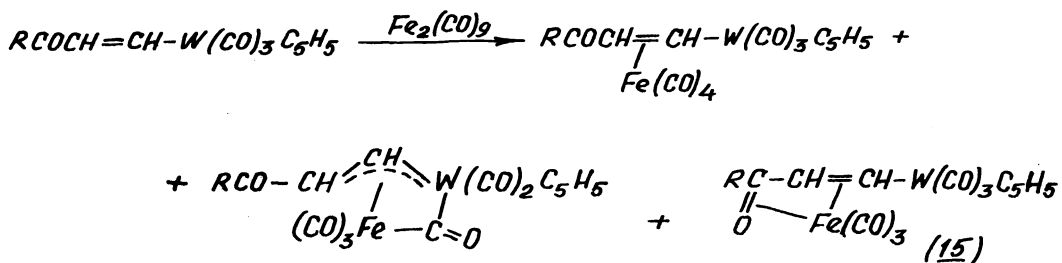
Similar σ-$RCH=CH-Fe(CO)_2C_5H_5$ compounds yielded only ferraallyl complexes (Refs.42,43). The structure of these compounds was confirmed by X-ray analysis (Ref.44).

$$RCH=CH-Fe(CO)_2\,C_5H_5 \xrightarrow{\ Fe_2(CO)_9\ } R-CH\overset{CH}{\diagdown}\!\!\!\!\diagdown Fe(CO)\,C_5H_5$$
$$(CO)_3Fe-CO$$

$$R = H,\ Ph,\ MeCO,\ PhCO$$
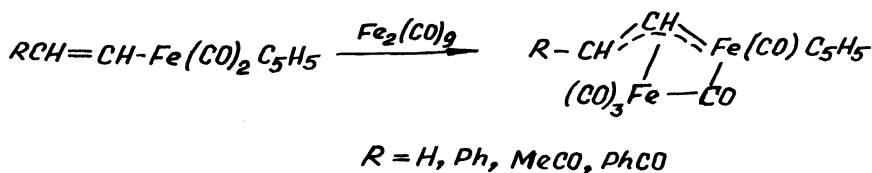
Similar complexes of type (16) with RS- and Hal- bridges were obtained on the basis vinylsulphides (Ref.45) and vinylhalogens (Ref.46). On the basis of X-ray analysis the authors of (Ref.46) suggested that these compounds be considered as complexes having a ferraallyl ligand.

$$RCH=CHEL \xrightarrow{\ Fe_2(CO)_9\ } R-CH\overset{CH}{\diagdown}\!\!\!\!\diagdown Fe(CO)_3$$
$$CO)_3Fe-EL \qquad (\underline{16})$$

$$EL = Hal,\ SR$$

Thus, the examples under study showed the structure type to be dependent on the nature of the heteroatom and on the ligands surrounding it (see scheme 2).

<div align="center">Scheme 2</div>

$$\begin{array}{c} ELnL'_m = SiR_3,\\ SiR_2Cl,\\ SiMe_2SiMe_2Vin,\\ Re(CO)_5,\\ W(CO)_3C_5H_5 \end{array}$$

$$\begin{array}{c}C=C\\ (CO)_4Fe\end{array}ELnL'_m$$

$$\begin{array}{c}C=C\\ ELnL'_m\end{array} + Fe_2(CO)_9 \longrightarrow$$

$$\begin{array}{c} ELnL'_{m-1}\\ (CO)_3Fe-L'\quad ELnL'_m=Fe(CO)_2C_5H_5,\\ W(CO)_3C_5H_5 \end{array}$$
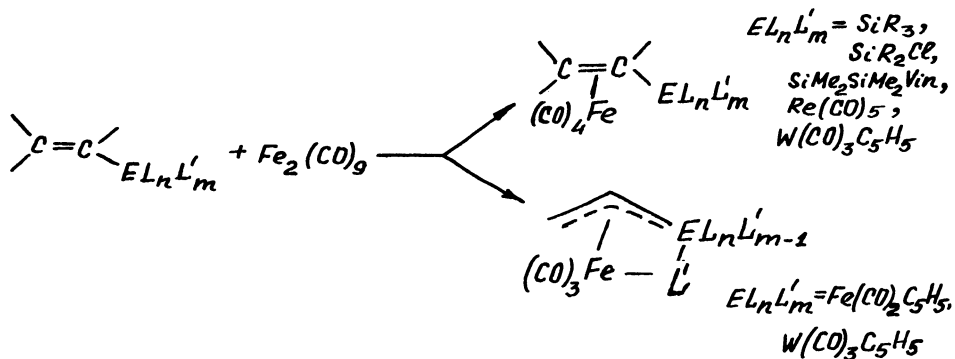
It should be noted that from among the transition metals used by us, the iron atom enters the ligand most readily. In this connection it should be added that complexes ($\underline{17}$) containing a ferrabutadiene ligand were obtained by different routes (see scheme 3) from derivatives of α, β -unsaturated amides and β-aminovinylketones isomeric to them (Refs.47,48).

Scheme 3.

$R'-CH=CH-C \overset{\nearrow O}{\underset{\searrow NR_2}{}} + Et_3\overset{+}{O}BF_4^-$
$R=Me,Et$
$R'=H,Me,Ph$

$R'-COCH=CH-NMe_2 + Et_3\overset{+}{O}BF_4^-$
$R'=Ph$

$R'-CH=CH-\overset{+}{\underset{OEt}{C}}-NR_2$
$R=Ph, R'=H,$

$R'-\overset{+}{\underset{OEt}{C}}-CH=CHNMe_2$
$R'=Ph$

$Fe_3(CO)_{12}$

$R'-CH=CH-\overset{+}{\underset{OEt}{C}}-NR_2$
$(CO)_4Fe$ $R'=Me, R=H$

(structure of complex 17 in center with $(CO)_3Fe$, $Fe(CO)_3$, R', R_2N, $(\underline{17})$)
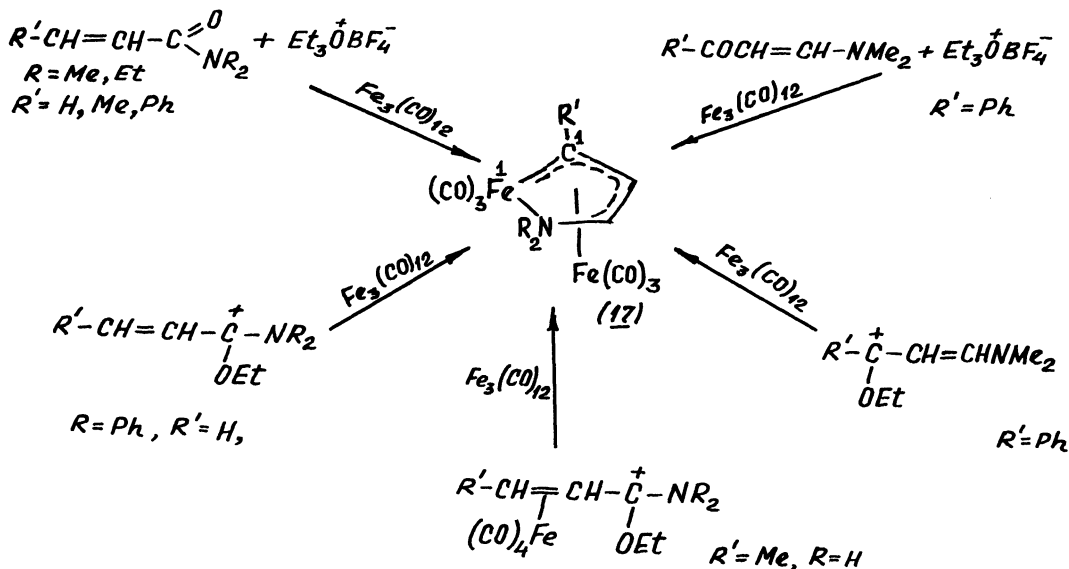
.X-ray analysis of complex ($\underline{17}$, R=Me, R'=H) (Fig.5) not only confirmed its structure, but also showed the $Fe_{(1)}-C_{(1)}$ bond to be slightly shorter (I.95Å) in comparison with the usual Fe-C bond (Ref.46).
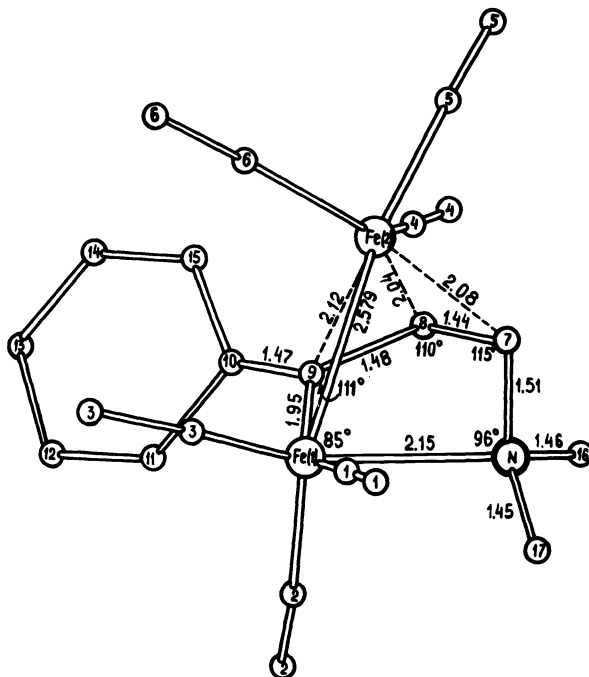
Fig.5. Molecular structure of complex ($\underline{17}$, R=Me,R'=H)

Thus, the irontricarbonyl group involved in a $\mathscr{K}$-bonded ligand is also to substitute Hal, SR, OEt and H.

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