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Iron-subgroup metal carbonyls in reactions with olefins having functional group substituents

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Abstract. The review covers the results of studies on the reactions of iron, ruthenium, and osmium carbonyls with olefins having functional group substituents, the behaviour of which differs significantly from that of simple olefins. Such studies have made it possible to create a new aspect of the chemistry of olefin complexes. The development of this field has led to the synthesis of previously unknown mononuclear and polynuclear complexes and to the discovery of unusual rearrangements of the complex compounds. The reactions of iron carbonyls differ from those of ruthenium and osmium carbonyls. In the last case, the hapticity of the unsaturated ligands increases and the ligands are found to be capable of giving rise to extremely unexpected structures. The present review surveys mainly the results of studies by the authors, who made a significant contribution to the development of this field. The bibliography includes 73 references.

I. Introduction

η^2-Olefin complexes occupy a special position in the chemistry of organometallic compounds of transition metals as the simplest compounds with a metal–organic ligand π-bond. They have served as a model for the development of the theory of the π-complex linkage. Furthermore, they are key intermediates in the catalytic reactions of olefins in the presence of transition metal compounds. Studies on such complexes have promoted the development of ideas about the mechanisms of catalytic hydrogenation, isomerisation, carbonylation, oligomerisation, and polymerisation of olefins. The chemistry of olefin complexes has therefore attracted for many years the attention of investigators.[1, 2] However, attention has been concentrated on the study of the properties of the complexes with ethylene and its homologues and to a lesser extent the complexes with olefins containing functional group substituents.

In the course of a number of years, we have carried out systematic studies on the thermal reactions of iron carbonyls with olefins having functional group substituents XCH=CHY and showed that the electronic nature of the substituents influences significantly the course of the reactions and the formation of the complexes $Fe(CO)_4$ (η^2-olefin).

These investigations have also shown that the coordination of an olefin to the $Fe(CO)_4$ group increases the electron density at the double bonds and the functional group adjoining it. The chemical reactions of these groups in the complexes have been used successfully to achieve the transition from η^2-olefin compounds to η^3-allyl or η^3-elementaallyl compounds, which made it possible to develop methods of synthesis of previously unknown organoiron compounds and also to discover and investigate new types of haptotropic rearrangements.

In order to deduce the general pattern for all the iron-subgroup metals, we included in the reactions with olefins having functional group substituents also ruthenium and osmium carbonyls. It was found as a result that, in contrast to iron carbonyls, which readily form the mononuclear complexes $Fe(CO)_4$ (η^2-olefin), the less reactive ruthenium and osmium carbonyls react with α,β-unsaturated ketones and esters under severe thermal conditions to form polynuclear compounds. The reactions proceed non-selectively and frequently lead to multicomponent mixtures which are difficult to separate. The elucidation of the structures of the complexes formed proved to be extremely useful, because it throws light on the possibility of the coordination of a polymetallic fragment to the organic ligand. The ligand in the sphere of the polynuclear fragment not only undergoes an increase in its hapticity compared with the mononuclear complexes but also proves capable of giving rise to different and frequently unexpected structures.

The data obtained are of interest for the understanding of the mechanisms of catalysis on clusters and, what is particularly important, heterogeneous catalysis on metallic surfaces.

II. η^2-Olefin complexes of iron carbonyls. Synthesis and properties

1. Interaction of iron carbonyls with substituted olefins

β-Substituted unsaturated ketones, acids and their derivatives[3–17] as well as the vinyl compounds of transition metals, silicon, and germanium,[18–29] have been used in the reactions with iron carbonyls as mono- and di-substituted olefins: XCH=CHY, where X and (or) Y = COR, COOH, COOR, COCl, COF, CONRR′, C(=NR)OEt, $C^+(OEt)NR_2$, CONHNHR, CONRNR′CO, $CON^-N^+R_3$, Cl, I, SPh, SO_2R, NR_2, NO_2, CF_3, SiRR′R″, $GeRR'_2$, $CpFeC_5H_4$, $Fe(CO)_2Cp$, $W(CO)_3Cp$, $Re(CO)_5$, etc.

The majority of these mono- and disubstituted olefins form η^2-olefin complexes:

$$XCH{=}CHY + Fe_2(CO)_9 \longrightarrow Fe(CO)_4(\eta^2\text{-}CHX{=}CHY)\,.$$

In certain cases, the substituents at the double bond can influence significantly the mode of these reactions and the nature of the products formed. It has been established[8] that, depending on the electronic effects of the substituent X, the unsaturated

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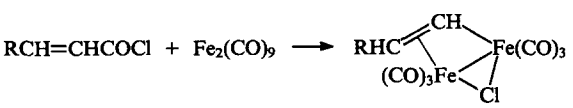
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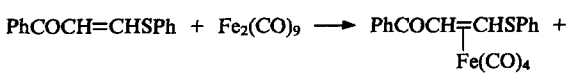
ketones RCOCH=CHX can give rise to qualitatively different results in reactions with iron carbonyls. When the substituent X is a strong electron-donating group, for example, the amino-group, a π-complex is not formed. When there are two strong electron-accepting groups at the double bond, as happens, for example, in β-nitrovinyl ketone, the reaction with iron carbonyls proceeds extremely vigorously but a polymeric product is formed. Vinyl ketones having substituents with stronger electron-donating or electron-accepting properties (X = Cl, H, COOR, etc.) form olefin complexes.

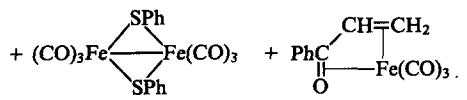
Such differences are determined by the difference between the energies of the lowest unoccupied π* orbital of the olefin and the 3*d* and 4*s* orbitals of iron. According to calculated data,[8] the unoccupied π* orbital is highest in amonovinyl ketone. For this reason, the formation of a π-complex by the latter is unlikely. The lowest orbital occurs in nitrovinyl ketone and in this instance there is a possibility of complete electron transfer from the metal to the ligand with subsequent polymerisation of the latter.

The energy of the π* orbitals in β-chlorovinyl ketone occupies an intermediate position, which ensures adequate reverse electron donation from the metal to the ligand and hence permits the formation of a stable π-bond.

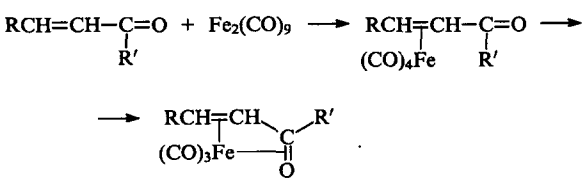
Certain substituents complicate the synthesis of η^2-olefin complexes by participating in reactions with iron carbonyls, for example:[14, 30]





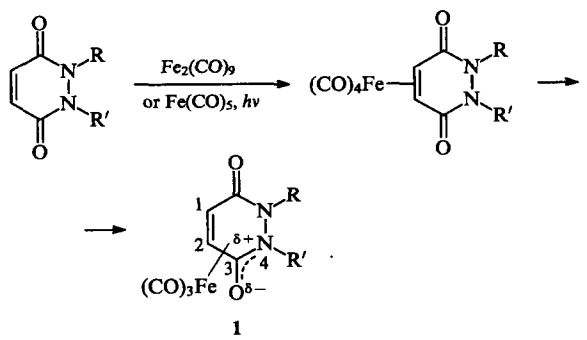


If the substituted olefins contain a heterodiene bond system, there is a possibility of the formation of heterodiene tricarbonyl complexes as a result of the $\eta^2 \rightarrow \eta^4$ transition in the initial η^2-olefin complexes:[5-9, 11, 31]



$\eta^2 \rightarrow \eta^4$ transition of this type have been observed also by other investigators.[32-34]

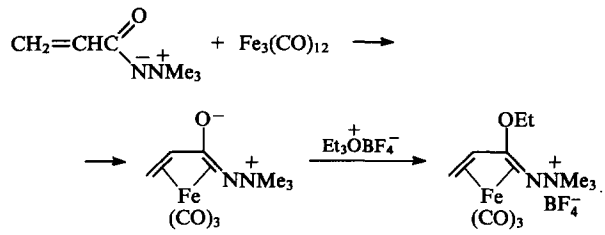
In the study of the reactions of unsaturated acid amides and related compounds with iron carbonyls, the possibility of the coordination of the metal to the amide fragment in the unsaturated ligand was demonstrated for the first time.[15] This was established unambiguously in the study of the reactions of cyclic maleic acid hydrazides with iron carbonyls.[17]



1

The structure of the η^4-complexes **1** was established by X-ray diffraction. The iron atom in complex **1** is linked to four neighbouring C(1), C(2), C(3), and N(4) ring atoms, i.e. the maleic acid hydrazide can be regarded as an azadiene ligand.

A stable η^4-complex of the azadiene type was also obtained for an open-chain compound, namely for the acrylic acid aminoimide.[15]



The interaction of the unsaturated acid amides themselves with iron carbonyls results in the formation, together with the complexes $Fe(CO)_4(\eta^2\text{-RCH=CHCONR'R''})$ as the main product of extremely unstable iron tricarbonyl compounds which can be characterised only with the aid of IR spectra. On the basis of the analogy between unsaturated amides, on the one hand, and maleic hydrazides and acrylic acid aminoimide on the other, one can postulate that the unstable $Fe(CO)_3$ complexes of unsaturated amides also have the η^4-azadiene structure. This hypothesis agrees with calculated data.[15]

2. The change in the properties of substituted olefins on π-coordination to zerovalent iron

Coordination to the iron carbonyl group entails significant changes in the electronic state, structural parameters, and reactivity of the η^2-olefin ligand with functional group substituents.

X-Ray diffraction study[35] of the complex $Fe(CO)_4$ (η^2-PhCOCH=CHCOPh) demonstrated a significant increase in the length of the coordinated double bond to 1.47 Å and a decrease in the bond angles of the olefinic carbon atoms by 5°–6° (Fig. 1). These structural changes indicate a decrease in the order of the double bond and partial sp^2-sp^3-rehybridisation of the olefinic carbon atoms, which is probably a result of the significant back-donation of electrons from the metal to the ligand in such complexes. A similar conclusion can be arrived at by analysing the spectroscopic data for the complexes $Fe(CO)_4$ (η^2-XCH=CHY).

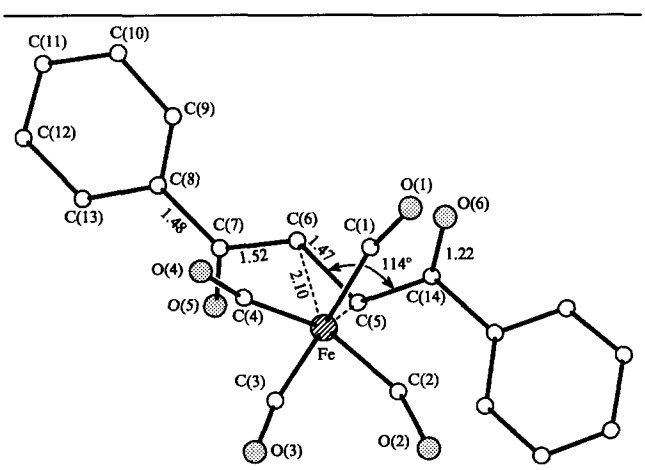
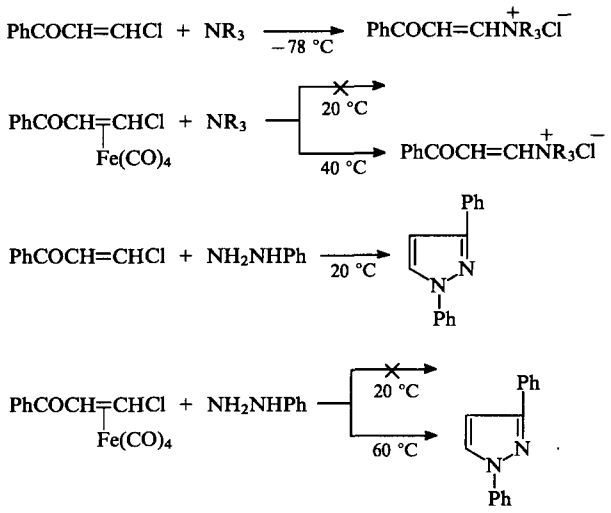


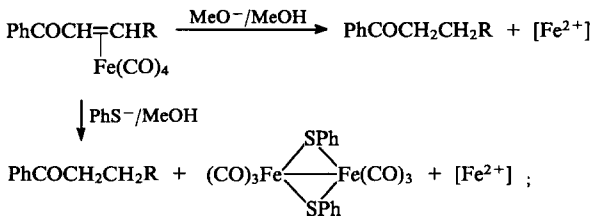
Figure 1. The structure of the $Fe(CO)_4(\eta^2\text{-PhCOCH=CHCOPh})$ molecule.

Such changes are reflected in the chemical properties of the olefin ligand and are manifested by a decrease in the electrophilicity of the double bond and of the functional groups in the ligand. For example, β-chlorovinyl ketones are known to react readily with nitrogen-containing bases,[36, 37] but their $Fe(CO)_4$ complexes are resistant under mild conditions to the action of these nucleophiles and the iron–olefin bond is ruptured only on heating.[16]



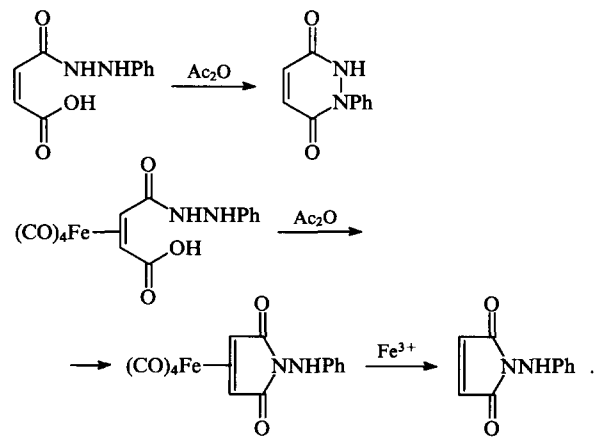
The cleavage of the π-bond accompanied by the reduction of the unsaturated ligand on treatment of stable olefin complexes with anionic nucleophiles has been observed.[30, 31]

Free β-substituted vinyl ketones combine with nucleophiles under these conditions.[38]



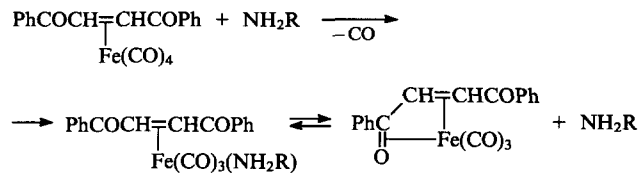
R = COPh, COOMe.

The change in the chemical properties of the unsaturated ligand on coordination to the $Fe(CO)_4$ group is manifested in the cyclisation of β-carboxyacryloylhydrazines: in the case of the substitution of the free olefin, six-membered rings are formed, whilst in the case of its $Fe(CO)_4$ complex the products are five-membered rings.[16]



This factor has been used for synthetic purposes in order to obtain substituted maleimides.

In addition, reactions due to the presence of iron carbonyl groups, for example, the reaction involving the substitution of CO ligands with retention of the metal–olefin bond, are characteristic of complexes of substituted olefins.[39]

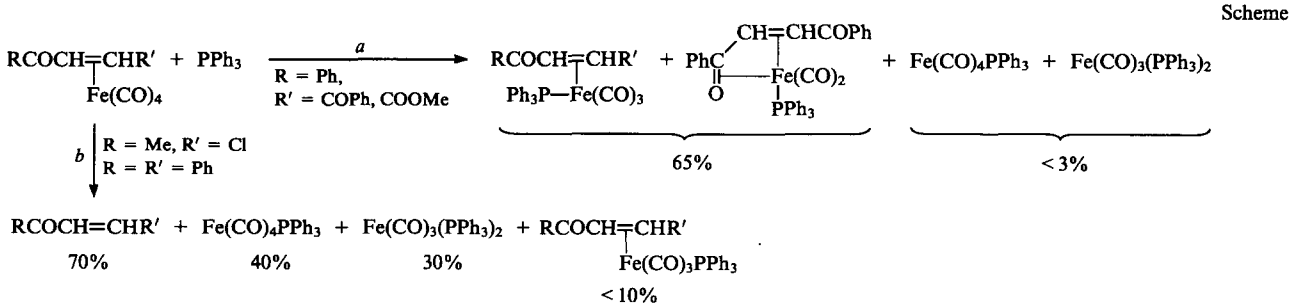


The reactions with triphenylphosphine may be used for the comparative characterisation of the strength of the Fe–CO and Fe–olefin bonds. It has been shown that the enhancement of the electron-accepting properties of the olefin and hence the increase in the strength of the π-bond alter the mode of the substitution reactions.[10] Thus the interaction of the complexes of α,β-dibenzoylethylene and methyl β-benzoylacrylate with PPh_3 results in the formation mainly of the products of the substitution of the CO ligand (Scheme 1, pathway *a*), whereas treatment of the less stable complexes of chalcone and methyl β-chlorovinyl ketone with phosphine leads to the preferential substitution of the unsaturated ligand (Scheme 1, pathway *b*).

3. The formation of the olefin, allyl, and elementaallyl structures in the iron carbonyl complexes. Haptotropic rearrangements.

The question of the interaction of the metal with the substituents is important in the study of complexes with substituted olefins. One can imagine two limiting cases: complexes of the η^2-olefin type **A** in which there is no such interaction and complexes **B** in which the metal is bound to the substituent.

Scheme 1





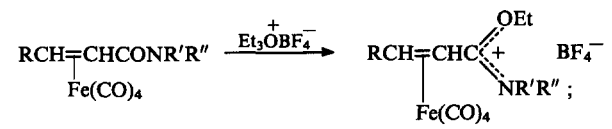
A B

In the general cases complexes **B** can be assigned to the η^3-allyl type if the metal is linked to X via a carbon atom, or to the η^3-elementaallyl type if the bond between the metal and the substituent X is formed via a non-carbon atom.

The question of the formation of the olefin and allyl structures has been investigated for complexes containing a positively charged substituent at the double bond. It was assumed that the degree of delocalisation of the charge can influence significantly the structure of such compounds.

a. Olefin complexes

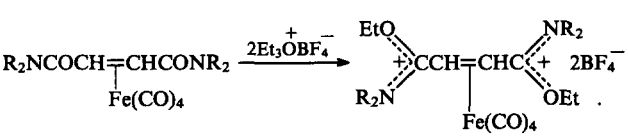
The olefin complexes with a positively charged substituent in the ligand can be synthesised by ethylating the amide group in the iron tetracarbonyl complexes of unsaturated acid amides.[40-42]



2

R = R′ = R″ = H; R = H, R′ = R″ = Me;
R = R′ = H, R″ = Me; R = Ph, R′ = R″ = H .

In the case of dibasic acid amides, dicationic complexes were obtained.



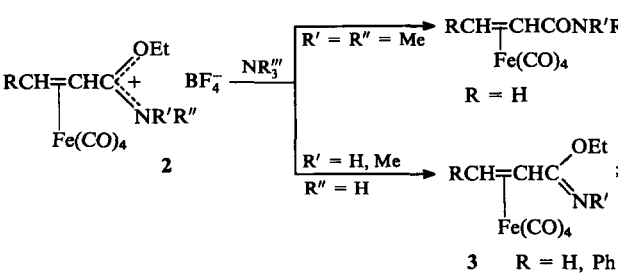
2a

Complexes **2** have the η^2-olefin structure. The signal of the α-carbon atom in the ^{13}C NMR spectra is significantly displaced downfield ($\delta \approx 180$ ppm) in comparison with the signals of olefinic carbon atoms (δ = 130–140 ppm), i.e. into the region characteristic of carbonium ions.

Complexes **2** were the first olefin complexes with a positively charged substituent.

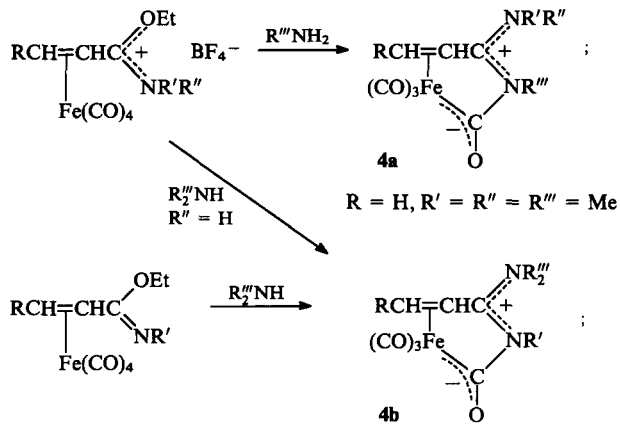
The reactions of complexes **2** with amines proceed with retention of the Fe–C(olefin) and Fe–C(carbonyl) bonds, which constitutes a fundamental difference between them and the reactions of the neutral olefin complexes of iron considered previously. Tertiary amines are dealkylating or deprotonating agents.

The deprotonation of the imidate group in the η^2-ligand in complexes **2** constitutes a method of synthesis of complexes of unsaturated acid iminoesters **3**. These complexes cannot be obtained directly from the iminoesters and iron carbonyls, whereas coordination to the $Fe(CO)_4$ group stabilises the unstable acrylic iminoesters.



3 R = H, Ph .

The dipolar chelate olefincarbamylate complexes **4** are formed in the reactions of the complexes of the iminoesters and their salts with primary and secondary amines.[40, 41, 49]



4a

R = H, R′ = R″ = R‴ = Me

4b

R = H, R′ = R‴ = Me, H; R′ = H, R‴ = Me;
R′ = Me, R_2''' = $(CH_2)_5$; R′ = H, R_2''' = $(CH_2)_5$;
R = Ph, R′ = H, R‴ = Me.

The structure of the chelate complexes **4** has been established by X-ray diffraction (Fig. 2).[40, 44]

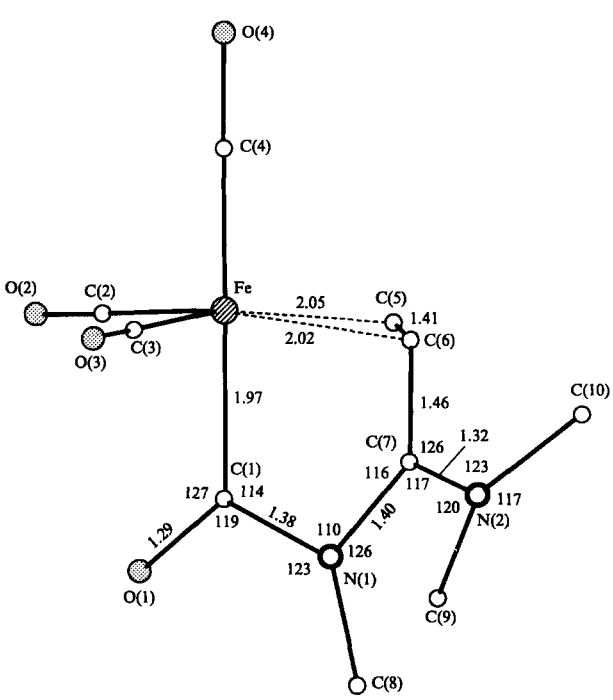
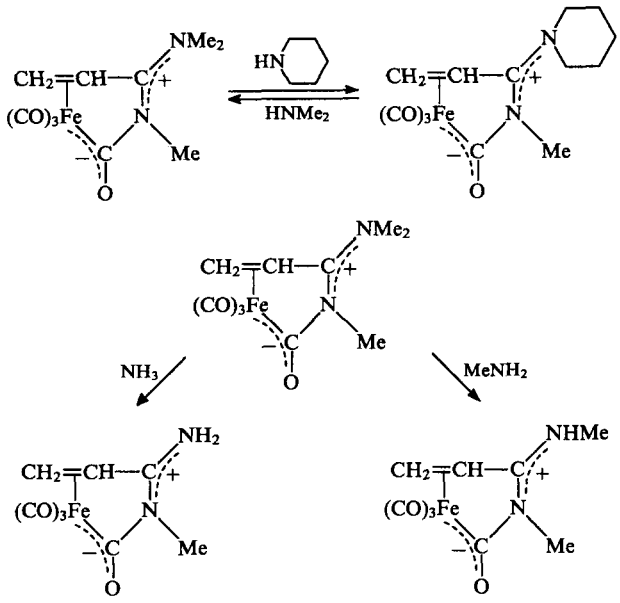
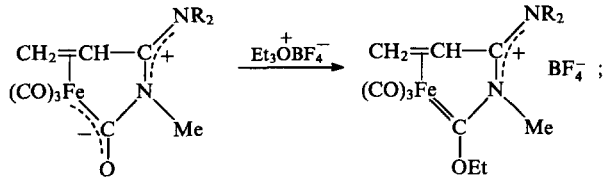


Figure 2. The structure of the molecule of complex **4** (R = H, R′ = R″ = R‴ = Me).

In conformity with the dipolar structure, complexes **4** react both with nucleophiles and electrophiles. The transamination reactions, which make it possible to convert a more readily available complex into others which are less easy to obtain, are important for synthetic purposes.[43]

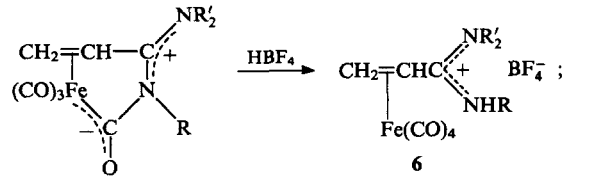


The reactions with electrophiles, for example, with the triethyloxonium cation and acids, lead to new olefin complexes with an α-cationic centre[40, 41, 43] — the vinylcarbene complex **5** and the acrylamidinium complex **6**.



R = Me, $R_2 = (CH_2)_5$.

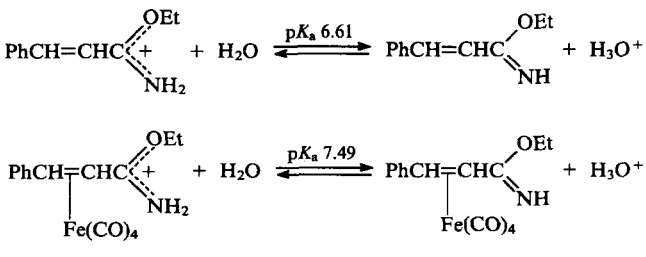
5



R = R′ = Me; R = Me, $R'_2 = (CH_2)_5$;
R = H, R′ = Me.

Examination of the characteristic features of the structures of complexes **2**–**6** permits the conclusion that the olefin structure with direct interaction between the metal and the cationic centre occurs in those cases where the charge is delocalised to a large extent owing to the presence of strong electron-donating substituents, for example, amino-groups.

The stabilising effect of the $Fe(CO)_4$ group in olefin complexes with a cationic centre has been estimated quantitatively by measuring and comparing the pK_a of ethyl cinnamidate and the corresponding iron tetracarbonyl complex.[45]

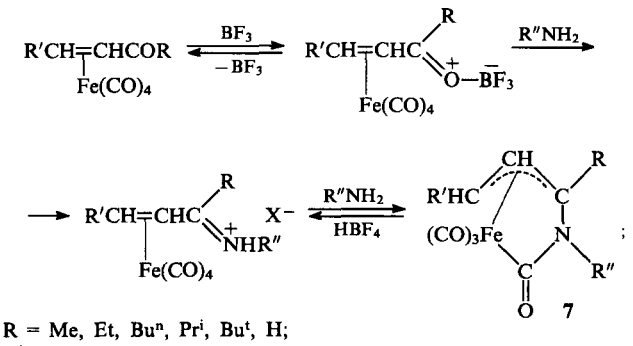


Comparison of the pK_a indicates a powerful electron-donating effect of the $Fe(CO)_4$ group, which more than compensates for the loss of conjugation as a result of the π-coordination.

b. Allyl complexes.

$\eta^3:\eta^1 \rightleftarrows \eta^2$-Tautomerism and the $\eta^2 \rightarrow \eta^1$(N) rearrangement.

The replacement of the strong electron-donating amino-group at the cationic centre in the olefincarbamylate complexes **4** by a weaker electron-donating group — an alkyl or aryl group — alters their structure, namely leads to a transition to compounds of the allyl type. Such compounds have been synthesised from the $Fe(CO)_4$ complexes of unsaturated ketones and cinnamaldehyde via their adducts with BF_3 and the subsequent reaction with amines.[39, 46, 47]



R = Me, Et, Bu^n, Pr^i, Bu^t, H;
R′ = Ph, PhCO, H;
R″ = H, Me, Et, Pr^i, Bu^n, Bu^t, n-C_6H_{13}, cyclo-C_6H_{11}, CH_2Ph .

The structure of the chelate $\eta^3:\eta^1$-allylcarbamoyl complexes **7** in the solid state has been established by X-ray diffraction (Fig. 3).[46, 48]

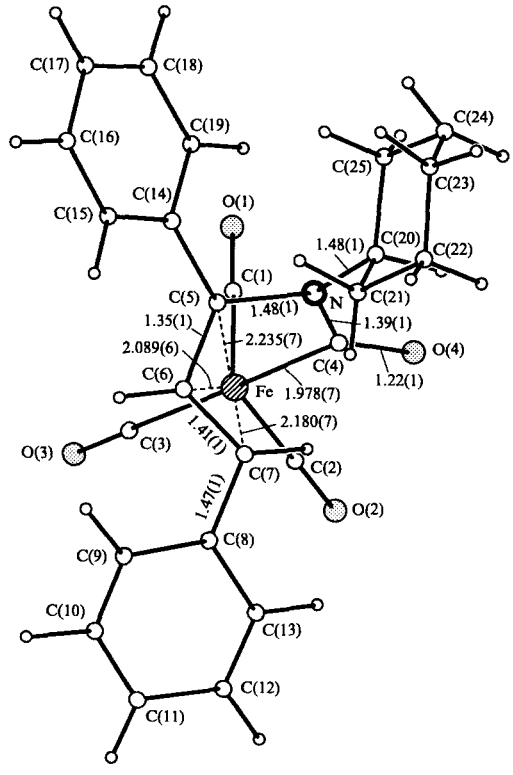
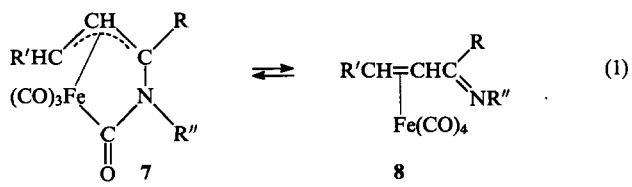


Figure 3. The structure of the molecule of complex **7** (R = R′ = Ph, R″ = cyclo-C_6H_{11}).

Table 1. Thermodynamic parameters of the equilibrium **7** ⇄ **8** (R = Me, R′ = Ph, R″ = cyclo-C_6H_{11}).

Solvent	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} deg^{-1}	ΔG/kJ mol^{-1}		
			295 K	250 K	210 K
Hexane	11.8	49.5	−2.8	−0.6	1.4
Hexane-CH_2Cl_2 (96:4)	20.3	72.8	−1.2	2.1	–

In solutions, complexes **7** rearrange reversibly to the isomeric η^2-olefin complexes **8**.[12, 41, 47]



(1)

The IR spectra of complex **7** with R = Me or n-alkyl, R′ = Ph or H, R″ = Me, Et, Pr^i, Bu^n, cyclo-C_6H_{11}, or CH_2Ph in non-polar solvents, for example in hexane, are seen to contain not only the three ν(C≡O) bands referring to the allylcarbamoyl form (~2065, 2010, and 1990 cm^{-1}) but also additional bands (~2085, 2020, 2010, and 1985 cm^{-1}), the positions and relative intensities of which indicate the presence in the molecule of the complex of the $Fe(CO)_4$ group η^2-linked to the olefin ligand.

The formation in solution of the η^2-olefin complexes **8** has been confirmed also by NMR spectroscopic data. Thus equilibrium (1) with R = Me, R′ = H, and R″ = Pr^i is displaced to the right so much that the ^{13}C NMR spectrum shows only signals due to the olefin form [$\delta(C_{olef})$ = 148.97 and 140.06 ppm and $\delta(C_\alpha)$ = 146.06 ppm; cyclopentane; 10 °C]. The ^1H NMR spectra can also serve as a demonstration of the appearance in solutions of the η^2-olefin form **8**. However, complex **8** could not be isolated in a pure state.

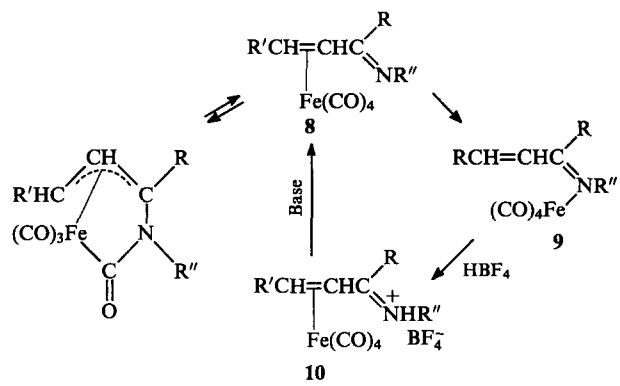
The dependence of the equilibrium position on the temperature, the solvent polarity, and the nature of the substituent in the ligand has been investigated quantitatively by IR spectroscopy.[12, 49]

The thermodynamic parameters of the reversible transition from the cyclic allyl form to the open-chain olefin form for the complex with R = Me, R′ = Ph, and R″ = cyclo-C_6H_{11} are presented in Table 1. With decrease in temperature, the equilibrium shifts towards the formation of the chelate form. The positive entropy change can probably be accounted for by the transition from the rigid chelate molecule to the more mobile molecule with an open chain. On passing to a more polar solvent, the relative stability of the more readily solvated chelate form also increases. The lower limit of the rate constant for the forward reaction ($k > 2.3 \times 10^{-3}$ s^{-1}) and the corresponding upper limit to the activation energy ($\Delta G^{\neq} < 90$ kJ mol^{-1}) were estimated.

The thermodynamic and kinetic parameters of the equilibrium isomerisation of the chelate alkylcarbamoyl complexes to the open-chain olefin complexes are within the limits of the corresponding scales for the tautomeric transformations.[50] Such isomerisation can be regarded as the first example of the ring–chain valence $\eta^3:\eta^1 \rightleftarrows \eta^2$-tautomerism. A characteristic feature of this process consists in the fact that, simultaneously with the opening and closure of the ring, the hapto-binding of the metal to the unsaturated ligand and the formal oxidation state of the metal change.

The steric requirements of the substituents R at the α-carbon atom and R″ at the nitrogen atom exert a significant influence on the equilibrium position.[12] An increase in the bulk of the substituent R leads to a sharp shift of the equilibrium towards the cyclic form. As a consequence of the increase in the bulk of the substituents R″ at the nitrogen atom, there is a smaller shift in the opposite direction.

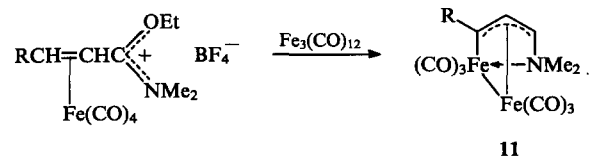
The η^2-olefin complexes **8**, formed as a result of the tautomeric shift, are capable of rearranging further to the η^1(N)-complexes **9**.[51] Such $\eta^2 \rightarrow \eta^1$(N) rearrangement occurs when the substituents R and R″ are small alkyl groups or one of them is a hydrogen atom. The rate of the rearrangement is appreciably lower than the rate of the tautomeric transformations. Complexes with R = H rearrange faster. The reverse η^1(N) → η^2 rearrangement occurs on protonation of complexes **9**. The deprotonation of the η^2-complexes **10** formed again opens the way to the $\eta^3:\eta^1 \rightleftarrows \eta^2$ tautomerism and the η^1(N) → η^2 rearrangement.



R = H, R″ = Me, cyclo-C_6H_{11}, Ph; R = Me, R″ = Me, Et; R = Et, Bu^n, R″ = Me, Et, Bu^n; R = Ph, Bu^t, R″ = H.

The tautomeric transformations and rearrangements investigated are characterised by the ease of the interconversions of various types of complexes containing unsaturated ligands with functional group substituents.

The conversion of the acrylimidate η^2-complexes **2** into the dinuclear η^3-aminoallyl† complexes **11** on heating with $Fe_3(CO)_{12}$ can also be formally classified as a hapto-transition.[42, 52]



The structure of these complexes was established by X-ray diffraction.[52]

c. Olefin and elementaallyl complexes

σ-Vinyl derivatives of elements of the type RCH=CHER′$_n$ occupy a special place among substituted olefins. The reactions of such compounds with iron carbonyls open the way to the synthesis of dinuclear and polynuclear complexes with a η^2-olefin or η^3-elementaallyl structure.

† Complexes **11** can also be regarded as compounds containing the azaferra-ring, which is η^4-coordinated to the other iron atom via its ferradiene system.

The structure of the complexes formed is influenced by the nature of the element. Thus the interaction of the σ-ketovinylrhenium compound with $Fe_2(CO)_9$ results in the formation of only the η^2-olefin complex without the Re–Fe bond.[26]

$$(CO)_5Re(\sigma\text{-}CH{=}CHCOMe) + Fe_2(CO)_9 \longrightarrow \longrightarrow MeCOCH{=}CHRe(CO)_5 \;.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Fe(CO)_4$$

The σ-ketovinyltungsten derivative affords under the same conditions the tungstaallyl complex with an intermetallic bond together with the olefin and oxadiene complexes.[24]

$$Cp(CO)_3W(\sigma\text{-}CH{=}CHCOPh) + Fe_2(CO)_9 \longrightarrow \longrightarrow PhCOCH{=}CHW(CO)_3Cp + Fe(CO)_4$$

$$+ \; PhC(O)CH{=}CHW(CO)_3Cp \; (Fe(CO)_3) + PhCOCH{=}CHW(CO)_2Cp \; ((CO)_3Fe{-}CO) \;.$$

On the other hand, in the case of the σ-vinyl derivatives of iron, the metallallyl complexes are the only reaction products.[23, 25, 26, 53]

$$Cp(CO)_2Fe(\sigma\text{-}CH{=}CHR) + Fe_2(CO)_9 \longrightarrow \longrightarrow RCH{=}CHFe(CO)Cp \;;$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad (CO)_3Fe \;\; CO{-}$$

R = H, Ph, COMe, COPh, CON⬡.

The structure of the ferraallyl complexes was established by X-ray diffraction.

The reactions of $Fe_2(CO)_9$ with various σ-vinyl derivatives of metals described above are the first examples of π-complex formation involving a σ-linked unsaturated ligand.

The nature of the complexes formed changes when the olefin contains two σ-linked iron carbonyl groups.[28]

In this case, a trinuclear complex with a bridging carbyne ligand, the formation of which requires an extensive rearrangement of the acryloyl ligand, was isolated together with the olefin and ferraallyl complexes. Its structure was demonstrated by X-ray diffraction (Fig. 4).[28]

$$Cp(CO)_2FeCOCH{=}CHFe(CO)_2Cp + Fe_2(CO)_9 \longrightarrow \longrightarrow Cp(CO)_2FeCOCH{=}CHFe(CO)_2Cp + Fe(CO)_4$$

48%

$$+ \; Cp(CO)_2FeCOCH{=}CHFe(CO)Cp \; ((CO)_3Fe{-}CO) + MeC{\equiv}CFeCp \; ((CO)_3Fe(CO)_3)$$

15% 2%

π-Complexes could not be obtained in the reactions of iron carbonyls with substituted σ-vinylpalladium(II) compounds.[29] At the same time it was found that, on heating in benzene, the σ-alkoxycarbonylvinylpalladium complexes undergo the $\eta^1 \rightarrow \eta^2$ rearrangement.

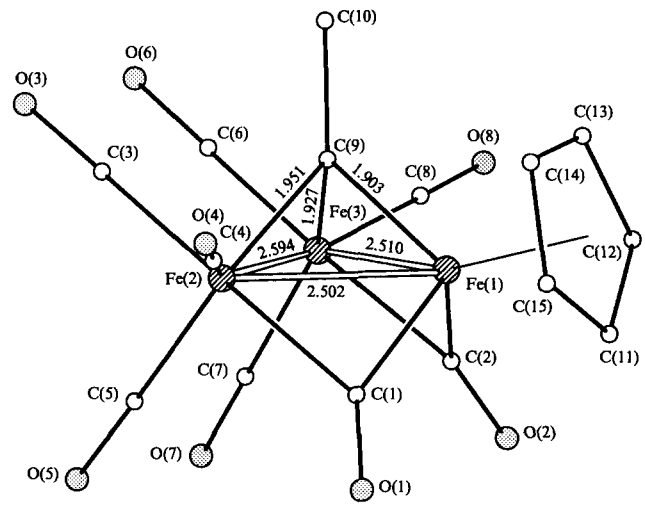


Figure 4. The structure of the molecule of the μ_3-ethylidyneoctacarbonyltriiron complex.

$$Ph_3P(X)Pd(CH{=}CHCOOR) \xrightarrow{80\ ^\circ C} X(Ph_3P)Pd^{-}(CH{-}COOR)(CH{-}PPh_3)^{+} \;;$$

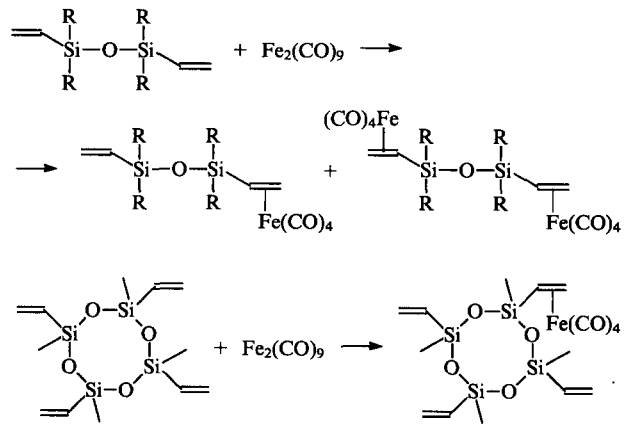
R = Me, Et; X = Cl, I.

Complexes in which the metal is coordinated only to the carbon–carbon double bonds have been obtained in the reactions of various vinyl compounds of silicon with iron carbonyls.[19, 20]

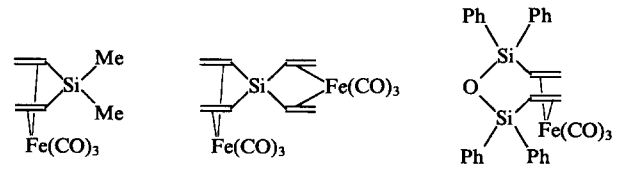
$$CH_2{=}CHSiRR'_2 + Fe_2(CO)_9 \longrightarrow CH_2{=}CHSiRR'_2 \;;$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Fe(CO)_4$$

R = R′ = Me, OMe;

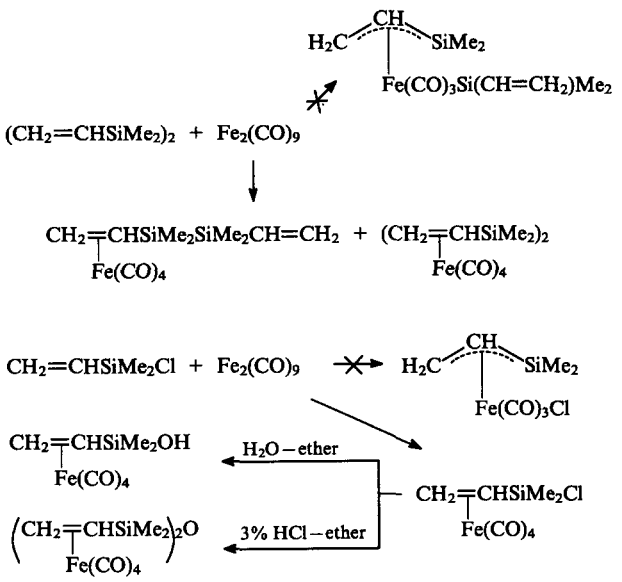
R = CH=CH$_2$, R′ = Me; R = R′ = CHCH$_2$;



η^4-Diene complexes have been obtained from dimethyldivinyl- and tetravinyl-silanes and also from 1,3-divinyltetraphenyldisiloxane and iron carbonyls.[20, 55]

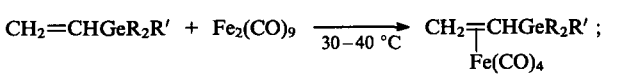


η^3-Silaallyl complexes could not be obtained from divinyldisilanes or chlorovinylsilane.[18]



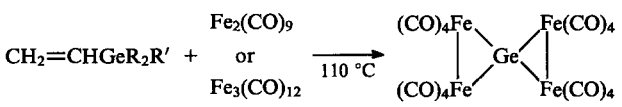
The absence of compounds of the silaallyl type among the reaction products can probably be explained by the fact that the stabilisation as a result of the formation of a π-complex with a metal is insufficient for the formation of stable structures with silicon–carbon multiple bonds.

The reactions of vinylgermanes and digermanes with $Fe_2(CO)_9$ also lead to complexes of the olefin type.[21]



R = R′ = Et, $CH{=}CH_2$;
R = $CH{=}CH_2$, R′ = $Ge(CH{=}CH_2)_3$.

The interaction of iron carbonyls with germanes containing at least one vinyl group leads, under more severe conditions, to the elimination of all the organic groups from germanium and the formation of an iron-germanium cluster.[21, 22]



III. Reactions of ruthenium and osmium carbonyl complexes with olefins having functional group substituents

The reactions of ruthenium and osmium carbonyl compounds with substituted olefins have been less investigated than those of their iron analogues. The main cause of the slow development of this field is apparently not only the high cost of the compounds of the above metals but also the specific features of the behaviour of the most readily available carbonyls $M_3(CO)_{12}$, the chemical properties of which are determined by the greater strength of their M–M and M–CO bonds compared with iron carbonyls (Table 2).[56]

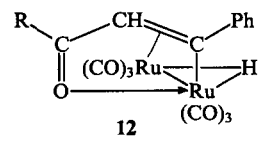
The products formed initially undergo further reactions under severe thermal conditions. This frequently results in the formation of mixtures of complexes which are difficult to separate. The metallic M_3 skeleton is either retained in these reactions or actually increases, whilst unsaturated hydrocarbons are dehydrogenated and undergo oxidative addition to the metal with formation of structures containing allyl, allenyl, alkyne, and vinylidene ligands.[57]

Table 2. The bond enthalpies in the carbonyls $M_3(CO)_{12}$ (in kJ mol^{-1}).

Bond	Fe	Ru	Os
M–M	80.37	117.2	130.2
M–CO	117.6	172.5	191.7

Trinuclear ruthenium and osmium carbanions react with olefins also under photochemical conditions. On UV irradiation, the M–M bonds are ruptured and mononuclear η^2-olefin complexes, similar to the η^2-olefiniron complexes already examined, are formed.[58–60]

The pattern becomes even more complicated after the introduction of functional groups into the olefin molecule. The study of the thermal reactions of $M_3(CO)_{12}$ (M = Ru, Os) with organic unsaturated carbonyl compounds showed that such systems can be coordinated in different ways to the polynuclear fragment. Thus, in the interaction of the unsaturated ketones $PhCH{=}CHCOR$ (R = Me, p-MeC_6H_4) with $Ru_3(CO)_{12}$ in boiling hydrocarbons (hexane, benzene, heptane), dinuclear complexes **12** are formed as the main products.[61]



12a: R = Me;
12b: R = p-MeC_6H_4.

The structure of complex **12a** was established by X-ray diffraction. Previously this complex had been obtained by the reaction of benzylideneacetone with mononuclear (η^4-cycloocta-1,5-diene)tricarbonylruthenium.[62] The ruthenium atoms in complex **12a** are linked by a metal–metal bond, a μ-hydride ligand, and an enone ligand which has lost one hydrogen atom. The last ligand chelates one Ru atom via the β-carbon atom (σ-bond) and the ketone oxygen atom (n-donor bond). The other ruthenium atom is η^2-coordinated to the same ligand.

Apart form complexes **12**, a series of other complexes are also formed in the reaction of $Ru_3(CO)_{12}$ with $PhCH{=}CHCOR$. The structure of one of them, namely complex **13**, was determined by X-ray diffraction (Fig. 5).[61]

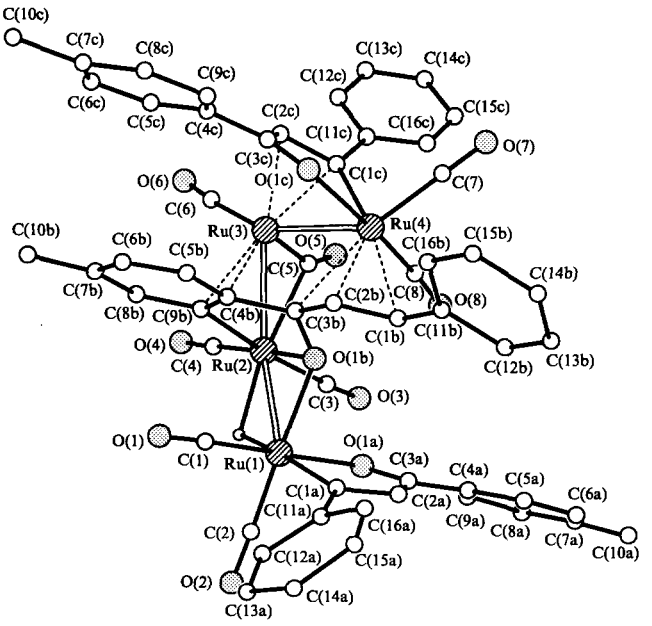
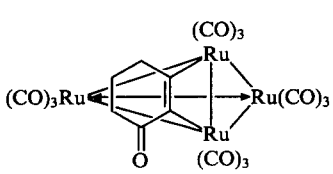


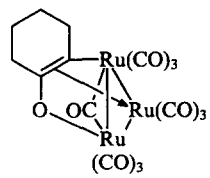
Figure 5. The structure of the molecule of complex **13**.

The molecule of complex **13** includes a chain made up of four ruthenium atoms and three organic ligands. One $PhC=CHCOC_6H_4Me$ ligand at the edge chelates the Ru(1) atom via the β-carbon atom (σ-bond) and the oxygen atom of the keto-group (n-donor bond), forming a five-membered metallocycle. Another similar ligand chelates the Ru(4) atom via the formation of σ-bonds with carbon and oxygen atoms and is also η^2-linked to Ru(3) via the C=C double bond.

The central ligand serves as a μ^4-bridge between all the ruthenium atoms and is linked to them in various ways. Its oxadiene fragment is converted into the hydroxyallyl fragment, which is η^3-linked to Ru(4) and is σ-O-linked to Ru(1) and Ru(2). In addition, Ru(2) forms a σ-bond with the *ortho*-carbon atom of the tolyl substituent and Ru(3) is involved in π-olefin coordination with the same substituent. Thus the ways in which the α,β-unsaturated ketones are coordinated in the ruthenium clusters are extremely varied. They depend primarily on the structure of the unsaturated ketone. When cyclohex-2-en-1-one was used in the thermal reaction with $Ru_3(CO)_{12}$, complexes **14** and **15** were obtained.[63, 64]



14



15

In complex **14**, the four ruthenium atoms form the 'butterfly' configuration. The metal atoms 'at the ends of the wings' are π-linked, while the axial metal atoms are σ-linked to the dehydrogenated cyclohexene.

Interesting examples of the wide variety of the ways in which bonding takes place in the ruthenium clusters are provided by the complexes formed in the reactions of unsaturated aldehyde imines (azadienes) with $Ru_3(CO)_{12}$.[65-69] Various types of bonds between the metal and the organic ligand are formed in these polynuclear compounds: σ-N, σ-C, η^2-C = C, η^2-C = N, η^3-allyl, and η^3-azaallyl.

Complex **16**, in which there is no intermetallic bond and the metal atoms are linked only to the common organic ligand, is formed in the reaction of $Ru_3(CO)_{12}$ with dimethylfumarate.[70] According to X-ray diffraction data (Fig. 6), the double bonds in the three dimethylfumarate ligands in complex **16** were opened [partly dissociated?] and two ligands dimerised with formation of three condensed metallacycles. One hydrogen atom was then transferred to the third ligand forming the fourth metallacycle.

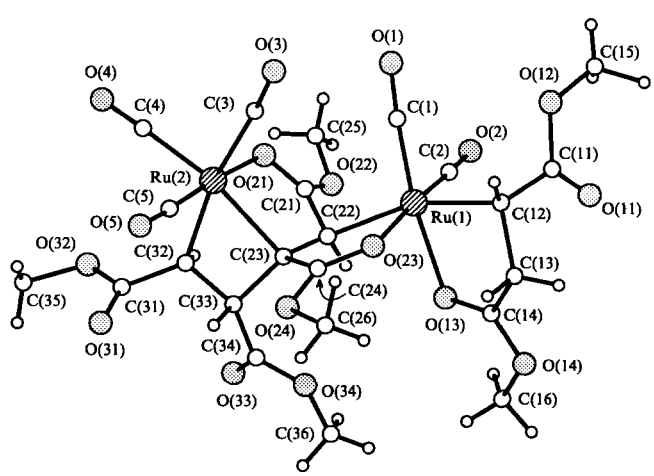
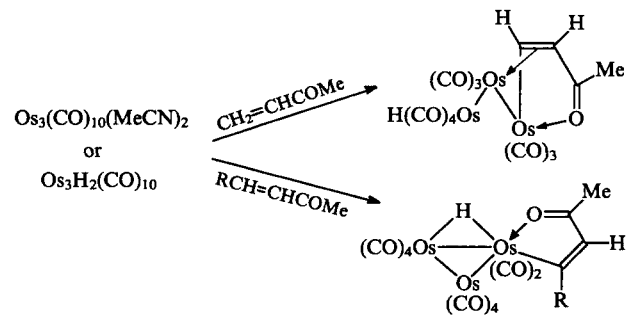


Figure 6. The structure of the molecule of complex **16**.

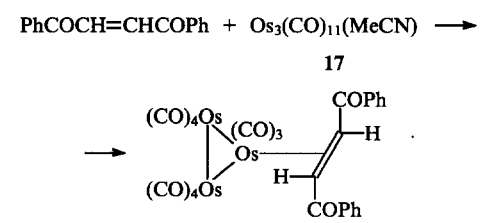
Several other complexes were obtained in this reaction, including the mononuclear complex $Ru(CO)_4(\eta_2$-MeOCOCH=CHCOOMe).

The examples examined above show that organic α,β-unsaturated carbonyl compounds in the ruthenium carbonyl complexes exhibit a tendency towards many-centre bonding, including the formation of σ-Ru–O and σ-Ru–C_β bonds.

The situation is similar also in the case of reactions of osmium carbonyl complexes with unsaturated ketones.[71]



For this reason, relatively few simple η^2-olefin complexes of transition metal clusters are known. In order to obtain a η^2-olefinosmium cluster complex, the monoacetonitrile derivative $Os_3(CO)_{11}(MeCN)$ **17** was used. The latter is normally employed for the synthesis of undecacarbonylosmium compounds.[72] When compound **17** was refluxed with *trans*-α,β-dibenzoylethylene in hexane, the η^2-olefin complex **18**, in which the Os_3 cluster skeleton is retained, was obtained.[73]



18

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