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Reaction of unsymmetrical thioalkynes $R{-}C{\equiv}C{-}SC_2H_5$, $R=CH_3$, C_6H_5, with iron and ruthenium carbonyls. How to build a polynuclear compound using the C–S cleavage

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Abstract

A thorough investigation of reactions of amino and phosphinoalkynes with metal carbonyls showed the significant influence of the nature of the heteroatom on the reaction This paper deals with the reactions of two unsymmetrical thioalkynes $RC{\equiv}CSC_2H_5$, $R=CH_3$ or C_6H_5, with iron and ruthenium carbonyls. About twenty characterized compounds helped to describe the sulfur influence on the behaviour of those two thioalkynes. (1) Two thioalkynes couple via the triple bond according to a classical reaction type. However, the alkyne asymmetry yields three types of coupling which were all observed. (2) The particular role of sulfur is displayed first by the cleavage of one or the other carbon–sulfur bond, or more seldomly both of them simultaneously, and second by the well known ability of sulfur to ligate metal. (3) The combination of these features led us to modulate the increase of nuclearity from two to five iron atoms.

1. Introduction

Various results have been published about reactions of metal carbonyls with functionalized alkynes having a phosphorus or a nitrogen atom directly fixed on the triple bond [1, 2]. Phosphinoalkynes have been shown to undergo an easy cleavage of the C–P bond leading to $RC{\equiv}C$ and PR'_2 fragments. The resulting fragments may bridge metallic atoms, building polynuclear cluster complexes. In contrast, the reactions of aminoalkynes are characterized either by the ligation of one alkyne molecule which behaves as an aminocarbene, or by the coupling of two alkyne molecules which build a metallacycle.

We then considered the case of thioalkynes in order to compare their reactivity with those of phosphinoalkynes and aminoalkynes. Some results have already been published by several authors using symmetrical dithioalkynes or unsymmetrical thioalkynes. Connor and Hudson [3] have observed the formation of the cyclopentadienone containing complex $[Fe(CO)_3\{\overline{C(SCH_3)}\text{-}C(SCH_3)C(O)C(SCH_3)\overline{C}(SCH_3)\}]$ when symmetrical $CH_3SC{\equiv}CSCH_3$ was reacted with $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$, without evidence of C–S cleavage. They also studied the reaction of the same thioalkyne with ruthenium carbonyl, chromium carbonyl, molybdenum carbonyl or tungsten carbonyl; no C–S bond cleavage occurred. Raubenheimer *et al.* [4] have synthesized the classical ferrole type complex $[Fe_2(CO)_6\{C_4(SCH_3)_4\}]$ by reacting $[Fe(CO)_5]$ with $CH_3SC{\equiv}CSCH_3$ under irradiation. Miller and Angelici [5] obtained π ligated alkyne products by reacting tungsten carbonyl with $CH_3SC{\equiv}CSCH_3$. Later, they studied the reaction of $CH_3SC{\equiv}CR$, $R=SCH_3$ or CH_3, with $[Ru\{P(CH_3)_3\}_2(C_5H_5)Cl]$ [6] and observed the formation of a sulfur bound thioalkyne complex cation $[Ru(C_5H_5)\{P(CH_3)_3\}_2(CH_3SC{\equiv}CR)]^+$; in the case of $R=SCH_3$, a rearrangement led to a cationic vinylidene complex $[Ru(C_5H_5)\{P(CH_3)_3\}_2\{C{=}C[S(CH_3)]_2\}]^+$ which can be reduced to give the thioacetylide containing compound $[Ru(C_5H_5)\{P(CH_3)_3\}_2(C{\equiv}CSCH_3)]$ after the cleavage of one C–S bond. They recently reported alkyne insertion reactions of $[Ir\{C_5(CH_3)_5\}(2,5\text{-dimethylthiophene})]$ with $CH_3SC{\equiv}CSCH_3$ and $CH_3SC{\equiv}CCH_3$, leading to tricyclocarbene complexes [7]. Fisher *et al.* [8] have reacted methylthioprop-1-yne with the carbene complex $[M(CO)_5\{C(OR)C{\equiv}CC_6H_5\}]$, where M was tungsten or chromium and R was a methyl or an ethyl group. They observed the insertion of the thioalkyne $C{\equiv}C$ bond, leading to ynenylcarbene complexes $[M(CO)_5$-

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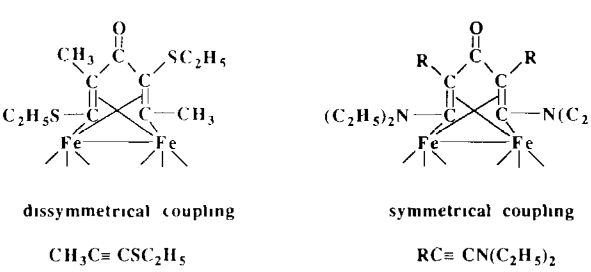
$\{C(SCH_3)[C(CH_3)=C(OR)C\equiv CC_6H_5]\}]$. It appears that in all these reactions the cleavage of the C–S bond is not often observed; Miller and Angelici [6] observed the cleavage of a C–S bond by hydrogenation.

We have now carried out the reaction of unsymmetrical thioalkynes $RC\equiv CSC_2H_5$, $R=CH_3$ or C_6H_5, with iron and ruthenium carbonyls. This review is dealing with the description of the various compounds we have obtained. Experimental details, collected in the thesis of Rosenberger [9], will be provided in papers in preparation.



Compound 1

Scheme 1

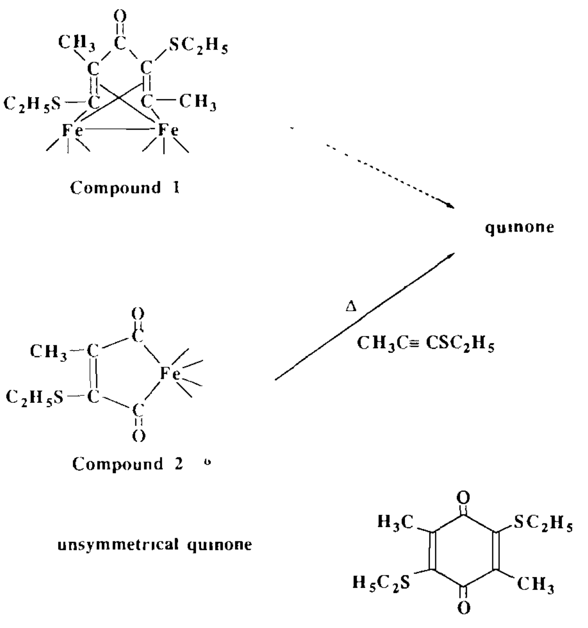
2. Where thioalkynes behave as alkynes or aminoalkynes; coupling reactions

Thioalkynes $RC\equiv CSC_2H_5$, $R=CH_3$ or C_6H_5, behave toward iron carbonyls in the same way as symmetrical alkynes or aminoalkynes, i.e. by coupling two molecules with or without incorporation of CO groups. Since thioalkynes and aminoalkynes are unsymmetrical molecules, three types of coupling are expected: two symmetrical couplings, $C(SC_2H_5)C(R)C(R)C(SC_2H_5)$ and $C(R)C(SC_2H_5)C(SC_2H_5)C(R)$, and one unsymmetrical coupling $C(R)C(SC_2H_5)C(R)C(SC_2H_5)$, respectively called in this paper head to head, tail to tail, and head to tail couplings.

The reactions of alkynes with iron carbonyl $[Fe_2(CO)_9]$ are well documented and various types of compounds have previously been described, including fly-over, cyclopentenedione, cyclopentadienone and ferrole type complexes. The same types of structures were formed by using $RC\equiv CSC_2H_5$, $R=CH_3$ or C_6H_5. They are discussed hereunder.

2.1. *The ligand incorporating a CO group*

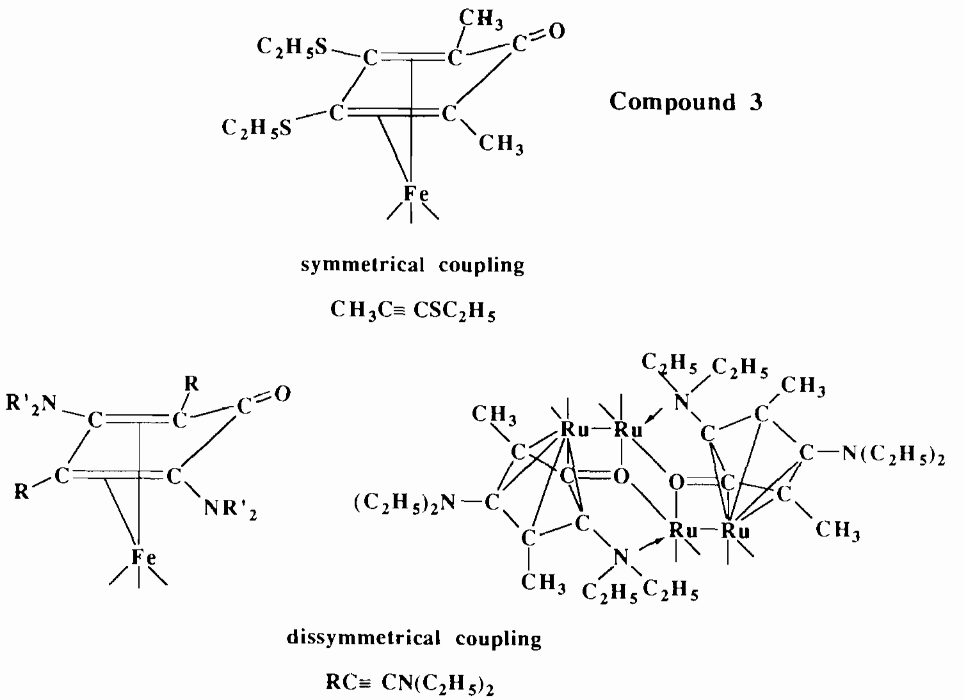
In compound **1**, $[Fe_2(CO)_6\{C(CH_3)C(SC_2H_5)C(O)C(CH_3)C(SC_2H_5)\}]$ (Scheme 1) which has the well known fly-over structure, the ligand is peculiar since it results from the combination of one CO group as a ketone group unsymmetrically linked to two thioalkynes, one by the $C(CH_3)$ carbon atom, one by the $C(SC_2H_5)$ carbon atom. The ligand is σ–π ligated to the metallic fragment $Fe_2(CO)_6$ in the fly-over manner. Such fly-over complexes were obtained with alkynes [10] or aminoalkynes [2g]. However in the case of aminoalkynes $RC\equiv CNR'_2$, both alkynes were symmetrically linked to CO by the CR carbon atom.



Scheme 2.

The interest of fly-over complexes is directly related to the formation of organic rings. Hübel [11] pointed out that those complexes obtained with symmetrical alkynes are precursors of quinones and/or cyclopentadienone. This behaviour has not been observed with aminoalkynes. In the case of thioalkynes, we formed together with compound **1** a quinone, the X-ray structure of which is directly related to the organic moiety of compound **1** (Scheme 2) since it shows the same linkage around the CO group. From the same reaction, the ferracyclopentenedione complex $[Fe(CO)_4\{C(O)C(SC_2H_5)C(CH_3)C(O)\}]$ (compound **2**, Scheme 2), was also separated. It contains a five-membered metallacycle enclosing one thioalkyne already bound to two CO groups. Then we wondered whether it was possible to replace the $Fe(CO)_4$ group of compound **2** by a second thioalkyne molecule in order to obtain a quinone. Actually, the reaction of an excess of $CH_3C\equiv CSC_2H_5$ with compound **2** yielded a quinone characterized by both IR and mass spectra.

Compound **3**, $[Fe(CO)_3\{C(SC_2H_5)C(CH_3)C(O)C(CH_3)C(SC_2H_5)\}]$ (Scheme 3), exhibits another classical ligand, that is a cyclopentadienone π bonded to a $Fe(CO)_3$ group. Nevertheless, in this compound, the ring resulted from the symmetrical coupling of two thioalkynes. The ring closure is made by one CO group linked to the two acetylenic carbons bearing methyl groups. The formation of tricarbonylcyclopentadienone-



Scheme 3.

iron has already been observed from dithioalkyne $CH_3SC{\equiv}CSCH_3$ by Connor and Hudson [3] or from aminoalkynes by King and Harmon [2f]. Let us point out that the coupling observed in the case of aminoalkynes is different to this one of thioalkyne. Aminoalkynes yielded a 2,4-bisdialkylaminocyclopentadienone, whereas thioalkyne yielded a 3,4-bisdiethylthiocyclopentadienone (Scheme 3). We observed the same 2,4-bisdialkylaminocyclopentadienone in a tetraruthenium compound [2h].

2.2. *Ferrole type complexes*

Another possibility of coupling two thioalkyne molecules $RC{\equiv}CSC_2H_5$ was observed in the dinuclear complex $[Fe_2(CO)_6L]$. This reaction was very smooth since it was carried out at room temperature. A tail to tail coupling yielded compound **4** $[Fe_2(CO)_6\{C(C_6H_5)C(SC_2H_5)C(SC_2H_5)C(C_6H_5)\}]$ (Fig. 1). This structure built on a 'ferrole' is quite common in alkyne reaction whatever the alkyne is, symmetrical or unsymmetrical, functionalized or not [2f, 2h, 4]. For instance, it is worth underlining that aminoalkynes $RC{\equiv}CNR'_2$ and dithioalkyne $CH_3SC{\equiv}CSCH_3$ both yielded this type of structure (Scheme 4).

Regular structural features are found in compound **4**, i.e. a non-planar ferrole with a dihedral angle between Fe(1)C(4)C(9) and C(4)C(3)C(8)C(9) equal to 166.9°, a C(23)–O(23) carbonyl semi-bridging the iron–iron bond with an O(23)–C(23)–Fe(2) angle equal to 164° (ν(CO) = 1930 cm^{-1}).

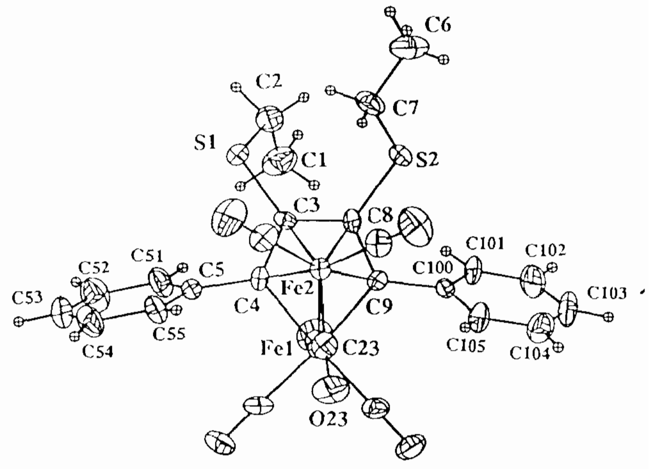
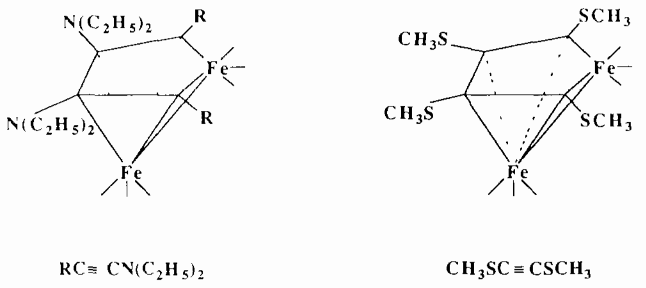
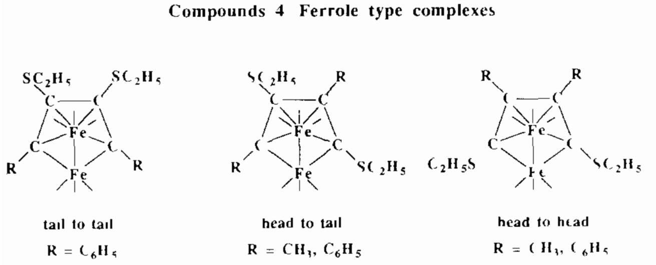


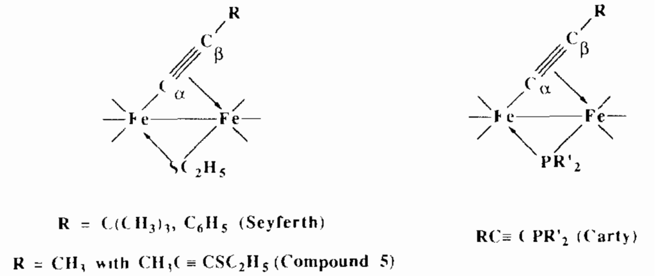
Fig. 1. Molecular structure of compound **4**, $[Fe_2(CO)_6\{\mu\text{-}C(C_6H_5)C(SC_2H_5)C(SC_2H_5)C(C_6H_5)\}]$, see Scheme 5, tail to tail coupling.



Scheme 4.



Scheme 5.



Scheme 6

The same tail to tail coupling in a dinuclear compound was observed for aminoalkynes; the two other couplings head to head [12] and head to tail [2g] of aminoalkynes were found only in trinuclear iron complexes (Scheme 5). With phenylethylthioethyne $C_6H_5C{\equiv}CSC_2H_5$, the three dinuclear isomers related to the three couplings were not fully separated on the silica column; only the tail to tail isomer crystallized and has been studied by X-ray (compound **4**, Fig. 1). The occurrence of the head to tail isomer has been proved by comparing the ^{1}H NMR spectrum of the tail to tail pure isomer with this one of a fraction of the chromatographed solution. A remarkable feature of this spectrum is the diastereotopic hydrogens of the two CH_3–CH_2S. The ^{1}H NMR did not allow the head to head isomer to be recognized. It will be seen later that reacting an excess of iron carbonyl with the chromatographed solution yielded a trinuclear complex which proved its occurrence in the solution.

For the methylethylthioethyne $CH_3C{\equiv}CSC_2H_5$, only head to head and head to tail isomers have been observed. This was proved by preparing corresponding tri- and tetrairon complexes by reacting an excess of iron carbonyl (see below).

3. Where one C–S bond is cleaved and another rebuilt

When phosphinoalkynes $RC{\equiv}CPR'_2$ were reacted with metal carbonyls, the C–P bond often cleaved, yielding two ligands acetylide and phosphide which then easily ligated the metal undergoing oxidative addition [1]. The same cleavage was observed for the C–S bond of thioalkynes $RC{\equiv}CSC_2H_5$, $R = CH_3$ or C_6H_5, when they were reacted with iron carbonyls. Are the structures obtained with phosphinoalkynes and ethylthioalkynes similar? This part deals with this question.

Carty and co-workers [1a, b] described a dinuclear iron compound $[Fe_2(CO)_6(\mu\text{-}C{\equiv}CR)(\mu\text{-}PR'_2)]$, $R = R' = C_6H_5$, with a phosphido bridge (Scheme 6). The same type of compound $[Fe_2(CO)_6(\mu\text{-}C{\equiv}CCH_3)(\mu\text{-}SC_2H_5)]$ is formed by using thioalkyne (compound **5**). The acetylide is σ–π ligated to iron atoms and the sulfide bridges the Fe–Fe bond.

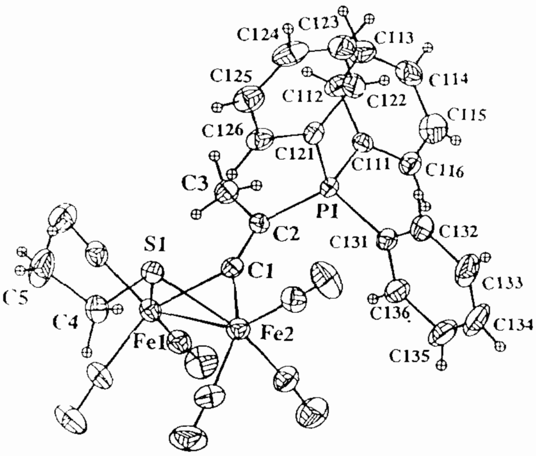
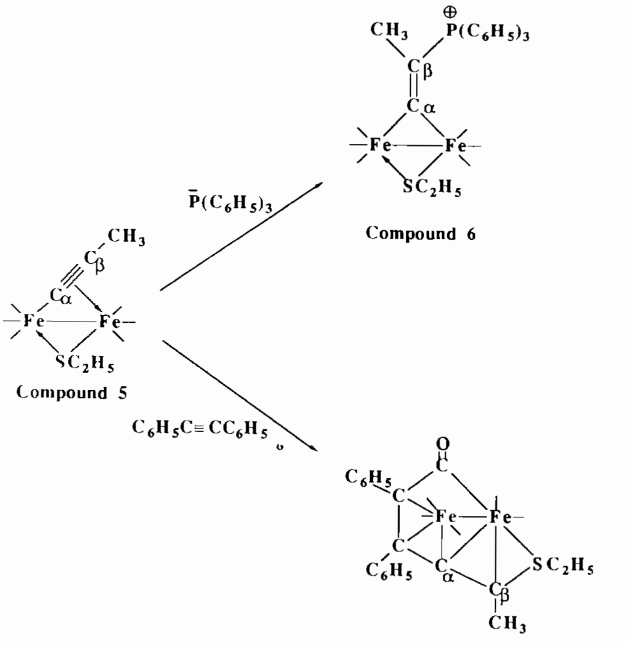


Fig. 2. Molecular structure of compound **6**, $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)\{\mu\text{-}C{=}C(CH_3)(P[C_6H_5]_3)\}]$, see Scheme 7.

Compound **5** was first identified by comparing its spectroscopic features with those of the similar complex $[Fe_2(CO)_6\{\mu\text{-}C_\alpha{\equiv}C_\beta C(CH_3)_3\}(\mu\text{-}SC_2H_5)]$ prepared by Seyferth *et al.* [13] by reacting a bromoalkyne with $[(C_2H_5)_3NH][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}SC_2H_5)]$. It has not been possible to check the structure of compound **5** by X-ray diffraction because it is an oil. However, it has been fully confirmed by its reactivity. As a matter of fact, it is known [1a, b, 14] that complexes containing a σ–π bridging acetylide ligand may undergo a nucleophilic attack, leading to zwitterionic complexes. This is due to the triple bond $C_\alpha{\equiv}C_\beta R$ polarization, which was described by Carty and co-workers using ^{13}C NMR chemical shifts $\delta(C_\alpha)$ and $\delta(C_\beta)$ [1a, b]. For compound **5**, following this method, the ^{13}C NMR spectrum gave $[\delta(C_\alpha) + \delta(C_\beta)] = 155.9$ ppm and $[\delta(C_\alpha) - \delta(C_\beta)] = -16.5$ ppm, which indicated a positive charge located on C_β. It is responsible for the nucleophilic attack on this carbon atom. Actually, $P(C_6H_5)_3$ reacted with compound **5** yielding the dinuclear complex $[Fe_2(CO)_6\{\mu\text{-}C{=}C[P(C_6H_5)_3](CH_3)\}(\mu\text{-}SC_2H_5)]$, the structure of which has been determined by X-ray diffraction (compound **6**, Fig. 2). The sulfide group still bridges the iron–iron bond. Triphenylphosphine is fixed on the C_β carbon atom making an ylide. The bond length $C(1)$–$C(2) = 1.32 \pm 0.02$ Å corresponds to a double bond

(Scheme 7) and the formed ligand $C{=}C[P(C_6H_5)_3](CH_3)$ is a μ-vinylidene which behaves as a three-electron donor.

A C–S bond may be rebuilt when diphenylacetylene is reacted with $[Fe_2(CO)_6(\mu\text{-}C^{(\alpha)}{\equiv}C^{(\beta)}CH_3)(\mu\text{-}SC_2H_5)]$ (compound **5**), yielding the dinuclear complex $[Fe_2(CO)_5\{\mu\text{-}C(O)C(C_6H_5)C(C_6H_5)CC(CH_3)S(C_2H_5)\}]$ (compound **7**, Fig. 3) characterized by X-ray analysis. One bond of $C_6H_5C{\equiv}CC_6H_5$ is opened so that the first carbon atom is bound to the C_α atom C(1) of the acetylide ligand and the second carbon atom is bound to a CO group C(6) also ligated to Fe(1). The so formed metallacycle Fe(1)C(6)C(7)C(8)C(1) is π bonded to the second iron atom Fe(2) by the allylic part C(7)C(8)C(1). Distances C(7)–C(8) and C(8)–C(1) are equal to 1.43 ± 0.03 and 1.41 ± 0.03 Å, respectively.



Scheme 7.

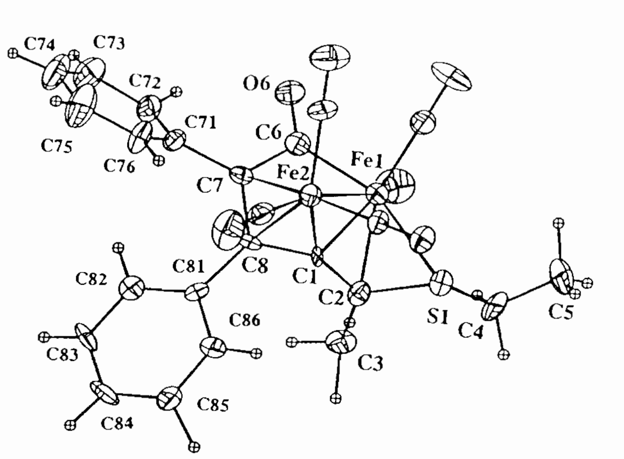
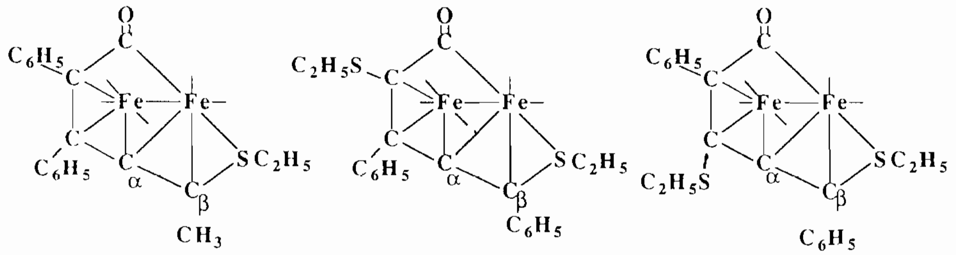


Fig. 3. Molecular structure of compound **7**, $[Fe_2(CO)_5\{\mu\text{-}C(O)C(C_6H_5)C(C_6H_5)CC(CH_3)S(C_2H_5)\}]$, see Scheme 7.

The most interesting feature of this structure is related to the ethylthio group. The C–S bond of $CH_3C_\beta{\equiv}C_\alpha SC_2H_5$ was broken to yield compound **5** which contains an SC_2H_5 bridge. Then this sulfur atom rebuilt a C–S bond to yield compound **7** [5]. The sulfur atom is now bound to the C_β carbon atom itself bearing the methyl group, C(2)–S(1) on Fig. 3. This sulfur atom is also bound to Fe(1) ligated to two CO ligands only. The acetylide group C(1)–C(2) is still σ–π ligated on iron atoms.

Since the formation of compound **5** implied the opening of the triple bond of a diphenylacetylene, it was thought that the same reaction might be carried out with the thioalkyne itself. This peculiar structure was indeed obtained from the direct reaction of $C_6H_5C^{(\beta)}{\equiv}C^{(\alpha)}SC_2H_5$ in slight excess with $[Fe_2(CO)_9]$ at room temperature. A first thioalkyne molecule was cleaved, yielding the ethylthio and the acetylide groups, and a second thioalkyne molecule replaced diphenylacetylene. However since the thioalkyne is unsymmetrical, two isomers are expected depending on whether the uncleaved thioalkyne is fixed to the C_α carbon atom C(3) of the acetylide by its C_β carbon atom C(8) (first isomer **8a**) or by its C_α carbon atom C(7) (second isomer **8b**). In compound **8a** the ligand is $C(O)\text{–}C(SC_2H_5){=}C(C_6H_5)\text{–}C{\equiv}C(C_6H_5)\text{–}S(C_2H_5)$ while in compound **8b** it is $C(O)\text{–}C(C_6H_5){=}C(SC_2H_5)\text{–}C{\equiv}C(C_6H_5)\text{–}S(C_2H_5)$ (Scheme 8). Both isomers were obtained; they were not separated by chromatography on silica, but two kinds of crystals were separated under the microscope and their structures were determined by X-ray methods. ^1H NMR spectra before chromatography of the solution showed that compound **8a** is the major isomer and compound **8b** the minor one.

Another dinuclear complex $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)\{\mu\text{-}S(C_2H_5)C[{=}C(CH_3)(C{\equiv}CCH_3)]\}]$, compound **9** (Fig. 4) [15], corresponds to the C–S cleavage of a first thioalkyne molecule and to the combination of the acetylide with a second uncleaved thioalkyne molecule. Compound **9** was obtained at room temperature by reacting $CH_3C^{(\alpha)}{\equiv}C^{(\beta)}SC_2H_5$ with $[Fe_2(CO)_9]$. The ethylthio group of the cleaved alkyne bridges the iron–iron bond. The acetylide group reacted with a second whole thioalkyne molecule. C_α, C(6), carbon atom of acetylide is now bonded to the C_β, C(2), carbon atom of the uncleaved thioalkyne. The resulting new ligand $C_2H_5S\text{–}C{=}C(CH_3)(C{\equiv}CCH_3)$ is ligated to iron atoms by S(1) and C(1) yielding a planar four-membered ring Fe(1)Fe(2)S(1)C(1) (Fig. 4). The dihedral angle between Fe(1)Fe(2)S(2) and Fe(1)Fe(2)S(1)C(1) is equal to 88.9°.



compound 7 compound 8a compound 8b

Scheme 8

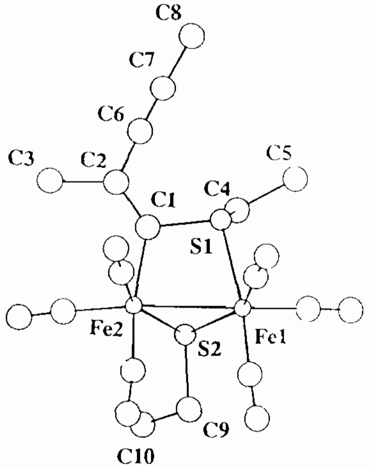
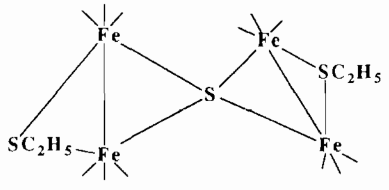


Fig. 4. Molecular structure of compound **9**, $[Fe_2(CO)_6(\mu\text{-}SC_2H_5)\{\mu\text{-}S(C_2H_5)C[C(CH_3)(C{\equiv}CCH_3)]\}]$.



$[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}SC_2H_5)_2]$

Scheme 9.

4. Where the nuclearity is increased

We have discussed in Section 2 the reactions of iron carbonyls with thioalkynes which yield dinuclear complexes $[Fe_2(CO)_6L]$ having a classical type of structure, i.e. a ferracyclopentadiene π bonded to a second iron atom; the two alkynes coupled to yield the ligand L. Since the alkyne is unsymmetrical, there are three types of coupling: $C(R)C(SC_2H_5)C(SC_2H_5)C(R)$, $C(R)C(SC_2H_5)C(R)C(SC_2H_5)$ and $C(SC_2H_5)C(R)C(R)C(SC_2H_5)$.

It has been observed earlier that the C–SR bond may be cleaved rather easily and that even both C–S–C bonds may be broken in some special rarer occasions as for $[Fe_4(CO)_{12}(\mu_4\text{-}S)(\mu\text{-}SC_2H_5)_2]$ [15] (Scheme 9). Thus, could we use the sulfur atom of $[Fe_2(CO)_6L]$ as a ligating atom to add an additional iron atom? Could we use the C–S bond so that it is cleaved by an additional iron atom which then undergoes an oxidative addition? It is the purpose of this part to investigate the various ways leading to an increase of nuclearity.

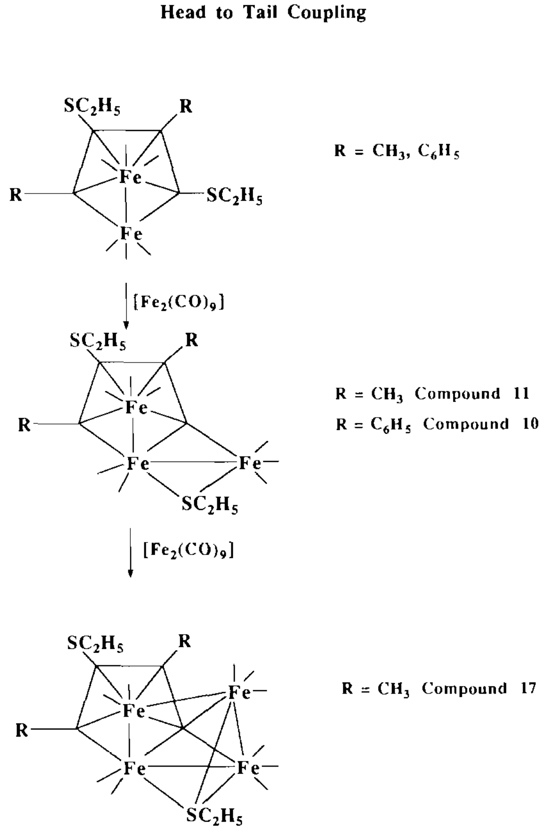
4.1. Three iron atoms

Let us start with the dinuclear species containing a head to tail coupled ligand (Scheme 5). One ethylthio group is linked to the carbon atom in α position with respect to the iron atom incorporated in the ferracyclopentadiene fragment, the other is not. That C–S bond in α position may be cleaved by a third iron atom which is then bonded to those C and S atoms now independent from each other (Scheme 10).

The X-ray structure has been determined only for $R=C_6H_5$, compound **10** (Fig. 5). The third iron atom is added to the framework of the original compound so that it forms only one Fe–Fe bond with the iron atom of the ferrapentadiene ring. This Fe–Fe bond is bridged by the ethylthio group. The additional iron atom is also linked to the carbon of the ring which has lost the ethylthio group. Thus, this carbon atom and the three iron atoms build a butterfly structure the Fe(1)–C(7) hinge of which is the iron atom of the ferracyclopentadiene ring and the carbon atom of the ring which has lost the SC_2H_5 group. The two nonbonded iron atoms are separated by 3.797 Å and the dihedral angle [C(7)Fe(1)Fe(2)]–[C(7)Fe(1)Fe(3)] is equal to 147.7°.

Since there are only two Fe–Fe bonds in compound **10**, it may be considered as an open triangle. It is easy to check that there are 50 valence electrons, 24 from iron atoms, 16 from CO ligands, 3 from the SR ligand and 7 from the organic moiety.

The structure of the methyl compound $[Fe_3(CO)_8\{C(CH_3)C(SC_2H_5)C(CH_3)C\}(\mu\text{-}SC_2H_5)]$ (compound **11**) is based upon its ^1H NMR spectrum compared to the one of $[Fe_3(CO)_8\{C(SC_2H_5)C(CH_3)C(CH_3)C\}(\mu\text{-}SC_2H_5)]$ which corresponds to a head to head coupling (compound **12**, Scheme 11); this last compound has also been studied by X-ray to check its structure.



Head to Tail Coupling

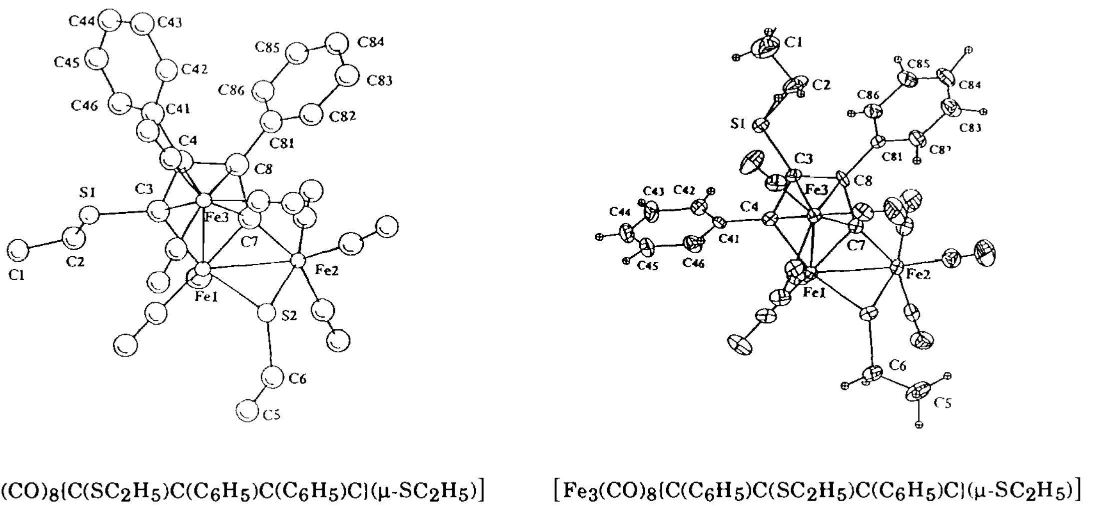
Scheme 10.

In particular, the ^{1}H NMR spectra of both **11** and **12** featured two C_2H_5 groups. For each of them, there is a strong diastereotopy. It is clear that both compounds **11** and **12** have the same bridging SC_2H_5 (triplet 3H of CH_3CH_2S at 1.23 and 1.23 ppm), with the same $^3J=7.4$ Hz. The other 3H of CH_3CH_2S do not have exactly the same chemical shift (3H triplet of CH_3CH_2S: 0.89 ppm for head to tail, 1.02 ppm for head to head) with again $^3J=7.4$ Hz (Fig. 6).

It must be underlined that the strength of the iron–sulfur bond is so high that such an open new structure is preferred to a *closo* structure derived from the *nido* $[Fe_2(CO)_6\{C(R)C(SC_2H_5)C(R)C(SC_2H_5)\}]$ structure by the simple addition of $Fe(CO)_2$ which would bring no electrons to the Fe_2C_4 skeleton. Such a *closo–nido* reversible transition has indeed been observed in the case of aminoalkynes which yielded the *closo* $[Fe_3(CO)_8\{\mu_3\text{-}C(R)C(N[C_2H_5]_2)C(N[C_2H_5]_2)\text{-}C(R)\}]$ [16]. As a matter of fact, $[Fe_2(CO)_9]$ reacted with the *nido* $[Fe_2(CO)_6\{\mu_2\text{-}C(C_6H_5)C(N[C_2H_5]_2)C(N[C_2H_5]_2)C(C_3H_5)\}]$ compound to provide the *closo* $[Fe_3(CO)_8\{\mu_3\text{-}C(C_6H_5)C(N[C_2H_5]_2)C(N[C_2H_5]_2)C(C_3H_5)\}]$ which in turn gave back the previous *nido* by heating (Scheme 12).

4.2. Four iron atoms

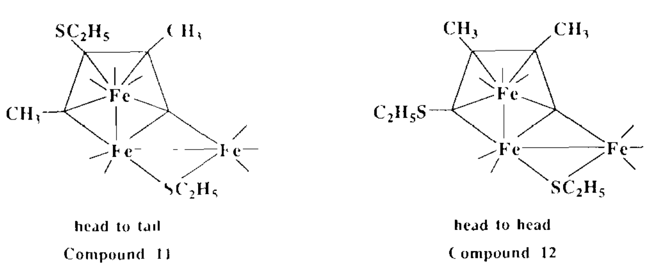
If one now considers the case of $C(SC_2H_5)\text{-}C(R)C(R)C(SC_2H_5)$ corresponding to a head to head coupling (Scheme 5), both CS are in α position with respect to the iron of the ferracyclopentadiene ring. An excess of iron carbonyl yields similarly a trinuclear compound with the same cleavage of the C–S bond and the same structure based upon X-ray (Fig. 5, $R=C_6H_5$) and NMR studies (compound **13**, Scheme 13). The SC_2H_5 cleaved fragment bridges a Fe–Fe bond. However, there is in this compound a second SC_2H_5 group in α position still connected to the other carbon



$[Fe_3(CO)_8\{C(SC_2H_5)C(C_6H_5)C(C_6H_5)C\}(\mu\text{-}SC_2H_5)]$ $[Fe_3(CO)_8\{C(C_6H_5)C(SC_2H_5)C(C_6H_5)C\}(\mu\text{-}SC_2H_5)]$

head to head head to tail

Fig. 5. Molecular structures of head to head compound **13** (see Scheme 13) and head to tail compound **10** (see Scheme 10) trinuclear complexes.



Scheme 11

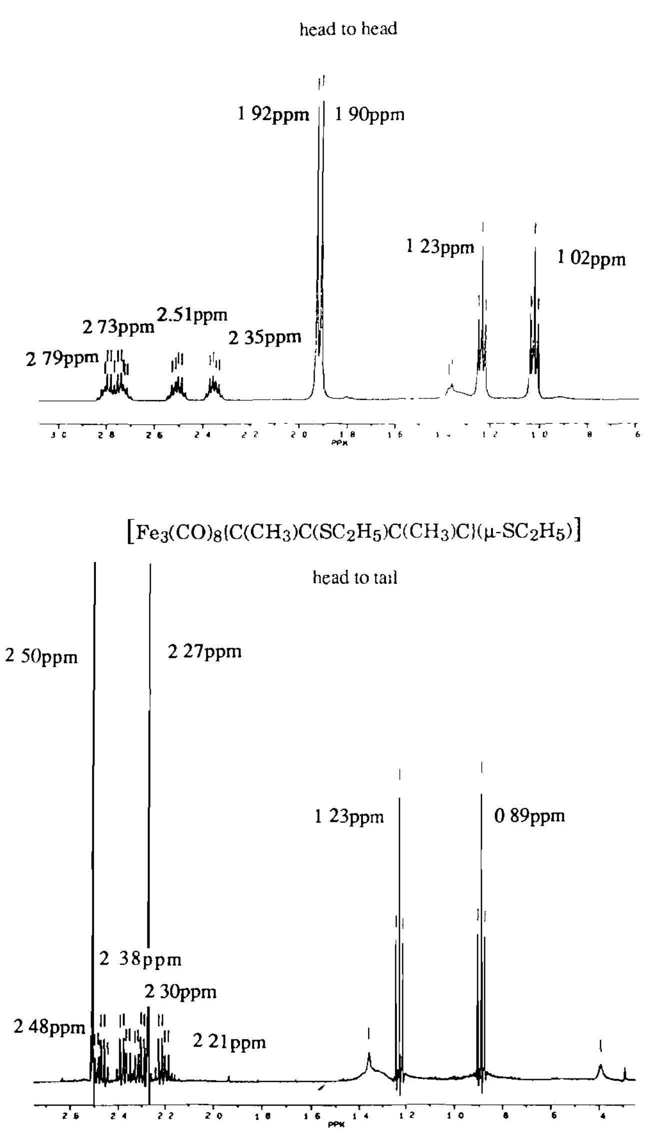
atom linked to the iron of the ferracyclopentadiene ring.

It seems clear that this C–SC_2H_5 bond should be similarly broken by an excess of iron carbonyl. This is what actually happens (Scheme 13). One now gets a symmetrical tetranuclear compound (yield 55% for $R = CH_3$, compound **14**, and 70% for $R = C_6H_5$, compound **15**, Fig. 7). The four iron atoms are set in a T shape. The upper bar of the T is not linear since the Fe(2)–Fe(1)–Fe(4) angle is 147.6°, being the same for both CH_3 and C_6H_5 compounds. Each of the two SC_2H_5 groups bridges a Fe–Fe bond, i.e. both sides of the bar of the T.

From a dinuclear compound, we have thus reached the stage of a tetranuclear compound. This T shaped compound may be considered as a butterfly shaped compound two edges of which were broken with 66 valence electrons.

4.3. Five iron atoms

When an excess of $[Fe_2(CO)_9]$ was reacted with $[Fe_3(CO)_8\{CC(CH_3)C(CH_3)C(SC_2H_5)\}(\mu\text{-}SC_2H_5)]$ to get the symmetrical tetranuclear compound $[Fe_4(CO)_{10}(\mu\text{-}SC_2H_5)_2\{CC(CH_3)C(CH_3)C\}]$, another minor compound was found (5% yield). From an X-ray study, it turned out that it was a pentanuclear compound $[Fe_5(CO)_{11}(\mu\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)\{CC(CH_3)C(CH_3)C\}]$ (Fig. 8, Scheme 13, compound **16**). Formally its structure is built from the preceding tetranuclear structure by adding a fifth iron atom which is bound to only two iron atoms by Fe–Fe bonds, i.e. the iron atom Fe(3) being π bonded to the ferracyclopentadiene ring and the iron atom Fe(5) being at one end of the upper bar of the T. The new Fe–Fe distances are 2.528(8) and 2.717(9) Å, the last one Fe(3)–Fe(4) being the longest of the six Fe–Fe distances of this compound. The two non-bonding Fe–Fe diagonals measure 3.378 and 3.766 Å. Thus, a quadrangle of four iron atoms Fe(1)Fe(3)Fe(4)Fe(5) is found. Actually, it is not planar; the dihedral angle between the moiety containing the three first iron atoms of the starting compound and the moiety containing the fifth iron atom and the two irons to which it is linked, is equal to 139°.


$[Fe_3(CO)_8\{C(SC_2H_5)C(CH_3)C(CH_3)C\}(\mu\text{-}SC_2H_5)]$

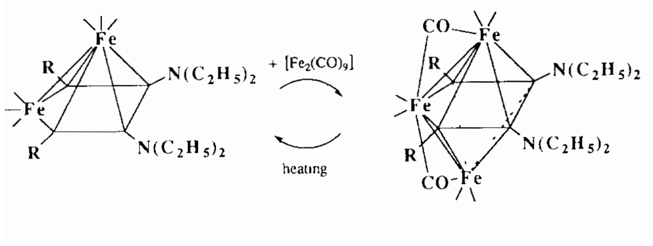
head to head

$[Fe_3(CO)_8\{C(CH_3)C(SC_2H_5)C(CH_3)C\}(\mu\text{-}SC_2H_5)]$

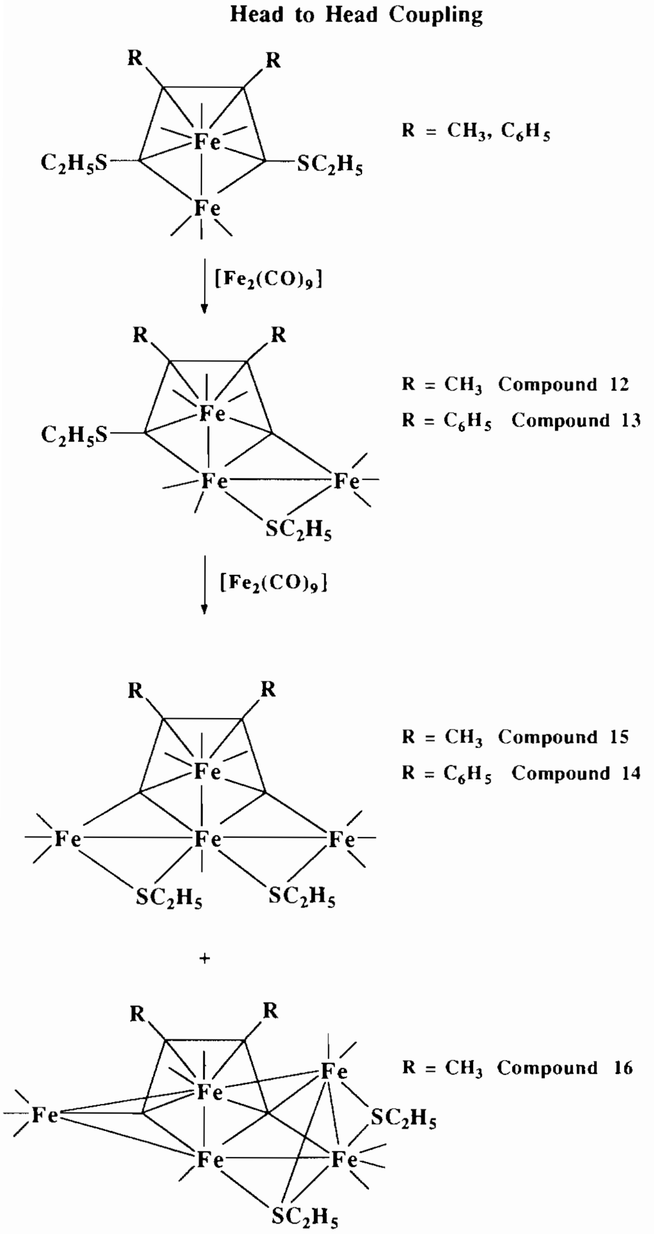
head to tail

Fig. 6 ^1H NMR spectrum (C_6D_6, 250 MHz) of the head to head compound **11** and the head to tail compound **12** trinuclear complexes. Upper part: singlets 1.90 and 1.92 ppm refer to methyl groups attached to the cycloferrapentadienyl ring; 1.02 ppm triplet and 2.75–2.79 ppm multiplets are related to the SC_2H_5 group linked to the ring; 1.23 ppm triplet and 2.35–2.51 ppm multiplets are related to the $\mu\text{-}SC_2H_5$ group. Lower part: singlets 2.27 and 2.50 ppm refer to methyl groups attached to the cycloferrapentadienyl ring; 0.89 ppm triplet and 2.21–2.30 ppm multiplets are related to the SC_2H_5 group linked to the ring, 1.23 ppm triplet and 2.38–2.48 ppm multiplets are related to the $\mu\text{-}SC_2H_5$ group.

This quadrangle makes a square pyramid with the carbon atom C(1) which has lost an SC_2H_5 group. This square pyramid has three iron atoms bridged by an SC_2H_5 group (S(2)).



Scheme 12.



Scheme 13.

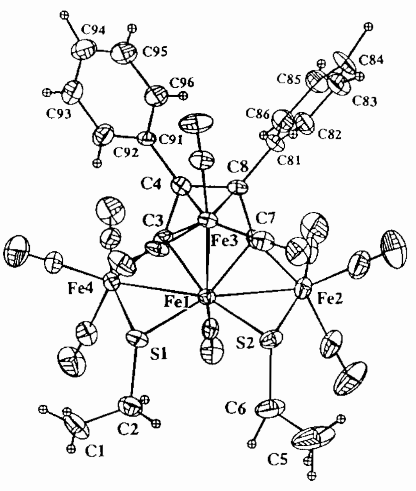


Fig. 7. Molecular structure of compound **15**, $[Fe_4(CO)_{10}(\mu\text{-}SC_2H_5)_2\{\mu_4\text{-}CC(C_6H_5)C(C_6H_5)C\}]$, see Scheme 13

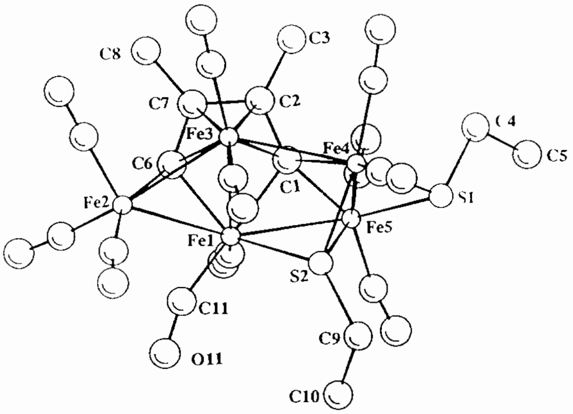


Fig. 8. Molecular structure of compound **16**, $[Fe_5(CO)_{11}(\mu\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)\{\mu_5\text{-}CC(CH_3)C(CH_3)C\}]$, see Scheme 13.

The second SC_2H_5 group has migrated from the other side of the molecule, from the other half of the T upper bar, now bridging two of the three iron atoms already μ_3-bridged by the first SC_2H_5. Consequently, a structural change happened on the side of the molecule where this second SC_2H_5 came from. The three iron atoms Fe(1)Fe(2)Fe(3) of this side now make a complete triangle capped by the carbon atom C(6) of the ferracyclopentadiene ring which has lost SC_2H_5.

It must be noted that such a pentanuclear structure has not been observed with the phenyl group.

Thus, on the T shaped tetranuclear compound, it is possible to add on one side of the T a fifth iron atom which builds up a quadrangle of metal atoms. Following this line, it was tempting to look for a six iron atom compound. Up to now, it has not been separated from the reaction medium.

4.4. *Four iron atoms again*

Turning back to $[Fe_3(CO)_8(\mu\text{-}SC_2H_5)\{CC(R)\text{-}C(SC_2H_5)C(R)\}]$ with $R=CH_3$ or C_6H_5, in which two alkynes are linked in the head to tail fashion, it is clear that the second SC_2H_5 group is not at the right position to yield a T shaped tetranuclear compound. However, one could wonder whether another iron atom could react, yielding a quadrangle as described in the preceding paragraph. Actually such a tetranuclear complex has been obtained by reacting an excess of iron carbonyls with $[Fe_3(CO)_8(\mu\text{-}SC_2H_5)\{CC(CH_3)C(SC_2H_5)C(CH_3)\}]$, to give a 30% yield (Fig. 9, Scheme 10, compound **17**).The same reaction was tried with $[Fe_3(CO)_8(\mu\text{-}SC_2H_5)\{CC(C_6H_5)C(SC_2H_5)C(C_6H_5)\}]$, but it did not work. One may wonder whether the phenyl is so bulky that it prevents another $Fe(CO)_n$ coming in.

In this compound **17**, a quadrangle Fe(1)Fe(2)-Fe(3)Fe(4) is similarly formed three iron atoms of which are bridged by a SC_2H_5 group, among them the added fourth iron atom. The non-bonding diagonal Fe–Fe distances are equal to 3.295 and 3.841 Å. This quadrangle is not planar; the dihedral angle between the original iron triangle and the triangle formed by the added iron and the two iron atoms to which it is linked, is equal to 139°. Thus, the situation is the same as above, with the difference of one $\mu\text{-}SC_2H_5$ bridge on one edge of the quadrangle for the pentanuclear compound, but not for this tetranuclear one.

It then seems that the addition of iron atoms is favoured by the formation of an ethylthio bridge.

4.5. Another type of tetranuclear iron compound

If both ethylthio groups are in α position one with respect to the other one, that is both of them in β position with respect to the iron atom of the ferracyclopentadiene ring (Fig. 1), one may wonder what would happen by reacting an excess of iron carbonyl. Could we obtain the same skeleton of iron–iron bonds, or could we use the lone pairs of both sulfur atoms to ligate additional iron atoms, or could we just build up a classical *closo* compound?

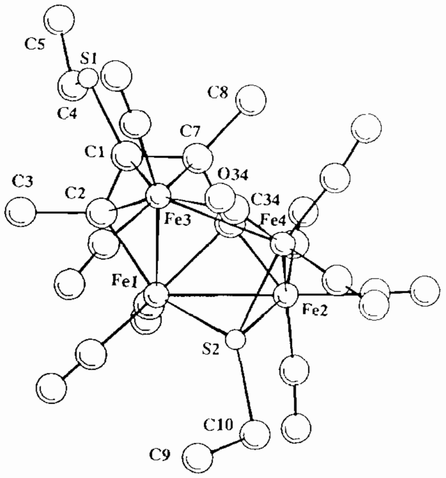


Fig. 9. Molecular structure of compound **17**, $[Fe_4(CO)_{10}(\mu_3\text{-}SC_2H_5)\{\mu_4\text{-}C(CH_3)C(SC_2H_5)C(CH_3)C\}]$, see Scheme 10

Actually, two complexes were obtained and the driving force for both of them was sulfur atoms. They are based on the starting classical dinuclear complex $[Fe_2(CO)_6\{C(C_6H_5)C(SC_2H_5)C(SC_2H_5)C(C_6H_5)\}]$. In the first one (compound **18**, Fig. 10), i.e. complex $[Fe_4(CO)_{12}\{\mu_4\text{-}C(C_6H_5)C(S)C(S)C(C_6H_5)\}]$, both $S\text{–}C_2H_5$ bonds were broken, but the sulfur atoms remained attached to the ring. Strangely, both ethyl groups were taken away (Scheme 14).

The cleavage now happened on the other side of the sulfur atom and the fate of these ethyl groups is not known. A $Fe_2(CO)_6$ group is ligated to these sulfur

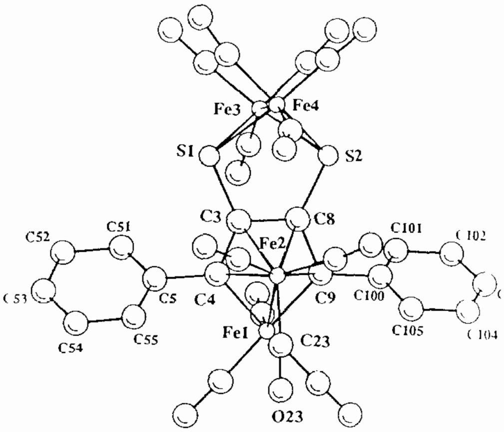
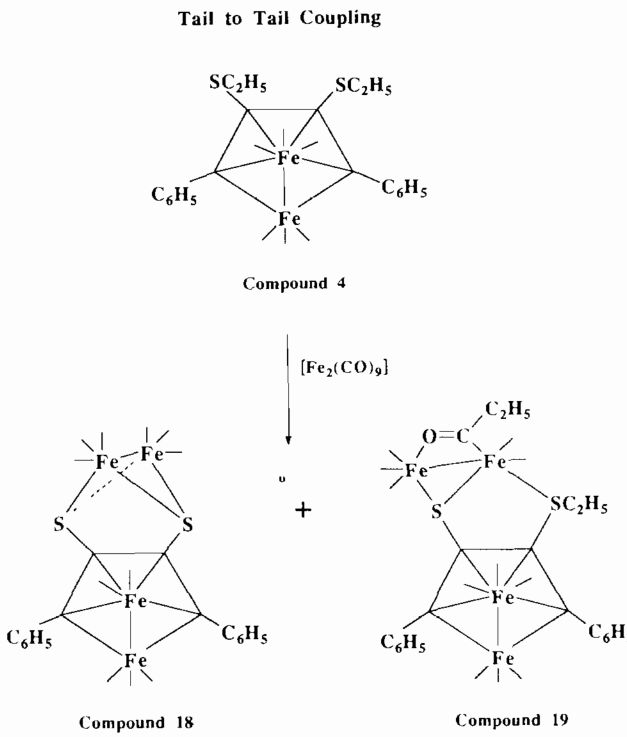


Fig. 10. Molecular structure of compound **18**, $[Fe_4(CO)_{12}\{\mu_4\text{-}C(C_6H_5)C(S)C(S)C(C_6H_5)\}]$, see Scheme 14



Scheme 14.

atoms, each iron atom being attached to both sulfurs by symmetrical Fe–S bonds, 2.267(8) and 2.26(1) Å for the first iron atom, 2.301(9) and 2.30(1) Å for the second one. Their carbonyl groups are in eclipsed positions

One could deduce from this reaction that, in the case where the heteroatom is fixed on this particular carbon atom, i.e. in β position with respect to the iron atom of the ferracyclopentadiene ring, the bond C_{ring}–S is stronger than the bond S–C_2H_5, maybe because of some multiple bond character. As a matter of fact, considering the starting dinuclear complex, the distances C_{ring}–S are C(8)–S(2) = 1.769(9) Å and C(3)–S(1) = 1.772(9) Å while the distances C_{ethyl}–S are longer: C(7)–S(2) = 1.82(1) and C(2)–S(1) = 1.84(1) Å. This is in contrast to the easy cleavage of the C_{ring}–S bond when S is in α position with respect to iron. This also might explain why the reaction of $[Fe_2(CO)_6\{C(CH_3)C(N[C_2H_5]_2)C(N[C_2H_5]_2)C(CH_3)\}]$ on copper to build up a complex using the lone pairs of nitrogen atoms failed; they certainly are more involved in the bond C_{ring}–N.

During the course of this reaction, another compound was made (compound **19**). It is again built upon $[Fe_2(CO)_6\{C(C_6H_5)C(SC_2H_5)C(SC_2H_5)C(C_6H_5)\}]$ but it is unsymmetrical (Fig. 11). A fragment $Fe_2(CO)_6$ was again added, but only one ethylthio group was cleaved.

The sulfur atom which has lost its ethyl group is unsymmetrically bonded to both iron atoms (2.278(6) and 2.228(6) Å). The second sulfur atom which has not lost its ethyl group is bound to only one iron atom (2.311(6) Å to Fe(4)), with a non-bonding distance of 3.645(6) Å to Fe(3). One ethyl group has migrated and attacked one CO group, making a propanoyl C_2H_5CO ligand bridging the two added iron atoms Fe(3) and Fe(4); the carbon of CO is ligated to the first iron atom Fe(3) and the oxygen to the second iron atom Fe(4) linked to the sulfur atom which has not lost its ethyl group: this is a rather unusual situation.

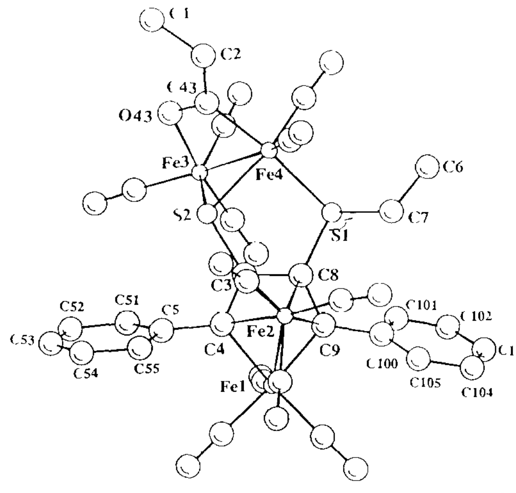


Fig 11 Molecular structure of compound **19**, $[Fe_4(CO)_{11}\{\mu_4\text{-}C(C_6H_5)C(SC_2H_5)C(S)C(C_6H_5)\}(\mu\text{-}OCC_2H_5)]$, see Scheme 14.

The line Fe(3)–Fe(4) makes an angle of 58.9° with the mean plane C(3)–C(4)–C(8)–C(9)–S(1)–S(2) while this angle is close to 90°, i.e. 83.5°, for compound **18**. It might be suggested that this compound is an intermediate in the production of $[Fe_4(CO)_{12}\{C(C_6H_5)C(S)C(S)C(C_6H_5)\}]$ in which both C–S bonds are broken. One then might think that the second C_2H_5 group attacked the C_2H_5CO group to yield pentan-3-one. This ketone has not yet been looked for in the reaction medium.

5. Reactions of thioalkynes with $[Ru_3(CO)_{12}]$

The complexes obtained from the reaction of iron carbonyls with thioalkynes showed two types of behaviour for the alkynes, coupling and C–S cleavage. It was tempting to consider the case of ruthenium carbonyl. Would the same behaviour of the organic entities be observed, as well as the same structural features of organometallic compounds? This part deals with the description of three clearly identified complexes of ruthenium. The first one is a trinuclear complex built on an open Ru_3 triangle, the second one is a tetranuclear complex containing an Ru_4 square plane, and the third one is particularly attractive, with a benzylidenecyclopentadienyl ligand formed by three molecules of alkyne and an Ru–Ru–Ru chain, providing an unusual structure.

These compounds illustrate the features previously met in the iron complexes: the easy C–S cleavage is the first constant feature, the attack of acetylide on another molecule of ligand is a second occasional feature, and the coupling of two alkynes to give a diene moiety is a third classical feature

The trinuclear complexes $[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CR)]$, R = CH_3 or C_6H_5, are based on a Ru_3 triangle with an open edge (Fig. 12) as previously observed by Carty *et al.* [1d] with phosphinoalkynes. The two ruthenium atoms of the open edge are connected by two bridges, the SC_2H_5 and the RC≡C ligands. As a matter of fact, the C–S bond joining the ethylthio and the acetylide moieties of the reactant $RC{\equiv}CSC_2H_5$ has been broken. The propynyl or phenylethynyl group is actually ligated to the three ruthenium atoms since it is bonded to Ru(1) and Ru(2) by its four π electrons and to Ru(3) by a σ bond involving the acetylide C atom previously bound to sulfur.

The five atoms C(1), C(2), C(3), C(4) and S are nearly located in the bissecting plane of the Ru(2)Ru(1)Ru(3) angle. These two compounds are characterized by 50 valence electrons, as expected for

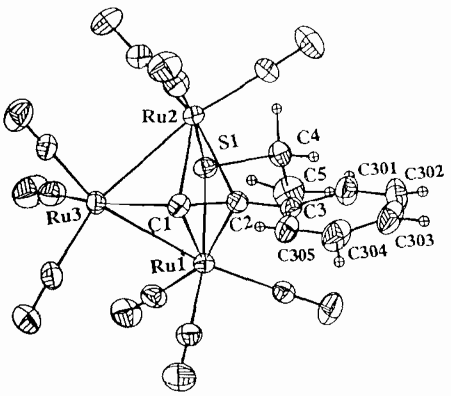


Fig. 12. Molecular structure of $[Ru_3(CO)_9(\mu_3\text{-}C{\equiv}CC_6H_5)(\mu\text{-}SC_2H_5)]$.

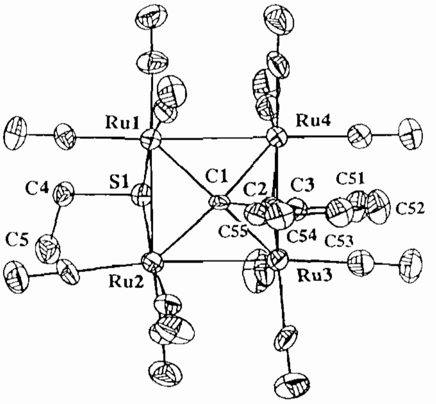
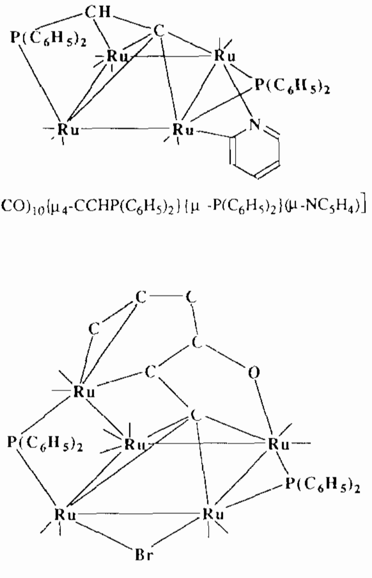


Fig. 13 Molecular structure of $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CC_6H_5)(\mu\text{-}SC_2H_5)]$, see Scheme 16

a cluster based upon a triangle having an open edge, i.e. 48+2. The SC_2H_5 group is a 3-electron donor and the $C{\equiv}CR$ group is a 5-electron donor.

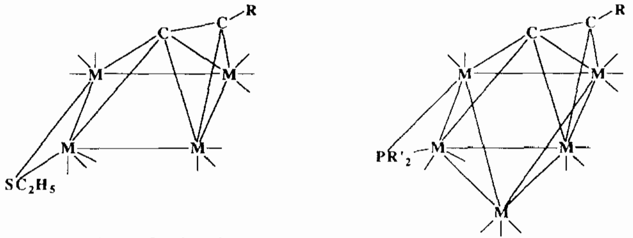
The tetranuclear complexes $[Ru_4(CO)_{12}(\mu\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CR)]$, with $R = CH_3$ or C_6H_5, are based upon a square planar core (Fig. 13). The acetylide $C{\equiv}CCH_3$ or $C{\equiv}CC_6H_5$ stretches over the surface of the square, and the ethylthio group bridges two ruthenium atoms on the opposite side of the square with respect to acetylide. The resulting structure is identical to that of $[Fe_4(CO)_{12}(\mu\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CR)]$ that we have previously obtained [15]. It must be pointed out that Bruce and co-workers [1g, 17] have isolated two compounds the structures of which are also square pyramidal. The first one is $[Ru_4\{\mu_4\text{-}CCHP[C_6H_5]_2\}\{\mu\text{-}P(C_6H_5)_2\}(\mu\text{-}NC_5H_4)(CO)_{10}]$ but its X-ray structure has not yet been published. The second one is a more complicated pentanuclear compound $[Ru_5\{\mu_5\text{-}CCC(O)CH_2CH{=}CH_2\}\{\mu\text{-}P(C_6H_5)_2\}_2(\mu\text{-}Br)(CO)_{11}]$; it may also be described as a square pyramidal structure built upon a Ru_4 plane sharing an edge with an open triangle of ruthenium atoms (Scheme 15).



$[Ru_4(CO)_{10}\{\mu_4\text{-}CCHP(C_6H_5)_2\}\{\mu\text{-}P(C_6H_5)_2\}(\mu\text{-}NC_5H_4)]$

$[Ru_5(CO)_{11}\{\mu_5\text{-}CCC(O)CH_2CH{=}CH_2\}\{\mu\text{-}P(C_6H_5)_2\}(\mu\text{-}Br)]$

Scheme 15



M = Fe, Ru R = CH_3, C_6H_5

$[M_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu\text{-}SC_2H_5)]$

$[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)(\mu\text{-}P(C_6H_5)_2]$

Scheme 16.

It is worthwhile comparing the structure of $[Ru_4(CO)_{12}(\mu\text{-}SC_2H_5)(\mu_4\text{-}C{\equiv}CR)]$, $R = CH_3$, C_6H_5, with that of $[Ru_5(CO)_{13}\{\mu\text{-}P(C_6H_5)_2\}(\mu_4\text{-}C{\equiv}CC_6H_5)]$ (Scheme 16).

In addition to the fifth ruthenium atom located on the other side of the Ru_4 plane with respect to the acetylide, this pentanuclear compound contains an isoelectronic $\mu\text{-}P(C_6H_5)_2$ bridge instead of a $\mu\text{-}SC_2H_5$ bridge. The position of the bridging atom with respect to the Ru_4 plane is different; the dihedral angle between the Ru–S–Ru plane and the mean square Ru_4 plane is close to 90° in the case of the tetranuclear sulfur containing compound, and equal to 170.7° in the case of the pentanuclear phosphorus containing compound, likely due to the steric hindrance of the $Ru(CO)_3$ group under the square plane.

The number of clusters with a square planar tetrametallic framework is rather small. For instance, compounds such as $[Fe_4(CO)_{11}\{P(C_6H_4CH_3)_2\}]$ or $[Ru_4(CO)_{11}\{P(C_6H_5)_2\}]$ or $[Fe_3Rh(CO)_8\{C_5(CH_3)_5\}\{P(C_6H_5)_2\}]$ have an octahedral M_4P_2 structure [18], with two phosphinidene ligands on each side of the square plane. The PSEPT (polyhedral skeleton electron pair theory) [19] rule leads to a 7 pairs 6 vertices *closo* structure. All these compounds correspond to 62 valence electrons. In the case of $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu\text{-}P(C_6H_5)_2\}]$ [1e, 20], the PSEPT rule leads again to a *closo* structure. Formally, the transformation of $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu\text{-}P(C_6H_5)_2\}]$ into $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu\text{-}SC_2H_5)]$ corresponds to the replacement of $Ru(CO)_3$ by two CO groups, leading to a *nido* structure. Actually, the 2-electron donor $Ru(CO)_3$ is replaced by two 2-electron donor CO groups, which results in an increase of the total number of valence electrons from 7 to 8 pairs: the PSEPT rule is no longer applicable, and $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu\text{-}SC_2H_5)]$ is then a compound having 64 valence electrons. There are other examples of electron rich clusters which all have 64 valence electrons. Most of them have an octahedral shape [18], while both compounds recently observed by Bruce and co-workers [1g, 17] and our $[M_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu\text{-}SC_2H_5)]$ complex have a square pyramidal shape.

It is interesting to compare the pair of compounds $[Ru_4(CO)_{12}(\mu_4\text{-}C{\equiv}CR)(\mu\text{-}SC_2H_5)]$ and $[Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CC_6H_5)\{\mu\text{-}P(C_6H_5)_2\}]$ [1e, 20] which offers a rather unique situation. As a matter of fact, the first one has a *nido* CRu_4 structure which does not follow the PSEPT rule but in which ruthenium atoms obey the electron precise extension of the inert gas rule. The second one has a *closo* CRu_5 structure which agrees with both these rules. Thus these two very closely related compounds are on both sides of the border separating the two fields of application of the two rules. The reason for this difference is not obvious. Perhaps the electronegativity of the heteroatom of the electron rich cluster would lower the first antibonding LUMO orbital so that it would become easily accessible to an additional electron pair.

The trinuclear complex $[Ru_3(CO)_7\{\mu_3\text{-}S(C_2H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CC(C_6H_5)\}(\mu\text{-}SC_2H_5)]$ (Fig. 14, Scheme 17) is based upon a Ru_3 triangle with an open edge; the Ru–Ru–Ru angle is more widely opened (131.3°) than in the case of compounds $[Ru_3(CO)_9(\mu\text{-}SC_2H_5)(\mu_3\text{-}C{\equiv}CR)]$ (71.8 and 72.3°). The organic moiety results from the head to tail coupling of two thioalkyne molecules, based upon C(11)–C(12) and C(8)–C(7) triple bonds, and one acetylide fragment C(3)–C(4) coming from a third thioalkyne molecule, yielding a substituted benzylidenecyclopentadiene ligand. The ring fragment C(8)–C(11)–C(12) is π bonded to a first ruthenium atom. The ring edge C(3)–C(7) and the C(3)–C(4) bond linking the benzylidene fragment are π bonded to a second ruthenium atom. The third ruthenium atom makes a second five-membered ring Ru(1)–C(4)–C(3)–C(7)–S(2) fused fo the first ring by sharing the C(3)–C(7) edge. The ethylthio group resulting from the C–S cleavage of the third thioalkyne molecule, the acetylide part of which is C(3)–C(4), builds a bridge between Ru(2) and Ru(3). Each ruthenium has 18 electrons and the total electron count gives 50 electrons, as expected for a chain of three metal atoms resulting from the opening of the triangle and as verified in both trinuclear ruthenium compounds.

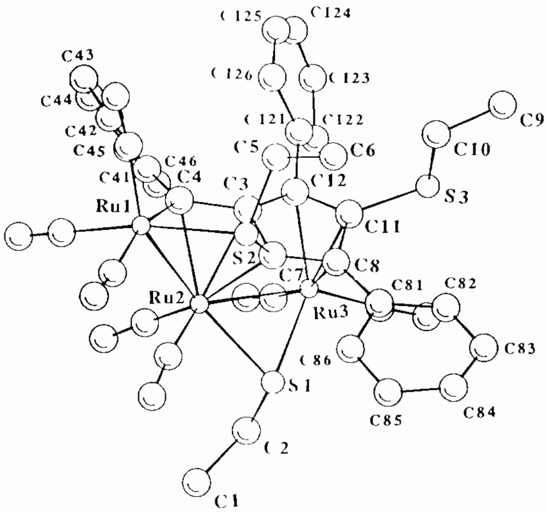
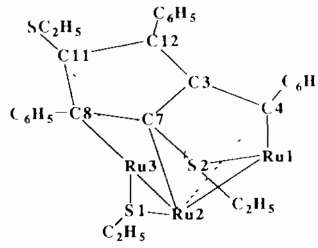


Fig. 14 Molecular structure of $[Ru_3(CO)_7\{\mu_3\text{-}C(C_6H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)CS(C_2H_5)\}(\mu\text{-}SC_2H_5)]$, see Scheme 17.



$[Ru_3(CO)_7\{\mu_3\text{-}C(C_6H_5)CC(C_6H_5)C(SC_2H_5)C(C_6H_5)S(C_2H_5)\}(\mu\text{-}SC_2H_5)]$

Scheme 17

6. Conclusions

From the characterization of about twenty complexes obtained by reacting two unsymmetrical thioalkynes $RC{\equiv}CSC_2H_5$, $R = CH_3$ or C_6H_5, with iron and ruthenium carbonyls, some characteristic features of the behaviour of thioalkynes have been established.

The triple bond allows the classical coupling of two thioalkyne molecules, and the asymmetry of thioalkyne allows three types of coupling, head to head, head to tail and tail to tail, all of which were observed.

Sulfur atom has a prevailing influence leading to the cleavage of one or, more seldomly, both C–S bonds, and to the stable Fe–S linkage. When the acetylenic carbon–sulfur bond is broken, the resulting acetylide group may attack a second thioalkyne molecule to form new ligands. The most frequently cleaved bond is the C–S bond joining the acetylide group and the ethylthio group. However, whatever the cleavage is, occurring or not, on one side or on the other of the sulfur atom, sulfur may ligate iron.

Playing with the cleavage of the C–S bond has allowed us to build up progressively and in a controlled manner trinuclear, tetranuclear and pentanuclear species.

In the case of ruthenium, both types of behaviour of the thioalkyne were also observed, leading to a particular assembly of three ruthenium atoms and of three thioalkyne molecules.

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