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# Dinuclear Iron Carbonyl Complexes with Nitrogen-containing Bridges

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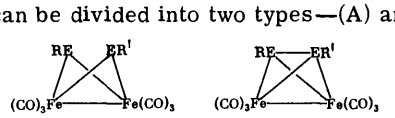
*The literature on the synthesis and properties of dinuclear complexes with the $N_2Fe_2(CO)_6$ group is surveyed. It is shown that these complexes are formed in reactions of a wide variety of nitrogen-containing organic compounds with iron carbonyls. The possibility of the formation of nitrene species and their complexes in these reactions is considered. The bibliography includes 123 references*

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## I. INTRODUCTION

Dinuclear iron carbonyl complexes with heteroatomic bridges are widely known in the chemistry of complex compounds. These compounds include also complexes containing the $Fe_2(CO)_6$ group, in which the iron atoms are linked by an intermetallic bond as well as one six-electron or two three-electron heteroatomic bridges. Depending on the electronic structure of the bridge, these complexes can be divided into two types—(A) and (B):



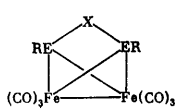

(A)




(B)

Among complexes with three-electron bridges [type (A)], compounds with RS bridges have been known longest (see, for example, Refs. 1–4). Analogous nitrogen-containing compounds were discovered comparatively recently. An example of six-electron bridges is provided by the –S–S–, –NR–NR–, and –PR–PR–† groups. Complexes of type (B) are formed with participation of such bridges.

In their turn three-electron heteroatomic groups can also be linked by a bridge (X):




However, as will be shown below, these compounds differ little in their structural parameters from complexes of type (A).

Interest in transition metal complexes with nitrogen-containing ligands was initially due to the fact that the compounds with the diazene ligand (HN=NH) were regarded as possibly intermediates in the enzymatic fixation of molecular nitrogen[5,6]. However, subsequently

† A.H.Cowley and K.E.Hill, Inorg.Chem., 12, 1446 (1973).

interesting data were obtained fairly rapidly, showing that this field of the chemistry of complex compounds may be of independent importance.

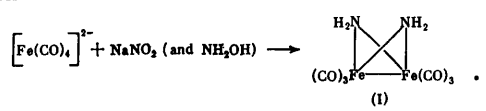
Complexes with nitrogen-containing bridges of types (A) and (B) were obtained by the interaction of various nitrogen compounds with iron carbonyls. During their synthesis, it was found that the formation of complexes of a particular type is controlled by a detailed balance between various factors. Thus it was discovered that the same complex may be generated from a wide variety of types of nitrogen compounds, and, just as surprisingly, compounds of one class, differing from one another merely by the nature of the substituents, can give rise to complexes of different types. This apparent contradiction was resolved on the hypothesis[7] of the intermediate formation in these reactions of either free nitrene species or such species coordinated to the metal. In many cases it was possible to isolate stable nitrene complexes.

Thus the chemistry of these complexes approached very closely that field of coordination chemistry, which has been developing vigorously in recent years, which is concerned with the problems of the stabilisation of unstable organic species as a result of coordination to transition metal complexes[8]. However, it would be incorrect to regard all the reactions of nitrogen compounds with iron carbonyls, leading to dinuclear complexes, as proceeding via the intermediate formation of nitrene species or their complexes. Otherwise the reactions with phenyl azide and azobenzene should have led to the same products, which is not the case. As will be shown below, the electronic and structural factors, the nature of the attacking transition metal complexes, and the reaction conditions determine the chemical behaviour of the nitrogen-containing ligand. It is not at present clear which of these factors predominates, but there is no doubt that the comparatively low strength of the N–N bond, whose dissociation energy is 37 kcal mole$^{-1}$ in certain cases[9] owing to the repulsion of the nitrogen *p* orbitals, does not play the least important role.

In the present review the literature data are classified in terms of the reactions of different organic nitrogen compounds in order to follow more clearly the specific features of the behaviour of each of them. Special reviews devoted to dinuclear iron carbonyl complexes have not yet been published, but these data are considered partially in a number of review articles[8,10–12]. Analogous dinuclear complexes of other transition metals will be briefly mentioned only, for comparison.

## II. REACTIONS OF NITROGEN-CONTAINING ORGANIC COMPOUNDS WITH IRON CARBONYLS LEADING TO DINUCLEAR COMPLEXES

The simplest type (A) complex is obtained (in low yield) in the interaction of the anion $[Fe(CO)_4]^{2-}$ with $NaNO_2$ or hydroxylamine under mild conditions[13–16]. It was assumed initially that this compound contains the N–N group. However, its structure was established as that of complex (I) on the basis of mass spectra[17,18] and X-ray diffraction studies[18]:

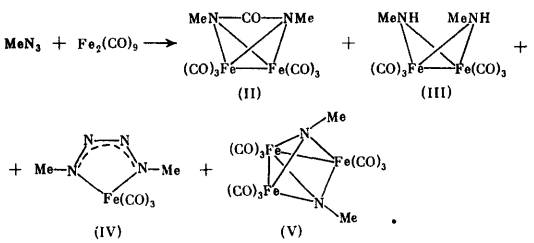



(I)

The reactions of organic nitrogen compounds with iron carbonyls lead as a rule to a mixture of different complexes.

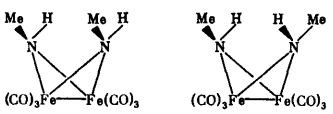
### 1. Reactions of Azides

Iron carbonyls catalyse the decomposition of organic azides under mild conditions. In most cases these reactions lead to the formation of a mixture of different complexes. The mixture composition varies considerably as a function of the type of organic group in the azide. Thus the reaction of methyl azide with $Fe_2(CO)_9$ gives rise to a mixture of complexes, where the main product is complex (II) with the ligand MeNCONMe‡.[7] The structure of this complex was demonstrated by the diffraction method[19]:




(II) (III) (IV) (V)

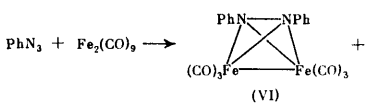
Complex (III) was obtained in a low yield and resolved into the stereoisomeric forms (IIIa) and (IIIb):



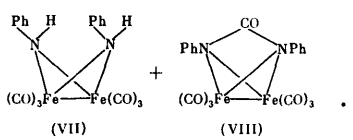

(IIIa) (IIIb)

Complex (IV), with a tetra-azadiene ligand, unknown in a free state, was isolated from the products of this reaction in a high yield (20%). The trinuclear complex (V) is formed in a moderate yield. The yield of the complex in the reaction of $MeNO_3$ with $Fe_2(CO)_9$ [7] is fairly high. Its structure was demonstrated by X-ray diffraction[20].

Phenyl azide reacts just as fast with $Fe_2(CO)_9$, but in this case the main product is the dinuclear complex (VI) with a six-electron ligand containing an N–N bond§[7]. A similar complex was not isolated from the products of the analogous reaction involving methyl azide:




(VI)




(VII) (VIII)

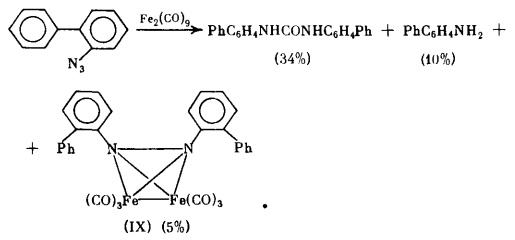
Furthermore, the reaction gives rise to complex (VII) in a low yield. In contrast to the analogous complex (III), obtained by the reaction with methyl azide, complex (VII) was isolated in only one stereoisomeric form. It is unstable in solution and decomposes spontaneously; the diphenylurea derivative (VIII) formed under these conditions was also isolated from the products of the reaction of phenyl azide with $Fe_2(CO)_9$.[7] The same compound is formed when $Fe_3(CO)_{12}$ is used (heating to 90°C).[21]

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‡ It is noteworthy that this product is obtained in a higher yield in the reaction of methyl isocyanate with $Fe_2(CO)_9$.[7]

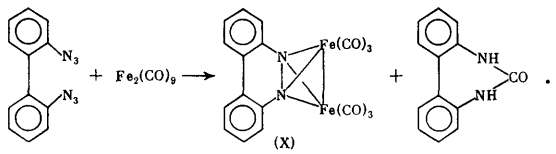
§ Free azobenzene was isolated in this reaction in a negligible yield.

The thermal decomposition of 2-azidobiphenyl is known to result in the formation of carbazole (in a high yield)[22]. However, when this azide decomposes in the presence of $Fe_2(CO)_9$, carbazole is formed in a negligible yield, while the main products of this reaction are *N*,*N*′-bis-(2-biphenylyl)urea (34%), 2-aminobiphenyl (10%), and the dinuclear complex (IX) (5%):[23]



(IX) (5%)

A similar dinuclear complex (X) is formed from a biphenyl derivative containing two azido-groups in the *ortho*-positions in different rings[23]:

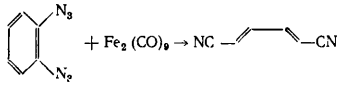


(X)

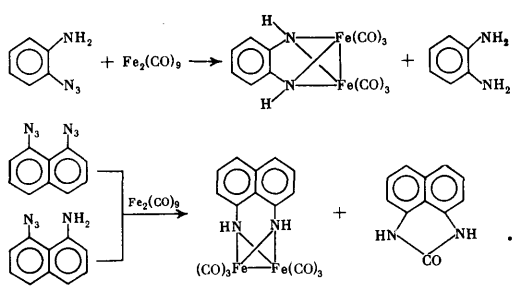
Together with complex (X), a cyclic urea derivative is also formed in this case. The determination of the structure of (X) and its specific synthesis from benzo[*c*]-cinnoline have already been described[24,25].

Thus in the above reactions aromatic azides give rise to dinuclear complexes of type (B) with six-electron nitrogen-containing ligands, while methyl azide gives rise mainly to dinuclear complexes of type (A) with three-electron bridges.

The course of these reactions differs somewhat when two azido-groups or an azido- and an amino-group are present in the *ortho*-positions of the benzene ring or in the *peri*-positions in the naphthalene molecule. Only *cis*,*cis*-muconitrile was isolated from the products of the reaction of *o*-diazidobenzene (27%):[23]



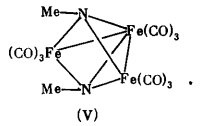

Under the same conditions, *o*-azidoaniline, 1,8-diazidonaphthalene, and 1-amino-8-azidonaphthalene form, together with purely organic products, dinuclear complexes in which the nitrogen atoms are linked by *o*-phenylene or *peri*-naphthalene bridges[23]:




These results show that steric factors can also play a significant role in the formation of products.

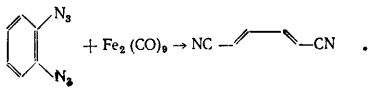
The hypothesis of the formation of nitrene species in the decomposition of azides in the presence of transition metal compounds does not lack justification, since in many cases complexes with such species have been isolated.

It has been shown by X-ray diffraction[19] that the trinuclear cluster (V), isolated from the products of the reaction of methyl azide with $Fe_2(CO)_9$,[7] is a complex in which each nitrene species $CH_3\dot{N}$: is coordinated to three iron atoms:



(V)

The iron complex (XI) of $Me_3Si\dot{N}$: was isolated from the products of the reaction of trimethylsilyl azide with $Fe_2(CO)_9$. This complex proved to be a trinuclear cluster incorporating a triply coordinated trimethylsilylnitrene species. It is of interest that one of the carbonyl groups in this cluster is also linked to three iron atoms[26,27]:




Stable nitrene complexes have also been obtained by the reaction of a polyfluorinated azide with ruthenium and osmium carbonyls[28]¶:

$$Ru_3(CO)_{12} + CF_3CHFCF_2N_3 \rightarrow Ru_3(CO)_9(NCF_2CHFCF_3)_2;$$
$$M(CO)_3(PPh_3)_2 + CF_3CHFCF_2N_3 \rightarrow M(NCF_2CHFCF_3)(CO)_2(PPh_3)_2;$$
$$M = Ru, \text{ or } Os.$$

Azides with other electron-accepting organic groups gave isocyanate complexes on interaction with the same ruthenium compound[29]:

$$RN_3 + Ru(CO)_3(PPh_3)_2 \rightarrow Ru(CO)_2(PPh_3)_2(RNCO);$$
$$R = PhCO,\ p\text{-}MeC_6H_4CO,\text{ or } p\text{-}MeC_6H_4SO_2.$$

In the presence of proton donors these complexes decompose with formation of isocyanate derivatives. It is of interest that the reaction of benzoyl azide or β-benzoylvinyl azide with $Fe_2(CO)_9$, carried out in aqueous alcohol, also led to derivatives of the corresponding isocyanates[30]:

$$RN_3 + Fe_2(CO)_9 \rightarrow [(RNCO)Fe(CO)_4] \xrightarrow[\text{alcohol, water}]{} [RN{=}C{=}O] \rightarrow RNHCOOC_2H_5 + RNH_2;$$
$$R = C_6H_5CO \text{ or } C_6H_5COCH{=}CH$$

Speaking of the formation of isocyanates, one should bear in mind that, in the absence of transition metal complexes, nitrenes combine with carbon monoxide under very severe conditions[31-34].

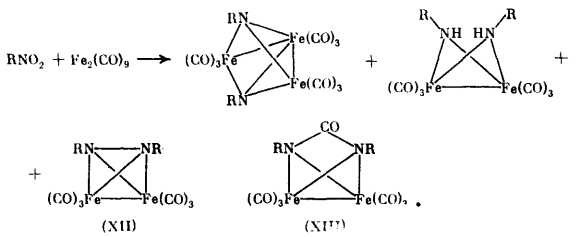
The interaction of 1-azidostyrene with $Fe_2(CO)_9$ [35] is examined below in the section dealing with the reactions of azirines.

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¶ See the review of Genini and La Monica[8] for information about other stable nitrene complexes of transition metals obtained from azides.

## 2. Reactions of Nitro-compounds

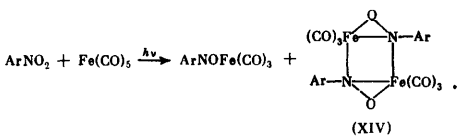
The reaction of nitromethane with $Fe_2(CO)_9$ gives the same mixture of products as the reaction with methyl azide [7]. Other aliphatic nitro-compounds, such as 1-nitro- and 2-methyl-2-nitropropanes, give rise to complexes (XII) with an N–N bond in addition to all the above products [36]. The main product of the reaction of 1-nitropropane with $Fe_2(CO)_9$ is, as for nitromethane, a trinuclear nitrene complex, while the reaction involving 2-methyl-2-nitropropane gives compound (XIII) in the highest yield:



(XII) (XIII).

Heating of aliphatic nitro-compounds with $Fe(CO)_5$ in diglyme at 120–132°C leads only to organic products—derivatives of formamide and urea [36]. The same products have been obtained on thermal degradation (120–130°C, diglyme) of certain iron carbonyl complexes isolated from the products of reactions with nitro-compounds. This suggested that iron carbonyl complexes may be intermediates in the formation of formamide and urea derivatives [36].

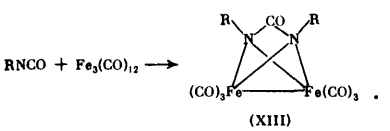
It is of interest that, on reaction with $Fe(CO)_5$ under ultraviolet or $\gamma$-irradiation, nitrobenzene forms nitrosobenzene complexes [37,38]. The structure of the dinuclear complex (XIV) was determined by X-ray diffraction [39]:



(XIV)

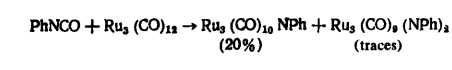
## 3. Reactions of Isocyanates

A report of the formation of an isocyanate complex on reaction of isocyanates RNCO (R = Me, n-Bu, or Ph) with $Fe_3(CO)_{12}$ was published in 1964. [21] Later studies established the presence of the ureylene group in these compounds and structure (XIII) was attributed to them [7,40], which was confirmed by X-ray diffraction [41]:



(XIII)

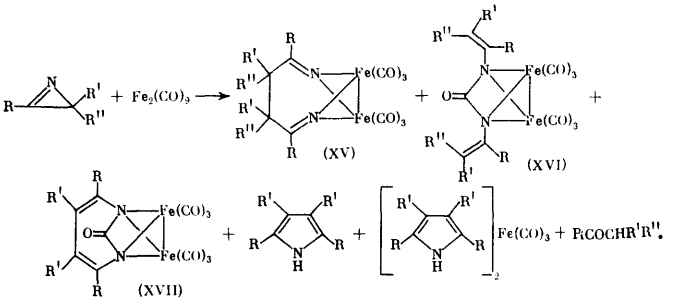
Intermediate complexes containing an isocyanate ligand can probably be formed in reactions with isocyanates. As shown above, such complexes were isolated in some cases [8]. At the same time it is important to note that nitrene complexes can also be obtained from isocyanates: this was observed in the reaction of phenyl isocyanate with $Ru_3(CO)_{12}$: [42]



## 4. Reactions of Azirines

The reactions of azirines with $Fe_2(CO)_9$ have been investigated in detail [35,43]. When these compounds are heated at 50°C (3–4 h) in dry benzene, the dinuclear complexes (XV), (XVI), and (XVII), which are stable in air, and certain organic substances are formed:

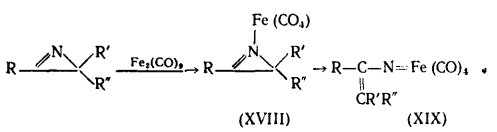
Scheme 1



a) R = Ph, R′ = R″ = H; b) R = *p*-$CH_3C_6H_4$, R′ = R″ = H; c) R = *p*-$BrC_6H_4$, R′ = R″ = H; d) R = Ph, R′ = Me, and R″ = H; e) R = Ph, R′ = $C_2H_5$, R″ = H; f) R = $CH_3$, R′ = $CH(Me)_2$, R″ = H; g) R = Ph, R′ = R″ = Me.

The structure of the products isolated was confirmed by spectroscopic data. It has been suggested [35] that a complex of type (XVIII) is involved in this reaction and is subsequently converted, with ring opening, into the nitrene derivative (XIX), which is the parent compound of all the products formed.

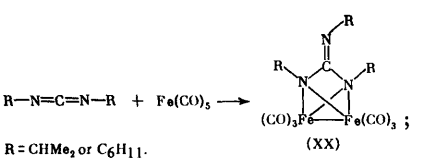
It is important to note that, on reacting with $Fe_2(CO)_9$, 1-azidostyrene gives rise to virtually the same products as phenylazirine, with the exception of pyrrole and its complex, which confirms the importance of the formation of the intermediate nitrene species (free or in the form of a metal carbonyl complex) [35]:



(XVIII) (XIX)

## 5. Reactions of Carbodi-imides

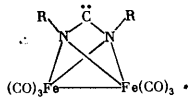
The reactions of carbodi-imides with $Fe(CO)_5$ give rise to dinuclear complexes (XX), whose acid hydrolysis indicates the presence in their molecules of the trialkylguanidine species linked to the $Fe_2(CO)_6$ group (see Section III). The infrared, NMR, and mass spectrometric data agree with formula (XX):



R = $CHMe_2$ or $C_6H_{11}$. (XX)

In the course of the discussion of the possible mechanism of the formation of this complex, a scheme involving the intermediate formation of the carbene species (XXI) was put forward. This species reacts further with a second carbodi-imide molecule and forms the complex (XX) and an isonitrile, isolated in the form of the compound

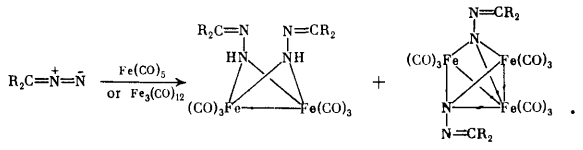
$(C_6H_{11}NC)Fe(CO)_4$:



(XXI)

6. Reactions of Diazo-compounds

Two types of complexes were isolated from the products of the reactions of diphenyl- and di-(*p*-tolyl)-diazomethanes with $Fe(CO)_5$ or $Fe_3(CO)_{12}$: an orange dinuclear complex (XXII) and a black trinuclear complex (XXIII).[44] The structures of the two complexes were confirmed by X-ray diffraction[44,45]:



(XXII) (XXIII)

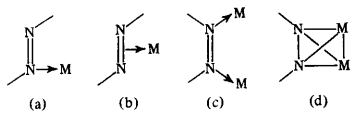
7. Reactions of Azo-compounds

Up to 1963, there was almost no information in the literature about the reactions of transition metal derivatives with azo-compounds, except for the description of certain metal chelate complexes of azo-dyes. However, from 1963, after the publication of the study of Kleiman and Dubeck[46] on the reactions of azobenzene with nickelocene, a series of other publications appeared in which complexes of azobenzene and its derivatives with platinum(II), palladium(II), and zerovalent iron were described[47-49].

Different ways of coordinating the N=N bond to transition metals (see Scheme 2) attracted the attention of chemists[10,11,24,50-54]. Of the four possible types of structures (a–d) of iron carbonyl complexes with azo-compounds, three structures were detected (a, c, and d), in which the nitrogen-containing ligand behaves as a donor of two, four, and six electrons respectively.

The type of coordination (b) is encountered in complexes of other transition metals, for example, $NiL_2(PhN=NPh)$[55-62] and $(C_5H_5)_2M(PhN=NPh)$ (M = Ti or V),[63] i.e. in those cases where the azo-compound is a comparatively poor σ-donor and the metal-containing fragment is a poor σ-acceptor.

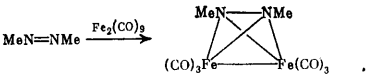
Scheme 2



(a) (b) (c) (d)

Azo-compounds with a wide variety of structures have been made to react with iron carbonyls. Studies have shown that the behaviour of aliphatic azo-compounds differs appreciably from that of azobenzene and its substituted derivatives.

The interaction of azomethane with di-iron nonacarbonyl leads to a dinuclear hexacarbonyl complex in which the initial compound retains its skeleton[64]. The ligand behaves in this case as a six-electron donor. The structure of the complex was demonstrated by X-ray diffraction:



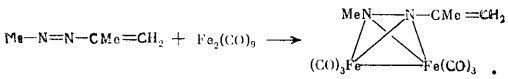
It is noteworthy that the dissociation of the bond between the nitrogen atoms has been observed for hexafluoroazomethane, which gives rise to a mixture of *cis*- and *trans*-isomers of the nitrene complexes $(Ph_2PMe)_2Ir(CO)(Cl)(NCF_3)$ on treatment with *trans*-$ClIr(CO)(Ph_2PMe)_2$:[65]

$(Ph_2PMe)_2Ir(CO)(Cl)(NCF_3)$[65]:

$$CF_3N{=}NCF_3 + \textit{trans}\text{-}ClIr(CO)(Ph_2PMe)_2 \rightarrow \textit{cis}\text{- and } \textit{trans}\text{-}(Ph_2PMe)_2Ir(CO)Cl(NCF_3).$$

Unfortunately the reactions of iron carbonyls with hexafluoroazomethane have not been investigated.

The reaction of di-iron nonacarbonyl with 2-(methylazo)propane is very remarkable[66]. In contrast to other butadiene systems, this compound gives rise to a dinuclear complex to which structure (XXIV) was attributed on the basis of spectroscopic data. The vicinal disposition of the nitrogen atoms in this compound has a decisive influence on the structure of the complex, while the C=C double bond is not involved in coordination[66]:

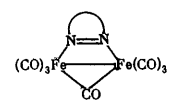


(XXIV)

This is not surprising if one takes into account the quantum-chemical calculations on the PhCH=CHPh and PhN=NPh molecules[67,68], where the energies of the highest occupied molecular orbitals (HOMO) are approximately equal, while the lowest unoccupied molecular orbital (LUMO), which is in both cases π*-antibonding, lies in a far lower position for azobenzene†.

Cyclic azo-compounds also retain their skeleton in reactions with iron carbonyls. Dinuclear iron carbonyl complexes of type (B) have been obtained from 2,3-diazabicyclo[2,2,1]hept-2-ene,[51-53] derivatives of 1,2-diazacyclopent-1-ene,[50,69,70] 1,3,4-thiadiazoline,[53] and dibenzo[1,4,5]oxadiazepine.[24,25]. It is noteworthy that in these reactions the first stage involves the formation of the mononuclear complexes $LFe(CO)_4$,[50,53] in which the metal atom is coordinated to one of the nitrogen atoms[70] and the ligand occupies an axial position.

Together with these compounds, complexes of the type $LFe_2(CO)_7$ were isolated in the reactions involving 2,3-diazabicyclo[2,2,1]hept-2-ene and 1,3,4-thiadiazoline[53]. On the basis of infrared and $^1H$ NMR spectra, the following structure was attributed to these complexes:

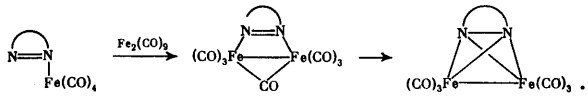


(XXV)

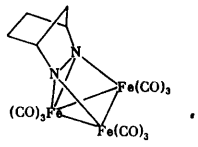
The infrared spectra of these compounds exhibit absorption by the metal carbonyl bridge groups in the range 1770–1820 $cm^{-1}$.[53] Compounds of type $LFe(CO)_4$ and $LFe_2(CO)_7$ are apparently intermediates[51,53] in the

† For information about the electronic structures of compounds with the –N=N– group, see, for example, Albini and Kisch's review[12].

formation of the dinuclear complexes $LFe_2(CO)_6$, since the conversion of $LFe(CO)_4$ into $LFe_2(CO)_7$ and then into $LFe_2(CO)_6$ can be followed by infrared spectroscopy in the region of approximately 2000 $cm^{-1}$.



It has been shown recently that a complex of type $LFe(CO)_4$, where L = diazanorbornene, reacts with iron carbonyls and can give rise to the trinuclear cluster (XXVI) together with a dinuclear complex of type $LFe_2(CO)_6$ and the former can also be synthesised by irradiating a dinuclear type (A) complex ($\lambda \geqslant 300$ nm) in the presence of iron carbonyls[51]:

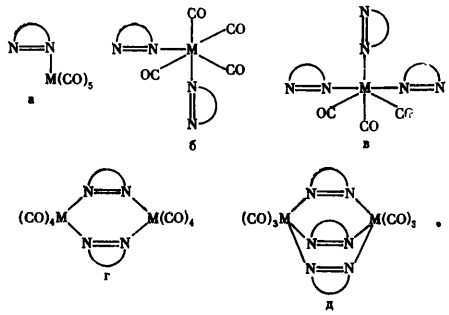


(XXVI)

Bearing in mind that the dinuclear complexes are diamagnetic, it follows that, in conformity with the effective atomic number rule, the metal atoms in them should be linked by an intermetallic bond, whose presence has been confirmed by X-ray diffraction (see below).

It is of interest that Group VIB metal carbonyls react with azo-compounds to give, together with mononuclear complexes (of types a–c, Scheme 3), also dinuclear complexes of types d and e in which the ligand behaves as a four-electron donor and the metal atoms are not linked to one another[6,71–75]:

Scheme 3



Thus Group VIB metals form a bond with nitrogen atoms solely via lone electron pairs, while the $\pi$ electrons of the N=N group are not involved in bonding to the metal, in contrast to iron carbonyl complexes. This can probably be attributed to the fact that the lowest unoccupied antibonding orbital of azo-compounds is located sufficiently low to make possible their interaction with Group VIB metals.

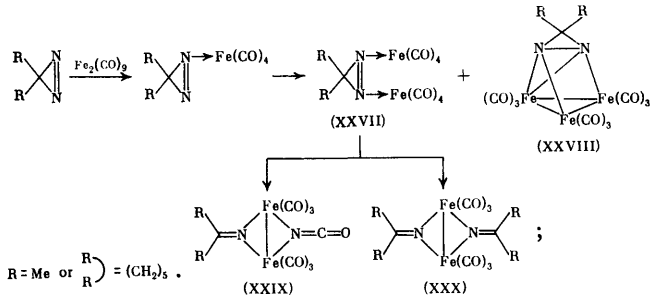
We may note that, instead of a mixed complex of type d, the reaction of $L_2Mo(CO)_4$ (where L = diazanorbornene) with $Fe_2(CO)_9$ gave a dinuclear di-iron hexacarbonyl complex of type $LFe_2(CO)_6$.

The reaction with diazirines, which are strained cyclic azo-compounds, is a special case. Diazirines contain the N=N group in a three-membered ring, and the distribution of electron density in these compounds differs significantly from that in other cyclic azo-compounds.

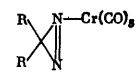
MINDO/2 calculation for 3,3-dimethyldiazirine[76] led to the conclusion that the orbitals of the C–N $\sigma$ bond are appreciably mixed with a linear combination of those of free pairs of $n_-$ and $n_+$ electrons of the nitrogen atoms, so that the concept of a "free pair" apparently loses its significance in these compounds. Calculation showed that the electrons are localised on the nitrogen atoms to an extent of only 56%,[76] so that the possibility of the formation of complexes of diazirines with metals appears to be problematical.

However, in reality it was found that[54] 3,3-dimethyl- and 3,3-pentamethylene-diazirines in tetrahydrofuran (THF) react with $Fe_2(CO)_9$ to form unstable complexes of the type $LFe(CO)_4$ (Scheme 4), which are subsequently converted into compounds (XXVII), giving rise also to a small amount of the trinuclear cluster (XXVIII). The diazirine skeleton is retained in all these compounds. Complexes (XXVII) decompose in solution with formation of new, more stable compounds (XXIX) and (XXX), which can be synthesised directly from diazirines and $Fe_2(CO)_9$ or $Fe(CO)_5$ on irradiation. This entails the dissociation of the C–N and N=N bonds and it is postulated that intermediate nitrene species are formed in the latter case[54]:

Scheme 4



Analogous results have been obtained in a study[77] in which the structure of complex (XXX) [where R–R = $(CH_2)_5$] was confirmed by X-ray diffraction. It is of interest that the aquopentammineruthenium derivative $[Ru(NH_3)_5(H_2O)]^{2+}$ used in the above study in the reaction with 3,3-pentamethylenediazirine promotes only the dissociation of the C–N bonds, which results in the formation of a complex with molecular nitrogen, namely $[Ru(NH_3)_5N_2]^{2+}$,[77] while in the reaction with $Cr(CO)_6$ the diazirine skeleton is retained and only complex (XXXI) is formed[54]:



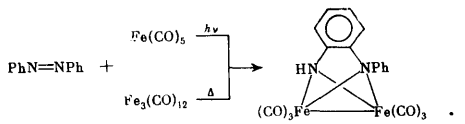
(XXXI)

The above examples provide a good illustration of the major influence of the metal in the attacking complex on the behaviour of the azo-compound.

The cleavage of the N=N bond is a new phenomenon in the chemistry of diazirines. However, a similar phenomenon is fairly usual in reactions of aromatic azo-compounds with iron carbonyls. At the same time it is important to note that the behaviour of such azo-compounds depends in many respects, as will be shown below, on the nature of the substituent in the aromatic ring.

The interaction of azobenzenes with $Fe_2(CO)_9$ was investigated for the first time by Bagga et al.[49] X-Ray diffraction analysis established[78,79] that the complex isolated has the structure (XXXII), indicating the dissociation

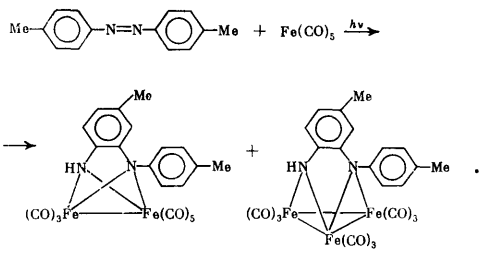
of the N=N bond as a result of an orthosemidine rearrangement‡:



(XXXII)

The yields of compound (XXXII) are only 2–3% both in the photochemical reaction of azobenzene with $Fe(CO)_5$ and in the thermal reaction with $Fe_3(CO)_{12}$.[80] At the same time in one of the reports[24] it is stated briefly that the reaction of azobenzene with $Fe_2(CO)_9$ at room temperature results in the formation of an unstable complex in which the azobenzene ligand is probably incorporated without serious changes, since azobenzene is liberated in attempts to purify the complex chromatographically or by sublimation. It is of interest that, as already stated above, a comparatively stable complex of type (B) with the azobenzene ligand is formed in the reaction of phenyl azide with $Fe_2(CO)_9$.[7]

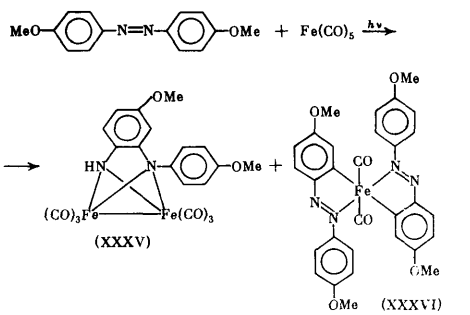
The behaviour of ring-substituted azobenzenes in reactions with iron carbonyls differs from the behaviour of azobenzene itself. Thus, when 4,4′-dimethylazobenzene reacts with $Fe(CO)_5$ under irradiation, two complexes with the *ortho*-semidine ligand are formed: a dinuclear complex (XXIII) in 2% yield and a trinuclear complex (XXXIV), which becomes the sole product when $Fe_2(CO)_9$ is used instead of $Fe(CO)_5$:[80]



(XXXIII) (XXXIV)

The structures of these complexes were assigned on the basis of spectroscopic studies and data derived from chemical reactions[80].

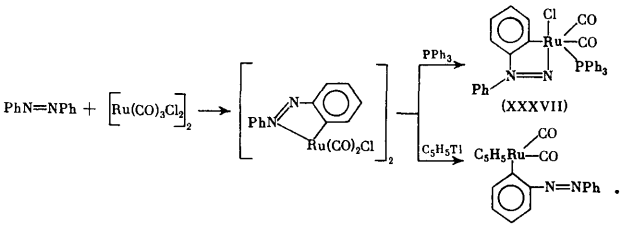
Under the same conditions, 4,4′-dimethoxyazobenzene gives a 22% yield of complex (XXXV) and a small amount of a completely new compound (XXXVI), which is a product of ring metallation[80]:



(XXXV) (XXXVI)

‡ When complexes of the type $\eta^5$-$C_5H_5M(CO)_2$, where M = Co (I) or Rh (I), are used in the reaction of azobenzene, dinuclear complexes with the *ortho*-semidine skeleton are also formed[81].

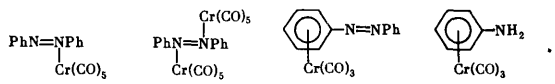
It is important to note that ring-metallated chelate complexes of type (XXXVI) are obtained fairly frequently when other metal carbonyls are used in the reaction with azobenzene[82–87]. Thus $[Ru(CO)_3Cl_2]_2$ yields a dimer, which is converted into complexes (XXXVII) and (XXXVIII) respectively on treatment with $Ph_3P$ and $C_5H_5Tl$:[84]



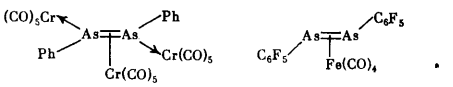
(XXXVII)

(XXXVIII)

Depending on the conditions, chromium hexacarbonyl yields at the same time four complexes[88]:



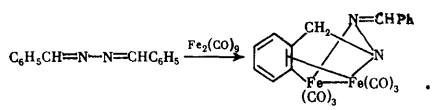
It is noteworthy that azobenzene does not react with metal carbonyls to form $\pi$ complexes via the N=N bond, while its arsenic analogue yielded the $\pi$ complexes (XXXIX) and (XL):[89,90]



(XXXIX) (XL)

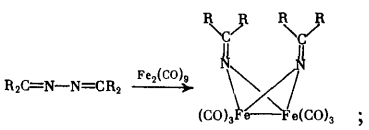
## 8. Reactions of Azines

There is at present no clear-cut hypothesis concerning the electronic and structural factors responsible for the different types of behaviour of azines in reactions with iron carbonyls. Thus the bond between the nitrogen atoms is retained in benzylideneazine on reaction with $Fe_2(CO)_9$ and a complex is formed to which the following structure was attributed on the basis of spectroscopic data[49]:



(XLI)

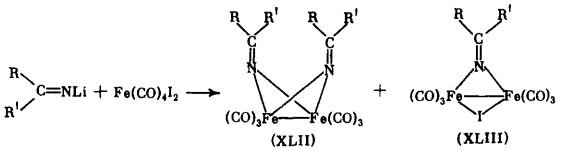
Benzophenone azine and its 4,4′-dimethyl derivative react with iron carbonyls to give low yields of di-iron hexacarbonyl complexes of type (XLII) whose formation involves the dissociation of the N–N bond[49]. The structure of these complexes has been demonstrated by X-ray diffraction in relation to compound (XLIIb):



(XLII): a) R = Ph; b) R = *p*-$MeC_6H_4$.

After unsuccessful attempts to improve this method of synthesis, a different procedure was proposed, which also leads to the formation of a small amount of compound

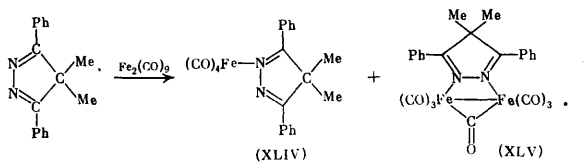
(XLIII):[92]



(XLII) (XLIII)

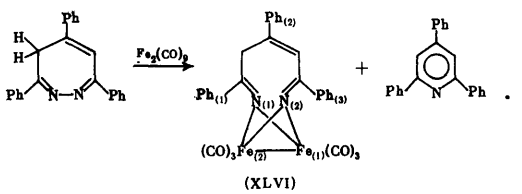
(a) R = R' = Ph; (b) R = R' = *n*-MeC$_6$H$_4$; (c) R = Ph, R' = t-Bu.

The unstrained cyclic azine 5,5-dimethyl-1,4-diphenyldiazacyclopentadiene reacts with $Fe_2(CO)_9$ under mild conditions (25°C) in pentane to form two complexes: a mononuclear complex (XLIV) and a dinuclear complex (XLV):[93]



(XLIV) (XLV)

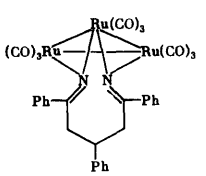
In agreement with infrared spectroscopic data, complex (XLV) incorporates a CO bridge group [$\nu$(CO) = 1736 $cm^{-1}$]. The nitrogen-containing ligand plays in this case the role of a four-electron donor. A cyclic seven-membered azine, such as 3,5,7-triphenyl-4*H*,1,2-diazepine, gives rise in this reaction to the dinuclear complex (XLVI) with dissociation of the N–N bond[94–96]:



(XLVI)

In the study of the Mössbauer spectra of this complex[94] the iron atoms were found to be non-equivalent, which was explained, after X-ray diffraction study, by differences between the Fe–N [$(Fe_1-N)_{av}$ and $(Fe_2-N)_{av}$] bond lengths (1.920 and 1.965 Å respectively). The differences between the bond lengths can be caused in their turn by the steric effects of the two phenyl substituents in the ring, namely $Ph_{(1)}$ and $Ph_{(3)}$, located on the same side of the ring as $Fe_{(2)}$.

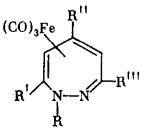
An analogous complex has been obtained as a result of the reaction of 3,5,7-triphenyl-4,5,6-trihydro-1,2-diazepine with $Fe_2(CO)_9$.[84] It is of interest that the use of $Ru_3(CO)_{12}$ in this same reaction led to the trinuclear cluster (XLVII):[94]



(XLVII)

At the same time the reactions of $[Rh(CO)_2X]_2$ (where X = Cl or Br) with seven-membered heterocycles give rise to complexes of type $LRh(CO)_2X$ in which the metal is coordinated to one of the nitrogen atoms[94]; this was confirmed by X-ray diffraction analysis of the compound with the 3,5,7-triphenyl-4*H*-1,2-diazepine ligand (X = Cl).[96]

As in the series of *N*-substituted 1(1*H*),2-diazepines, the breakdown of the diazepine system leads to mononuclear complexes of type (XLVIII) with coordination between the metal atom and the diene group in the heterocycle[97–99]:

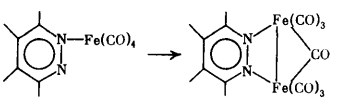


(XLVIII)

9. Reactions of Aromatic Heterocycles with Two Vicinal Nitrogen Atoms

Since the resonance hybrid of aromatic heterocycles incorporates structures with both N=N and =N–N= groups, it is not surprising that iron carbonyls react with these heterocycles in the same way as with azo-compounds and diazines.

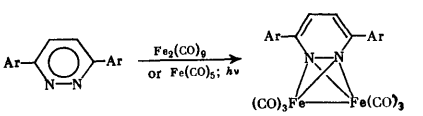
The simplest representative of this class of compounds, namely pyridazine, and also 3,6-dimethylpyridazine react with $Fe_2(CO)_9$ to form in the first stage mononuclear complexes of type $LFe(CO)_4$ in which the metal atom is bound to one of the nitrogen atoms[53,100]. Next, according to Herberhold and Leonard[53], complexes of type $LFe(CO)_4$, formed from pyridazine and phthalazine, are converted into dinuclear compounds (XLIX). In these compounds the ligand behaves as a four-electron donor coordinated to the $Fe_2(CO)_7$ group and containing the CO bridge group in the pyridazine complex [$\nu(CO)_{bridge}$ = 1851 $cm^{-1}$ in KBr and 1775 $cm^{-1}$ in THF solution]. The presence of seven carbonyl groups in the complexes (XLIX) has been confirmed convincingly by mass spectrometry[53]:



(XLIX)

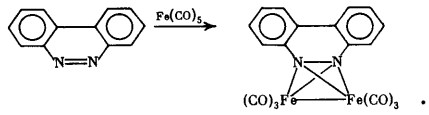
It is noteworthy that the attempt to convert compounds of type $LFe_2(CO)_7$ into $LFe_2(CO)_6$, which was achieved for dinuclear iron carbonyl complexes of aliphatic azo-compounds, was unsuccessful[53]. On heating or irradiation in the presence of CO the complex (pyridazine)$Fe_2(CO)_7$ regenerates (pyridazine)$Fe(CO)_4$.[53]

The reaction of 3,6-diarylpyridazine with $Fe_2(CC)_9$ gives rise to iron carbonyl complexes (L)[123] Their structure was demonstrated by X-ray diffraction analysis of the monotriphenylphosphine derivative[101]:



(L)

An analogous dinuclear complex (LI) was obtained (in 79% yield) from benzo[*c*]cinnoline [24] §:



(LI)

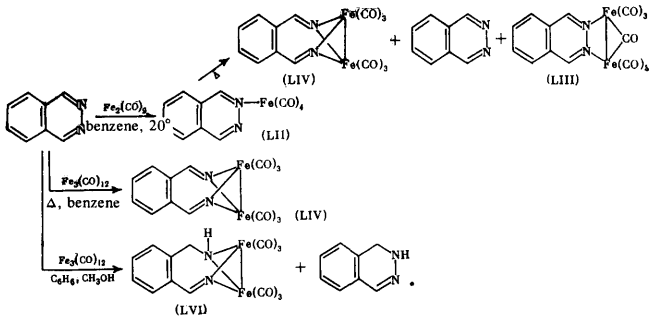
Its structure was also confirmed by X-ray diffraction [25]. In the reaction involving benzo[*c*]cinnoline the formation of an intermediate di-iron heptacarbonyl complex with a CO bridge group was noted [53]. Thermal or photochemical decarbonylation of $LFe_2(CO)_7$ (L = benzocinnoline) leads to complex (LI). The synthesis of dinuclear complexes from 1,10-dichloro- and 3,8-dichloro-benzo[*c*]cinnolines and from 4,5,9,10-tetra-azapyrene has also been mentioned [24], both N=N fragments in the last compound being coordinated to $Fe_2(CO)_6$ groups.

The above examples suggest that the formation of the $N_2Fe_2(CO)_6$ group is energetically fairly favourable, since it occurs despite the losses of resonance energy as a result of the breakdown of the aromatic system of the heterocycle.

Phthalazine forms mononuclear and dinuclear complexes with iron carbonyls (Scheme 5). When it is treated with $Fe_2(CO)_9$ in n-hexane or benzene at 20°C, a mononuclear complex of type $LFe(CO)_4$ (LII) is formed, in which the nitrogen-containing ligand occupies an axial position. Furthermore, a dinuclear heptacarbonyl complex $LFe_2(CO)_7$ (LIII) with a CO bridge group is formed [$\nu$(C=O) = 1745 $cm^{-1}$ in KBr or 1775 $cm^{-1}$ in THF]. [53,104]

According to Alper's data [104], on heating in benzene complex (LII) is converted into a compound $LFe_2(CO)_6$, to which structure (LIV) was assigned. In contrast to di-iron hexacarbonyl complexes of 3,6-diarylpyridazine, there is no bond between the nitrogen atom in compound (LIV). The latter is formed also when phthalazine is heated with $Fe_3(CO)_{12}$ in benzene [104]. The alternative *ortho*-xylylene structure (LV) for this substance has been rejected on the grounds that the ligand in (LIV) retains its benzenoid structure.

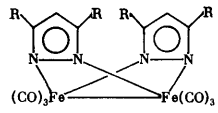
Scheme 5



A dinuclear complex (LVI) (Scheme 5) was detected in the products of the interaction of phthalazine with $Fe_3(CO)_{12}$ in benzene in the presence of methanol [104].

§ It is noteworthy that the reaction of benzo[*c*]cinnoline with Group VIB metal hexacarbonyls gives rise to complexes $LM(CO)_5$, in which the metal is coordinated to one of the nitrogen atoms [102,103].

The reactions of five-membered heterocycles have so far been little investigated. It has been shown that, when pyrazole or 3,5-dimethylpyrazole reacts with $Fe_2(CO)_9$ in ether, dinuclear hexacarbonyl complexes of type (LVII), whose structure has been assigned on the basis of spectroscopic data, are formed together with other products [105,106]:

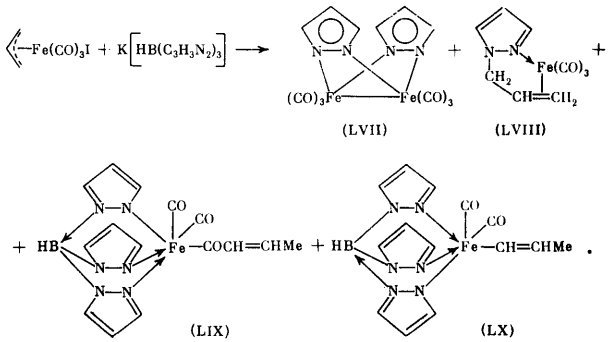


R = H, or Me.

The same dinuclear complex (LVII) (R = H) has been obtained by the interaction of $Fe(CO)_4I_2$ with pyrazolylsodium [106]:

$$2Fe(CO)_4I_2 + 2C_3H_3N_2Na \rightarrow (C_3H_3N_2)_2Fe_2(CO)_6 + 2NaI + 2CO$$

and has also been isolated from the products of the reaction of $\pi$-(allyl)$Fe(CO)_3I$ with $K[HB(C_3H_3N_2)_3]$. [107] The mononuclear complexes (LVIII)–(LX) were obtained together with this product in the latter case:



(LVII) (LVIII)



(LIX) (LX)

## III. CHEMICAL PROPERTIES OF DINUCLEAR COMPLEXES

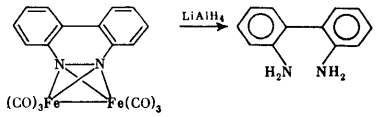
The reactivity of the dinuclear complexes has still been little investigated. Studies have been made mainly on reactions designed to demonstrate the structures of these compounds and, particularly, in order to elucidate the nature of the nitrogen-containing ligand incorporated in them. Thus, *N*,*N*',*N*''-tricyclohexaguanidine, identified as the picrate, was isolated after the acid hydrolysis of complexes of type (XX) (R = $C_6H_{11}$): [108]

$$(XX) \xrightarrow{H^+} C_6H_{11}NHCNHC_6H_{11} \quad (\text{with } NC_6H_{11})$$

*N*,*N*'-Diphenylurea was obtained in 50% yield by treating complex (VIII) with $LiAlH_4$, which confirms the presence of this ligand in the complex [41]:

$$(VIII) \xrightarrow{LiAlH_4} PhNHCONHPh$$

On interaction with $LiAlH_4$, the dinuclear benzo[*c*]cinnoline complex forms 2,2-diaminobiphenyl in 56% yield [24]:



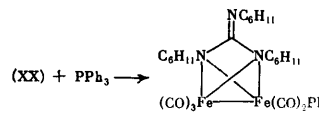
Under the same conditions, free benzo[*c*]cinnoline is resistant to the action of $LiAlH_4$, but, when the complex

is treated with an oxidant, such as $Ce^{4+}$, free benzo[*c*]-cinnoline may be produced.

The CO ligand substitution reactions involving these complexes are also striking. It has been shown in many instances that phosphines, phosphites, arsines, and isonitriles substitute one and in some cases two CO groups without change in the main skeleton of the complex.

Triphenylphosphine substitutes one or two CO groups in the complex $[Fe_2(CO)_6(NH_2)_2]$ giving rise to compounds of type $[Fe_2(CO)_5PPh_3(NH_2)_2]$ and $[Fe_2(CO)_4(PPh_3)_2(NH_2)_2]$.[17,109] It is of interest that the latter can be very readily oxidised by iodine with formation of the dication $[Fe_2(CO)_4.(PPh_3)_2(NH_2)_2]^{2+}$.[17] It is also noteworthy that NO completely displaces the CO ligands from the complex $[Fe_2(CO)_6(NH_2)_2]$.[14,15]

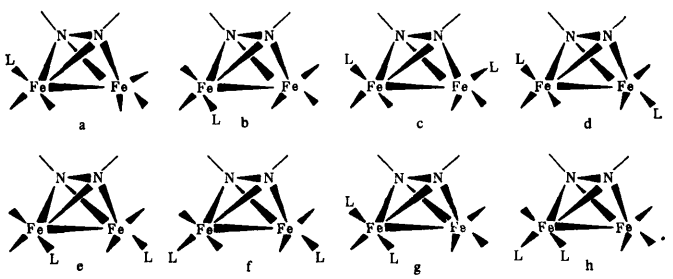
Only one CO group is substituted in a complex of type (XX) (R = $C_6H_{11}$) by $PPh_3$ even in the presence of an excess of the latter; this reaction results in the formation of a monophosphine derivative, which is very stable in air[108]:



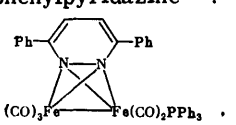
When the di-iron hexacarbonyl complex of benzo[*c*]cinnoline is treated with phosphines, phosphites, arsines, and isonitriles, both mono- and di-substituted derivatives are formed[24,110]. Here it is significant that the substitution of one of the CO groups by another ligand should theoretically lead to two isomers [(a) and (b) (Scheme 6)], while substitution of two CO groups should lead to six isomers [(c)–(h) (Scheme 6)].

Analysis of the infrared spectra of monosubstituted benzo[*c*]cinnoline complexes suggested that these compounds have the structure of the *trans*-isomers (a):[110]

Scheme 6



*trans*-Substitution¶ relative to the Fe–Fe bond has been demonstrated by the X-ray diffraction study of the triphenylphosphine complex (LXI) obtained from di-iron hexacarbonyl-3,6-diphenylpyridazine[101]:

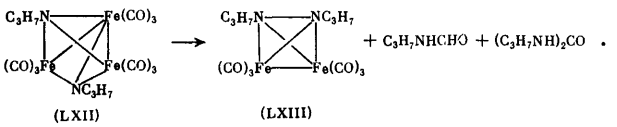


(LXI)

The problem of the structure of the disubstituted derivatives has still not been finally solved. Isomers of types (g) and (h) (Scheme 6) were ruled out on the grounds that the mass spectra of the diphosphite and di-isonitrile complexes investigated, obtained from di-iron hexacarbonyl–benzo[*c*]cinnoline, failed to reveal fragment ions containing one iron atom linked to two $P(OCH_3)_3$ or $C_6H_{11}NC$ molecules[110]. It is extremely difficult to choose between isomers (c)–(f) (Scheme 6). On the basis of the number of bands in the metal carbonyl part of the spectrum, it was concluded that a mixture of isomers is formed in most instances, but it could not be resolved chromatographically[110].

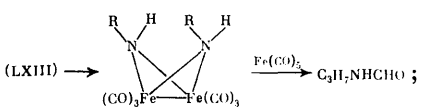
Extremely useful information about the reactivity of dinuclear iron carbonyl complexes was obtained in a study of the interconversions and thermal degradation of these compounds. The study of the products of the reactions makes it possible to some extent to infer the sequence of stages in the formation of dinuclear complexes.

It has been shown[36] that, when the trinuclear complex (LXII) is heated in diglyme at 120–130°C, complex (LXIII) and traces of $C_3H_7NHCHO$ and $(C_3H_7NH)_2CO$ are formed:



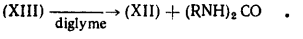
(LXII) (LXIII)

On further heating, complex (LXIII) is converted into (LXIV) with rupture of the N–N bond in the bridge ligand:



(LXIV) R = $C_3H_7$.

When this compound is heated with iron pentacarbonyl, a formamide derivative is formed. Thermal degradation of complex (XIII) (R = $C_3H_7$) with a ureylene ligand led to the formation of *N*,*N*′-disubstituted urea and the formation of a small amount of complex (XII):



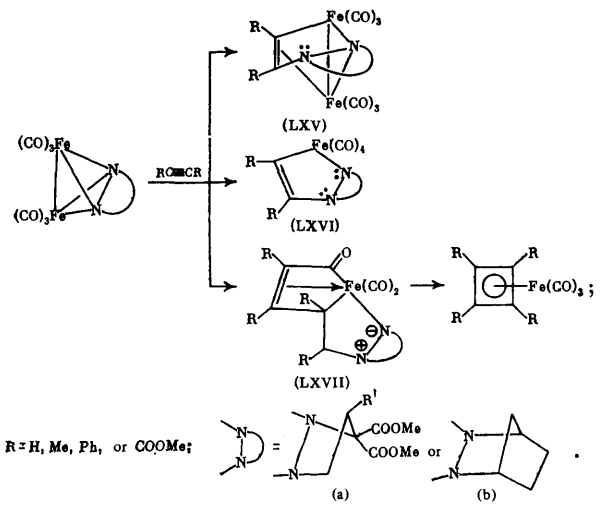
One should note here that the nature of the substituent R can influence the course of the reaction. Thus spontaneous reconversion of complex (XII) into (XIII) for R = Ph has been observed[7]. Prolonged heating of a type (XIII) complex (R = t-Bu) yields substituted formamide and urea[36].

Thus trinuclear complexes of type (LXII) can behave as precursors of binary compounds when the latter are formed from azides and nitro-compounds. Reactions involving insertion in the N–Fe bond can be assigned to the most interesting and hitherto little investigated branch of the chemistry of dinuclear complexes. The insertion of CO molecules in this bond has already been mentioned. Thermal and photochemical reactions of dinuclear complexes with alkynes were investigated recently[111–113] and it was found that alkyne molecules are inserted in the N–Fe bond with formation of complex (LXV)–(LXVII)

¶ We have in mind the *trans*-substitution relative to the Fe–Fe bond in the distorted octahedron at each Fe atom.

Scheme 7):[111,112]

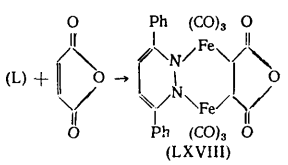
Scheme 7




It was found that complex (LXV) is readily converted into (LXVI) and the latter into (LXVII). The structures of compounds (LXVa) and (LXVIIa) (R = R′ = Ph) were confirmed by X-ray diffraction. In contrast to compounds with ligands (a) and (b), the complex obtained on the basis of benzo[*c*]cinnoline reacts with alkynes to give only a compound of type (LXV).

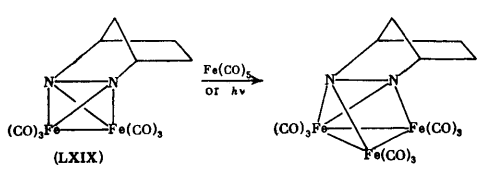
It is of interest to note that, when compounds of type (LXVII) (R = Ph) were heated *in vacuo* to 150°C, tetraphenylcyclobutadieneiron tricarbonyl was obtained. This compound can be synthesised in a single stage by heating the initial di-iron hexacarbonyl complex with a sixfold excess of diphenylacetylene (yield 70%).[111] The authors[111] noted that they were unable to obtain analogous results using aliphatic alkynes[12].

The interaction of the dinuclear complex (L) (Ar = Ph) with maleic anhydride has been assigned to reactions of the same type[113]†:




The structure of complex (LXVIII) obtained was demonstrated by X-ray diffraction[113].

Finally, a very interesting conversion into a trinuclear cluster was observed in the interaction of complex (LXIX) with $Fe(CO)_5$ or simply on its irradiation ($\lambda \geqslant 300$ nm):[51]




† Other workers[113] regard this reaction as cycloaddition.

## IV. RESULTS OBTAINED BY PHYSICAL RESEARCH METHODS

The common fragment in the dinuclear complexes investigated is the group $N_2Fe_2(CO)_6$, which determines the main properties of these compounds. According to X-ray diffraction studies, the $N_2Fe_2$ fragment in this group has tetrahedral or a distorted tetrahedral geometry and the presence or absence of the bond between nitrogen atoms‡ in the fragment clearly divides all the complexes into two groups (see Tables 1 and 2):

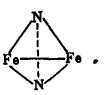
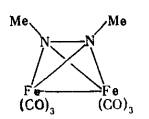
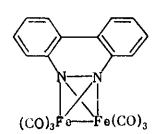
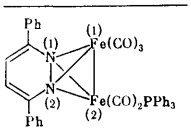
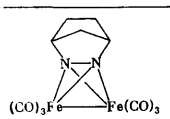


Table 1. Certain structural parameters of dinuclear complexes of type (B) (the bond lengths are quoted in angstroms and the angles in degrees).

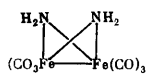
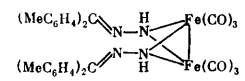
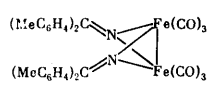
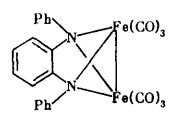
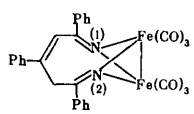
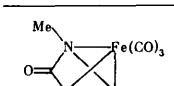
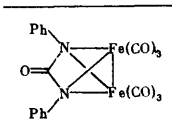
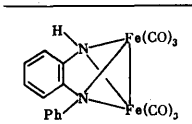
| Complex | Fe—Fe | Fe—N | N—N | Fe—N—Fe | N—Fe—N | Refs. |
|---|---|---|---|---|---|---|
|  | 2.496 | 1.878 | 1.366 | 83.4 | 42.7 | 64 |
|  | 2.508 | 1.914 | 1.399 | 81.9 | 42.90 | 25 |
|  | 2.53 | 1.93($Fe_{(1)}$—$N_{(1)}$); 1.95($Fe_{(2)}$—$N_{(2)}$) | 1.43 | 82.00 | 42.0 | 101 |
|  | 2.990 | 1.932 | 1.405 | 81.3 | 43.1 | 121 |

The distance between the nitrogen atoms in dinuclear complexes with an N—N bond [(type B), Table 1] is approximately 1.40 Å, which corresponds to a single bond[44,114,115]. The distance between the nitrogen atoms in the other group of complexes [type (A), Table 2] varies in the range 2.15—2.50 Å, which undoubtedly leads to the conclusion that there is no bond between them. It has been observed that in complexes with an N—N bond the length of the Fe—Fe bond (2.50 Å) is always greater by approximately 0.1 Å than in the other group, where the Fe—Fe bond length is approximately 2.40 Å. This tendency was

‡ A dashed line NN implies that a bond between nitrogen atoms is not obligatory.

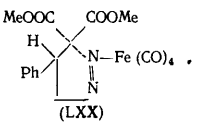
first noted by Doedens and Ibers [64] and was subsequently confirmed by Doedens [25]. The shortening of the Fe–Fe bond (to 2.40 Å) in complexes without an N–N bond is probably due to the constancy of the Fe–N bond length [116]. In the dinuclear complexes considered this bond length varies from 1.91 to 2.00 Å, but it cannot vary within limits as wide as in the case of the Fe–Fe bond [116–119]. Indeed, Table 3, taken from Vahrenkamp [116], shows that the Fe–Fe bond length can vary from 2.40 to 3.05 Å, i.e. by more than 0.6 Å. Thus, in order to keep the Fe–N bond length constant on passing from complexes of type (B) to those of type (A), the Fe–Fe bond must be somewhat shortened with a consequent obligatory decrease of the Fe–N–Fe angle (from 83° to 72°, cf. Tables 1 and 2).

Table 2. Certain structural parameters of dinuclear complexes of type (A) (the bond lengths are quoted in angstroms and the angles in degrees).

| Complex | Fe–Fe | Fe–N | N–N | Fe–N–Fe | N–Fe–N | Refs. |
|---|---|---|---|---|---|---|
|  | 2.402 | 1.98 | 2.50 | 74.4 | 77.8 | 18 |
|  | 2.40 | 2.00 | — | — | — | 44 |
|  | 2.403 | 1.94 | — | — | — | 91 |
|  | 2.37 | 2.00 | — | 72.50 | 73.00 | 78 |
|  | 2.393 | 1.920(Fe$_1$—N)<br>1.965(F$_2$—N) | 2.25 | — | — | 95 |
|  | 2.39 | 1.975 | — | 75.37 | 65.00 | 19 |
|  | 2.402<br>2.416 | 2.01<br>1.99 | | 74<br>74.5 | 65<br>64.9 | 41<br>122 |
|  | 2.372 | 2.00 | 2.38 | 72.5 | 72.9 | 79 |

Furthermore, the data in Table 3 show that the dependence of the Fe–Fe bond length on the Fe–heteroatom bond length is common to dinuclear iron complexes.

At the same time it is important to note that virtually identical Fe–N bond lengths have been found both in dinuclear complexes of types (A) and (B) and in iron tetracarbonyl derivatives $LFe(CO)_4$. X-Ray diffraction studies on complex (LXX) [70] showed that the Fe–N bond length in this complex is 1.979 Å and the nitrogen–nitrogen bond length is 1.242 Å, which corresponds to the N=N double bond:




It follows from X-ray diffraction data that the $N_2Fe_2(CO)_6$ group in the complexes considered has $C_{2v}$ symmetry, like other structurally related bridge groups in the compounds $LFe(CO)_6$. [64]

Table 3. Certain results of the X-ray diffraction analysis of dinuclear complexes with heteroatomic bridges [116].

| Complex | Bridge heteroatom | Fe–heteroatom distance, Å | Fe–Fe, Å |
|---|---|---|---|
| $[(CO)_3FeNH_2]_2$ | N | 1.98 | 2.40 |
| $(CO)_5Fe_2Cp(PMe_2)$ | P | 2.19 | 2.63 |
| $(CO)_8FeMnAsMe_2$ | As | 2.35 | 2.85 |
| $[(NO)_2FeI]_2$ | I | 2.58 | 3.05 |

Group theoretical analysis makes it possible to predict five infrared-active vibrations for terminal carbonyl groups: $2A_1 + 2B_2 + B_1$. [120]

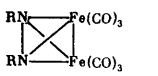
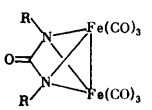
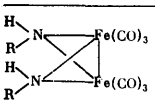
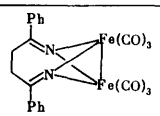
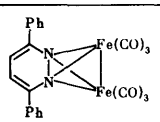
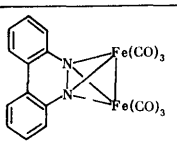
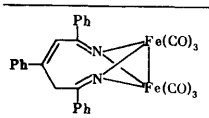
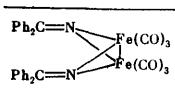
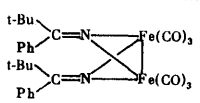
Table 4 presents the stretching vibration frequencies of the CO ligands for certain complexes containing the $N_2Fe_2(CO)_6$ group. It shows that the spectra of the majority of complexes in the region of $\nu(C{\equiv}O)$ are very similar. In a number of studies this similarity between the spectra enabled the presence of the $N_2Fe_2(CO)_6$ group in the complexes to be observed [69,92,94].

It is much more difficult to conclude whether or not the nitrogen–nitrogen bond is present on the basis of infrared spectra. In this instance the influence of the ligand as a whole is probably more important. It may consist both in the breakdown of the symmetry of the metal carbonyl fragment, which leads to an increase of the number of absorption bands [92], and in an enhancement or weakening of the electron-donating properties of the ligand, which causes a band shift [53]. Such a band shift is manifested to an even greater extent on passing to $LF_2(CO)_6$ systems with other bridge heteroatoms (S, P, As, etc.) [120].

At the same time infrared spectra of the complexes $LFe_2(CO)_7$ yield undoubtedly important information. Apart from the four stretching vibration bands of the terminal CO ligands, they include the characteristic absorption at 1820–1730 $cm^{-1}$, which convincingly demonstrates the presence of a carbonly bridge group [83,93]. The mass spectra of many complexes contain molecular ions

and indicate the successive elimination of all the carbonyl groups[18,53,92,108]. The fragmentation of the $LFe_2^+$ ions formed in this process is determined mainly by the nature of the ligand L.

**Table 4.** The stretching vibration frequencies of the CO ligands in certain complexes $LFe_2(CO)_6$.

| Complex | ν (C=O), cm$^{-1}$ | Refs. |
|---|---|---|
|  R = n-Pr<br>R = t-Bu | 2072, 2032, 1999, 1911, 1972 (sh.)<br>2060, 2022, 1994, 1972 (sh.) | 36 |
|  R = n-Pr<br>R = t-Bu | 2082, 2046, 2002, 1991<br>2082, 2045, 1998 | 36 |
|  R = n-Pr<br>R = t-Bu | 2075, 2051, 2034, 1998, 1992<br>2066, 2047, 1033, 1992 | 36<br>36 |
|  | 2070, 2030, 1995, 1975, 1960 (sh.) ($CHCl_3$) | 36<br>36<br>35 |
|  | 2065, 2025, 1985, 1970 (cyclohexane) | 123 |
|  | 2073, 2033, 1982, 1972 ($CS_2$) | 24 |
|  | 2068, 2031, 1998, 1986, 1972 (sh.), 1967 (hexane) | 94 |
|  | 2047, 2041, 1994, 1979 (cylcohexane) | 92 |
|  | 2073, 2036, 1994, 1987, 1971 (cyclohexane) сан) | 92 |

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