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Chalcogeniron Carbonyl Clusters

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The literature data and the methods of synthesis, structure, and physicochemical properties of chalcogeniron carbonyl clusters and their derivatives are surveyed and described systematically.
The bibliography includes 163 references.

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I. INTRODUCTION

Iron clusters are particularly abundant among transition metal carbonyl complexes with sulphur-containing ligands.[1] Typical representatives of chalcogeniron carbonyl clusters are dichalcogendiiron hexacarbonyl $(\mu\text{-}X)_2Fe_2(CO)_6$ (I) and dichalcogentriiron nonacarbonyl $(\mu_3\text{-}X)_2Fe_3(CO)_9$ (II), where X = S, Se, or Te [for brevity, the formulae used subsequently will be $X_2Fe_2(CO)_6$ and $X_2Fe_3(CO)_9$].

The chemistry of these clusters has so far developed extensively, but some of their features have not been adequately explained. The study of the methods of synthesis and the properties of clusters (I) and (II) under comparable conditions involves considerable experimental difficulties. Very few thoroughly developed methods of synthesis of the above cluster compounds are so far available. Their chemical properties have likewise not been studied systematically.

Chalcogeniron carbonyl complexes, which are the compounds of a large number of cluster derivatives, in particular the cubane systems $[S_4Fe_4(SR_4)]^{n-}$, themselves possess a series of unique properties, which are considered in the present review. For example, sulphur-containing iron clusters enter into the composition of polynuclear enzymes (ferredoxins)—a new class of biocatalysts which play an exceptional role in vitally important processes such as the fixation of molecular nitrogen. The chemical modelling of the catalytic properties of cluster enzymes will make it possible to create fundamentally new effective catalysts of many industrial processes.

The aim of the present review is a critical consideration of the methods of synthesis and the structure of chalcogeniron carbonyl clusters together with the discussion of their physicochemical properties. Although more than 150 communications have been published on this subject, so far no attempt has been made to survey them and to give a systematic account. We believe that a review of the methods of synthesis and chemical properties of chalcogeniron carbonyl clusters is extremely urgently required in connection with the vigorous development of a new scientific discipline—the chemistry of cluster compounds.[2]

II. METHODS OF SYNTHESIS

As already mentioned, there are as yet very few thoroughly developed methods of synthesis of chalcogeniron carbonyl clusters. The majority of these clusters have been obtained non-specifically. The interaction of aqueous alcoholic solutions of alkali metal tetracarbonylferrate salts with sulphurous acid (or selenous and tellurous acid respectively) must be regarded as the most general method whereby such compounds can be obtained. This method synthesis is so far the most convenient and the one most frequently used for preparative purposes. A survey of the methods of synthesis shows that molecules with different chemical properties can serve as sources for the preparation of the same chalcogeniron carbonyl clusters. Thus for sulphur these are compounds exhibiting differences from the standpoint of the formal valence of sulphur, such as S_8, H_2S, SO_2, CS_2, RSH, etc. These compounds will be considered below in greater detail as sources of sulphur.

Analysis of the literature data (see the Table below) has shown that the most effective methods of synthesis of iron carbonyl clusters involve the reaction of elemental sulphur S_8 [3] or hydrogen sulphide[4] with dodecacarbonyltriangulotriiron (DDCI) $Fe_3(CO)_{12}$. A novel method of synthesis of clusters of types (I) and (II), where X = S, based on the interaction of elemental sulphur with the triethylammonium salt of undecacarbonyltriiron hydride (TSUTH) $[(C_2H_5)_3NH]^+[HFe_3(CO)_{11}]^-$ is noteworthy.[3] Satisfactory results have also been obtained in the synthesis of the compound $S_2Fe_3(CO)_9$ from DDCI and 3-chloropropenyl sulphide[5] or by the reaction of $(C_6H_5)_3CSH$ with DDCI.[6] The reaction conditions and the method used to isolate the products apparently play a significant role in the synthesis of chalcogeniron carbonyl clusters.

We shall consider initially the method of synthesis of chalcogeniron carbonyl clusters in which a mixture of compounds (I) and (II) is formed.

1. Interaction of Elemental Sulphur and Hydrogen Sulphide with Iron Carbonyls

The compounds $X_2Fe_2(CO)_6$ and $X_2Fe_3(CO)_9$ where X = S, Se, or Te) can be regarded as the products of the substitution of the bridging carbonyl groups in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ by chalcogens.[7]

Until recently, there has been no information in the literature about the direct interaction of sulphur, selenium, and tellurium with iron carbonyls. It has been reported only that iron pentacarbonyl (IPC) does not react with elemental sulphur in the cold in solutions in carbon tetrachloride and xylene.[8] It has been shown[9-11] that elemental sulphur reacts with iron pentacarbonyl, iron nonacarbonyl (INC), and iron dodecacarbonyl in solution in benzene in

the course of 1–2 h at 80 °C to form very small amounts (2–5%) of the sulphur-containing clusters $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$ in proportions of 1 : 3.

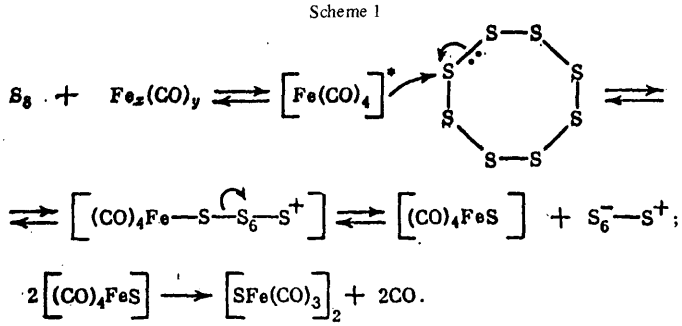
The reaction of elemental sulphur with iron carbonyls has been studied in greater detail by Mavlonov,[3] who examined the influence of the composition of the iron carbonyl, the reaction time, the reaction temperature, the reactant ratio, and the nature of the solvent and activating agents on the yield and ratio of compounds of types (I) and (II) and described the conditions for the chromatographic separation of these clusters.

The increase in reactivity of iron carbonyls in the sequence $Fe(CO)_5 < Fe_2(CO)_9 < Fe_3(CO)_{12}$ in the reaction with elemental sulphur agrees well with the hypothesis that the reactivity of iron carbonyls depends not only on the rate of formation and the amount of the coordination-unsaturated intermediate $[Fe(CO)_4]^*$ but also on the nuclearity of the cluster.[12–15]

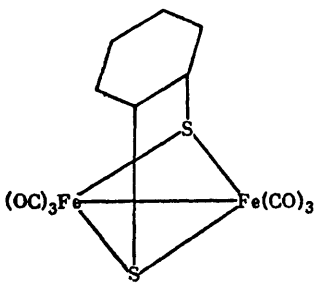
On the basis of available data on the interaction of sulphur compounds with iron carbonyls,[16–19] the reaction presumably proceeds via Scheme 1.

In certain cases where large amounts of the starting materials were used [0.075 mole of S_8 and 0.1 mole of $Fe_3(CO)_{12}$], it was possible to isolate in addition a further two substances in very small amounts.[3] One of these compounds is dithiodiiron heptacarbonyl $S_2Fe_2(CO)_7$ (III). It is a pale-orange crystalline substance with a melting point of 81–82 °C, which is readily soluble in organic solvents and is relatively stable in the solid state, while in solutions it is quantitatively converted on standing into $S_2Fe_2(CO)_6$ with evolution of CO.

Scheme 1



The structure of cluster (III) has been confirmed by elemental analysis, infrared spectroscopy, mass spectrometry, and X-ray diffraction.[20] The interaction of $Fe_3(CO)_{12}$ with a methanolic solution of NaOH and subsequent acidification of the solution in the presence of Na_2SO_3 yielded the cluster $SFe_3(CO)_{10}$ (IV).[21] At the same time the reaction of S_8 with an excess of cyclohexene or hex-1-ene in the presence of $Fe_3(CO)_{12}$ resulted in the formation,[22] apart from compound (IV), also of $S_2Fe_2(CO)_6$, $S_2Fe_3(CO)_9$, and the dithiolandiiron hexacarbonyl cluster having the structure



When cyclohexene is used, sulphur atoms are inserted in the double bond with formation of cyclic polysulphides. The structure of cluster (IV) has been studied by X-ray diffraction.[22]

The second compound formed together with compound (III) is apparently a polynuclear high-molecular-weight cluster $[S_xFe_y(CO)_z]$ (V), which is soluble only in polar organic solvents and is generated on heating compounds (I) or (II). The formation of a polynuclear cluster has also been noted in the interaction of elemental sulphur with dicobalt octacarbonyl.[23–25]

The methods of synthesis of clusters of types (I) and (II).

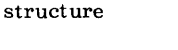
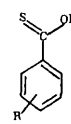
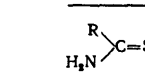
Initial compounds		Reaction conditions	Product (yield, %)	Refs.
sulphur compound	iron carbonyl			
S_8	$Fe(CO)_5$	CCl_4; $(CH_3)_2C_6H_4$; in the cold	—	[8]
S_8	$Fe(CO)_5$; $Fe_2(CO)_9$; $Fe_3(CO)_{12}$	C_6H_6; 80°; 1–2 h	(I):(II)=1:3 (2–5)	[9]
S_8	$Fe_3(CO)_{12}$	C_6H_6; 60°; 4 h	(I):(II)=4:1 (23.6)	[3]
S_8	$Fe_3(CO)_{12}$	THF; 60°; 6 h	(I)+(II); (36.7)	[3]
H_2S	$Fe_3(CO)_{12}$	C_6H_6; 52–54°, 2 h	(I):(II)=2:1 (90)	[4]
S_8	$[(C_2H_5)_3NH]\times$ $\times[HFe_3(CO)_{11}]$	C_6H_6; 60°; 6 h	(I):(II)=1:3 (33)	[3]
H_2XO_3; $Na_2S\times$ $\times 9H_2O$, X=S, Se, Te	$Fe(CO)_5$+CH_3OH+ +KOH	H_2O; 0°	(I)+(II) *	[32]
	$Fe_3(CO)_{12}$	C_6H_6; 80°; 4 h	(II) (10)	[5]
	$Fe_3(CO)_{12}$	C_6H_6; 80°; 4 h	(II) (55)	[5]
SO_2	$Fe_2(CO)_9$	petroleum ether; −10–−20°; 2 h	(II) **	[41]
$S_4(H_{28}CC_6H_5)_2$	$Fe_3(CO)_{12}$	C_6H_6; 50°; 9 h	(II)	[16]
	$Fe_2(CO_9)$	C_6H_{14}; 70°; 3 h	(II) (19)	[43]
$F_3C-S-S-CF_3$	$Fe_2(CO)_9$	C_6H_{14}; 70°	(I) (0.3); (II) (0.1)	[47]
t-C_4H_9SH	$Fe_3(CO)_{12}$	C_6H_6; 80°; 12 h	(II) (10)	[49]
$(C_6H_5)_3CSH$	$Fe_3(CO)_{12}$	$CH_3C_6H_5$; 80°; 4 h	(II) (57)	[6]
	$Fe(CO)_5$	C_6H_6; 78–80°; 14 h	(II) (26.7)	[54]
	$Fe_2(CO)_9$	C_6H_6; room temp.	(II) (5.4–18.3)	[56,57]
	$Fe_2(CO)_9$	C_6H_6; room temp.	(II) (0.7–7.5)	[58,59]
	$Fe_2(CO)_9$	C_6H_6; room temp.	(II) (0.1–2.5)	[17]

Table (contd.).

Initial compounds		Reaction conditions	Product (yield, %)	Refs.
sulphur compound	iron carbonyl			
	$Fe_2(CO)_9$	THF; room temp.	(II) (5.5)	[17,60]
Thiocamphenone	$Fe_2(CO)_9$	—	(II) (1.9)	[61]
Thiofenchone	$Fe_2(CO)_9$	—	(I) (4.57); (II) (15.7)	[61]
2-Thiono-1,3-dioxolan-chromium pentacarbonyl	$Fe(CO)_5$	THF	(II) **	[62]
Diphenylthionocyclopropene	$Fe_2(CO)_9$	THF	(II) **	[63]
R—N=S—N—R	$Fe_2(CO)_9$	C_6H_{14} or C_6H_6; 70-80°; 2-3 days	(II (1.5)	[65,67]
CS_2	$Fe_3(CO)_{12}$	C_6H_{14}; 80°; 7.5 h	(II) **	[68]
1,3-dithiole-2-thione	$Fe_2(CO)_9$	—	(II) (8.0)	[69]

*The yield is not quoted.
**Traces.

A mixture of clusters of types (I) and (II) in proportions of 2:1 has been isolated in 90% yield on passing an excess of hydrogen sulphide through a benzene solution of DDCI (52–54 °C, 2 h):[4]

$$H_2S + Fe_3(CO)_{12} \rightarrow S_2Fe_2(CO)_6 + S_2Fe_3(CO)_9.$$

It has been shown that TSUTH, which is an intermediate in the synthesis of DDCI, can be used successfully to obtain sulphur-containing compounds of types (I) and (II) [yield 33%, C_6H_6, 6 h, 60 °C, ratio (I):(II) = 1:3].[3] This method can be of preparative value in view of the availability of IPC and the possibility of regenerating triethylamine whose reactivity is relatively low in the substitution of CO groups in the clusters obtained.

It is noteworthy that, when iron carbonyls react with elemental sulphur or hydrogen sulphide and also when TSUTH reacts with sulphur, the initial reaction product is, according to thin-layer chromatographic (TLC) data, dithiodiiron hexacarbonyl, which is subsequently converted into a compound of type (II):[3]

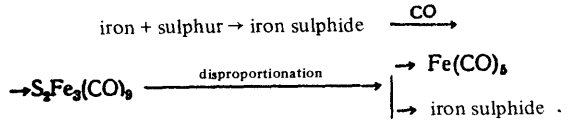
$$S_2Fe_2(CO)_6 \xrightarrow{Fe_3(CO)_{12}} S_2Fe_3(CO)_9.$$

In earlier studies it was reported that the reaction of DDCI with 2-mercaptobenzothiazole, thiosemicarbazide, thioacetamide, or parathioformaldehyde leads to the formation of the compound $(H_2C)S_2Fe_3(CO)_{10}$ [26] in a low yield. Later it was demonstrated that in reality this compound is dithiotriiron nonacarbonyl $S_2Fe_3(CO)_9$.[27]

Spongy iron and matte, granulated iron, and certain natural ores are used as the iron-containing raw material in the industrial preparation of IPC.[28] The iron matte consists of an alloy of iron (in the form of filings) and iron pyrite FeS_2 in proportions of 3:1. The alloy contains ~92% of iron and 8% of sulphur. A number of studies have been devoted to the influence of sulphur compounds on the formation of iron, molybdenum, and nickel compounds.[29–31]

In the development of preparative methods for the synthesis of IPC from the metal in the absence of solvents, it has been established that small amounts of sulphur or selenium have a favourable effect on the reaction.[29] A systematic investigation has therefore been made of the influence of added sulphur, selenium, and tellurium on the formation of IPC[7] and it was suggested that these elements act as catalysts, forming intermediate clusters such as $S_2Fe_3(CO)_9$, which subsequently decompose under the influence of carbon monoxide to form IPC and sulphur. It was shown that the formation of nickel carbonyl is appreciably accelerated under the influence of hydrogen sulphide.[31] The first intermediate formed in this process is nickel γ-sulphide, which is reformed in subsequent transformations together with segregation of $Ni(CO)_4$, and catalyses the reaction at very minute concentrations.

An interesting phenomenon, the activation of the formation of iron, molybdenum, and nickel carbonyls by friction in the presence of sulphur-containing substances, has been described.[31] According to the authors, friction causes the breakdown of the crystal lattices of iron and the metal sulphide and the reaction proceeds via the disproportionation of the carbonyl sulphide formed:



The mechanism of iron carbonyl formation via a stage involving the appearance of the intermediate $S_2Fe_3(CO)_9$, which was described previously,[29] does not operate solely in a high-pressure reactor but also under the conditions of mechanical treatment.

Analysis of the literature data on the synthesis of IPC under various conditions from iron and carbon monoxide in the presence of small amounts of elemental sulphur has shown that in certain cases dithiotriiron nonacarbonyl, which is a catalyst of this reaction, is formed.[29–31]

Thus, as shown above, the interaction of elemental sulphur and hydrogen sulphide with iron carbonyls and TSUTH leads to the formation of a mixture of clusters (I) and (II) in satisfactory yields.

2. The Synthesis from Tetracarbonylferrates

Chalcogeniron carbonyls of type (II) were first obtained[32] by the interaction of aqueous alcoholic solutions of alkali metal tetracarbonylferrate salts with sulphurous acid (and similarly with selenous and tellurous acids):

$$3[Fe(CO)_4]^{2-} + 2XO_3^{2-} + 10H^+ \rightarrow X_2Fe_3(CO)_9 + CO_2 + 2CO + 5H_2O.$$

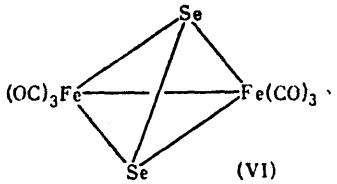
The reactions with $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ take place in the same way and in this case $Fe_3(CO)_{12}$ is formed as well. It is noteworthy that, as established subsequently, a mixture of compounds (I) and (II) is formed in all cases.[27–31,33]

Under analogous conditions, when the tetracarbonylferrate ion is acidified with hydrochloric acid, it reacts with sodium polysulphide to form a mixed precipitate of $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$ [32] (these compounds can be separated by subliming the first *in vacuo* at 40 °C):

$$5[Fe(CO)_4]^{2-} + S_5^{2-} + 2H^+ \rightarrow S_2Fe_2(CO)_6 + S_2Fe_3(CO)_9 + H_2S + 5CO.$$

The cluster $Se_2Fe_2(CO)_6$ (VI) has also been obtained by treating with KOH a solution of $Fe(CO)_5$ in methanol at 0 °C in an atmosphere of N_2 with subsequent addition of selenium and then a solution of $Na_2Se.9H_2O$ in water, the reaction mixture being stirred for 1 h and then acidified with a 15% HCl solution.[32] The properties of cluster (VI) have been recently described in detail.[34]

The cluster $Se_2Fe_3(CO)_9$ (VII) has been synthesised analogously[32] and its structure has been determined[35] by X-ray diffraction:



(VI)

The clusters $Te_2Fe_3(CO)_9$ (VIII)[32,36] and $Te_2Fe_2(CO)_6$ (IX) have been obtained by adding K_2TeO_3 to a solution of $Fe(CO)_5$ and KOH in aqueous methanol with subsequent acidification of the reaction mixture with HCl. Under analogous conditions, IPC reacts with compounds (IX) to form $Te_2Fe_3(CO)_{10}$ (X), which the authors suggest[36] is an intermediate in the formation of compound (VIII). The reaction of $Fe(CO)_5$ with compound (IX) in the presence of $(CH_3)_3NO$ affords compound (VIII):

$$Te_2Fe_2(CO)_6 + Fe(CO)_5 + 2(CH_3)_3NO \rightarrow Te_2Fe_3(CO)_9 + 2CO_2 + 2(CH_3)_3N.$$

The structure of cluster (VIII) has been established by X-ray diffraction.[37]

Iron clusters containing two different chalcogen atoms in one molecule were first obtained from the tetracarbonylferrate ion.[38] Despite certain difficulties in the isolation of these substances (repeated thin-layer chromatography), the reaction is of practical interest, since it leads to the formation in one stage of clusters which are otherwise difficult to obtain:

$$[Fe(CO)_4]^{2-} + XO_3^{2-} + YO_3^{2-} + H^+ \rightarrow X_2Fe_3(CO)_9 + XYFe_3(CO)_9 + Y_2Fe_3(CO)_9 + CO_2 + CO + H_2O;$$
$$X \text{ и } Y = S, Se, Te;\ X \neq Y.$$

The compounds $XYFe_3(CO)_9$ are solid crystalline substances whose external appearance and properties are very similar to clusters of type (II), which are already known. They do not dissolve in water but do dissolve in organic solvents, namely aliphatic and aromatic hydrocarbons, ether, carbon tetrachloride, chloroform, and especially CS_2; they are stable in the solid state in air, while in solution they are also stable in an inert atmosphere but in air they decompose to form brown amorphous insoluble deposits.[38]

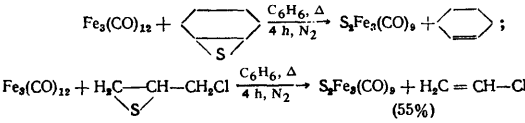
The formation of a cluster of type (II) in satisfactory yield by the reaction of the tetracarbonylferrate ion with sulphoxylic acid has been mentioned.[39]

Thus the synthesis of a mixture of chalcogeniron carbonyl clusters (I) and (II) from aqueous alcoholic solutions of alkali metal tetracarbonylferrate salts and the corresponding acids must be regarded as the most general method of their synthesis.

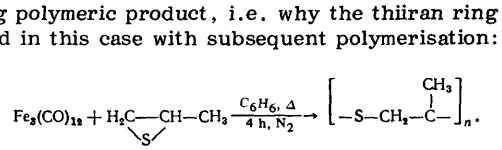
We shall now consider the reactions of various organosulphur compounds with iron carbonyls which lead to the formation of the compound $S_2Fe_3(CO)_9$ as a side product.

(a) Reactions of cyclohexene sulphide and 3-chloropropene sulphide with DDCI. The reaction of DDCI with cyclohexene or 3-chloropropene sulphide in boiling benzene involves the cleavage of the carbon–sulphur bond and the formation of a substance which was initially believed to be an isomer of $S_2Fe_3(CO)_9$.[5]

The decomposition of the thiiran ring with elimination of the sulphur atom and the formation of alkenes is a characteristic property of thiirans.[40] The method of synthesis of $S_2Fe_3(CO)_9$ from cyclohexene and 3-chloropropene sulphides is based on the desulphurisation of thiirans:[5]

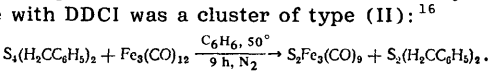


The conditions governing the elimination of sulphur in such cases are much milder compared with thermal desulphurisation, which indicates the preliminary coordination of DDCI or its decomposition products to the sulphur atom. At the same time it is not clear why the main product of the reaction of methylthiiran with $Fe_3(CO)_{12}$ is the corresponding polymeric product, i.e. why the thiiran ring is opened in this case with subsequent polymerisation:[40]



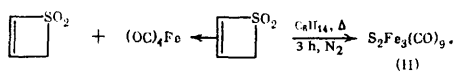
(b) The reaction of sulphur dioxide, polysulphides, and thiacyclobutene sulphone with iron carbonyls. The interaction of INC with sulphur dioxide in the absence of irradiation leads to $Fe_2(CO)_8SO_2$; a small amount of $S_2Fe_3(CO)_9$ was isolated together with the above product.[41] The reaction was carried out by passing SO_2 through petroleum ether containing a suspension of $Fe_2(CO)_9$ or in liquid SO_2 at −10° or −20 °C. However, Field and Newlands[42] did not detect $S_2Fe_3(CO)_9$ in the reaction product (−10 °C, inert atmosphere, 2 h); the reaction mixture contained $Fe_2(CO)_8SO_2$ and $Fe(CO)_5$. Analogous products have been isolated using DDCI.

One of the products of the interaction of bibenzyl tetrasulphide with DDCI was a cluster of type (II):[16]

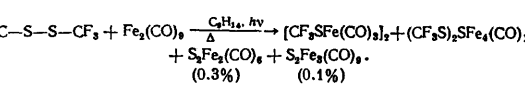


A suspension of 1,1-dioxothiacyclobuteneiron tetracarbonyl, obtained from thiocyclobutene sulphone and $Fe_2(CO)_9$, gives rise to cluster (II) in 19% yield on refluxing with thiacyclobutene sulphone in hexane[43] (Scheme 2). It is of interest to note that not even traces of $Fe_2(CO)_8SO_2$ and a compound of type (I) were detected in the reaction products.

Scheme 2



(c) The reactions of thiols and disulphides with iron carbonyls. It is well known that dialkyl sulphides, dialkyl disulphides, primary aliphatic thiols, and the corresponding aryl derivatives react with iron carbonyls to form bis(alkyl-, arylthioiron tricarbonyls) (bis-ATITC) having the general formula $[RSFe(CO)_3]_2$ (XI).[44–46] Only two cases where the sulphur atom was eliminated from disulphides and thiols have been described. Thus very small amounts of clusters of types (I) and (II) have been isolated on treating bis(trifluoromethyl) disulphide with $Fe_2(CO)_9$. The main product was the corresponding bis(trifluoromethylthioiron tricarbonyl).[47] Compounds (I) and (II) were not formed when $Fe(CO)_5$ was used:



A higher yield (10%) of compound (II) was achieved in the reaction of $Fe_3(CO)_{12}$ with secondary and tertiary aliphatic thiols:[48,49]

$$t\text{-}C_4H_9SH + Fe_3(CO)_{12} \xrightarrow[12\ h]{C_6H_6,\ \Delta} [t\text{-}C_4H_9SFe(CO)_3]_2 + (t\text{-}C_4H_9S)_3Fe_3(CO)_9 + (t\text{-}C_4H_9S)_2SFe_4(CO)_{12} + S_2Fe_3(CO)_9.$$
(35%) (5%) (5%) (10%)

Winter and co-workers[6,50–53] carried out a series of studies on the deprotonation and substitution reactions with trinuclear iron clusters $(RS)(H)Fe_3(CO)_9$ (XII) and $(\mu_3\text{-}X)(\mu_3\text{-}S)Fe_3(CO)_9$ (XIII), where X = PR, AsR, or SO. The compound $S_2Fe_3(CO)_9$ has been obtained in a high yield (57%) by the reaction of $Fe_3(CO)_{12}$ with RSH, where R = $C(C_6H_5)_3$ (toluene, 80 °C, 4 h) together with clusters (XII).[6]

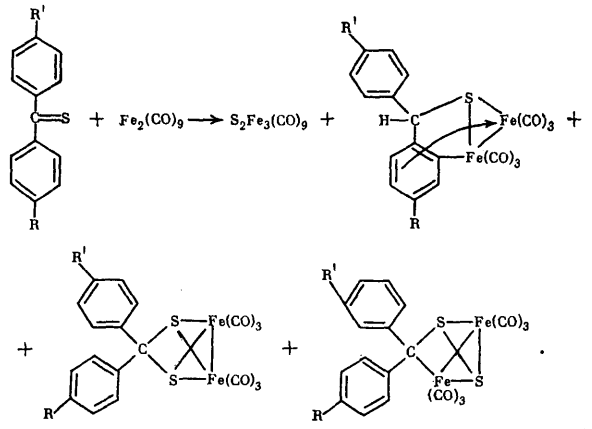
On decomposition, bis(fluorocarbonyl)disulphane also acts as a source of elemental sulphur and gives rise to a cluster of type (II) on interaction with $Fe(CO)_5$:[54]

$$F\text{—}\overset{O}{\overset{\|}{C}}\text{—}S\text{—}S\text{—}\overset{O}{\overset{\|}{C}}\text{—}F + Fe(CO)_5 \xrightarrow[14\ h,\ Ar]{C_6H_6,\ 78\text{–}80^\circ} S_2Fe_3(CO)_9.$$
(26.7%)

A compound of type (II) has been detected when industrial pipes through which a mixture of carbon monoxide and methane had been passed for a long time under a high pressure were disassembled.[55] This cluster might have been formed with participation of sulphur compounds behaving as donors of atomic sulphur and present in the gas mixture as an impurity, via a stage involving the preliminary formation of iron carbonyls.

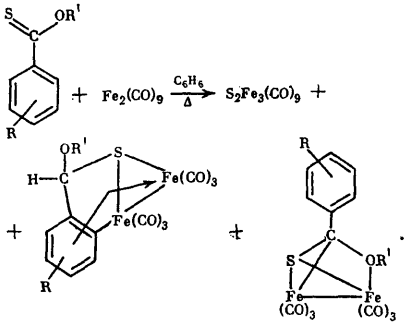
(d) Reactions of thiobenzophenones with INC. A cluster of type (II) has been obtained as a side product in 5.4–18.3% yield by the reaction of various thiobenzophenones with $Fe_2(CO)_9$ in benzene at room temperature together with clusters of the type $(C_6H_5)_2CS_2.Fe_2(CO)_6$ (Scheme 3).[56,57] The main compounds were the corresponding *ortho*-metallated complexes formed in most cases in high yields.

Scheme 3



(e) Reactions of thioesters with INC. In contrast to the reaction described above, treatment of various o-alkyl- and o-aryl-thioesters in benzene at room temperature leads mainly to the formation of mixed isomeric diiron hexacarbonyl clusters containing oxygen and sulphur as electron-donating ligands (Scheme 4). Insignificant amounts of the *ortho*-metallated product and a compound of type (II) have been isolated (0.7–7.5%).[51,58,59]

Scheme 4

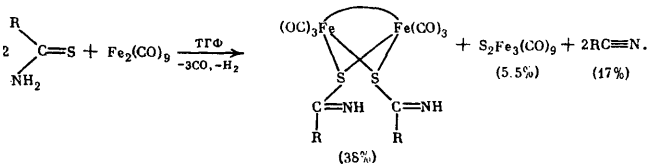


(f) Reactions of thiourea and thioamides with INC. Under analogous conditions, substituted thiourea and a series of thioamides react with $Fe_2(CO)_9$ to produce iron tetracarbonyl clusters containing sulphur as the ligand, diiron hexacarbonyl clusters with mixed ligands, and traces (0.1–2.5%) of cluster (II):[17,60–62]

$$RNHC(=S)R' + Fe_2(CO)_9 \xrightarrow[\Delta]{C_6H_6} S_2Fe_3(CO)_9 + RNHC(=S\rightarrow Fe(CO)_4)R' + [RNHC(=S\text{—})R'\text{—}Fe(CO)_3]_2 + + (RNCR')_2Fe_3(CO)_8.$$

Compound (II) is formed in 5.5% yield on treatment of $Fe_2(CO)_9$ with *p*-methoxythiobenzamide in tetrahydrofuran (THF) at room temperature for 24 h.[17] It is of interest to note that compound (II) is formed via a stage involving the formation of the diiron hexacarbonyl cluster (38%) with subsequent substitution of part of the ligand by the iron tricarbonyl fragment and the isolation of *p*-methoxybenzonitrile (yield 17%, Scheme 5):[60,61]

Scheme 5



(g) Reactions of thionoadamantanes with INC. The main product of the interaction of thionoadamantane with $Fe_2(CO)_9$ is the complex $C_{16}H_{14}S_2Fe_2O_6$ (71.5%) which is sensitive to air and differs from the product of the reaction of thiobenzophenone, containing both bridging and terminal carbonyl groups and two sulphur atoms attached to the same carbon atom.

At the same time in the reactions of thiocamphenilone with the complexes mentioned above, compound (II) was isolated as a side product (1.9%), while the reaction of thiofenchone gives rise to a mixture of compounds (I) and (II) (4.6 and 15.7% respectively)[61] [Ref.62? (Ed. of Translation)].

In addition traces of compound (II) have been isolated in the reaction of 2-thiono-1,3-dioxolanchromium pentacarbonyl with $Fe(CO)_5$ on irradiation in THF[63] and on interaction of diphenylthionocyclopropene with $Fe_2(CO)_9$ in THF.[64] Later the formation of ligands of a new type on treatment of diphenylthionocyclopropene with the carbonyl $Fe_2(CO)_9$ and the study of the crystal structures of carbene complexes with a cluster skeleton, namely Fe_3S_2, $C_3(C_6H_5)_2Fe_3S_2(CO)_8$, and the dithiodiketone derivative

$C_6(C_6H_5)_4S_2Fe_2(CO)_6$ were described.[65] When the sulphur diimide R–N=S=N–R [R = t-C_4H_9 or 4-$(CH_3)C_6H_4$] was treated with $Fe_2(CO)_9$, very small amounts of clusters (I) and (II) were isolated and analysed by a highly sensitive liquid chromatographic technique[66] together with dinuclear and trinuclear iron carbonyl clusters (Scheme 6).[67,68]

(h) Reactions of carbon disulphide with DDCI. The compound $S_2Fe_3(CO)_9$ was obtained together with the main product $(CS)SF_4(CO)_{12}$ and two unidentified complexes in the reaction of carbon disulphide with $Fe_3(CO)_{12}$ (in hexane at 80 °C, 10 atm, CO : Ar = 1 : 1, 7.5 h).[69] Only the overall yield of the four compounds is quoted (4%). In addition, the compound $S_2Fe_3(CO)_9$ was isolated in 8% yield together with the octacarbonyl cluster $(C_3H_2S_2)Fe_3(CO)_8S_2$ (43%) as the main product in the reaction of a 1,3-dithiole2-thione with $Fe_2(CO)_9$.[70]

The cluster $S_2Fe_3(CO)_9$ was also obtained as a side product in the reaction of $C_6H_5P(S)Cl_2$ with DDCI in the presence of magnesium in THF together with the mixed-ligand trinuclear cluster $(\mu_3\text{-}S)(\mu_3\text{-}PC_6H_5)Fe_3(CO)_9$ (17%) and the already known $(\mu_3\text{-}PC_6H_5)_2Fe_3(CO)_9$.[71]

The formation of hydrothiocarbonylferrate cluster anions $H_{2-n}Fe_3(CO)_9S^{n-}$ (n = 1,2) has been reported.[72] Such anions, $HFe_3(CO)_9S^-$ or $Fe_3(CO)_9S^{2-}$, are formed when the hydride clusters $HFe_3(CO)_9(SR)$ are heated in polar solvents.[73,74]

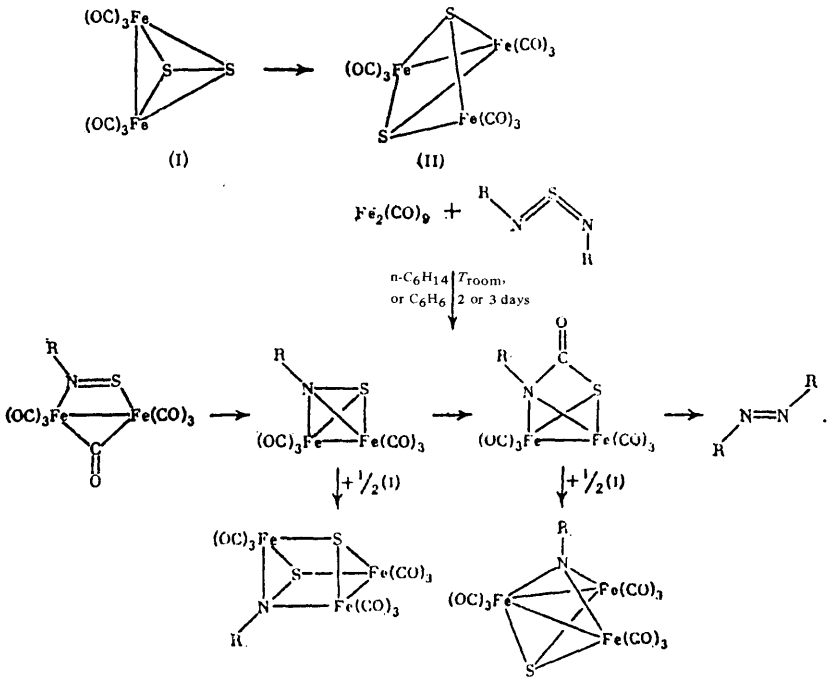
Thus it is seen from the foregoing that the trinuclear cluster $S_2Fe_3(CO)_9$ is a permanent side product in the interaction of iron carbonyls with various organosulphur compounds; it has been shown[3] that, according to TLC data, the initial product is dithiodiiron hexacarbonyl $S_2Fe_2(CO)_6$, which is subsequently converted into a compound of type (II). Methods for the separation of mixtures of compounds (I) and (II) are described in the same communication.[3] It has been found that cluster (II) is fully decomposed and cluster (I) is quantitatively isolated in column chromatography using alumina and n-hexane as the eluent. Refluxing of alcoholic solutions of a mixture of compounds (I) and (II) also decomposes fully compound (II), while cluster (I) is isolated in 72% yield (methanol) and 92% yield (isopropyl alcohol). On the other hand, refluxing of benzene solutions leads to the formation of only the trinuclear cluster (II) in 92% yield. The above results are important not only for the separation of a particular cluster in a pure form but also for the selection of conditions for reactions involving these compounds.

The principal methods of synthesis of the compounds $S_2Fe_2(CO)_9$ and $S_2Fe_3(CO)_9$ are surveyed in the Table. Analysis of the tabulated literature data shows that three methods are the most promising for the synthesis of a mixture of clusters (I) and (II): (1) from elemental sulphur and DDCI (in THF);[3] (2) from hydrogen sulphide and DDCI (in benzene);[4] (3) from elemental sulphur and TSUTH (in benzene).[3] The interaction of $H_2C\text{–}\underset{\underset{S}{\diagup}}{CH}\text{–}CH_2Cl$[5] or $(C_6H_5)_3CSH$[6] with DDCI must be regarded as the most effective method of synthesis of the trinuclear cluster (II).

III. STRUCTURE AND PHYSICAL RESEARCH METHODS

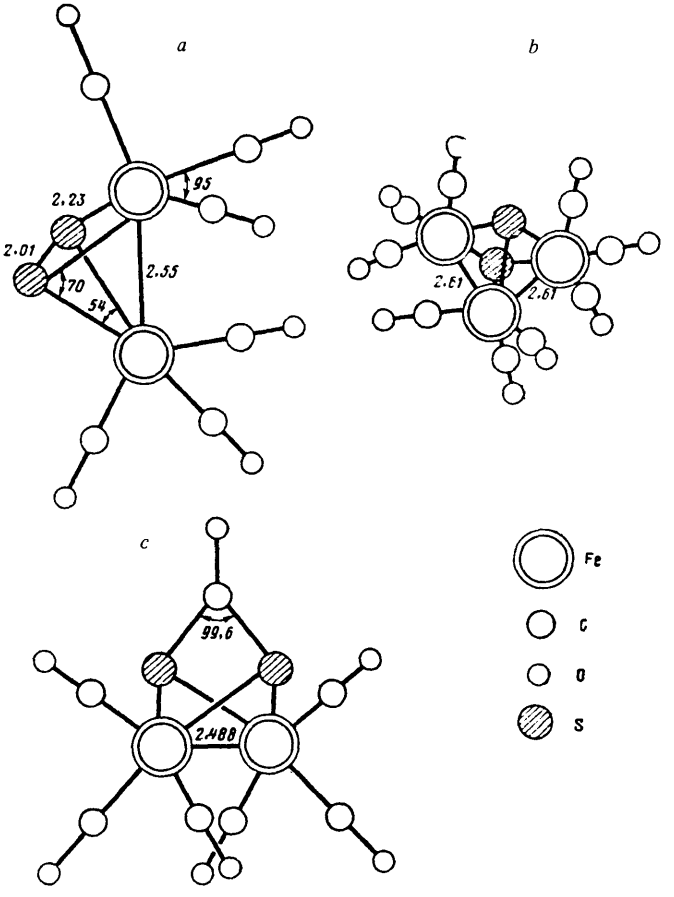
The structures of the compounds $S_2Fe_2(CO)_6$,[75] $S_2Fe_2(CO)_7$,[20] $S_2Fe_3(CO)_9$,[76] $SFe_3(CO)_{10}$,[22] $Se_2Fe_3(CO)_9$,[35] and $Te_2Fe_3(CO)_9$[37] were established by X-ray diffraction. Fig. *a* illustrates the structure of a sulphur-containing cluster of type (I). Evidently the –S–S– ligand is a bridge linking symmetrically two iron atoms; the iron–iron distance corresponds

Scheme 6



to the formation of a metal–metal bond. Fig.*b* shows that the sulphur-containing cluster of type (II) contains a triangle of iron atoms: the lengths of the two Fe–Fe bonds are on average 2.6 Å, while the third side of the triangle is 3.37 Å long. Subsequently it was established that, on passing to the analogous clusters containing selenium[35] and tellurium,[37] all the metal–metal bonds become so much longer that in the structure of the $Te_2Fe_3(CO)_9$ cluster the three $Fe(CO)_3$ fragments are in essence linked to one another only via μ_3-tellurium bridges.

It has been shown by X-ray diffraction that the structure of the cluster $[\mu\text{-S–C(O)–S–}]Fe_2(CO)_6$ corresponds to the insertion of CO in the S–S bond (Fig.*c*).[20] It has also been demonstrated with the aid of the same method that the μ_3-bridging sulphide and CO ligands in the cluster $(\mu_3\text{-S})(\mu_3\text{-CO})Fe_3(CO)_9$ "build-up" the triangle of Fe atoms to a trigonal bipyramid (the number of valence electrons associated with the three Fe atoms is 48).[22]



The structures of the $(\mu\text{-S})_2Fe_2(CO)_6$ (*a*), $(\mu_3\text{-S})_2Fe_3(CO)_9$ (*b*), and $[\mu\text{-S–C(O)–S–}]Fe_2(CO)_6$ (*c*) clusters.

The relation between the number of atoms, the number of bonding electron pairs (skeletal electrons) and the geometrical structure of cluster compounds has been examined[77,78] and the different types of geometrical structures of cluster compounds have been classified as a function of the number of atoms in the cluster, and simple rules have been formulated for the calculation of the number of bonding electron pairs in cluster compounds of different types. Such calculation makes it possible to explain the known structures and to predict the unknown structures of the known compounds as well as the existence of new compounds and methods for their synthesis. In particular, certain possible transformations of geometrical structures of one type into those of another type in reactions accompanied by a change in the number of skeletal electrons of a given cluster have been examined and the interaction of compound (II) with $L_3M(CO)_3$ has been described, but has not so far been confirmed experimentally:

$$S_2Fe_3(CO)_9 + L_3M(CO)_3 \rightarrow (OC)_3MS_2Fe_3(CO)_9 + 3L;$$
$$L = CO, RCN;\ M = Cr, Mo, W.$$

The results of quantum-chemical calculations by the self-consistent field method ($SCF\text{–}X_\alpha\text{–}SW$) have been compared[79,80] with data obtained from the photoelectron spectra of the $S_2Fe_2(CO)_6$ molecule and it has been established that the Fe–Fe bond is best described in terms of a simple "bent" bond, while the orbital corresponding to it has the character of the highest occupied molecular orbital (HOMO).

The infrared and Raman spectra of $S_2Fe_2(CO)_6$ and the $(CH_3S)_2Fe_2(CO)_6$ isomers have shown[81] that the Fe–Fe bond stretching vibrations are at 191 cm^{-1}; the force constant of this bond is 1.3 mdyn A^{-1} and is close to the value expected for a single Fe–Fe bond. Study of the infrared spectra in the CO group stretching region, in hexane solutions of a series of dinuclear bridged carbonyl complexes of the type $Y_2Co_2(CO)_6$, where Y = CO, P, As, or CR, and $X_2Fe_2(CO)_6$, where X = S, SR, Se, PRR', Br, or I, both with normal and enriched in ^{13}CO, established that the difference between the force constants for the axial and equatorial CO groups (the latter are in the *trans*-position relative to the bridging ligand) characterises the π interaction of the metal with the bridging group.[82]

The dimeric character of the clusters $[XFe(CO)_3]_2$, where X = S, Se, SC_2H_5, SeC_2H_5, or SC_6H_5, has been demonstrated by their diamagnetism and also by the results of cryoscopic studies of these compounds (in benzene). The dipole moments of type (I) clusters considered, with X = S, Se, or SC_2H_5, in benzene and of a compound of type (I), with X = SC_2H_5, dissolved in cyclohexane are respectively 1.63 ± 0.1, 2.20 ± 0.07, 2.69 ± 0.05, and 2.66 ± 0.04 D,[83] which also indicates their dimeric character. The authors proposed for them non-planar bridged structures analogous to those which were later established by X-ray diffraction (Fig.*a*).

The ^{13}C NMR spectra have been investigated in a series of studies[84–87](including the observation of satellites due to the ^{57}Fe nucleus) for a series of clusters: $S_2Fe_2(CO)_6$ and the *syn*- and *anti*-isomers of $(CH_3S)_2Fe_2(CO)_6$ and $Fe_3(CO)_{12}$. The information obtained indicates the retention in solution of the structures established for these compounds in the crystal state. On varying the experimental temperature, intramolecular dynamic processes were discovered but their nature has not been accurately established.

The electronic structure of the dinuclear clusters (I) and their analogues containing metal–metal bonds has been studied[88] with the aid of He(I) and He(II) photoelectron spectra.

The Mössbauer spectra of the compounds $S_2Fe_3(CO)_9$, $Se_2Fe_3(CO)_9$, and $R_3PS_2Fe_3(CO)_8$ have been investigated by γ-nuclear resonance.[89–92] The mass spectra of $X_2Fe_2(CO)_6$ (X = S or Se) and $X_2Fe_3(CO)_9$ (X = S, Se, or Te) have been

published.[93] The data obtained have been compared with the results of thermogravimetric analysis of thermal decarbonylation, of the same clusters in the temperature range 25–600 °C. After decarbonylation, the residues were subjected to X-ray diffraction and magnetic investigations.[93]

The mass spectrum of compound (II) contains the molecular ion as well as ions formed as a result of the successive elimination of the nine CO groups. The maximum peak is that of the $S_2Fe_3^+$ ion, which subsequently decomposes with formation of $S_2Fe_2^+$ and Fe_2^+.[94] Mass spectrometric studies on the negative ions formed from $X_2Fe_3(CO)_9$ (X = S, Se, or Te) have been reported.[95] The peak of the $X_2Fe_3(CO)_7^-$ ion proved to be the most intense and a weak molecular peak due to $Te_2Fe_3(CO)_8^-$ was also observed.

Study of the oxidation-reduction reactions of the cluster $Cp_3Fe_3(CO)_2(S)(SR)$ by the cyclic voltamperometric method revealed the presence of two waves on the voltage–current plots corresponding to two reversible oxidation-reduction processes.[96,97] The voltage–current plot for $S_2Fe_3(CO)_9$ showed only one wave, whose potential was more negative than for $Cp_3Fe_3(CO)_2(S)(SR)$. The smaller chemical shift in the ^{57}Fe Mössbauer spectra of the cluster $Cp_3Fe_3(CO)_2$. .(S)(SR) compared with $S_2Fe_3(CO)_9$ shows that the CO groups in the former cluster are more powerful π-acceptor ligands than the terminal CO groups in the latter cluster.[97]

IV. CHEMICAL PROPERTIES

The advance achieved nowadays in the chemistry and physics of cluster compounds have brought to the fore the task of investigating their reactivities and their unique properties, which in many respects have altered traditional ideas about the reactivity of coordination and organometallic compounds.

1. The Conversion of Type (I) Clusters into Cubane Clusters

Considerable advances have been made in the synthesis and study of clusters having the general formula $[Fe_4S_4(SR)_4]^{n-}$, where R is an alkyl or aryl group. The structures of these synthetic analogues of proteins, established by X-ray diffraction, and their spectroscopic and magnetic properties are very similar to those of clusters found in the so-called "proteins with a high potential" (PHP) and in oxidised ferredoxin.[98] The synthesis of cubane clusters of the Fe_4S_4 type from a carbonyl-containing compound of type (I) has been described.[99] The preparation of the corresponding cluster and the specific syntheses from known compounds proceed in accordance with the following scheme:

$$FeCl_3 + ArSH + NaOCH_3 + NaSH \rightarrow [Fe_4S_4(SAr)_4]^{2-}$$

$$S_2Fe_2(CO)_6 \rightarrow [Fe_4S_4(SAr)_4]^{2-} \xrightarrow{ArSH} [Fe_4S_4(S\text{-}t\text{-}C_4H_9)_4]^{2-}$$

$$S_2Fe_2(CO)_6 \xrightarrow{ArSSAr^{++}} \{Fe_4S_4[SC_6H_4N(CH_3)_3]_4\}^{2+} \xrightarrow{ArSH^+} [Fe_4S_4(S\text{-}t\text{-}C_4H_9)_4]^{2-}$$

The reaction mixture containing $S_2Fe_2(CO)_6$, $C_6H_5SSC_6H_5$, and $C_6H_5S^-$ in molar proportions of 1 : 1 : 2 yields $[Fe_4S_4(SC_6H_5)_4]^{2-}$ as the only product, which was isolated and identified in the form of the tetraphenylarsonium salt (65% yield):

$$S_2Fe_2(CO)_6 + C_6H_5SSC_6H_5 + C_6H_5SH + (C_6H_5)_4AsCl \xrightarrow[1\text{ h, }CH_3OH,\ \Delta]{CH_3ONa,\ N_2} [(C_6H_5)_4As]_2\{Fe_4S_4(SC_6H_5)_4\} + CO + NaCl.$$

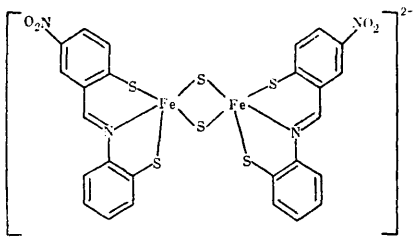
The cationic tetramer was obtained in the following way:

$$S_2Fe_2(CO)_6 + (n\text{-}(CH_3)_3NC_6H_4S)_2(PF_6)_2 + [n\text{-}(CH_3)_3NC_6H_4SH]PF_6^+ + CH_3ONa \xrightarrow[N_2,\ 1\text{ h, }\Delta]{CH_3OH\text{–}CH_3CN} \{Fe_4S_4[SC_6H_4N(CH_3)_3\text{-}n]_4\}^{3+} + CO + NaPF_6.$$

According to the authors,[99] the carbonyl groups in compound (I) are initially fully substituted by the thiyl fragment with formation of the Fe_2S_2 cluster, which is followed by thermal or catalytic dimerisation:

$$S_2Fe_2(CO)_6 + RSSR + 2RS^- \rightarrow [S_2Fe_2(SR)_4]^{2-} + 6CO;$$
$$2[S_2Fe_2(SR)_4]^{2-} \rightarrow [S_3Fe_4(SR)_4]^{2-} + RSSR + 2RS^-.$$

The interaction of 2,2-bis{benzo[*d*]thiazoline}-4,4-dinitrodiphenyl disulphide with compound (I) in the presence of sodium methoxide was investigated in the same study.[99] The corresponding anionic cluster, free from carbonyl groups, was identified in the form of the tetraphenylarsonium salt. The authors suggest that the cluster contains pentacoordinate iron(III). An analogous cluster has been obtained by the reaction of $FeCl_3$, NaSH, and a base with thiazoline disulphide.



2. Reduction Reactions of Type (I) Clusters

Treatment with reducing agents such as KH, metallic sodium, and the RLi–LiBr (R = CH_3 or C_4H_9) system leads to the cleavage of the S–S bond in compound (I).[100,101] The authors suggest the initial formation of both the monoanion (A) and the corresponding dianion (B), which subsequently readily enters into condensation reactions, for example, in accordance with the following scheme:

$$S_2Fe_2(CO)_6 + CH_3Li/LiBr \xrightarrow[-78^\circ]{(C_2H_5)_2O,\ N_2} \underset{(A)}{[(CH_3S)_2Fe_2(CO)_6]^-} \xrightarrow[12\text{ h}]{CH_3I} \underset{(82\%)}{(CH_3S)_2Fe_2(CO)_6};$$

$$S_2Fe_2(CO)_6 + KH \xrightarrow[4\text{ h}]{THF,\ N_2} \underset{(B)}{[S_2Fe_2(CO)_6]^{2-}} \xrightarrow{CH_3I} \underset{(53\%)}{(CH_3S)_2Fe_2(CO)_6}.$$

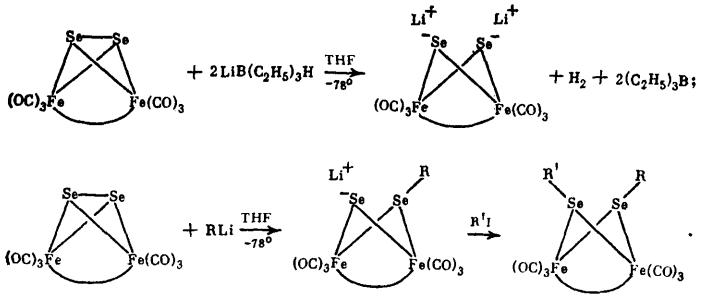
This leads to a way of synthesising various asymmetric bis(alkylthio)diiron hexacarbonyl clusters from the monoanion (A). The dianion (B) is of considerable interest for the synthesis of already known iron sulphide clusters containing both acyclic and cyclic groups.[101] An improved method of synthesis of the dianion (B) for compound (I) into THF by treatment with $LiB(C_2H_5)_3H$ has been proposed.[102]

The reactions of the dianion (B) with organic halides and with tin, germanium, silicon, and nickel halides have also been reported.[102] The protonation of the dianion (B) by treatment with CF_3COOH leads to the formation of the bridged thiol cluster $(HS)_2Fe_2(CO)_6$ in a quantitative yield. Its synthesis and some of its properties have been described in detail in two communications.[103,104] This thiol cluster has been used to synthesise the $S_2Fe_2(CO)_6$ clusters in the study of the chemistry of these compounds.[105]

It has been found[34] that the reactivity of diselenodiiron carbonyl $Se_2Fe_2(CO)_8$ (VI) is the same as that of the usual organic diselenides RSeSeR. Thus the reaction with two molar equivalents of $LiB(C_2H_5)_3H$ converts compound (VI) into the dianion $(LiSe)_2Fe_2(CO)_6^{2-}$. Organolithium reagents

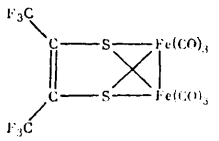
cleave the Se–Se bond in compound (VI), affording (μ-LiSe).(μ-RSe)$Fe_2(CO)_6$ [34] by analogy with the sulphur-containing cluster (Scheme 7).[101]

Scheme 7



3. Interaction of Compounds of Type (I) with Activated Acetylenes

The photochemical effect of activated acetylenes (hexafluorobut-2-yne or dimethyl or diethyl acetylenedicarboxylate) on dithiodiiron hexacarbonyl $S_2Fe_2(CO)_6$ in THF leads to their insertion in the cluster not in the Fe–Fe bond, as happens for $(RS)_2Fe_2(CO)_6$,[106] but in the S–S bond[107] with formation of a dithiolene cluster of the type



whose structure has been demonstrated by specific synthesis.[107]

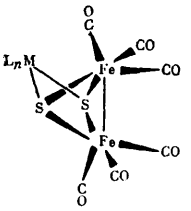
4. Reactions Involving Addition to Type (I) Clusters

It has been shown recently[108] that lithium alkyls also add to $S_2Fe_2(CO)_6$ at the S–S bond.

An unexpected intramolecular nucleophilic substitution in the anionic complex of $Fe_2(CO)_6$ with an organosulphur ligand has been observed.[109] It can be regarded as a new method of synthesis of complexes of $Fe_2(CO)_6$ with dithioformic acid esters. Later the same workers[110] discovered the formation of an exocluster sulphonium group from the product of the deprotonation of the diiron hexacarbonyl complex of thioformic acid ester.[111]

5. Reactions of Type (I) Compounds with Metal Complexes

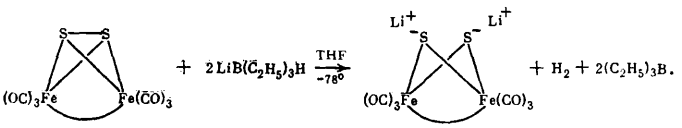
The reactions of dithiodiiron hexacarbonyl can only involve the S–S bond, which constitutes a feature of this compound similar to that of organic disulphides. The reaction of compounds (I) with metal complexes in the zerovalent state, such as $[(C_6H_5)_3P]_4Pt$, $[(C_6H_5)_3P]_3Pd(CO)$, and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Ni(CO)_2$ entails the insertion of Ni, Pt, and Pd in the S–S bond, and under mild conditions (benzene, 20 °C, 2.5–24 h) the products are the coloured crystalline complexes $QM(S)_2Fe_2(CO)_6$ where Q = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ or $[(PC_6H_5)_3]_2$ and M = Ni, Pd, or Pt, which are stable in air.[112]



Analogous products have been obtained by the reaction of the dianion (B) with the corresponding metal chlorides.[112]

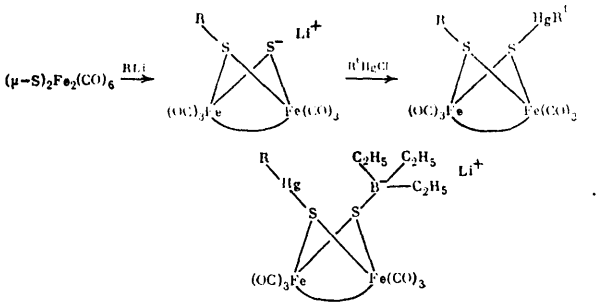
The transfer of the alkyl group from the boron atom to the sulphur atom in the reactions of lithium hydrotriethylborate derivatives of the bis(μ-thiolato)-bis(tricarbonylferrate) dianion with mercury and alkylmercury chlorides has been described.[113] The reactions of $(\mu\text{-LiS})_2Fe(CO)_6$, obtained by the interaction of $S_2Fe_2(CO)_6$ and $LiB(C_2H_5)_3H$ with $HgCl_2$ in THF in accordance with Scheme 8, in methyl, ethyl, or propyl alcohol, or in THF give rise to the product of the previously unknown transfer of the alkyl group from the boron atom to the sulphur atom: $(\mu\text{-SC}_2H_5)$. $(\mu\text{-SHgC}_2H_5)Fe_2(CO)_6$.

Scheme 8



The formation of elemental mercury in this reaction led the authors[112] to the hypothesis that RHgCl acts as an oxidant, oxidising the intermediate complex [shown in Scheme 9] and leading to the transfer of the ethyl group from boron to sulphur, yielding ultimately the observed product, for which four isomers are possible according to ^1H and ^{13}C NMR spectra (Scheme 9).[113]

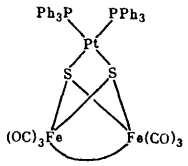
Scheme 9



An interesting comparison of the reactivities of the carbonyl dianion $[S_2Fe_2(CO)_6]^{2-}$ and the anion of Roussin's red salt $[S_2Fe_2(NO)_4]^{2-}$ has been made in a report,[114] which describes also certain chemical properties of Roussin's red salt, in particular its reactions with monofunctional electrophiles RX[R = CH_3, C_2H_5, $CH_2=CHCH_2$, $C_6H_5CH_2$, CH_3Sn, $(C_6H_5)_3Sn$, $(C_6H_5)_3Pb$, C_6H_5Hg, or $CpFe(CO)_2$; X = halogen], resulting in the formation of the related nitrosyl complexes $(RS)_2Fe_2(NO)_4$ and NaX.

The synthesis and the structure of the bridged platinum derivative of Roussin's red salt (Scheme 10) are described in the subsequent communication by the same authors.[115]

Scheme 10



$$+ 4NO \longrightarrow (Ph_2P)_2PtS_2Fe_2(NO)_4 + 6CO.$$

The same derivative has been synthesised by the reaction of $Na_2[Fe_2(S)_2(NO)_4]$ with *cis*-$[(C_6H_5)_3P]PtCl_2$ in THF.[115]

6. The Insertion of Group IVB Elements in Type (I) Clusters

Group IVB elements can be inserted into a cluster (I) both in the S–S and Fe–Fe bonds. The compounds formed may be of definite interest, because fragments capable of entering into numerous reactions remain in both cases.

It has been shown[116] that the reaction of compound (I) with the triethylamine complex of trichlorosilane (pentane, 1 h, 40 °C) results in the formation of bis(hexacarbonyldithiodiiron)silicon (73%):

$$S_2Fe_2(CO)_6 + HSiCl_3\cdot(C_2H_5)_3N \rightarrow Si[S_2Fe_2(CO)_6]_2.$$

When methanolic solutions of compound (I) and the triethylamine complex of trichlorogermane are mixed, a brown-red precipitate of bis(dithiodiiron)germanium is formed instantly at room temperature (82%):[116,117]

$$S_2Fe_2(CO)_6 + HGeCl_3\cdot(C_2H_5)_3N \rightarrow Ge[S_2Fe_2(CO)_6]_2.$$

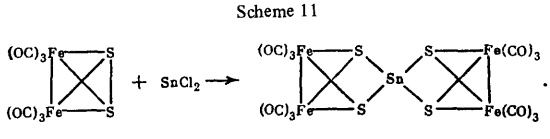
The structure of this cluster has been established.[118]

The reaction involving the dissociation of the S–S bond in compound (I) after preliminary treatment with various reducing agents (with formation of the corresponding dianions) has also been achieved and a complex containing the $(CH_3)_2Sn$ fragment has been obtained.[101] In contrast to the triethylammonium salts of trihalogenogermanes(silanes), the corresponding $HSnCl_3$ salt does not react with dithiodiiron hexacarbonyl.[3] At the same time refluxing of a solution of a type (I) cluster in absolute ethanol with the tribromostannane–amine complex leads to the formation of a product containing two molecules of the amine complex and one molecule cluster (I) (according to the results of elemental analysis and the infrared spectra):

$$S_2Fe_2(CO)_6 + (C_2H_5)_3N\cdot HSnBr_3 \rightarrow S_2Fe_2(CO)_6\cdot 2(C_2H_5)_3N\cdot HSnBr_3.$$

Treatment of compound (I) with tin dichloride in solution in methanol, ethanol, and a methanol–ethyl acetate mixture (4 h, 65 °C) gives rise to a compound in which the $SnCl_2$: (I) ratio is 1 : 2 (on the basis of the results of elemental analysis) (Scheme 11).[3]

Scheme 11



7. Reactions of Compound (I) with Diazomethane

When compound (I) was allowed to react with diazomethane in ether at temperatures ranging from −40° to 20 °C, a brown deposit consisting of fractions having different molecular weights was obtained.[119] Treatment of the deposit with pentane and subsequent chromatography on Al_2O_3 or silica gel led to the isolation of various methylene-, bismethylene-, methyl-, and trismethylene-dithiodiiron hexacarbonyl clusters with the main high-molecular-weight $[H_2C = S_2Fe_2(CO)_6]_x$ fraction, which is insoluble in the usual organic solvents.[119]

8. The Effect of Halogens on Compounds (I) and (II)

The first data concerning the effects of the halogens on sulphur cluster complexes have been published by Hieber and Kaiser.[120] The reactions of dinuclear carbonyliron mercaptides $(C_2H_5S)_2Fe_2(CO)_6$ with halogens leads to compounds of the type $[C_2H_5SFe(CO)_3X]_2$ (X = Br or I). The phosphine-substituted compounds $[Fe(CO)_2LX]_2$ [L = $P(C_6H_5)_3$; X = S, SC_2H_5, or SC_6H_5] react with iodine to form the periodides $[Fe(CO)_2LXI_{0.5}]_2^+I_3$, while salts of a trinuclear cation of the type $[Fe_3(CO)_4L_2X_2Hal_4]^+Hal^-$ are formed when the unsubstituted compounds $[Fe(CO)_3LX]_2$ react with chlorine, bromine, or iodine (Hal). Compounds of the last two types are isolated from aqueous mediums as salts, for example, $[Fe(CO)_2LXHal_{0.5}]_2^+[PF_6]^-$.[120]

The reactions of the trinuclear dithiotriiron carbonyl of type (II) with the halogens lead to the formation of a trinuclear cluster cation under the same conditions: $[Fe_3(CO)_6\cdot S_2Hal_4]^+Hal^-$.[120]

9. Reactions Involving the Substitution of Ligands in Compounds (I)

We shall consider initially the reactions leading to the cleavage of the S–S bond in compounds (I) and in the same reactions involving compounds (II).

For the carbonylthio-clusters considered, there exist two examples of the complete substitution of carbonyl groups. The first concerns the preparation of synthetic analogues of iron- and sulphur-containing proteins (ferredoxins)[99] and the second the reaction of compounds (II) with bis(trifluoromethyl)dithioethane.[121]

The reaction of compound (II) with $S_2C_2(CF_3)_2$ affords a high yield of $S_2Fe_3[S_2C_2(CF_3)_2]_4$,[121] which has also been synthesised from $(CF_3)_2C_2S_2Fe_2(CO)_6$ and sulphur.[122] This is a novel method of synthesis of trinuclear clusters not containing carbonyl fragments.

Certain carbonyl groups in metal carbonyls are known to be readily substituted by phosphines, arsines, and stibines, but for the majority of metal carbonyls the removal of all the carbonyl groups presents considerable difficulties; this can be achieved only in reactions with triphenylphosphine.[7,45,123,126]

The interaction of the sulphur-containing cluster (I) with triphenylphosphine at room temperature has been described. It leads to the formation of a disubstituted cluster whose molecular weight has been determined:[127]

$$S_2Fe_2(CO)_6 + 2P(C_6H_5)_3 \xrightarrow[20°]{C_7H_{16}} [(H_5C_6)_3P]_2S_2Fe_2(CO)_4] + 2CO.$$

The reactions of $X_2Fe_2(CO)_6$, where X = S or Se, with a ligand L lead to various products, whose formation depends on the nature of both L and X.

When the less reactive $Se_2Fe_2(CO)_6$ is treated with $As(C_6H_5)_3$ or $P(OC_6H_5)_3$, mainly the monosubstituted product (A) and to a lesser extent the disubstituted compound (B) are formed; polynuclear complexes were not detected.[127]

$$Se_2Fe_2(CO)_6 + L \rightarrow \underset{(A)}{LSe_2Fe_2(CO)_5} + CO;$$

$$LSe_2Fe_2(CO)_5 + L \rightarrow \underset{(B)}{L_2Se_2Fe_2(CO)_4} + CO;$$

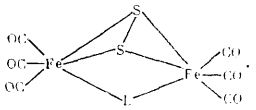
$$L = As(C_6H_5)_3,\ P(OC_6H_5)_3.$$

It is important to note that the interaction of compound (I) with $P(C_6H_5)_3$ leads initially to the formation of the compound $(C_6H_5)_3PS_2Fe_2(CO)_6$, which, however, has not been isolated.[127] It has been characterised only by infrared spectroscopy, together with $(C_6H_5)_3PS_2Fe_2(CO)_5$. The difficulty of isolating this cluster is probably associated with its instability and high reactivity. The main reaction products are the corresponding mono- and di-substituted derivatives (I) and (II).

The same workers[127] have shown that, when $P(OC_6H_5)_3$ is used, the unstable compound $(C_6H_5O)_3PS_2Fe_2(CO)_5$ is formed as an intermediate. The reaction mixture also contains mono- and di-substituted derivatives of compounds (I) and (II). It has been suggested that the trinuclear clusters are formed via a stage in which an intermediate complex is produced on interaction of compound (I) with the mono-derivative or the adduct.[127]

The greater difference between the reactivities of $As(C_6H_5)_3$ and $P(n\text{-}C_4H_9)_3$ in their reactions with compound (I) shows that the preliminary dissociation of the initial complex is unlikely and that the ligand is coordinated to compound (I) with formation of an adduct:

$$S_2Fe_2(CO)_6 + L \rightarrow LS_2Fe_2(CO)_6;$$
$$L = P(C_6H_5)_3,\ P(n\text{-}C_4H_9)_3;$$



A structure in which the ligand is formally coordinated to two iron atoms, forming a labile three-centre donor–acceptor bond, has been proposed for the adduct.

The dinuclear chalcogeniron carbonyl clusters $L_2(CH_3S)_2.Fe_2(CO)_4$, formed in the reactions of compounds (I) with a proton[128] and $HgCl_2$,[129] as well as the salt-like complexes with the halogens, namely $[Fe(CO)LL'(SR)]_2$ (L' = CO, phosphine, or phosphite), frequently have a similar structure.[130] An additional piece of evidence for the formation of adducts in the above systems is, according to the authors,[131] the oxidative addition of $(CF_3)_2C_2S_2$ or $NOPF_6$ to compounds (I), leading to the formation of the cationic complex $[Fe_2(SR)_3.(CO)_6]^+$, in which the SR group is inserted in the Fe–Fe bond. The structure of this compound has been established by X-ray diffraction.[132]

Monosubstituted derivatives of compound (I) are readily generated from the adduct as a result of the migration of the ligand to one of the iron atoms with the simultaneous elimination of a CO group in accordance with the equation

$$LX_2Fe_2(CO)_6 \rightarrow LX_2Fe_2(CO)_5 + CO.$$

The subsequent attack by the iron atom on a second molecule of L leads to the formation of a disubstituted derivative of compound (I).[130]

The stability of the substitution products depends on the nature of the ligand,[45] apparently owing to the formation, on successive substitution, of a system having an exess electron density of the iron atoms, which promotes the mutual repulsion of the latter. An analogous influence of the nature of the cations on the stability of compounds with an Fe–Fe bond has been demonstrated in another study.[133]

The kinetics of CO substitution in $X_2Fe_2(CO)_6$ clusters (where X = S or Se) by ligands such as $As(C_6H_5)_3$, $P(OC_2H_5)_3$, $P(OC_6H_5)_3$, or $P(C_6H_5)_3$ has been investigated by infrared and ultraviolet spectroscopy.[134] A possible mechanism of the reactions of compounds (I) with L has been proposed, according to which the rate-determining reaction stage involves the formation of the associated species $X_2Fe_2(CO)_6L$, which subsequently loses a CO group with formation of a monosubstituted product or again reacts with a molecule of compound (I), giving rise to a trinuclear derivative via an intermediate of the type $X_2Fe_2(CO)_6L...X_2Fe_2(CO)_6$:

$$X_2Fe_2(CO)_6 \underset{-L}{\overset{+L}{\rightleftarrows}} X_2Fe_2(CO)_6L \begin{cases} \xrightarrow{+L} \text{products;} \\ \xrightarrow{-CO} X_2Fe_2(CO)_5L \xrightarrow{+L} X_2Fe_2(CO)_4L_2; \\ \xrightarrow{+X_2Fe_2CO_6} [X_2Fe_2(CO)_6L...X_2Fe_2(CO)_6] \rightarrow X_2Fe_3\text{-derivatives.} \end{cases}$$

The proposed structure of the "secondary" adduct is extremely doubtful, although it does not conflict with the possibility of the coordination of compound (I) to the initial adduct at the S–S bond.[134]

The adduct can react via different mechanisms, serving as the starting compound for the preparation of polynuclear clusters. It has been noted[134] that the yield of these clusters is a maximum when the concentrations of compound (I) and of L are a maximum.

The rate constants for the above reactions indicate the high sensitivity of compound (I) to the nature of the attacking ligand L, which can be explained, according to the authors,[134] by the ease of their coordination to the Fe atom.

10. Ligand Substitution Reactions Involving Compounds (II)

Numerous studies involving the substitution of the CO groups in the compounds $X_2Fe_3(CO)_9$ (X = S, Se, or Te) with phosphines, phosphites, and arsines have been carried out[126,135–140] and it has been shown[135] that, for X = S or Se, a mixture of mono- and di-substituted derivatives of compound (II) is formed:

$$X_2Fe_3(CO)_9 + L \rightarrow LX_2Fe_3(CO)_8 + CO;$$
$$LX_2Fe_3(CO)_8 + L \rightarrow L_2X_2Fe_3(CO)_7 + CO;$$
$$L = As(C_6H_5)_3,\ P(OC_6H_5)_3,\ P(n\text{-}C_4H_9)_3.$$

$Te_2Fe_3(CO)_9$, behaves differently in the reactions considered. It is characterised by the formation in the first stage of the corresponding adduct with subsequent elimination of a CO group:[135]

$$Te_2Fe_3(CO)_9 + L \rightarrow LTe_2Fe_3(CO)_9;$$
$$LTe_2Fe_3(CO)_9 \rightarrow LTe_2Fe_3(CO)_8 + CO.$$

The synthesis and properties of heterometallic cluster compounds obtained from $Te_2Fe_3(CO)_9$ have been described recently.[141]

The reactivity of the mixed cluster $XYFe_3(CO)_9$ (X and Y = S, Se, or Te; $X \neq Y$) in the reaction involving the displacement of a CO group by a triphenylarsine and triphenylphosphine corresponds to the reactivity of $X_2Fe_3(CO)_9$.[138]

The complexes $LXYFe_3(CO)_8$ and $L_2XYFe_3(CO)_7$ have more than one isomer. The ligand L in the monosubstituted complexes is probably coordinated to the Fe atom adjoining the chalcogen atoms, while in the disubstituted complexes two L molecules are coordinated to two iron atoms owing to steric hindrance. However, it cannot be ruled out that the existence of two and more isomers is a result of the ligand exchange between the iron atoms in the cluster.[138]

The synthesis of derivatives of compound (II) by the substitution of one, two, or three CO groups by triphenylphosphine and nitrogen-containing ligands (phenanthroline, α,α'-bipyridyl, acetonitrile, triethylamine, pyridine, and piperidine) has been described.[140] The character of the

infrared spectra of the compounds obtained in the carbonyl region depends on the strength of the d_π bonds between the ligand and the metal.

11. The Reactions of Compounds (I) and (II) with Transition Metal Carbonyls

The rapid rearrangements of the adduct $X_2Fe_2(CO)_6 \cdot L \ldots X_2Fe_2(CO)_6$ lead to the formation of $X_2Fe_3(CO)_9$ or $LX_2Fe_3(CO)_8$ with loss of L or CO respectively. In this case the adduct behaves as a ligand containing a sulphur atom as the nucleophilic fragment. A similar behaviour of the $AsCo_3(CO)_9$ [84] and $SFeCo_2(CO)_9$ [142,143] clusters, in which the As and S atoms manifest the character of Lewis bases in reactions with $Fe(CO)_5$ and $M(CO)_6$ (M = Cr, Mo, or W), has been reported:

$$SFeCo_2(CO)_9 + M(CO)_6 \rightarrow (OC)_5MSFeCo_2(CO)_9 + CO;$$
$$SFeCo_2(CO)_9 + Fe(CO)_5 \rightarrow (OC)_4FeSFeCo_2(CO)_9 + CO;$$
$$AsCo_3(CO)_9 + M(CO)_6 \rightarrow (OC)_5MAsCo_3(CO)_9 + CO.$$

In the adduct the ligand weakens the S–S bond by increasing the electron density in the X_2Fe_2 fragment. Steric and electronic factors influence the electron-donating character of the adduct. For example, tributyl phosphite, which is a powerful ligand donor, ensures a high yield of the trinuclear cluster. The above mechanism makes it possible to interpret the difference between the reactions involving the direct substitution of the CO groups in compound (II) and the formation of $LX_2Fe_3(CO)_8$ from the adduct. On the basis of ^{13}C NMR spectra, the authors[143] concluded that the substituted trinuclear clusters synthesised by the two different methods are identical.

It has been shown[144] that heating of a mixture of $(PHR)_2 \cdot Fe_2(CO)_6$ with $Fe_3(CO)_{12}$ leads to the formation of $(PR)_2 \cdot Fe_3(CO)_9$ together with the clusters $(PR)_2Fe_4(CO)_{11}$ and $(PR)_2Fe_4(CO)_{12}$.

The structure of the cluster $(\mu_3\text{-}S)(\mu_3\text{-}PR)Fe_3(CO)_9$ (where $R = p\text{-}CH_3OC_6H_4$), obtained by the reaction of $Fe_3(CO)_{12}$ with the Lawesson reagent cyclo-$[p\text{-}CH_3OC_6H_4P(S)S]_2$, has been determined recently.[145,146]

Treatment of compound (I) with $Fe_3(CO)_{12}$ or $(C_2H_5)_3N \cdot H_2Fe_3(CO)_{11}$ leads to the formation of a compound of type (II):[3]

$$S_2Fe_2(CO)_6 + Fe_3(CO)_{12} \rightarrow S_2Fe_3(CO)_9 + CO.$$

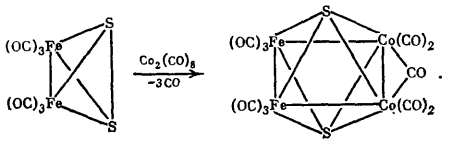
The presence of insignificant amounts of dithiodiiron heptacarbonyl $S_2Fe_2(CO)_7$ in the reaction mixture and the instability of this cluster, which is quantitatively converted into compound (I) in solution, suggests that the above dinuclear cluster can be an intermediate in the formation of the trinuclear cluster (II).[3] The reaction apparently proceeds via a stage involving the formation of compound (I) with subsequent insertion of the $Fe(CO)_3$ fragment in the S–S bond.

Dicobalt octacarbonyl does not react with compound (II), while the sulphur-containing cluster (I) reacts under mild conditions to give a relatively high yield (56%) of $SFeCo_2(CO)_9$,[147] whose structure has been established by X-ray diffraction:[148]

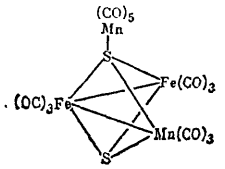
$$S_2Fe_2(CO)_6 + Co_2(CO)_8 \xrightarrow[\Delta]{C_6H_{14},N_2} SFeCo_2(CO)_9 + Fe(CO)_5 + S.$$

Vahrenkamp and Wucherer[149] were the first to synthesise a tetranuclear cluster from two initial dinuclear complexes of type (I). As expected, the substitution by cobalt carbonyl under mild conditions leads to the formation of the new tetranuclear cluster $S_2Fe_2Co_2(CO)_{11}$ (Scheme 12).

Scheme 12



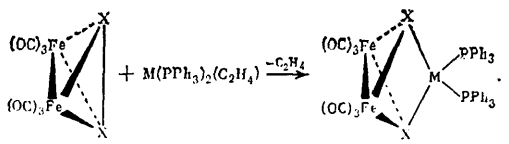
The photoinduced reaction of $S_2Fe_2(CO)_6$ with $Mn_2(CO)_{10}$ in solution in THF gives rise to a cluster having the composition $S_2Fe_2Mn_2(CO)_{14}$.[150] The composition and structure of this cluster, established by elemental analysis, mass spectrometry, Mössbauer spectroscopy, and X-ray diffraction, can be represented by $Fe_2Mn(CO)_9 \cdot (\mu_3\text{-}S)(\mu_4\text{-}S)Mn(CO)_5$, where the Fe_2Mn system contains one Fe–Fe bond and one Fe–Mn bond.[150]



12. Oxidative Addition of Metal Complexes

New heterometallic chalcogenide clusters $X_2Fe_2(CO)_6M(PPh_3)_2$ (where X = S, Se, or Te; M = Pt or Pd), characterised by means of elemental analysis, molecular weight measurements, and infrared and NMR spectroscopic data (Scheme 13), have been obtained in quantitative yields by the oxidative addition of $M(PPh_3)_2(C_2H_4)$ to $X_2Fe_2(CO)_6$:[151]

Scheme 13



This reaction has been used to obtain heteronuclear clusters.[152] It formally involves the homolytic cleavage of the X–X bond in the initial $\mu\text{-}X_2$ complexes and leads to a new way of obtaining mixed metallic clusters.[152,153]

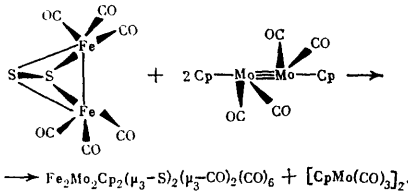
13. The Interaction of Compounds (I) with Transition Metal π-Complexes

The interaction of $S_2Fe_2(CO)_6$ with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ in heptane led to the synthesis in 15% yield of the first iron-nickel cluster in which the sulphur atom at the apex (centre) is symmetrically linked to three metal atoms: $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3S$. Its structure has been confirmed by X-ray diffraction.[154]

The interaction of $S_2Fe_2(CO)_6$ with $(C_5H_5)_2Mo_2(CO)_4$ in toluene at 0 °C has been described.[155] It leads to the formation of the red crystalline dimer $[(C_5H_5Mo(CO)_3]_2$

and red-brown crystals of a new iron–molybdenum sulphur-containing cluster of the "butterfly" type having the composition $Fe_2Mo_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6$ and characterised by infrared spectroscopy (Scheme 14):

Scheme 14



$\longrightarrow Fe_2Mo_2Cp_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6 + [CpMo(CO)_3]_2.$

The structure of this cluster has been demonstrated by X-ray diffraction.[155]

The reaction of compound (I) with $R_2Mo_2(CO)_4$, where R = Cp, Cp', or $\eta^5\text{-}CH_3C_5H_4$, leading to new isomeric iron–molybdenum sulphur-containing clusters, has been investigated:[156]

$$S_2Fe_2(CO)_6 + 2\,R_2Mo_2(CO)_4 \rightarrow Cp_2Mo_2(CO)_6 + \\ + R_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2 + R_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2.$$

The $Cp'_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2$ cluster has been analysed by X-ray diffraction.[156]

A new heterotetrametallic cluster $(\eta^5\text{-}C_2H_5)_2Cr_2Fe_2(\mu_3\text{-}CO)_2.(\mu_3\text{-}S)_2(CO)_6$, whose structure has been demonstrated by X-ray diffraction, has been obtained by refluxing $S_2Fe_2(CO)_6$ with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ for 30 min in a hexane–toluene mixture.[157]

14. Catalytic Properties of Clusters (I) and (II)

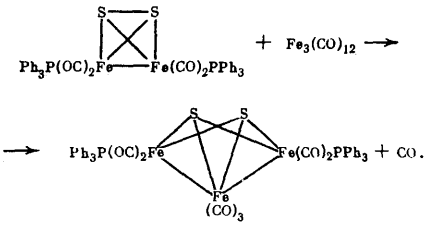
It has been established[3] that cluster (I) and (II) exhibit catalytic activity in the conversion of thiols into disulphides:[158,159]

$$2\,RSH \xrightarrow{\text{(I) or (II)}} RSSR + H_2.$$

This reaction has served as the basis for a new method of eliminating mercaptans from hydrocarbon mixtures.[160] Cluster (II) has a greater catalytic activity in this reaction than cluster (I).

In order to elucidate the causes of the different behaviour of clusters (I) and (II) in the conversion of thiols into disulphides, triphenylphosphine-substituted compounds (I) and (II) were used and their relative activities in the above process were tested. It was found that the monoderivatives of compounds (I) and (II) differ insignificantly in their activities from the corresponding unsubstituted clusters. On the other hand, bis(triphenylphosphine)-substituted clusters (I) virtually lose their ability to convert thiols into disulphides. Steric factors associated with the presence of the bulky triphenylphosphine ligand, which prevents the coordination of the thiol, apparently exert an appreciable influence on the rate of reaction in this case. A different type of behaviour has been observed using a disubstituted derivative of the trinuclear clusters (II) obtained by the reaction of $Fe_3(CO)_{12}$ with a disubstituted derivative of compound (I):

Scheme 15



The activity of the latter cluster is comparable to that of the unsubstituted cluster (II). Bearing in mind the data concerning the interaction of the dinuclear cluster (I) with iron carbonyls and Group IVB elements, obtained by Mavlonov,[3] the $Fe(CO)_3$ cluster is presumably inserted in the S–S bond in this case also.

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The data described above permit the conclusion that the abundance of the reactions of clusters (I) and (II) compared with the mononuclear complexes can apparently be accounted for by the presence of several active centres at the Fe atoms. The activity of tetra- and poly-nuclear clusters is probably still greater.

---o0o---

During the preparation of the manuscript for the press, a number of studies concerning the synthesis and properties of chalcogeniron carbonyl clusters were published.[161–163]

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