

Synthesis of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ )  
and reactivity with electron-rich molecules, triphenylphosphine,  
diphenylacetylene, ethylthio(phenyl) ethyne and (diethylamino) propyne.  
Preparation of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SCCC}_6\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  and formation  
of  $[\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-S})(\mu\text{-CCC}_6\text{H}_5)_2]$

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Abstract

Compounds  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$  with  $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ , were prepared and allowed to react with triphenylphosphine, diphenylacetylene, (ethylthio)phenylethyne, 1-(diethylamino)prop-1-yne. These four reactants are electron-rich molecules able to attack at the acetylide carbon atoms  $\text{C}_\alpha \equiv \text{C}_\beta \text{R}$ . The structures of nine complexes were determined by X-ray diffraction.

For  $\text{R} = \text{CH}_3$  or  $\text{P}(\text{C}_6\text{H}_5)_3$  reaction occurred at  $\text{C}_\beta$  leading to  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-C}=\text{C}[\text{P}(\text{C}_6\text{H}_5)_3](\text{CH}_3))]$ . In the case of  $\text{R} = \text{C}_6\text{H}_5$ , a monosubstituted complex  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)\}]$  and a disubstituted complex  $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  were obtained. With  $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ ,  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{R})\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$  was obtained ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ). The opening of the triple bond of the incoming alkyne led to two C–C bonds, one with acetylide  $\text{C}_\alpha$ , one with a carbonyl group. The  $\text{SC}_2\text{H}_5$  moved around an iron atom from a bridging position to be linked to  $\text{C}_\beta$ . In addition, for  $\text{R} = \text{C}_6\text{H}_5$  an isomer was obtained the structure of which is based on a *nido*  $\text{Fe}_2\text{C}_3$  framework. It readily transformed into  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$ . With  $\text{C}_6\text{H}_5\text{C}\equiv\text{CSC}_2\text{H}_5$  two complexes,  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{SC}_2\text{H}_5)\text{C}(\text{O})\}]$  (80%) and  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{SC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$  (20%), were obtained. They are of the same structural type as above. The major product resulted from the coupling of thioalkyne  $\text{C}_\beta$  with acetylide  $\text{C}_\alpha$ .

With  $\text{CH}_3\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  the complex obtained,  $[\text{Fe}_2(\text{CO})_6\{\text{C}[\text{C}(\text{O})\text{SC}_2\text{H}_5]\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)\text{C}[\text{N}(\text{C}_2\text{H}_5)_2]\}]$ , has a structure based on a ferracyclopentadienyl fragment ligated to a second iron atom by a Fe–Fe bond and by an allylic fragment. An unprecedented CO insertion occurred in a side chain, yielding an ethylthiocarboxy radical. Both CS bonds were eventually cleaved using  $\text{S}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$  as a starting alkyne. First,  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}\equiv\text{CC}_6\text{H}_5)(\mu\text{-C}\equiv\text{CC}_6\text{H}_5)]$  was prepared. Second, an excess of iron carbonyl yielded  $[\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-S})(\mu\text{-C}\equiv\text{CC}_6\text{H}_5)_2]$ . The four iron atoms belong to two dinuclear entities and form a tetrahedron around sulfur.

Keywords: Iron; Carbonyls; Sulfur; Alkyne; Thiolate; Cluster

1. Introduction

The chemistry of aminoalkynes  $\text{RC}\equiv\text{CNR}'_2$  that we recently developed showed that the carbon–nitrogen bond does not cleave [1] when aminoalkynes react with iron carbonyl. In contrast the carbon–phosphorus bond of phosphinoalkynes  $\text{RC}\equiv\text{CPR}'_2$  is easily broken and there is an oxidative addition [2]. The reactions of alkynes such as  $\text{HC}\equiv\text{CR}$  are also oxidative additions [3]. For example,  $\text{HC}\equiv\text{CC}(\text{CH}_3)_3$  reacts with  $[\text{Ru}_3(\text{CO})_{12}]$  yielding  $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu_3\text{-CCC}$

$(\text{CH}_3)_3)]$ . The reaction may go further since a coupling of a second alkyne molecule and of the acetylide provides the ligand  $(\text{CH}_3)_3\text{CCCHCHCC}(\text{CH}_3)_3$ .

A question which arises is whether the thioalkyne  $\text{RC}\equiv\text{CSR}'$  reacts as an aminoalkyne, that is without cleavage of the C–S bond, or undergoes an oxidative addition, eventually followed by coupling with another alkyne.

In order to answer this, the reaction of  $\text{RC}\equiv\text{CSC}_2\text{H}_5$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ) was carried out with iron and ruthenium carbonyls [4]. CS cleavage has been

Table 1  
Formulae and numerical designation of compounds described in this paper

1	$[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCCH}_3)]$
2	$[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$
3	$[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CC}(\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3])]$
4	$[\text{Fe}_2(\text{CO})_4(\text{P}(\text{C}_6\text{H}_5)_3)_2(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$
5	$[\text{Fe}_2(\text{CO})_5(\text{P}(\text{C}_6\text{H}_5)_3)(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$
6	$[\text{Fe}_2(\text{CO})_5(\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O}))]$
7	$[\text{Fe}_2(\text{CO})_5(\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O}))]$
8	$[\text{Fe}_2(\text{CO})_6\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}(\text{SC}_2\text{H}_5)(\text{C}_6\text{H}_5))]$
9	$[\text{Fe}_2(\text{CO})_5(\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{SC}_2\text{H}_5)\text{C}(\text{O}))]$
10	$[\text{Fe}_2(\text{CO})_5(\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{SC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O}))]$
11	$[\text{Fe}_2(\text{CO})_6(\mu\text{-C}(\text{N}(\text{C}_2\text{H}_5)_2)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\text{S}(\text{C}_2\text{H}_5))]$
12	$[\text{Fe}_2(\text{CO})_6(\mu\text{-SCCC}_6\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$
13	$[\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-S})(\mu\text{-CCC}_6\text{H}_5)_2]$

observed. Among various products,  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SR})(\mu\text{-CCR})]$  has been found. This paper deals with the synthesis of this compound which was carried out

with  $\text{R} = \text{CH}_3$  and  $\text{C}_6\text{H}_5$ , and  $\text{R}' = \text{C}_2\text{H}_5$  and  $\text{C}\equiv\text{CC}_6\text{H}_5$ . Structurally similar compounds were described by Seyferth et al. [5], with  $\text{R}' = \text{But}$ ,  $\text{R} = \text{C}_6\text{H}_5$ , and by Carty and co-workers [2], with  $\text{R} = \text{C}_6\text{H}_5$  and a diphenylphosphide bridge instead of an ethylthiolate bridge. These authors demonstrated the ability of electron-donating amines and phosphines to react with the acetylide fragment. In this work, because  $\text{SC}_2\text{H}_5$  is a different group, the reaction of triphenylphosphine was reinvestigated and this is described below. The reaction of electron-rich alkynes has also been undertaken, and a variety of dinuclear species has been synthesized.

Finally, a sulfur-containing molecule able to undergo a double CS cleavage,  $\text{S}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ , has been considered. A single and then a double cleavage have been observed.

Table 1 shows the product formulae and their corresponding numerical designations.

Table 2  
Crystallographic data collection and structure refinements for compounds 4, 6 and 8

	Compound 4	Compound 6	Compound 8
Formula	$\text{Fe}_2\text{C}_{50}\text{O}_4\text{P}_2\text{SH}_{40}$	$\text{Fe}_2\text{C}_{25}\text{O}_6\text{SH}_{18}$	$\text{Fe}_2\text{C}_{30}\text{O}_6\text{SH}_{20}$
Cryst. color	Purple	Orange	Orange
Mol. weight (g)	910	558	620
Cryst. size (mm)	$0.8 \times 0.7 \times 0.3$	$0.24 \times 0.12 \times 0.06$	$0.26 \times 0.1 \times 0.2$
$\rho$ calc ( $\text{g cm}^{-3}$ )	1.353	1.552	1.415
$\mu$ (Mo K $\alpha$ ) ( $\text{cm}^{-1}$ )	8.055	13.353	11.385
Cryst. system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/a$
$a$ (Å)	21.745(1)	10.177(2)	13.885(6)
$b$ (Å)	10.924(1)	11.019(5)	21.235(6)
$c$ (Å)	19.108(6)	12.837(5)	10.068(5)
$\alpha$ (°)	90.	65.32(4)	90.
$\beta$ (°)	99.98(3)	70.07(3)	108.44(1)
$\gamma$ (°)	90.	69.76(4)	90.
$V$ (Å <sup>3</sup> )	4470	1194	2816
$Z$	4	2	4
Diffractometer	Philips PW 1100	CAD4 Enraf-Nonius	Philips PW 1100
Radiation, $\lambda$ (Å)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)
Scan type	$\theta$ - $2\theta$	$\theta$ - $2\theta$	$\theta$ - $2\theta$
Scan range (°)	$0.9 + 0.345\text{tg } \theta$	$0.8 + 0.34\text{tg } \theta$	$0.9 + 0.345\text{tg } \theta$
$2\theta$ range (°)	4–50	2–40	4–36
Reflections measured	$hkl, \bar{h}kl$	$hkl, \bar{h}kl, h\bar{k}l, \bar{h}k\bar{l}$	$hkl, \bar{h}kl$
No. of reflections collected	8568	2373	2182
No. of independent reflections merged	7814	2235	1911
No. of reflections kept for refinement	4437 ( $I > 3\sigma(I)$ )	936 ( $I > 3\sigma(I)$ )	435 ( $I > 3\sigma(I)$ )
Form factors	[12]	[12]	[12]
Weighting scheme	$w = 1$	$w = 1$	$w = 1$
Secondary extinction param	$1.2 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	/
Absorption correction	Difabs [13]	Difabs [13]	Difabs [13]
Av. shift/esd (last cycle)	0.02	0.015	0.02
Nref./Nvar. par.	8.3	3.04	2.77
Max. height in final difference			
Fourier synthesis ( $e \text{ Å}^{-3}$ )	0.5	0.2	0.3
$R^a$	0.037	0.030	0.068
$R_w^a$	0.038	0.034	0.081

<sup>a</sup>  $R$  and  $R_w$  are defined as follows:  $R = \sum \|F_o\| - |F_c| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ .

## 2. Experimental section

### 2.1. General procedure

The reactions of 1-ethylthioprop-1-yne, ethylthio-(phenyl)ethyne  $RC\equiv CSC_2H_5$  ( $R = CH_3$  or  $C_6H_5$ ), or bis(phenylethynyl)sulfur  $C_6H_5C\equiv CSC\equiv CC_6H_5$  with iron carbonyl were carried out under argon using standard Schlenk techniques. Solvents used for syntheses were freshly distilled under dinitrogen over appropriate drying agents. Alkynes were prepared following previously reported methods of Pourcelot and Cadot [6] for  $R = CH_3$ , of Makosza and Fedorynski [7] for  $R = C_6H_5$ , and of Lang et al. [8] for  $C_6H_5C\equiv CSC\equiv CC_6H_5$ . Nonacarbonyldiiron was synthesized from pentacarbonyliron [9]; dodecacarbonyltriiron was used as purchased at Strem Chemical Inc. Reactions were monitored by thin layer chromatography. Separations of products were performed by column chromatography

using silica gel 60 (70-230 mesh ASTM) under dry dinitrogen. Compounds **4**, **5**, and **11** were separated using Merck precoated preparative TLC plates (silica gel 60 F<sub>254</sub>, 2 mm).

IR spectra were recorded with a Perkin-Elmer 457 or with a Nicolet FT spectrometer using either KBr pellets or heptane solutions. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker 250, 300 or 500 MHz spectrometer, and chemical shifts were referenced to Si(CH<sub>3</sub>)<sub>4</sub>. Mass spectra were recorded with a Nermag R1010, usually by chemical ionisation with NH<sub>3</sub>.

### 2.2. X-ray structure analysis

All measurements were carried out at room temperature using a Philips PW 1100 diffractometer, except for compounds **6**, **9**, **13** for which a Nonius CAD4 diffractometer was used. Details concerning the crystallographic data collection and structure determinations for

Table 3  
Crystallographic data collection and structure refinements for compounds **11**, **12** and **13**

	Compound <b>11</b>	Compound <b>12</b>	Compound <b>13</b>
Formula	Fe <sub>2</sub> C <sub>24</sub> O <sub>7</sub> NSH <sub>23</sub>	Fe <sub>2</sub> C <sub>22</sub> O <sub>6</sub> SH <sub>10</sub>	Fe <sub>4</sub> C <sub>28</sub> O <sub>12</sub> SH <sub>10</sub>
Cryst. color	Yellow	Red	Red
Mol. weight (g)	581	514	794
Cryst. size (mm)	0.4 × 0.4 × 0.06		0.3 × 0.06 × 0.4
$\rho$ calc (g cm <sup>-3</sup> )	1.493	1.533	1.717
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	12.396	14.257	19.773
Cryst. system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$
<i>a</i> (Å)	10.474(4)	11.433(4)	15.368(3)
<i>b</i> (Å)	10.802(6)	7.634(6)	10.279(2)
<i>c</i> (Å)	12.273(3)	25.529(8)	19.503(4)
$\alpha$ (°)	80.39(1)	90.	90.
$\beta$ (°)	83.72(3)	92.14(4)	94.46(2)
$\gamma$ (°)	71.12(3)	90.	90.
<i>V</i> (Å <sup>3</sup> )	1288	2227	3071
<i>Z</i>	2	4	8
Diffractometer	Philips PW 1100	Philips PW 1100	CAD4 Enraf-Nonius
Radiation $\lambda$ (Å)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)
Scan type	$\theta$ -2 $\theta$	$\theta$ -2 $\theta$	$\theta$ -2 $\theta$
Scan range (°)	1.1 + 0.345tg $\theta$	1.1 + 0.345tg $\theta$	0.8 + 0.34tg $\theta$
2 $\theta$ range (°)	4–50	4–40	2–50
Reflections measured	<i>hkl</i> , $\bar{h}kl$ , $h\bar{k}l$ , $\bar{h}\bar{k}l$	<i>hkl</i> , $\bar{h}kl$	<i>hkl</i> , $\bar{h}kl$
No. of reflections collected	4791	2357	
No. of independent reflections merged	4524	2064	2686
No. of reflections kept for refinement	2202 ( $I > 3\sigma(I)$ )	695 ( $I > 3\sigma(I)$ )	1703 ( $I > 3\sigma(I)$ )
Form factor	[12]	[12]	[12]
Weighting scheme	$w = 1$	$w = 1$	$w = 1$
Secondary extinction param	/	$8.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$
Absorption correction	Difabs [13]	Difabs [13]	Difabs [13]
Av. shift/esd (last cycle)	0.0003	0.04	0.05
Nref./Nvar. par.	7	5.5	8.3
Max. height in final difference			
Fourier synthesis (e Å <sup>-3</sup> )	0.3	0.99	0.35
<i>R</i> <sup>a</sup>	0.044	0.092	0.035
<i>R</i> <sub>w</sub> <sup>a</sup>	0.049	0.107	0.036

<sup>a</sup> *R* and *R*<sub>w</sub> are defined as follows:  $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ .

compounds **4**, **6**, **8**, **11**, **12**, and **13** are given in Tables 2 and 3. Data for compounds **3**, **5**, **7**, **9**, and **10** are given in Tables 4 and 5. Suitable crystals, sometimes very tiny, were chosen and set into Lindeman glass capillary tubes. Cell dimensions were determined from 25 reflections dispersed in reciprocal space. Two standard reflections were monitored every 2 h during data collection to check crystal orientation and absence of decomposition. The usual correction for Lorentz and polarization effects was applied. Direct methods (SHELXS-86) [10] and successive Fourier maps were used to locate the positions of all atoms. Full-matrix least-squares refinement of atomic parameters and isotropic (compounds **7**, **8**, and **12**) or anisotropic (compounds **3**, **4**, **5**, **6**, **9**, **10**, **11**, and **13**) thermal parameters were carried out using CRYSTALS programs [11] and a DEC Microvax II. The size of the crystal and the number of recorded reflections for compounds **7**, **8**, and **12** did not allow the refinement of

anisotropic thermal parameters. The form factors, including anomalous dispersion corrections, were provided by CRYSTALS. Only hydrogen atoms located in a difference Fourier map were included in refinement in fixed positions with an overall isotropic thermal parameter. Fractional parameters, selected distances and bond angles are given in Tables 6 to 17 for compounds **4**, **6**, **8**, **11**, **12**, and **13**. Compounds **3**, **5**, **7**, **9**, and **10** correspond to structural types already described, either in this paper or previously. Their structure determinations were used as an identification tool. All their crystallographic details are not given herein (atomic parameters, bond lengths and bond angles), but they have been deposited with the Cambridge Crystallographic Data Centre, as supplementary material (atomic and thermal parameters and complete lists of bond distances and angles). These data and structure factor tables are also available from the authors.

Table 4  
Crystallographic data collection and structure refinements for compounds **3** and **5**

	Compound 3	Compound 5
Formula	Fe <sub>2</sub> C <sub>29</sub> O <sub>6</sub> SPH <sub>23</sub>	Fe <sub>2</sub> C <sub>33</sub> O <sub>5</sub> SPH <sub>25</sub>
Cryst. color	Orange	Red
Mol. weight (g)	642	676
Cryst. size (mm)	0.8 × 0.3 × 0.2	0.2 × 0.3 × 0.06
$\rho$ calc (gcm <sup>-3</sup> )	1.460	1.419
$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> )	11.534	10.663
Cryst. system	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	10.840(6)	10.930(4)
<i>b</i> (Å)	11.413(5)	13.308(3)
<i>c</i> (Å)	13.582(8)	13.841(7)
$\alpha$ (°)	74.09(4)	61.41(2)
$\beta$ (°)	77.37(4)	68.06(3)
$\gamma$ (°)	65.58(3)	66.92(2)
<i>V</i> (Å <sup>3</sup> )	1436	1508
<i>Z</i>	2	2
Diffractometer	Philips PW 1100	Philips PW 1100
Radiation $\lambda$ (Å)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)
Scan type	$\theta$ - $2\theta$	$\theta$ - $2\theta$
Scan range (°)	1.2 + 0.345tg $\theta$	1.0 + 0.345tg $\theta$
$2\theta$ range (°)	4–50	4–40
Reflections measured	<i>hkl</i> , $\bar{h}kl$ , <i>hk<math>\bar{l}</math>, <math>\bar{h}\bar{k}l</math></i>	<i>hkl</i> , $\bar{h}kl$ , <i>hk<math>\bar{l}</math>, <math>\bar{h}\bar{k}l</math></i>
No. of reflections collected	4849	3119
No. of independent reflections merged	4641	2923
No. of reflections kept for refinement	3139 ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))	1335 ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))
Form factors	[12]	[12]
Weighting scheme	{1-[ $\Delta F$ /6. $\sigma$ ( <i>F</i> <sub>o</sub> )] <sup>2</sup> } <sup>2</sup>	w = 1
Secondary extinction param.	/	/
Absorption correction	Difabs [13]	Difabs [13]
Av. shift/esd (last cycle)	0.02	0.02
Nref./Nvar. par.	8.9	3.5
Max. height in final difference		
Fourier synthesis (e <sup>-3</sup> )	0.6	0.4
<i>R</i> <sup>a</sup>	0.055	0.049
<i>R</i> <sub>w</sub> <sup>a</sup>	0.057	0.055

<sup>a</sup> *R* and *R*<sub>w</sub> are defined as follows:  $R = \Sigma \|F_o| - |F_c| / \Sigma F_o|$ ;  $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ .

### 2.3. Syntheses

Only syntheses of compounds of interest for this paper are described here. These reactions also yielded compounds corresponding to other structural types which have been described elsewhere [4].

**2.3.1. Syntheses of acetylide compounds**  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$ , **1**  $R = \text{CH}_3$ , **2**  $R = \text{C}_6\text{H}_5$ , and  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SCCC}_6\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  **12** and of  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{SC}_2\text{H}_5)\text{C}(\text{O})\}]$  **9** and  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{SC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$  **10**

Compound **1**: a solution of  $[\text{Fe}_2(\text{CO})_9]$  (0.9 g, 2.6 mmol),  $\text{CH}_3\text{C}\equiv\text{SC}_2\text{H}_5$  (0.2 g, 2 mmol) and  $(\text{CH}_3)_3\text{NO}$  (0.2 g, 2.6 mmol) in heptane-dichloromethane (40–20) was stirred at room temperature during

4 h. The resulting solution was filtered and concentrated under vacuum. The residue was chromatographed on silica gel. Compound **1** was eluted as the first red fraction with heptane. Yield 10%. Red oil.

IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2090, 2060, 2000  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 381. (electronic impact):  $\text{M}^{+\cdot}$  ( $m/z$ ) = 380,  $\text{M}^{+\cdot}-\text{CO}$  = 352,  $\text{M}^{+\cdot}-2\text{CO}$  = 324,  $\text{M}^{+\cdot}-3\text{CO}$  = 296,  $\text{M}^{+\cdot}-4\text{CO}$  = 268,  $\text{M}^{+\cdot}-5\text{CO}$  = 240,  $\text{M}^{+\cdot}-6\text{CO}$  = 212,  $\text{HSFe}_2\text{C}\equiv\text{CCH}_3$  = 184,  $\text{SFe}_2\text{C}\equiv\text{CCH}_3$  = 183,  $\text{HSFe}_2\text{C}\equiv\text{C}$  = 169,  $\text{HSFe}_2$  = 145,  $\text{SFe}_2$  = 144,  $\text{FeC}\equiv\text{CCH}_3$  = 95,  $\text{HSC}\equiv\text{CCH}_3$  = 72,  $\text{Fe}$  = 56.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$  at 7.16 ppm, 250 MHz): t 3H 0.74 ppm  $^3J_{(\text{CH}_3, \text{CH}_2)} = 7.4$  Hz for  $\text{CH}_3\text{CH}_2\text{S}$ , q 2H 1.58 ppm  $^3J_{(\text{CH}_3, \text{CH}_2)} = 7.4$  Hz for  $\text{CH}_3\text{CH}_2\text{S}$ , s 3H 1.51 ppm for  $\text{CH}_3\text{C}\equiv$ .  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$  at 128.4 ppm, 300 MHz): 209.0 ppm CO terminal, 106.1 ppm  $\text{C}\equiv\text{CCH}_3$ ,

Table 5  
Crystallographic data collection and structure refinements for compounds **7**, **9** and **10**

	Compound <b>7</b>	Compound <b>9</b>	Compound <b>10</b>
Formula	$\text{Fe}_2\text{C}_{30}\text{O}_6\text{SH}_{20}$	$\text{Fe}_2\text{C}_{26}\text{O}_6\text{S}_2\text{H}_{20}$	$\text{Fe}_2\text{C}_{21}\text{O}_6\text{S}_2\text{H}_{18}$
Cryst. color	Orange	Red	Dark red
Mol weight (g)	620	604	604
Cryst. size (mm)	$0.3 \times 0.4 \times 0.16$	$0.72 \times 0.3 \times 0.2$	$0.44 \times 0.5 \times 0.64$
$\rho$ calc ( $\text{g cm}^{-3}$ )	1.495	1.519	1.514
$\mu$ (Mo K $\alpha$ ) ( $\text{cm}^{-1}$ )	11.657	12.865	12.822
Cryst. system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
$a$ (Å)	10.386(2)	9.606(1)	10.783(7)
$b$ (Å)	13.793(4)	18.709(3)	11.809(1)
$c$ (Å)	19.230(4)	14.838(2)	20.848(9)
$\alpha$ (°)	90.	90.	90.
$\beta$ (°)	90.	92.14(4)	94.46(2)
$\gamma$ (°)	90.	90.	90.
$V$ (Å <sup>3</sup> )	2755	2642	2651
$Z$	4	4	4
Diffractionmeter	Philips PW 1100	CAD4 Enraf Nonius	Philips PW 1100
Radiation $\lambda$ (Å)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)	Mo K $\alpha$ (0.71069)
Scan type	$\theta$ - $2\theta$	$\theta$ - $2\theta$	$\theta$ - $2\theta$
Scan range (°)	$1.1 + 0.345\text{tg } \theta$	$0.8 + 0.345\text{tg } \theta$	$0.9 + 0.345\text{tg } \theta$
$2\theta$ range (°)	4–50	2–50	2–50
Reflections measured	$hkl$	$hkl, \bar{h}kl$	$hkl, \bar{h}kl$
No. of reflections collected	2776	5000	5050
No. of independent reflections merged	2730	4644	4594
No. of reflections kept for refinement	841 ( $I > 3\sigma(I)$ )	3086 ( $I > 3\sigma(I)$ )	1581 ( $I > 3\sigma(I)$ )
Form factors	[12]	[12]	[12]
Weighting scheme	1	1	1
Secondary extinction param	/	/	/
Absorption correction	Difabs [13]	Difabs [13]	Difabs [13]
Av. shift/esd (last cycle)	0.003	0.02	0.001
Nref./Nvar. par.	5.64	9.5	4.9
Max. height in final difference			
Fourier synthesis ( $e \text{ Å}^{-3}$ )	0.3	0.99	0.35
$R^a$	0.051	0.033	0.038
$R_w^a$	0.059	0.032	0.040

<sup>a</sup>  $R$  and  $R_w$  are defined as follows:  $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ ;  $R_w = [\sum w(\|F_o\| - \|F_c\|)^2 / \sum w \|F_o\|^2]^{1/2}$ .



89.8 ppm  $C\equiv CCH_3$ , 29.8 ppm  $CH_3CH_2S$ , 14.7 ppm  $CH_3CH_2S$ , 1.8 ppm  $CH_3C\equiv$ .

Compounds **2**, **9**, and **10**: a solution of  $[Fe_2(CO)_9]$  (1.1 g, 3.1 mmol),  $C_6H_5C\equiv CSC_2H_5$  (0.38 g, 2.4 mmol) and  $(CH_3)_3NO$  (0.23 g, 3.1 mmol) in heptane-dichloromethane (40:20) was stirred at room temperature during 3 h. The solution was then filtered and concentrated under vacuum. The residue was chromatographed on silica gel. After evaporating the third red fraction eluted with heptane, compound **2** was obtained as a red oil in mixture with an excess of  $C_6H_5C\equiv CSC_2H_5$ .

Compound **2**: IR (KBr pellet):  $\nu_{CO}$  terminal: 2080, 2040, 2000  $cm^{-1}$ ,  $\nu_{C\equiv C}$ : 2160  $cm^{-1}$  weak. Mass spectrometry (chemical ionisation with  $NH_3$ ):  $[M + H]^+$  ( $m/z$ ) = 443,  $[M + H] - CO = 415$ . (electronic impact):  $M^{+} - CO = 414$ ,  $M^{+} - 2CO = 386$ ,  $M^{+} - 3CO = 358$ ,  $M^{+} - 4CO = 330$ ,  $M^{+} - 5CO = 302$ ,  $M^{+} - 6CO = 274$ ,  $HSFe_2C\equiv CC_6H_5 = 246$ ,  $SFe_2C\equiv CC_6H_5 = 245$ ,  $Fe_2C\equiv CC_6H_5 = 189$ ,  $HSFeCC_6H_5 = 178$ ,  $HSFe_2C\equiv C = 169$ ,  $FeC\equiv CC_6H_5 = 157$ ,  $HSFe_2 = 145$ ,  $SFe_2 = 144$ ,  $HSC\equiv CC_6H_5 = 106$ ,  $Fe = 56$ .  $^1H$  NMR ( $C_6D_6$  at 7.28 ppm, 500 MHz): t 3H 0.86 ppm  $^3J_{(CH_3,CH_2)} = 7.3$  Hz for  $CH_3CH_2S$ , q 2H 1.88 ppm

Table 9

Selected interatomic distances (Å) and bond angles ( $^\circ$ ) for compound **6**  $[Fe_2(CO)_5(S(C_2H_5)_2C_3(CH_3)_2C_6H_5)_2C(O)]$

Fe(1)–Fe(2)	2.629(3)	Fe(1)–S(1)	2.348(4)
Fe(1)–C(1)	1.94(1)	Fe(1)–C(2)	2.10(1)
Fe(1)–C(6)	1.93(1)	Fe(2)–C(1)	1.95(1)
Fe(2)–C(7)	2.19(1)	Fe(2)–C(8)	2.11(1)
C(6)–O(6)	1.22(1)	C(1)–C(2)	1.36(1)
C(1)–C(8)	1.41(1)	C(2)–C(3)	1.51(2)
C(4)–C(5)	1.52(2)	C(6)–C(7)	1.52(2)
C(7)–C(8)	1.43(1)	C(7)–C(71)	1.53(2)
C(8)–C(81)	1.49(2)	C(86)–H(86)	0.93(1)
S(1)–Fe(1)–Fe(2)	92.6(1)	C(1)–Fe(1)–Fe(2)	47.7(4)
C(1)–Fe(1)–S(1)	73.3(3)	C(2)–Fe(1)–Fe(2)	83.0(4)
C(2)–Fe(1)–S(1)	46.6(3)	C(2)–Fe(1)–C(1)	39.0(4)
C(6)–Fe(1)–Fe(2)	69.1(4)	C(6)–Fe(1)–S(1)	155.6(5)
C(6)–Fe(1)–C(1)	82.3(6)	C(6)–Fe(1)–C(2)	112.8(5)
C(1)–Fe(2)–Fe(1)	47.3(3)	C(7)–Fe(2)–Fe(1)	72.4(3)
C(7)–Fe(2)–C(1)	67.6(4)	C(8)–Fe(2)–Fe(1)	74.4(3)
C(8)–Fe(2)–C(1)	40.3(4)	C(8)–Fe(2)–C(7)	38.8(4)
C(2)–S(1)–Fe(1)	59.2(4)	C(4)–S(1)–Fe(1)	110.6(4)
C(4)–S(1)–C(2)	106.8(6)	Fe(2)–C(1)–Fe(1)	85.0(4)
C(2)–C(1)–Fe(1)	76.8(7)	C(2)–C(1)–Fe(2)	144.6(9)
C(8)–C(1)–Fe(1)	118.9(8)	C(8)–C(1)–Fe(2)	75.7(7)
C(8)–C(1)–C(2)	139.6(11)	S(1)–C(2)–Fe(1)	74.1(5)
C(1)–C(2)–Fe(1)	64.2(7)	C(1)–C(2)–S(1)	110.3(9)
C(3)–C(2)–Fe(1)	133.7(8)	C(3)–C(2)–S(1)	122.8(9)
C(3)–C(2)–C(1)	126.5(11)	C(5)–C(4)–S(1)	108.4(9)
O(6)–C(6)–Fe(1)	128.5(11)	C(7)–C(6)–Fe(1)	111.4(10)
C(7)–C(6)–O(6)	120.0(12)	C(6)–C(7)–Fe(2)	89.2(8)
C(8)–C(7)–Fe(2)	67.5(6)	C(8)–C(7)–C(6)	112.7(11)
C(71)–C(7)–Fe(2)	125.4(9)	C(71)–C(7)–C(6)	120.2(11)
C(71)–C(7)–C(8)	124.8(11)	C(1)–C(8)–Fe(2)	63.9(6)
C(7)–C(8)–Fe(2)	73.7(6)	C(7)–C(8)–C(1)	109.2(10)

Table 10

Fractional atomic coordinates for compound **8**  $[Fe_2(CO)_6(C(C[SC_2H_5](C_6H_5))C(C_6H_5))C(C_6H_5)]$

Atom	x	y	z	$U_{iso}$
Fe(1)	0.1882(8)	0.9085(5)	0.080(1)	0.064(4)
Fe(2)	0.2044(8)	0.8182(5)	0.242(1)	0.055(3)
S(1)	0.438(1)	0.9295(7)	0.105(2)	0.062(6)
C(1)	0.298(4)	0.850(2)	0.183(6)	0.02(2)
C(2)	0.362(4)	0.858(3)	0.100(6)	0.05(2)
C(3)	0.349(5)	0.806(3)	−0.024(7)	0.08(3)
C(4)	0.560(5)	0.898(3)	0.109(7)	0.09(3)
C(5)	0.626(7)	0.889(4)	0.217(9)	0.17(4)
C(7)	0.228(5)	0.919(3)	0.273(7)	0.09(2)
C(8)	0.333(5)	0.879(3)	0.316(7)	0.07(2)
C(11)	0.147(6)	0.884(4)	−0.103(9)	0.12(3)
C(12)	0.218(5)	0.982(4)	0.064(8)	0.11(3)
C(13)	0.069(5)	0.924(3)	0.094(7)	0.09(3)
C(21)	0.149(4)	0.773(3)	0.112(7)	0.05(2)
C(22)	0.095(7)	0.823(4)	0.289(9)	0.14(3)
C(23)	0.26(1)	0.752(6)	0.38(1)	0.25(7)
C(31)	0.366(4)	0.836(2)	−0.139(6)	0.02(2)
C(32)	0.355(5)	0.793(3)	−0.238(7)	0.08(3)
C(33)	0.353(4)	0.728(3)	−0.210(6)	0.03(2)
C(34)	0.359(5)	0.702(3)	−0.106(7)	0.07(2)
C(35)	0.358(4)	0.746(3)	0.036(6)	0.06(2)
C(71)	0.204(5)	0.958(3)	0.378(8)	0.08(2)
C(72)	0.162(5)	1.021(3)	0.322(6)	0.07(2)
C(73)	0.127(5)	1.060(3)	0.435(8)	0.10(3)
C(74)	0.128(5)	1.034(3)	0.557(7)	0.07(2)
C(75)	0.161(5)	0.975(3)	0.578(7)	0.08(2)
C(76)	0.193(4)	0.933(3)	0.506(7)	0.06(2)
C(81)	0.416(5)	0.882(3)	0.457(7)	0.07(2)
C(82)	0.442(5)	0.931(3)	0.538(7)	0.06(2)
C(83)	0.531(5)	0.926(3)	0.659(7)	0.09(3)
C(84)	0.603(6)	0.871(4)	0.695(8)	0.12(3)
C(85)	0.571(4)	0.827(3)	0.562(6)	0.04(2)
C(86)	0.474(4)	0.828(2)	0.470(5)	0.02(2)
O(11)	0.120(3)	0.857(2)	−0.200(5)	0.07(1)
O(12)	0.237(3)	1.034(2)	0.022(5)	0.10(2)
O(13)	−0.022(3)	0.935(2)	0.083(4)	0.09(2)
O(21)	0.114(3)	0.742(2)	−0.006(5)	0.09(2)
O(22)	0.035(4)	0.824(2)	0.343(5)	0.11(2)
O(23)	0.309(4)	0.716(2)	0.431(6)	0.12(2)

$^3J_{(CH_3,CH_2)} = 7.3$  Hz for  $CH_3CH_2S$ , unresolved multiplets between 6.8 and 7.8 ppm for  $C_6H_5$ .

$^1H$  NMR ( $C_6D_6$  at 7.28 ppm, 500 MHz) for  $C_6H_5C\equiv CSC_2H_5$ : t 1.25 ppm for  $CH_3CH_2S$ , q 2.48 ppm for  $CH_3CH_2S$ , 2 unresolved multiplets centred at 7.1 and 7.5 ppm for  $C_6H_5$ .

Note: while keeping the mixture of the oily compound **2** with the alkyne  $C_6H_5C\equiv CSC_2H_5$  at  $-20^\circ C$ , compound **2** transformed into compounds **9** and **10**. The new solution was chromatographed on silica gel, and compounds **9** and **10** were eluted together with pure dichloromethane as an orange-red fraction. Both compounds crystallized in two different forms at  $-20^\circ C$  and their structures were determined by X-ray diffraction (Table 5). Total yield 10%.

Compounds **9** and **10**: IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2050, 2010, 1990, 1960,  $\nu_{\text{C}=\text{O}}$ : 1615,  $\nu_{\text{C}=\text{C}}$ : 1450  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 605.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$  at 7.16 ppm, 500 MHz): Compound **9** (major, 80%) t 0.56 ppm for  $\text{CH}_3\text{CH}_2\text{S}$  and 2 unresolved multiplets centred at 1.45 and 1.95 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2\text{S}$ , t 1.09 ppm for  $\text{CH}_3\text{CH}_2\text{S}$  and 2 unresolved multiplets centred at 2.85 and 3.70 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2\text{S}$ , unresolved multiplets between 6.7 and 7.7 ppm for  $\text{C}_6\text{H}_5$ . Compound **10** (minor, 20%) t 0.61 ppm for  $\text{CH}_3\text{CH}_2\text{S}$  and 2 unresolved multiplets centred at 1.60 and 2.10 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2\text{S}$ , t 0.66 ppm for  $\text{CH}_3\text{CH}_2\text{S}$  and 2 unresolved multiplets centred at 2.10 and 2.45 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2\text{S}$ , unresolved multiplets between 6.7 and 7.7 ppm for  $\text{C}_6\text{H}_5$ .

Compound **12**: a solution of  $[\text{Fe}_3(\text{CO})_{12}]$  (0.39 g, 0.78 mmol), and  $\text{C}_6\text{H}_5\text{C}\equiv\text{CSC}\equiv\text{CC}_6\text{H}_5$  (0.21 g, 0.91 mmol) was stirred during 1 h in refluxing hexane. After cooling, the solution was filtered and concentrated under vacuum. The residue was chromatographed on silica gel. Compound **12** was eluted with heptane as the second red fraction just after residual  $[\text{Fe}_3(\text{CO})_{12}]$ . Yield 15%. Compound **12** crystallized at  $-20^\circ\text{C}$  and its structure was determined by X-ray diffraction (Tables 3, 14, 15).

Table 11  
Selected interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for compound **8**  $[\text{Fe}_2(\text{CO})_6(\text{C}(\text{C}(\text{SC}_2\text{H}_5)(\text{C}_6\text{H}_5))\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5))]$

Fe(1)–Fe(2)	2.48(1)	Fe(1)–C(1)	1.98(5)
Fe(1)–C(7)	1.86(7)	Fe(2)–C(1)	1.73(5)
Fe(2)–C(7)	2.17(7)	Fe(2)–C(8)	2.14(6)
S(1)–C(2)	1.84(6)	S(1)–C(4)	1.81(6)
C(1)–C(2)	1.40(6)	C(1)–C(8)	1.41(6)
C(2)–C(3)	1.64(7)	C(3)–C(31)	1.40(7)
C(3)–C(35)	1.39(7)	C(4)–C(5)	1.20(9)
C(7)–C(8)	1.62(8)	C(7)–C(71)	1.46(8)
C(8)–C(81)	1.52(7)		
C(1)–Fe(1)–Fe(2)	43.8(16)	C(7)–Fe(1)–Fe(2)	58.0(21)
C(7)–Fe(1)–C(1)	66.6(27)	C(1)–Fe(2)–Fe(1)	52.5(16)
C(7)–Fe(2)–Fe(1)	46.4(18)	C(7)–Fe(2)–C(1)	64.2(25)
C(8)–Fe(2)–Fe(1)	69.6(17)	C(8)–Fe(2)–C(1)	41.1(20)
C(8)–Fe(2)–C(7)	44.1(20)	C(4)–S(1)–C(2)	103.2(29)
Fe(2)–C(1)–Fe(1)	83.7(21)	C(2)–C(1)–Fe(1)	98.2(39)
C(2)–C(1)–Fe(2)	158.9(48)	C(8)–C(1)–Fe(1)	101.7(39)
C(8)–C(1)–Fe(2)	85.3(39)	C(8)–C(1)–C(2)	114.6(52)
C(1)–C(2)–S(1)	123.1(47)	C(3)–C(2)–S(1)	119.6(46)
C(3)–C(2)–C(1)	116.3(53)	C(31)–C(3)–C(2)	108.2(57)
C(35)–C(3)–C(2)	107.5(60)	C(35)–C(3)–C(31)	140.2(63)
C(5)–C(4)–S(1)	121.4(72)	Fe(2)–C(7)–Fe(1)	75.5(25)
C(8)–C(7)–Fe(1)	99.3(49)	C(8)–C(7)–Fe(2)	66.9(33)
C(71)–C(7)–Fe(1)	140.2(54)	C(71)–C(7)–Fe(2)	126.7(51)
C(71)–C(7)–C(8)	119.3(59)	C(1)–C(8)–Fe(2)	53.6(31)
C(7)–C(8)–Fe(2)	69.0(33)	C(7)–C(8)–C(1)	87.8(51)
C(81)–C(8)–Fe(2)	130.6(44)	C(81)–C(8)–C(1)	146.7(61)
C(81)–C(8)–C(7)	125.3(62)		

Table 12  
Fractional atomic coordinates for compound **11**  $[\text{Fe}_2(\text{CO})_6(\text{C}(\text{C}(\text{O})\text{SC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{N}(\text{C}_2\text{H}_5)_2))]$

Atom	x	y	z	$U_{\text{eq}}$
Fe(1)	0.1012(1)	0.2633(1)	0.85283(9)	0.0366
Fe(2)	0.1017(1)	0.2635(1)	0.64341(9)	0.0370
S(1)	0.4079(2)	−0.0579(3)	0.8789(2)	0.0641
N(1)	−0.1746(6)	0.2359(6)	0.8559(5)	0.0437
C(1)	0.2109(7)	0.1298(6)	0.7635(5)	0.0313
C(2)	0.1409(7)	0.0653(6)	0.7134(5)	0.0314
C(3)	0.2095(7)	−0.0575(7)	0.6622(6)	0.0388
C(4)	0.5874(9)	−0.119(1)	0.854(1)	0.0631
C(5)	0.634(1)	−0.209(2)	0.773(1)	0.1331
C(6)	0.3612(8)	0.0748(7)	0.7686(6)	0.0397
C(7)	−0.0483(7)	0.2045(7)	0.8113(6)	0.0329
C(8)	−0.0037(7)	0.1291(7)	0.7186(5)	0.0338
C(9)	−0.0863(8)	0.0807(8)	0.6490(7)	0.0487
C(11)	−0.0064(9)	0.4257(9)	0.8731(7)	0.0559
C(12)	0.1060(8)	0.1684(9)	0.9870(7)	0.0488
C(13)	0.2444(9)	0.3166(8)	0.8654(7)	0.0494
C(21)	−0.0390(9)	0.4109(9)	0.6375(7)	0.0523
C(22)	0.097(1)	0.2324(8)	0.5064(7)	0.0572
C(23)	0.2312(8)	0.3411(7)	0.6081(7)	0.0454
C(31)	0.1799(8)	−0.1714(8)	0.7055(7)	0.0519
C(32)	0.253(1)	−0.2907(8)	0.6676(8)	0.0634
C(33)	0.352(1)	−0.2946(9)	0.5861(8)	0.0649
C(34)	0.3822(9)	−0.183(1)	0.5417(7)	0.0564
C(35)	0.3115(8)	−0.0641(8)	0.5786(7)	0.0490
C(51)	−0.2135(9)	0.286(1)	0.9642(9)	0.0722
C(52)	−0.329(1)	0.402(1)	0.973(1)	0.0891
C(53)	−0.2921(8)	0.2140(9)	0.8130(7)	0.0508
C(54)	−0.3624(9)	0.323(1)	0.7260(8)	0.0640
O(6)	0.4449(6)	0.1115(6)	0.7113(6)	0.0636
O(11)	−0.0659(8)	0.5336(7)	0.8825(7)	0.0848
O(12)	0.1099(6)	0.1023(7)	1.0691(5)	0.0706
O(13)	0.3337(7)	0.3514(7)	0.8736(6)	0.0728
O(21)	−0.1311(7)	0.5041(6)	0.6337(6)	0.0700
O(22)	0.0947(8)	0.2130(7)	0.4170(5)	0.0729
O(23)	0.3103(6)	0.3935(6)	0.5843(5)	0.0629

IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2083, 2052, 2021, 1998, 1994, 1937,  $\nu_{\text{C}=\text{C}}$ : 2167 (weak)  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 515.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$  at 7.28 ppm, 500 MHz): unresolved multiplets centered on 6.90, 7.37, and 7.48 ppm for  $\text{C}_6\text{H}_5$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  at 77 ppm, 300 MHz): 207.9 ppm CO terminal, 132.2, 131.9, 129.0, 128.9, 128.6, 128.3, 124.7, and 122.2 ppm for  $\text{C}_6\text{H}_5$ , 85.9, 86.5, 92.7, and 111.2 ppm for  $\text{C}\equiv$ .

2.3.2. Addition of triphenylphosphine  $\text{P}(\text{C}_6\text{H}_5)_3$ : compounds  $[\text{Fe}_2(\text{CO})_5(\mu\text{-SC}_2\text{H}_5)\{\mu\text{-C}=\text{C}[\text{P}(\text{C}_6\text{H}_5)_3]-(\text{CH}_3)\}]$  **3**  $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  **4** and  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  **5**

On compound **1**: synthesis of compound **3**.  $\text{P}(\text{C}_6\text{H}_5)_3$  (0.013 g, 0.05 mmol) was reacted with compound **1** (0.02 g, 0.05 mmol) at room temperature in 10 ml THF during 4 h. After concentrating the solution, the residue



Table 13

Selected interatomic distances (Å) and bond angles (°) for compound **11** [ $\text{Fe}_2(\text{CO})_6(\text{C}(\text{C}(\text{O})\text{SC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{N}(\text{C}_2\text{H}_5)_2))$ ]

Fe(1)–Fe(2)	2.569(1)	Fe(1)–C(1)	1.945(6)
Fe(1)–C(7)	2.010(7)	Fe(2)–C(1)	2.038(7)
Fe(2)–C(2)	2.094(6)	Fe(2)–C(8)	2.133(7)
S(1)–C(4)	1.789(9)	S(1)–C(6)	1.780(8)
N(1)–C(7)	1.333(9)	N(1)–C(51)	1.48(1)
N(1)–C(53)	1.49(1)	C(1)–C(2)	1.404(9)
C(1)–C(6)	1.50(1)	C(2)–C(3)	1.495(9)
C(2)–C(8)	1.447(9)	C(3)–C(31)	1.37(1)
C(3)–C(35)	1.39(1)	C(4)–C(5)	1.44(2)
C(6)–O(6)	1.190(8)	C(7)–C(8)	1.457(9)
C(8)–C(9)	1.53(1)		
C(1)–Fe(1)–Fe(2)	51.4(2)	C(7)–Fe(1)–Fe(2)	67.1(2)
C(7)–Fe(1)–C(1)	82.2(3)	C(1)–Fe(2)–Fe(1)	48.3(2)
C(2)–Fe(2)–Fe(1)	74.8(2)	C(2)–Fe(2)–C(1)	39.7(3)
C(8)–Fe(2)–Fe(1)	74.7(2)	C(8)–Fe(2)–C(1)	69.4(3)
C(8)–Fe(2)–C(2)	40.0(3)	C(6)–S(1)–C(4)	102.1(4)
C(51)–N(1)–C(7)	123.2(6)	C(53)–N(1)–C(7)	126.4(6)
C(53)–N(1)–C(51)	110.2(6)	Fe(2)–C(1)–Fe(1)	80.3(2)
C(2)–C(1)–Fe(1)	116.2(5)	C(2)–C(1)–Fe(2)	72.3(4)
C(6)–C(1)–Fe(1)	122.3(5)	C(6)–C(1)–Fe(2)	128.5(5)
C(6)–C(1)–C(2)	120.0(6)	C(1)–C(2)–Fe(2)	68.0(4)
C(3)–C(2)–Fe(2)	129.6(5)	C(3)–C(2)–C(1)	123.1(6)
C(8)–C(2)–Fe(2)	71.4(4)	C(8)–C(2)–C(1)	112.8(6)
C(8)–C(2)–C(3)	124.0(6)	C(31)–C(3)–C(2)	119.1(7)
C(35)–C(3)–C(2)	122.3(7)	C(35)–C(3)–C(31)	118.3(7)
C(5)–C(4)–S(1)	115.4(9)	C(1)–C(6)–S(1)	111.4(5)
O(6)–C(6)–S(1)	120.8(6)	O(6)–C(6)–C(1)	127.8(7)
N(1)–C(7)–Fe(1)	125.9(5)	C(8)–C(7)–Fe(1)	110.8(5)
C(8)–C(7)–N(1)	123.1(6)	C(2)–C(8)–Fe(2)	68.6(4)
C(7)–C(8)–Fe(2)	89.5(4)	C(7)–C(8)–C(2)	111.9(6)
C(9)–C(8)–Fe(2)	120.5(5)	C(9)–C(8)–C(2)	116.5(6)
C(9)–C(8)–C(7)	129.6(6)		

Table 14

Fractional atomic coordinates for compound **12** [ $\text{Fe}_2(\text{CO})_6(\text{CCC}_6\text{H}_5)(\text{SCCC}_6\text{H}_5)$ ]

Atom	x	y	z	$U_{\text{iso}}$
Fe(1)	0.8753(5)	0.0472(8)	0.8648(2)	0.044(2)
Fe(2)	1.0284(5)	0.2582(9)	0.8999(2)	0.044(2)
S(1)	0.8965(9)	0.328(2)	0.8333(4)	0.050(4)
C(1)	0.784(4)	0.450(6)	0.858(1)	0.05(1)
C(2)	0.705(4)	0.537(6)	0.874(2)	0.07(1)
C(3)	0.612(4)	0.627(7)	0.897(2)	0.08(2)
C(4)	1.031(3)	0.057(5)	0.844(1)	0.03(1)
C(5)	1.125(3)	0.104(5)	0.838(1)	0.05(1)
C(6)	1.244(3)	0.139(5)	0.818(2)	0.04(1)
C(11)	0.912(3)	−0.127(5)	0.906(1)	0.04(1)
C(12)	0.810(4)	−0.064(7)	0.813(2)	0.07(2)
C(13)	0.745(3)	0.081(5)	0.897(1)	0.04(1)
C(21)	1.111(4)	0.144(5)	0.943(2)	0.05(1)
C(22)	1.120(4)	0.464(6)	0.894(2)	0.06(1)
C(23)	0.930(4)	0.318(6)	0.949(2)	0.07(1)
C(31)	0.611(4)	0.647(7)	0.950(2)	0.08(2)
C(32)	0.518(5)	0.732(9)	0.975(2)	0.12(2)
C(33)	0.435(5)	0.799(8)	0.941(2)	0.10(2)
C(34)	0.526(4)	0.713(7)	0.864(2)	0.09(2)
C(35)	0.430(5)	0.799(8)	0.889(3)	0.12(2)
C(61)	1.332(4)	0.231(6)	0.840(1)	0.06(1)
C(62)	1.443(4)	0.235(7)	0.823(2)	0.07(1)
C(63)	1.467(5)	0.157(7)	0.777(2)	0.10(2)
C(64)	1.385(6)	0.057(9)	0.752(2)	0.13(2)
C(65)	1.272(4)	0.044(7)	0.773(2)	0.07(1)
O(11)	0.938(2)	−0.249(4)	0.933(1)	0.073(9)
O(12)	0.770(3)	−0.138(5)	0.776(1)	0.10(1)
O(13)	0.666(3)	0.115(4)	0.921(1)	0.08(1)
O(21)	1.168(3)	0.053(5)	0.974(1)	0.10(1)
O(22)	1.176(3)	0.582(5)	0.896(1)	0.11(1)
O(23)	0.871(2)	0.371(4)	0.981(1)	0.07(1)

was chromatographed on silica gel. Only compound **3** was eluted with heptane as a red fraction. Compound **3** crystallized at  $-20^\circ\text{C}$  and its structure was determined by X-ray diffraction (Table 4). The amount prepared was too small to carry out all spectrometric measurements.

On compound **2**: syntheses of compound **4** and **5**. A slight excess of  $\text{P}(\text{C}_6\text{H}_5)_3$  (0.027 g, 0.1 mmol) was allowed to react with compound **2** (0.033 g, 0.07 mmol), and the mixture was stirred during 4 h in refluxing hexane. The solution was separated on a silica plate using a 50:50 heptane-dichloromethane eluant (200 ml). The first fraction was the excess of  $\text{P}(\text{C}_6\text{H}_5)_3$ , the second red fraction ( $R_f = 0.55$ ) was compound **5**, and the third purple one ( $R_f = 0.35$ ) was compound **4**.

Compound **5** is unstable. If kept in solution, it is rapidly transformed into compound **4**, but the reaction can be reversed by bubbling carbon monoxide into compound **5**.

Compound **4** crystallized at  $-20^\circ\text{C}$  and compound **5** crystallized at the same temperature under CO. Their structures were determined by X-ray diffraction (Tables 2, 4, 6, 7).

Table 15

Selected interatomic distances (Å) and bond angles (°) for compound **12** [ $\text{Fe}_2(\text{CO})_6(\text{CCC}_6\text{H}_5)(\text{SCCC}_6\text{H}_5)$ ]

Fe(1)–Fe(2)	2.519(8)	Fe(1)–S(1)	2.30(1)
Fe(1)–C(4)	1.87(3)	Fe(2)–S(1)	2.29(1)
Fe(2)–C(4)	2.09(4)	Fe(2)–C(5)	2.28(4)
S(1)–C(1)	1.73(4)	C(1)–C(2)	1.20(5)
C(2)–C(3)	1.41(6)	C(3)–C(31)	1.37(5)
C(3)–C(34)	1.42(6)	C(4)–C(5)	1.15(4)
C(5)–C(6)	1.49(5)	C(6)–C(61)	1.33(5)
C(6)–C(65)	1.41(5)		
S(1)–Fe(1)–Fe(2)	56.6(3)	C(4)–Fe(1)–Fe(2)	54.4(11)
C(4)–Fe(1)–S(1)	75.6(12)	S(1)–Fe(2)–Fe(1)	57.0(3)
C(4)–Fe(2)–Fe(1)	46.8(10)	C(4)–Fe(2)–S(1)	72.1(10)
C(5)–Fe(2)–Fe(1)	77.0(10)	C(5)–Fe(2)–S(1)	86.1(10)
C(5)–Fe(2)–C(4)	30.2(11)	Fe(2)–S(1)–Fe(1)	66.4(4)
C(1)–S(1)–Fe(1)	106.7(15)	C(1)–S(1)–Fe(2)	109.6(13)
C(2)–C(1)–S(1)	178.7(39)	C(3)–C(2)–C(1)	174.6(50)
C(31)–C(3)–C(2)	119.8(49)	C(34)–C(3)–C(2)	120.2(48)
C(34)–C(3)–C(31)	119.7(51)	Fe(2)–C(4)–Fe(1)	78.7(13)
C(5)–C(4)–Fe(1)	162.3(36)	C(5)–C(4)–Fe(2)	84.1(28)
C(4)–C(5)–Fe(2)	65.7(25)	C(6)–C(5)–Fe(2)	128.3(28)
C(6)–C(5)–C(4)	165.2(42)	C(61)–C(6)–C(5)	129.2(39)
C(65)–C(6)–C(5)	115.7(37)	C(65)–C(6)–C(61)	114.6(37)

Compound **5**: IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2044, 1996, 1983, 1965, 1944  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^{+\cdot}$  ( $m/z$ ) = 677.

Compound **4**: IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2081, 2042, 2006, 1999, 1988, 1953  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} - \text{P}(\text{C}_6\text{H}_5)_3]^{+\cdot}$  ( $m/z$ ) = 649,  $[\text{M} - \text{P}(\text{C}_6\text{H}_5)_3 + \text{CO}]^{+\cdot}$  ( $m/z$ ) = 677, and  $[\text{M} + \text{H}]^{+\cdot}$  ( $m/z$ ) = 798 (weak peak).

2.3.3. Addition of alkynes: compounds  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{R})\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$  **6**  $\text{R} = \text{CH}_3$  **7**  $\text{R} = \text{C}_6\text{H}_5$   $[\text{Fe}_2(\text{CO})_6\{\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}[\text{C}(\text{C}_6\text{H}_5)\text{-}(\text{SC}_2\text{H}_5)]\}]$  **8** and  $[\text{Fe}_2(\text{CO})_6\{\mu\text{-C}[\text{C}(\text{O})(\text{SC}_2\text{H}_5)]\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)\text{C}[\text{N}(\text{C}_2\text{H}_5)_2]\}]$  **11**

$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$  on compound **1**: synthesis of compound **6**. An excess of  $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$  (0.02 g, 0.1 mmol) was added to compound **1** (0.02 g, 0.05 mmol) in 25 ml hexane. The mixture was stirred during 2 d at room temperature. The solution was chromatographed on silica gel. Compound **6** was eluted as the third yellow fraction with dichloromethane. Crystals were obtained at  $-20^\circ\text{C}$ , and the structure was determined by X-ray diffraction (Tables 2, 8, 9). Because of a low yield, only the mass spectrum was recorded. Chemical ionisation with  $\text{NH}_3$  gave a signal at  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 558.

$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$  on compound **2**: syntheses of compounds **7** and **8**.  $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$  (0.02 g, 0.1 mmol)

Table 16  
Fractional atomic coordinates for compound **13**  $[\text{Fe}_4(\text{CO})_{12}(\text{S})(\text{CCC}_6\text{H}_5)_2]$

Atom	x	y	z	$U_{\text{eq}}$
Fe(1)	-0.13078(5)	0.29204(8)	0.22211(4)	0.0462
Fe(2)	-0.06203(5)	0.12084(8)	0.15024(4)	0.0464
S(1)	0.0000	0.2013(2)	0.2500	0.0412
C(1)	-0.0733(4)	0.3246(5)	0.1417(3)	0.0463
C(2)	-0.0289(4)	0.3149(5)	0.0916(3)	0.0487
C(3)	0.0161(4)	0.3245(5)	0.0300(3)	0.0467
C(11)	0.0240(4)	0.0482(6)	0.1038(3)	0.0542
C(12)	-0.0945(5)	-0.0176(7)	0.1947(3)	0.0711
C(13)	-0.1506(4)	0.0987(7)	0.0849(3)	0.0679
C(21)	-0.1250(4)	0.4495(7)	0.2624(3)	0.0680
C(22)	-0.2321(4)	0.3082(6)	0.1719(3)	0.0588
C(23)	-0.1801(4)	0.2023(7)	0.2881(3)	0.0624
C(31)	-0.0284(4)	0.3047(6)	-0.0332(3)	0.0586
C(32)	0.0142(5)	0.3104(7)	-0.0927(3)	0.0713
C(33)	0.1016(5)	0.3388(7)	-0.0894(3)	0.0710
C(34)	0.1459(4)	0.3604(8)	-0.0286(4)	0.0773
C(35)	0.1049(4)	0.3534(7)	0.0317(3)	0.0689
O(11)	0.0742(3)	0.0057(4)	0.0706(2)	0.0737
O(12)	-0.1162(4)	-0.1061(5)	0.2249(3)	0.0957
O(13)	-0.2069(3)	0.0878(6)	0.0439(3)	0.0964
O(21)	-0.1223(4)	0.5508(5)	0.2846(3)	0.0992
O(22)	-0.2959(3)	0.3174(5)	0.1380(2)	0.0840
O(23)	-0.2118(3)	0.1433(6)	0.3289(3)	0.0875

Table 17  
Selected interatomic distances (Å) and bond angles ( $^\circ$ ) for compound **13**  $[\text{Fe}_4(\text{CO})_{12}(\text{S})(\text{CCC}_6\text{H}_5)_2]$

Fe(1)–Fe(2)	2.531(1)	Fe(1)–S(1)	2.244(1)
Fe(1)–C(1)	1.889(6)	Fe(2)–S(1)	2.256(1)
Fe(2)–C(1)	2.107(5)	Fe(2)–C(2)	2.375(5)
C(1)–C(2)	1.239(7)	C(2)–C(3)	1.435(7)
C(3)–C(31)	1.379(7)	C(3)–C(35)	1.394(8)
Fe(2)–Fe(1)–S(1)	55.99(4)	Fe(2)–Fe(1)–C(1)	54.6(2)
S(1)–Fe(1)–C(1)	78.9(2)	Fe(1)–Fe(2)–S(1)	55.55(4)
Fe(1)–Fe(2)–C(1)	47.0(2)	S(1)–Fe(2)–C(1)	74.4(1)
Fe(1)–Fe(2)–C(2)	78.3(1)	S(1)–Fe(2)–C(2)	90.9(1)
C(1)–Fe(2)–C(2)	31.4(2)	Fe(1)–S(1)–Fe(1')	130.86(9)
Fe(1)–S(1)–Fe(2)	68.46(3)	Fe(1)–S(1)–Fe(2')	132.21(3)
Fe(2)–S(1)–Fe(2')	137.0(1)	Fe(1)–C(1)–Fe(2)	78.4(2)
Fe(1)–C(1)–C(2)	164.4(5)	Fe(2)–C(1)–C(2)	86.3(4)
Fe(2)–C(2)–C(1)	62.3(3)	Fe(2)–C(2)–C(3)	126.6(4)
C(1)–C(2)–C(3)	170.3(6)	C(2)–C(3)–C(31)	120.1(5)
C(2)–C(3)–C(35)	122.0(5)	C(31)–C(3)–C(35)	118.0(5)

was added to compound **2** (0.046 g, 0.1 mmol.) in 15 ml hexane. The mixture was stirred during 5 h in refluxing hexane. The solution was filtered and the filtrate was chromatographed on silica gel. Compound **8** was eluted as the second brown fraction just after residual  $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ , with 80:20 heptane-dichloromethane. Compound **7** was eluted with dichloromethane as the third red fraction. Both compounds crystallized at  $-20^\circ\text{C}$ , and their structures were determined by X-ray diffraction (Tables 2, 5, 10, 11).

Compound **8**: IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2055, 2008, 1991, 1978, 1946  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^{+\cdot}$  ( $m/z$ ) = 621,  $[\text{M} + \text{NH}_4]^{+\cdot}$  ( $m/z$ ) = 638.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$  at 7.16 ppm, 300 MHz): t 0.45 ppm for  $\text{CH}_3\text{CH}_2\text{S}$ , unresolved multiplet centred at 2.1 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2\text{S}$ , unresolved multiplets between 6.6 and 7.8 ppm for 3  $\text{C}_6\text{H}_5$ .

Compound **7**: IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2054, 2008, 1991, 1978, 1946,  $\nu_{\text{C}=\text{O}}$ : 1590  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^{+\cdot}$  ( $m/z$ ) = 621,  $[\text{M} + \text{NH}_4]^{+\cdot}$  ( $m/z$ ) = 638.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$  at 7.16 ppm, 300 MHz): t 0.62 ppm for  $\text{CH}_3\text{CH}_2\text{S}$ , 2 unresolved multiplets centred at 2.10 and 1.60 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2\text{S}$ , unresolved multiplets between 6.6 and 7.8 ppm for 3  $\text{C}_6\text{H}_5$ .

$\text{CH}_3\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  on compound **2**: synthesis of compound **11**. An excess of  $\text{CH}_3\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  (0.02 g, 0.18 mmol) was added to compound **2** (0.01 g, 0.03 mmol) in 15 ml hexane. The mixture was stirred during 4 d at room temperature. The solution was concentrated under vacuum and the residue was separated on a pre-coated silica plate with a 30-70 heptane-dichloromethane eluant. Yellow compound **11** was the major product of the reaction in 16% yield. Crystals were obtained at  $-20^\circ\text{C}$ , and the structure was determined by X-ray diffraction (Tables 3, 12, 13).

Compound **11**: IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2057, 2012, 1987, 1959, 1943  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 582,  $[\text{M} + \text{NH}_4]^+$  ( $m/z$ ) = 599.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$  at 7.16 ppm, 300 MHz): s 3H 1.94 ppm for  $\text{CH}_3$ , t 3H 0.94 ppm for  $\text{CH}_3\text{CH}_2$ , 2 t between 1.14 and 1.21 ppm under peaks of residual heptane for 2  $\text{CH}_3\text{CH}_2$ , 3 unresolved multiplets centred at 2.63, 3.25, and 3.37 ppm for two diastereotopic H of  $\text{CH}_3\text{CH}_2$ , unresolved multiplets between 7.21 and 7.30 ppm for  $\text{C}_6\text{H}_5$ .

### 2.3.4. Addition of $[\text{Fe}_2(\text{CO})_9]$ on compound **12**: compound **13** $[\text{Fe}_4(\text{CO})_{12}\{\mu_4\text{-S}\}(\mu\text{-CCC}_6\text{H}_5)_2]$

$[\text{Fe}_2(\text{CO})_9]$  (0.012 g, 0.034 mmol) was added to compound **12** (0.017 g, 0.036 mmol) in 15 ml heptane. The solution was stirred at room temperature during 4 h. The solution was concentrated and chromatographed on silica gel column. Some  $[\text{Fe}_3(\text{CO})_{12}]$  was formed. Compound **13** was eluted with heptane as the major product. Yield 20%. X-ray structures of **12** and **13** were determined using crystals which grew from a hexane solution (Tables 3, 16, 17).

IR (KBr pellet):  $\nu_{\text{CO}}$  terminal: 2092, 2066, 2038, 1988, 1970  $\text{cm}^{-1}$ . Mass spectrometry (chemical ionisation with  $\text{NH}_3$ ):  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 795.  $^1\text{H}$  NMR ( $\text{CDCl}_3$  at 7 ppm, 300 MHz): unresolved multiplets centered on 7.2, 7.4, and 7.6 ppm for  $\text{C}_6\text{H}_5$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 205.0 and 206.0 ppm CO terminal, 124.7, 128.6, and 131.9 ppm for  $\text{C}_6\text{H}_5$ , 97.4 ppm  $\text{C}\equiv$ .

## 3. Discussion

Compounds  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$  were obtained beside several other products [4]. The yield was 10% for compound **1** ( $\text{R} = \text{CH}_3$ ) and 5% for compound **2** ( $\text{R} = \text{C}_6\text{H}_5$ ).

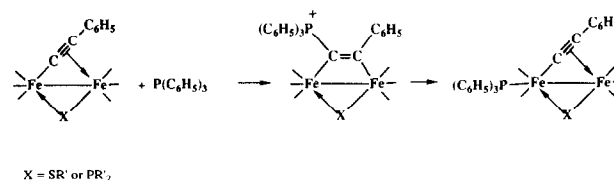
$\text{R}-\text{C}\equiv\text{C}-\text{SC}_2\text{H}_5 + [\text{Fe}_2(\text{CO})_9] \rightarrow [\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$ : this compound is structurally identical to the compound obtained by Seyferth et al. [5] who carried out the reaction of  $\text{RC}\equiv\text{CBr}$  with  $[(\text{C}_2\text{H}_5)_3\text{NH}][\text{Fe}_2(\text{CO})_6(\mu\text{-SR}')(\mu\text{-CO})]$ , and structurally equivalent to the compound obtained by Carty et al. [2] from the reaction of phosphinoalkynes  $\text{RC}\equiv\text{CPR}'_2$  with iron carbonyl,  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PR}'_2)(\mu\text{-CCR})]$ . Those two compounds contain an acetylide bridging fragment



$\text{R}' = \text{C}_2\text{H}_5$ ,  $\text{R} = \text{CH}_3$  compound **1**

$\text{R} = \text{C}_6\text{H}_5$  compound **2**

Scheme 1.



Scheme 2.

$\sigma$ -bonded to one iron atom and  $\pi$ -bonded to the second (Scheme 1).

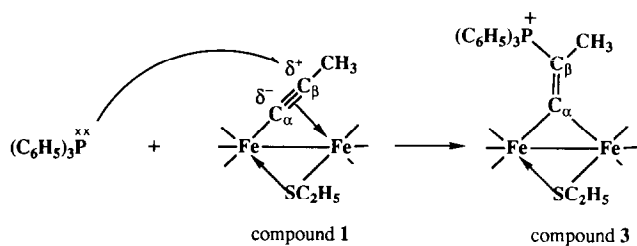
A thorough  $^{13}\text{C}$  NMR study of the acetylide  $\text{C}_\alpha$  and  $\text{C}_\beta$  chemical shifts has been carried out by Carty and co-workers [14]. It was shown that the polarity depends on the nature of the R group of the ligated  $\text{C}_\alpha\equiv\text{C}_\beta\text{-R}$  acetylide.  $\text{C}_\alpha$  is more positive than  $\text{C}_\beta$  if R is an electron acceptor such as a phenyl group, while  $\text{C}_\alpha$  is less positive than  $\text{C}_\beta$  if R is an electron donor such as a tertio-butyl group. In order to confirm those results, a reactivity study of acetylide complexes with amines or phosphines has been undertaken. Seyferth et al. [5] showed that the reaction of  $(\text{C}_2\text{H}_5)_2\text{NH}$  with  $[\text{Fe}_2(\text{CO})_6(\mu\text{-X})(\mu\text{-CCR})]$  is similar for  $\text{X} = \text{P}(\text{C}_6\text{H}_5)_2$  and  $\text{X} = \text{SC}(\text{CH}_3)_3$  in that  $[\text{Fe}_2(\text{CO})_6(\mu\text{-X})\{\mu\text{-CHC}(\text{C}_6\text{H}_5)=\text{N}(\text{C}_2\text{H}_5)_2\}]$  was obtained in both cases. The nature of X does not alter the polarity of the acetylide carbon atoms of the triple bond  $\text{C}_\alpha\text{C}_\beta\text{C}_6\text{H}_5$ . Mechanistically those results do not fit very well with the expected polarity since the nucleophilic amine attacks at the electron-rich carbon atom of the acetylide. In fact,  $\text{P}(\text{C}_6\text{H}_5)_3$  reacted as expected at the  $\text{C}_\alpha$  electron-poor carbon atom generating a phosphonium ylide  $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SC}(\text{CH}_3)_3\}\{\mu\text{-C}[\text{P}(\text{C}_6\text{H}_5)_3]\text{C}(\text{C}_6\text{H}_5)\}]$  identified by NMR spectroscopy; this species was then shown to be an intermediate in the formation of the CO-substituted compound  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-SC}(\text{CH}_3)_3\}\{\mu\text{-CCC}_6\text{H}_5\}\{\text{P}(\text{C}_6\text{H}_5)_3\}]$  (Scheme 2) [5].

### 3.1. Reaction of triphenylphosphine

Both compounds  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$ ,  $\text{R} = \text{CH}_3$ , **1**, and  $\text{R} = \text{C}_6\text{H}_5$ , **2**, were prepared as red oils. They were characterized by comparing their spectroscopic data (mass spectrometry using electronic impact,  $^1\text{H}$  NMR, and IR) with those published by Seyferth et al. [5], though they contain  $\text{SC}_2\text{H}_5$  instead of  $\text{SC}(\text{CH}_3)_3$ .

The reaction of triphenylphosphine  $\text{P}(\text{C}_6\text{H}_5)_3$  was another way to characterize them indirectly.

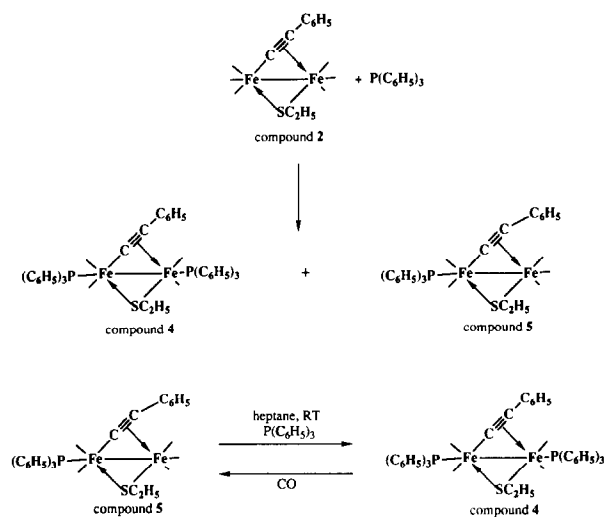
In the case of the methylated thioalkyne, the  $^{13}\text{C}$  NMR study of pure  $\text{CH}_3\text{C}_\beta\equiv\text{C}_\alpha\text{SC}_2\text{H}_5$  showed that  $\delta(\text{C}_\alpha) + \delta(\text{C}_\beta) = 158.9$  ppm and  $\delta(\text{C}_\alpha) - \delta(\text{C}_\beta) = -22.3$  ppm. These values suggest that  $\text{C}_\beta$  is more electrophilic than  $\text{C}_\alpha$  following the reasoning of Mott and Carty [14a]. Assuming that the polarity of the acetylide fragment  $\text{C}_\alpha\equiv\text{C}_\beta\text{CH}_3$  in compound **1** is the



Scheme 3.

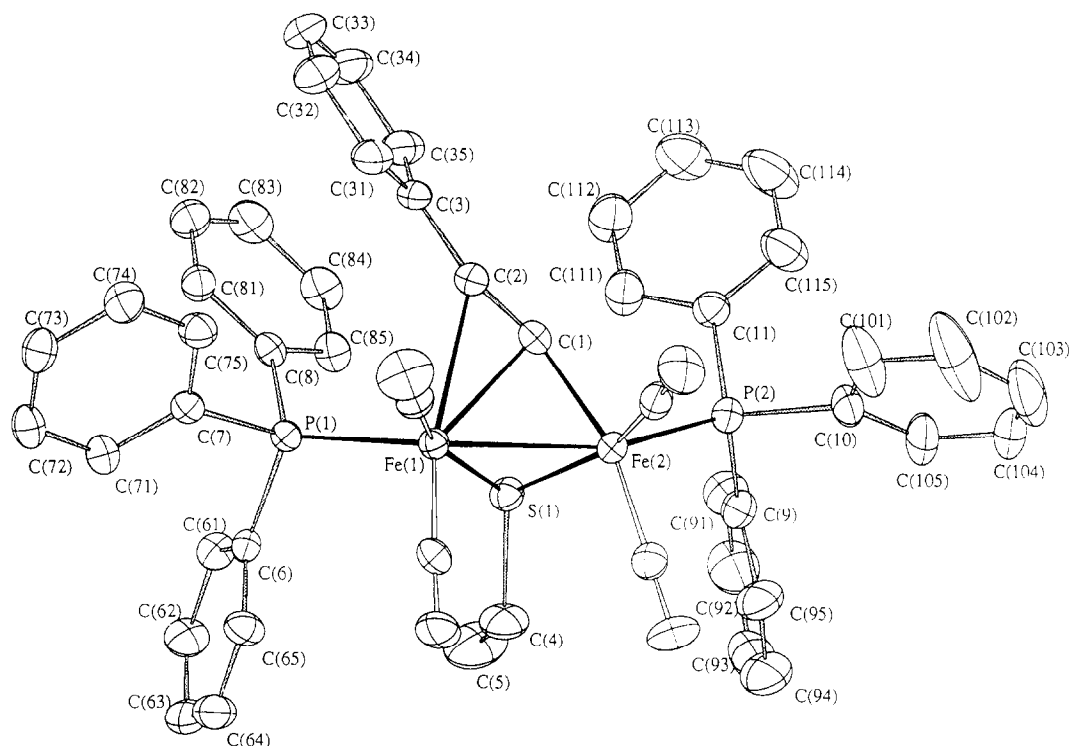
same as in free thioalkyne,  $\text{P}(\text{C}_6\text{H}_5)_3$  should attack the  $\text{C}_\beta$  carbon atom. X-ray analysis of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-C}=\text{C}[\text{P}(\text{C}_6\text{H}_5)_3][\text{CH}_3])]$  (compound 3) confirmed the above expectation, as shown in Scheme 3 (Table 4). Since the very similar crystal structure of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P}(\text{C}_6\text{H}_5)_2)(\mu\text{-C}=\text{C}[\text{PH}(\text{C}_6\text{H}_{11})_2](\text{C}_6\text{H}_5))]$  has been described [14d], all crystallographic details dealing with compound 3 are not given here but have been deposited.

In the case of  $\text{R} = \text{C}_6\text{H}_5$ , the  $^{13}\text{C}$  NMR spectrum of  $\text{C}_6\text{H}_5\text{C}_\beta\equiv\text{C}_\alpha\text{SC}_2\text{H}_5$  gave  $\delta(\text{C}_\alpha) + \delta(\text{C}_\beta) = 175.2$  ppm and  $\delta(\text{C}_\alpha) - \delta(\text{C}_\beta) = +13.8$  ppm. This suggests that  $\text{C}_\alpha$  is now more electrophilic than  $\text{C}_\beta$ , i.e. the polarity of the triple bond is inverted compared to the case with  $\text{R} = \text{CH}_3$ . Consequently, making the same assumption as above, triphenylphosphine should attack at the  $\text{C}_\alpha$  carbon atom of the acetylide complex 2, as observed by Seyferth et al [5] (Scheme 2).  $\text{P}(\text{C}_6\text{H}_5)_3$  was allowed to react with compound 2. When the



Scheme 4.

reaction was carried out at room temperature, a chromatographic follow up showed two weak spots which developed very slowly. The reaction temperature was then progressively raised to the temperature of boiling hexane. Both spots, one red and one purple, became intense. Compounds 4 and 5 were obtained by separation using precoated silica plate chromatography. The structure of 4 was determined by X-ray diffraction (Tables 2, 6, 7). It shows a double substitution, with one phosphine on each iron atom  $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$ .

Fig. 1. Molecular structure of compound 4  $[\text{Fe}_2(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_5)_3\}_2(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$ .

$\text{SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  (Fig. 1). The angle between vectors  $\text{Fe}(1)\text{P}(1)$  and  $\text{Fe}(2)\text{P}(2)$  is  $113^\circ 88'$  and the four atoms are nearly in the same plane with deviations from this least-squares plane  $\text{P}(1)$ :  $-0.029$ ,  $\text{Fe}(1)$ :  $+0.069$ ,  $\text{Fe}(2)$ :  $-0.066$ , and  $\text{P}(2)$ :  $+0.025$  Å.

Red compound **5** is unstable in solution, and transformed itself spontaneously into purple compound **4** at room temperature. Assuming that the unstable compound **5** is an ylide analogous to the intermediate ylide compound described by Seyferth et al. [5] on a spectroscopic basis (Scheme 2), carbon monoxide was bubbled into a solution of the purple compound **4**, with the expectation that the CO molecule would push one  $\text{P}(\text{C}_6\text{H}_5)_3$  molecule towards the  $\text{C}_\alpha$  of the acetylide. The solution then contained only one red compound which is thought to be compound **5** since the  $R_f = 0.55$  is the same. Bubbling now argon in this red solution transformed it back into purple compound **4**. The transformation of **5** into **4** is thus reversible (Scheme 4).

Crystals of **5** were obtained (Table 4). X-ray analysis showed that it is not an ylide but the monosubstituted complex  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$  (Fig. 2). Triphenylphosphine is ligated to  $\text{Fe}(2)$   $\sigma$ -bonded carbon atom  $\text{C}(1)$  of the acetylide, as

inferred by Seyferth et al. [5] for  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-SC}(\text{CH}_3)_3)(\mu\text{-CCC}_6\text{H}_5)]$  and as found by X-ray by Cherkas et al. [14b] for  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-P}(\text{C}_6\text{H}_5)_2)(\mu\text{-CCC}_6\text{H}_5)]$ . Since the crystal structure of  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-P}(\text{C}_6\text{H}_5)_2)(\mu\text{-CCC}_6\text{H}_5)]$  has been published, and **5** differs only by the bridge  $\text{SC}_2\text{H}_5$  instead of  $\text{P}(\text{C}_6\text{H}_5)_2$ , and since **5** is a mono-phosphine substituted compound while **4** is a bis(phosphine) derivative, the crystallographic details are not included here but have been deposited.

The structures of **4** and **5** may be compared with each other and to that of  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-P}(\text{C}_6\text{H}_5)_2)(\mu\text{-CCC}_6\text{H}_5)]$  [2b] (Scheme 5). This last compound is characterized by two *trans* phosphorus

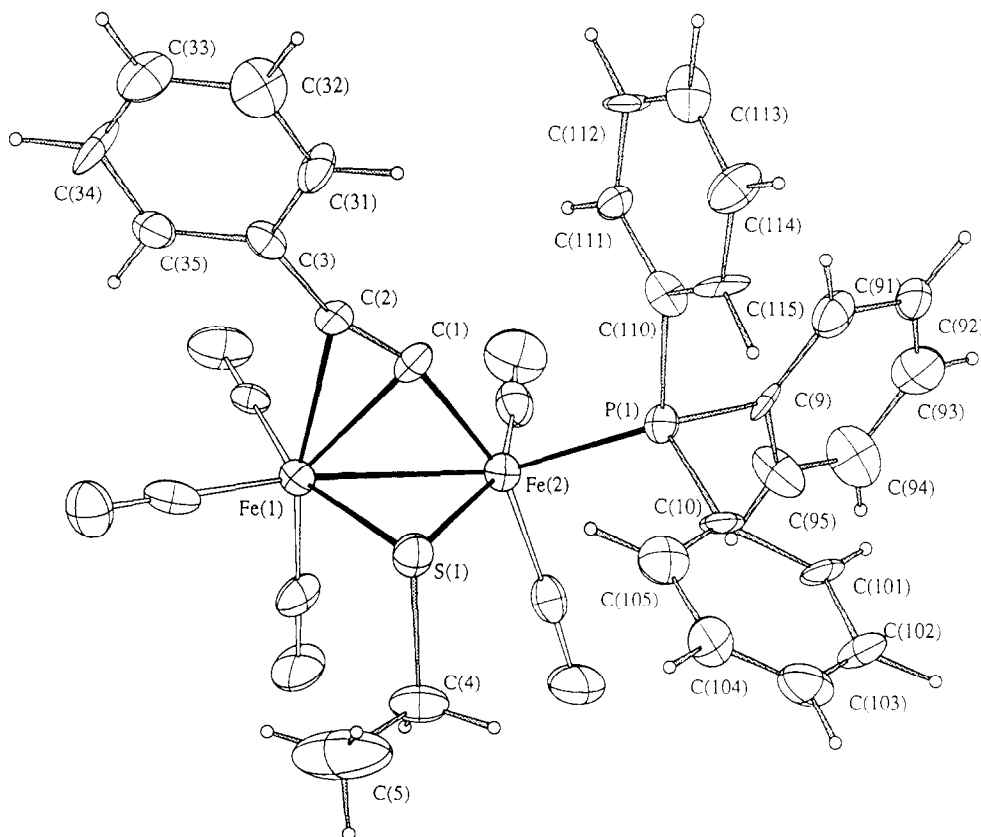
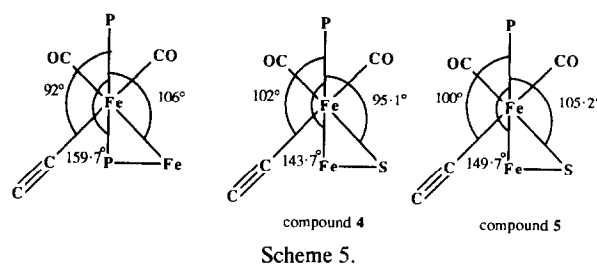


Fig. 2. Molecular structure of compound **5**.  $[\text{Fe}_2(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)]$ . Space group:  $P\bar{1}$ . Cell parameters:  $a = 10.930(4)$ ,  $b = 13.308(3)$ ,  $c = 13.841(7)$  Å,  $\alpha = 61.41(2)^\circ$ ,  $\beta = 68.06(3)^\circ$ ,  $\gamma = 66.92(2)^\circ$ . Selected interatomic distances (Å) and bond angles ( $^\circ$ ):  $\text{Fe}(1)\text{-Fe}(2)$ : 2.537(3),  $\text{Fe}(1)\text{-S}(1)$ : 2.294(5),  $\text{Fe}(2)\text{-S}(1)$ : 2.274(5),  $\text{Fe}(1)\text{-C}(1)$ : 2.10(2),  $\text{Fe}(1)\text{-C}(2)$ : 2.27(2),  $\text{Fe}(2)\text{-C}(1)$ : 1.89(2),  $\text{Fe}(2)\text{-P}(1)$ : 2.230(5),  $\text{Fe}(1)\text{-S}(1)\text{-Fe}(2)$ :  $67.5(1)$ ,  $\text{Fe}(1)\text{-C}(1)\text{-Fe}(2)$ :  $78.8(6)$ ,  $\text{Fe}(1)\text{-Fe}(2)\text{-P}(1)$ :  $149.7(2)$ .

atoms. The P–Fe–P angle is  $159.7^\circ$  while the P–Fe–Fe angle is  $106.0^\circ$ . In different ways, for both **4** and **5**, phosphorus atoms are *cis* to sulfur with P–Fe–S angles equal to  $95.1^\circ$  and  $105.2^\circ$ , respectively. This *cis* arrangement of  $\text{P}(\text{C}_6\text{H}_5)_3$  with respect to the  $\text{SC}_2\text{H}_5$  bridging group may be attributed to the less bulky bridge. Phosphorus atoms are *trans* to iron with P–Fe–Fe angles of  $148.6^\circ$  and  $143.7^\circ$  for **4**, and  $149.7^\circ$  for **5**.

### 3.2. Reaction of alkynes

As mentioned above,  $[\text{Fe}_2(\text{CO})_6(\mu\text{-X})(\mu\text{-CCC}_6\text{H}_5)]$  [**5**] reacts with amines and triphenylphosphine, as shown by Seyferth et al. ( $\text{X} = \text{SC}_2\text{H}_5$ ) and by Cherkas et al. [14b] ( $\text{X} = \text{P}(\text{C}_6\text{H}_5)_2$ ). Amines and triphenylphosphine are electron donors. Since alkynes are electron-rich molecules, and since Cherkas et al. showed that alkynes react at the acetylide of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-P}(\text{C}_6\text{H}_5)_2)(\mu\text{-CCC}_6\text{H}_5)]$  [15], the reaction of three alkynes  $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5\text{C}\equiv\text{CSC}_2\text{H}_5$ , and  $\text{CH}_3\text{C}\equiv\text{CN}(\text{C}_2\text{H}_5)_2$  with  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ) was investigated.

#### 3.2.1. Reaction of $\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$

$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$  reacts with  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$  to give  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{R})\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$  (compound **6** with  $\text{R} = \text{CH}_3$ , com-

pound **7** with  $\text{R} = \text{C}_6\text{H}_5$ ) (Fig. 3). Their crystal structures were determined. However, because **7** is of a structural type identical to that of **6** (Tables 2, 8, 9), crystallographic details of **7** are not included here but have been deposited (Table 5)

Those compounds are characterized by two features. First of all, diphenylacetylene forms two C–C bonds by triple bond opening. At one end, it coupled with the  $\text{C}_\alpha$  carbon atom of the acetylide; at the other end, it coupled with a carbonyl group which became a ketone inserted between iron atom Fe(1) and carbon atom C(7). The second feature is the position of the thiolate group which moved around Fe(1) from the Fe–Fe bridging position to form a bridge between Fe(1) and  $\text{C}_\beta$  of  $\text{C}_\alpha\equiv\text{C}_\beta\text{R}$  group.

Remarkably, the C(1) carbon atom, which was the  $\text{C}_\alpha$  of the acetylide, is now linked to both iron atoms (Fe(1)–C(1) =  $1.94(1)$  and Fe(2)–C(1) =  $1.95(1)$  Å for  $\text{R} = \text{CH}_3$ ; Fe(1)–C(1) =  $1.97(2)$  and Fe(2)–C(1) =  $1.97(2)$  Å for  $\text{R} = \text{C}_6\text{H}_5$ ) and to two carbon atoms C(2) and C(8) (C(1)–C(2) =  $1.36(1)$  and C(1)–C(8) =  $1.41(1)$  Å for  $\text{R} = \text{CH}_3$ ; C(1)–C(2) =  $1.36(2)$  and C(1)–C(8) =  $1.42(3)$  Å for  $\text{R} = \text{C}_6\text{H}_5$ ). Distances along the chain Fe(1)–S(1)–C(2)–C(1)–C(8)–C(7)–C(6)–Fe(1) are the same for **6** and **7** within standard deviations ( $2.348(4)$ ,  $1.77(2)$ ,  $1.36(1)$ ,  $1.41(1)$ ,  $1.43(1)$ ,  $1.52(2)$ ,  $1.93(1)$  Å for  $\text{R} = \text{CH}_3$ ;  $2.345(7)$ ,  $1.79(2)$ ,  $1.36(2)$ ,  $1.42(3)$ ,  $1.38(3)$ ,

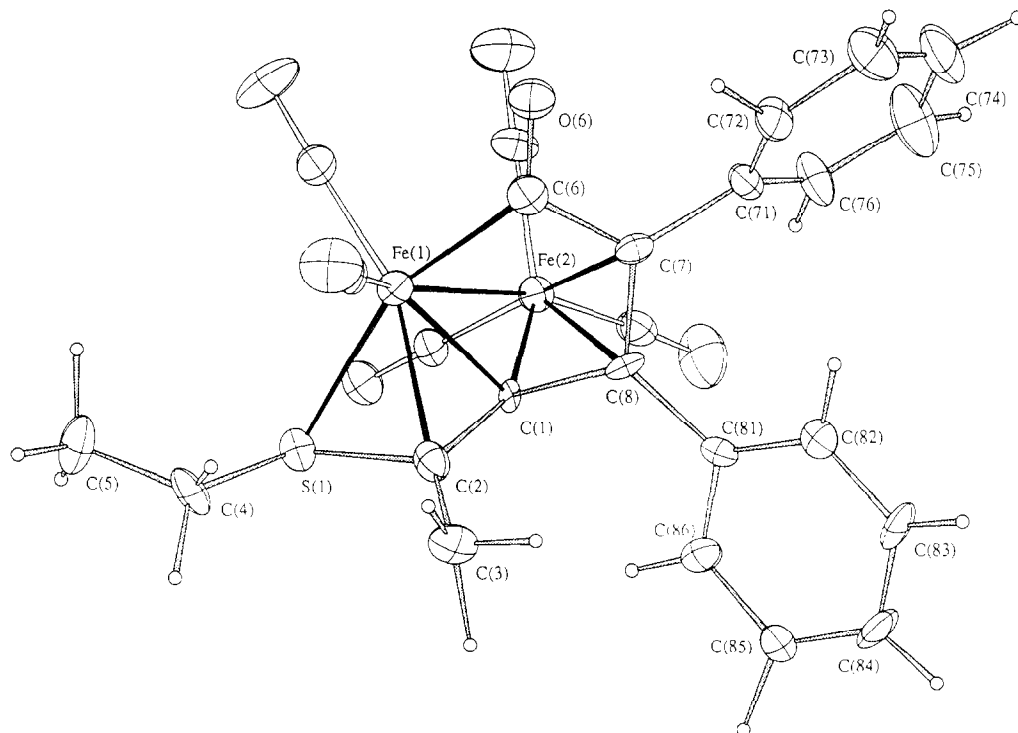


Fig. 3. Molecular structure of compound **6**  $[\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{CH}_3)\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}]$ .

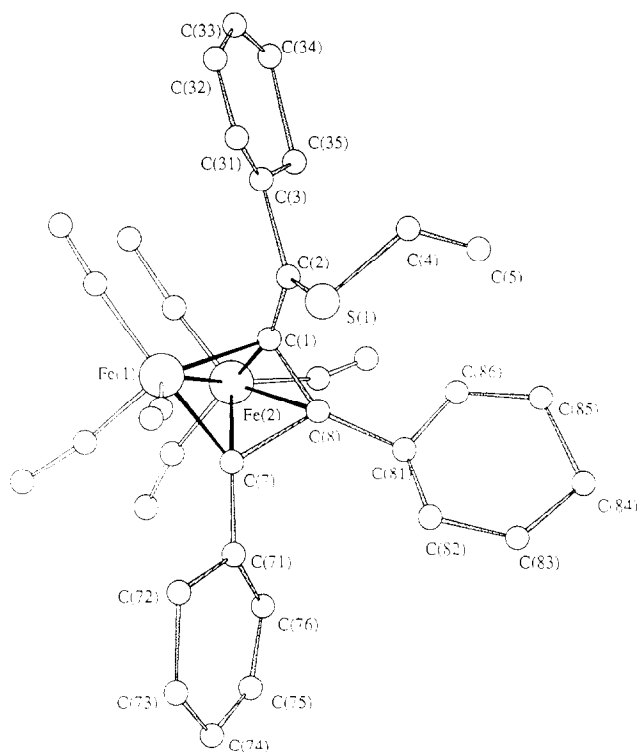


Fig. 4. Molecular structure of compound **8** [ $\text{Fe}_2(\text{CO})_6\{\mu\text{-C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}[\text{C}=(\text{SC}_2\text{H}_5)(\text{C}_6\text{H}_5)]\}$ ].

1.54(3), 1.93(2) Å for  $\text{R} = \text{C}_6\text{H}_5$ ). Thus, the phenyl ring seems to have no influence on the electronic distribution of the cluster framework.

Considering the electron count, this compound may be described as two fused clusters [16]. The first is an *arachno*  $\text{Fe}_2\text{C}_4$  cluster, Fe(1), Fe(2), C(1), C(8), C(7), and C(6), with  $14n + 6 - 4 \times 10 = 50$  valence electrons. The second one is a butterfly, i.e. an *arachno*  $\text{FeC}_2\text{S}$  cluster, Fe(1), C(1), C(2), and S(1) with  $14n + 6 - 3 \times 10 = 32$  valence electrons. Those two units share one edge, Fe(1)–C(1); one then gets  $50 + 32 - 24 = 58$  valence electrons. It may be easily checked that it is consistent with the structural formula [ $\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{R})\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}$ ].

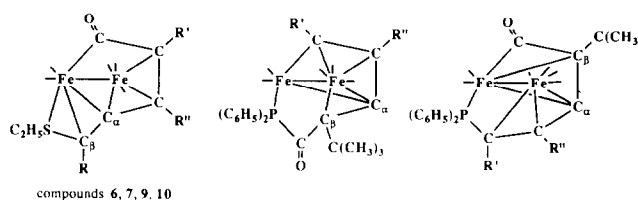
When the reactional mixture in the case of  $\text{R} = \text{C}_6\text{H}_5$  was chromatographed, an orange fraction eluted with 80:20 heptane-dichloromethane. This fraction (compound **8**) is different from the red fraction eluted with pure dichloromethane (compound **7**). Mass spectrometry gave the same molecular peak for both fractions ( $[\text{M} + \text{H}]^+(m/z) = 621$ ). However the IR band at  $1590 \text{ cm}^{-1}$  which corresponded to the inserted  $\text{C}=\text{O}$  of compound **7** was not observed for compound **8**. X-ray analysis of this isomer corresponding to the formula [ $\text{Fe}_2(\text{CO})_6\{\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}[\text{C}(\text{C}_6\text{H}_5)(\text{SC}_2\text{H}_5)]\}$ ] showed a different structure based on a square pyramid  $\text{Fe}_2\text{C}_3$  (Fig. 4) that is a *nido* structure (Tables 2, 10, 11). The apical vertex is occupied by the iron atom Fe(2), and the four basal plane vertices are occupied by

Fe(1), C(7) and C(8) of diphenylacetylene, and the  $\text{C}_\alpha$  carbon atom C(1) of the acetylide. The thiolate group is bound to the  $\text{C}_\beta$  carbon atom C(2) of the acetylide, as for compound **7**. Unfortunately, the number of recorded data was small and distances and angles are consequently not very accurate. However, the Fe–Fe distance, 2.48(1) Å, is significantly different from the Fe–Fe distance of compound **7**, 2.622(5) Å. Distances in the basal plane are Fe(1)–C(1) = 1.98(5), C(1)–C(8) = 1.41(6), C(8)–C(7) = 1.62(8), and C(7)–Fe(1) = 1.86(7) Å, and angles are Fe(1)–C(7)–C(8) =  $99.1(5)^\circ$ , C(7)–C(8)–C(1) =  $87.8(5)^\circ$ , C(8)–C(1)–Fe(1) =  $101.6(4)^\circ$ , and C(1)–Fe(1)–C(7) =  $66^\circ 6(3)$ . The Fe(1), C(1), C(7), and C(8) atoms define a mean-squares plane to which distances are  $-0.092$  Å for Fe(1),  $+0.121$  Å for C(1),  $+0.111$  Å for C(7), and  $-0.140$  Å for C(8). The C(1) carbon atom appears linked by a double bond to C(2) of the  $\text{C}(\text{C}_6\text{H}_5)(\text{SC}_2\text{H}_5)$  group, since C(1)–C(2) is 1.40(7) Å.

The skeleton electron count corresponds to 7 pairs, that is to a *nido* structure.

Considering the structures of compounds **7** and **8** together, compound **8** may be described as an intermediate in the formation of compound **7**. Indeed, when compound **8** was carefully separated by chromatography, and the product crystals were dissolved in  $\text{C}_6\text{D}_6$ , an NMR study revealed a small amount of **7** which increased with time as the amount of **8** decreased. The intramolecular insertion of one carbonyl coming from Fe(1) into the Fe(1)–C(7) bond would yield compound **8**. The resulting vacant site on Fe(1) would then be filled by an electron pair from the sulfur atom.

Smith et al. have described the reaction of various alkynes  $\text{RC}\equiv\text{CR}$  ( $\text{R} = \text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{CF}_3$ ,  $\text{C}_2\text{H}_5$ , or  $\text{C}_6\text{H}_5$ ) with [ $\text{Fe}_2(\text{CO})_6\{\mu\text{-P}(\text{C}_6\text{H}_5)_2\}(\mu\text{-CC}^t\text{Bu})$ ] [15] (Scheme 6). This diiron compound differs from **2** by the bulkier  $\text{P}(\text{C}_6\text{H}_5)_2$  instead of  $\text{SC}_2\text{H}_5$ , and by a *t*-butylacetylide instead of a phenylacetylide. Alkynes coupled with  $\text{CC}^t\text{Bu}$ . The organic moiety also incorporated a CO molecule and the bridging group, as for the reaction of [ $\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCC}_6\text{H}_5)$ ] with diphenylacetylene. However, there are two differences in the linking of the four groups, the acetylide, CO, the oncoming alkyne, the phosphido or the thiolate. First, CO is inserted between one end of the incoming alkyne and iron in compounds **6** and **7**. It is linked to the acetylide  $\text{C}_\beta$  and either to phosphorus or to iron in the com-



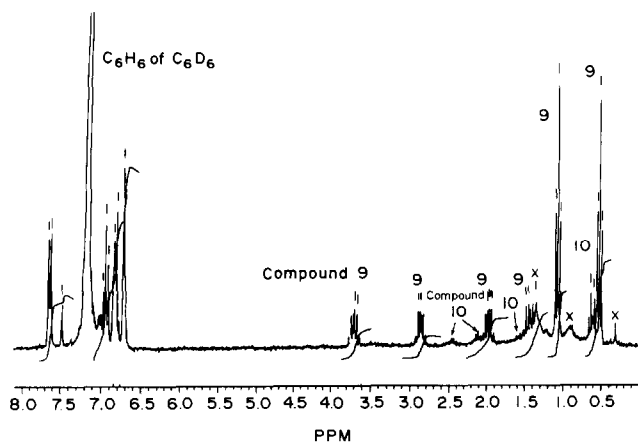


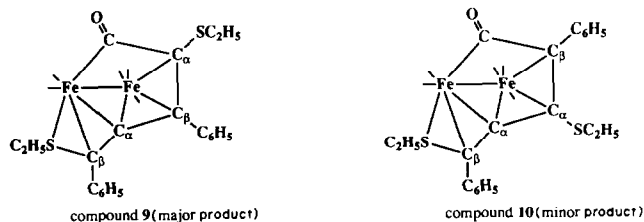
Fig. 5.  $^1\text{H}$  NMR Spectrum ( $\text{C}_6\text{D}_6$  at 7.16 ppm, 250 MHz) of the mixture of compounds **9** and **10** [ $\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{SC}_2\text{H}_5)\text{C}(\text{O})\}$ ], compound **9** and [ $\text{Fe}_2(\text{CO})_5\{\mu\text{-S}(\text{C}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CC}(\text{SC}_2\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{O})\}$ ], compound **10**.

pounds of Smith et al. Second, the thiolate is inserted between the acetylde  $\text{C}_\beta$  and iron for **6** and **7**; the phosphide inserted either between iron and CO or between iron and one end of the incoming alkyne in the compounds of Carty et al. Thus the chains of atoms are as follows: for compounds **6** and **7**,  $\text{C}_2\text{H}_5\text{SC}(\text{R})\text{CC}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)\text{CO}$  with  $\text{R} = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ , compared with  $\text{RCC}(\text{R})\text{CC}(\text{t-Bu})\text{C}(\text{O})\text{P}(\text{C}_6\text{H}_5)_2$  and  $\text{P}(\text{C}_6\text{H}_5)_2\text{C}(\text{R})\text{C}(\text{R})\text{CC}(\text{t-Bu})\text{CO}$  ( $\text{R} = \text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{CF}_3$ ,  $\text{C}_2\text{H}_5$ , or  $\text{C}_6\text{H}_5$ ) for the others.

### 3.2.2. Reaction of $\text{C}_6\text{H}_5\text{C}\equiv\text{CSC}_2\text{H}_5$

Since diphenylacetylene reacts with [ $\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})$ ], we wanted to see whether the thioalkyne  $\text{RC}\equiv\text{CSC}_2\text{H}_5$  ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ) behaves similarly.

(Ethylthio)phenylethyne reacts at room temperature with compound **2** to yield a red fraction, eluted with dichloromethane. The IR spectrum displayed not only several bands typical of terminal CO around  $2000\text{ cm}^{-1}$ , but also two bands at  $1615\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ , typical of either a ketone or a  $\text{C}=\text{C}$  double bond. Mass spectrometry gave only one peak,  $[\text{M} + \text{H}]^+$  ( $m/z$ ) = 605, although the  $^1\text{H}$  NMR spectrum was relatively complicated, corresponding to a mixture of two compounds, a major one, compound **9**, and a minor one, compound **10** (Fig. 5). As far as the thiolate group



Scheme 7.

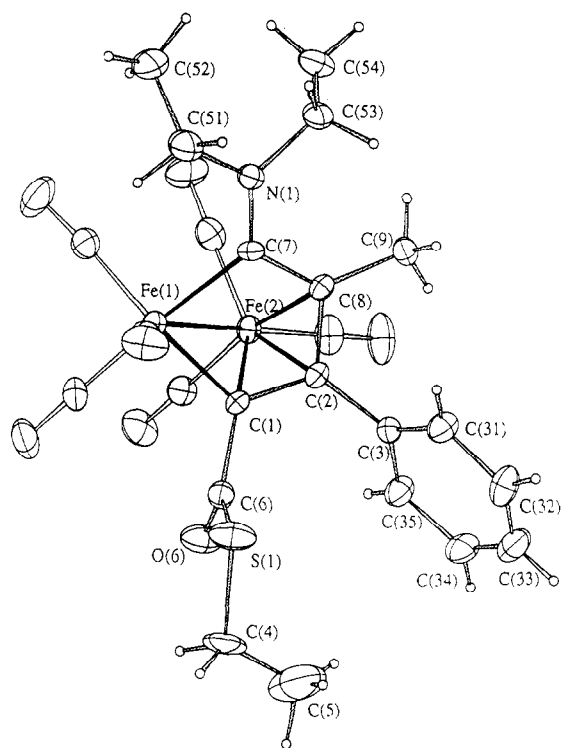
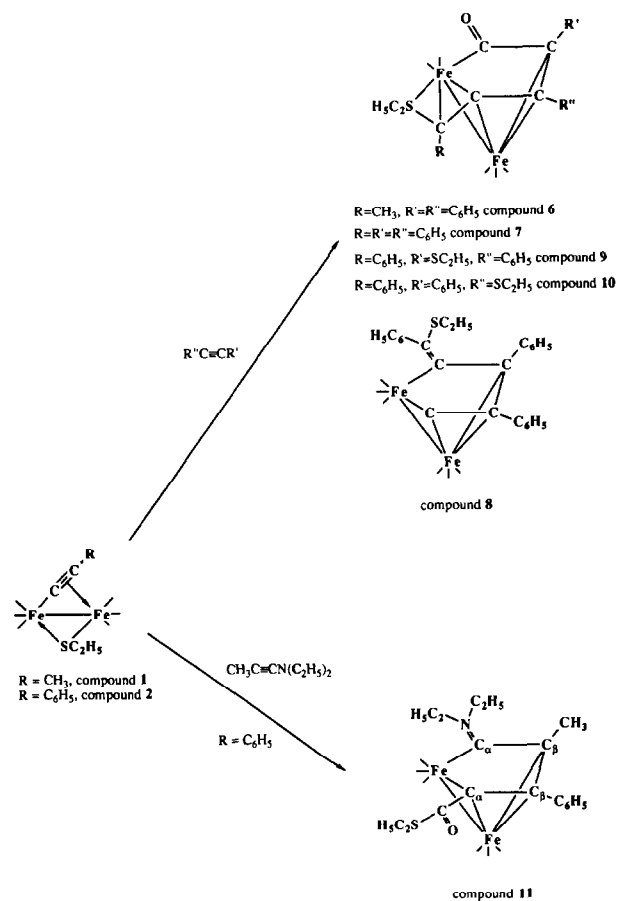


Fig. 6. Molecular structure of compound **11** [ $\text{Fe}_2(\text{CO})_6(\mu\text{-Cl} = \text{N}(\text{C}_2\text{H}_5)_2)\text{C}(\text{CH}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}(\text{O})\text{SC}_2\text{H}_5)]$ ].



Scheme 8.



SC<sub>2</sub>H<sub>5</sub> is concerned, the two hydrogen atoms of CH<sub>2</sub> are not equivalent. They form an AB system coupled with the three hydrogen atoms of CH<sub>3</sub>. This results in four unresolved multiplets for two diastereotopic H of CH<sub>2</sub>CH<sub>3</sub>, two multiplets of higher intensity, centred at 1.40 and 1.90 ppm, corresponding to the triplet at 0.56 ppm, two centred at 2.85 and 3.70 ppm corresponding to the triplet at 1.09 ppm, two multiplets of lower intensity, centred at 1.60 and 2.10 ppm corresponding to the triplet at 0.61 ppm, and finally two centred at 2.10 and 2.45 ppm corresponding to the triplet at 0.66 ppm. This strongly suggests a mixture of two isomers each isomer containing two non-equivalent SC<sub>2</sub>H<sub>5</sub> groups, which could not be separated by chromatography.

After crystallization from a hexane solution, careful examination under the microscope revealed two kinds of crystals which were separated mechanically. They were studied by X-ray diffraction (Table 5). They have molecular structures similar to that of compounds **6** and **7**. The incoming thioalkyne is coupled at one end to the C<sub>α</sub> of the acetylide CCC<sub>6</sub>H<sub>5</sub>. A CO has inserted into the other end of the incoming thioalkyne and iron. Since the reacted alkyne C<sub>6</sub>H<sub>5</sub>C≡CSC<sub>2</sub>H<sub>5</sub> is unsymmetrical, two arrangements are possible. They lead to the major compound **9** [Fe<sub>2</sub>(CO)<sub>5</sub>{μ-S(C<sub>2</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)CC(C<sub>6</sub>H<sub>5</sub>)-C(SC<sub>2</sub>H<sub>5</sub>)C(O)}], and to the minor compound **10** [Fe<sub>2</sub>(CO)<sub>5</sub>{μ-S(C<sub>2</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)CC(SC<sub>2</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)C(O)}]. **9** and **10** correspond to the two species observed by <sup>1</sup>H NMR spectroscopy, 80% for compound **9**, and 20% for compound **10** from peak intensities (Scheme 7).

Since these two compounds **9** and **10** are structurally similar to **6**, crystallographic details are not included here but they have been deposited.

### 3.2.3. Reaction of CH<sub>3</sub>-C≡C-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>

The aminoalkyne CH<sub>3</sub>-C≡C-N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> reacts with [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-SC<sub>2</sub>H<sub>5</sub>)(μ-CCC<sub>6</sub>H<sub>5</sub>)]. The <sup>13</sup>C NMR spectrum of CH<sub>3</sub>C<sub>β</sub>≡C<sub>α</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> shows δ(C<sub>α</sub>) + δ(C<sub>β</sub>) = 140.8 ppm and δ(C<sub>α</sub>) - δ(C<sub>β</sub>) = 26.04 ppm. This suggested that C<sub>β</sub> is more nucleophilic than C<sub>α</sub> and was confirmed by organic reactivity [17]. It would then be expected that the nucleophilic carbon C<sub>β</sub> of the aminoalkyne would be directed to the electrophilic carbon atom C<sub>α</sub> of the acetylide of compound **2**.

After reaction and separation using a precoated silica plate, compound **11** was characterized. The peak [M + H]<sup>+</sup> (m/z) = 582 for the mass spectrum is 28 units higher than the 553 expected for a compound resulting from the addition of one molecule of aminoalkyne to compound **2**.

The X-ray structure determination shows the formula to be [Fe<sub>2</sub>(CO)<sub>6</sub>{C[C(O)(SC<sub>2</sub>H<sub>5</sub>)]C(C<sub>6</sub>H<sub>5</sub>)C(CH<sub>3</sub>)C[N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]}] (Fig. 6, Tables 3, 12, and 13).

The structure is based on a ferracyclopentadienyl fragment Fe(1)C(1)C(2)C(8)C(7) which is ligated to a

second iron Fe(2) by an iron–iron bond and by three adjacent C(1)C(2)C(8) carbon atoms, forming an allyl fragment. The C(1)–C(2) and C(2)–C(8) distances are 1.404(9) and 1.447(9) Å, with an angle of 112.8(6)°. Corresponding iron-carbon distances are Fe(2)–C(1) = 2.038(7), Fe(2)–C(2) = 2.094(6), Fe(2)–C(8) = 2.133(7) Å. The Fe(2) iron atom is not connected to the last C(7) atom of the ferracyclopentadiene ring because the separation is 2.573(7) Å. Correspondingly, the nitrogen atom has donated its lone pair to C(7) and the C(7)–N distance is 1.333(9) Å.

There are three other features distinguishing this structure from the preceding ones (Scheme 8). First, there is no CO inserted into the iron-carbon framework, as in compounds **6**, **7**, **9**, and **10**. Secondly, there is one CO inserted in a lateral chain, between sulfur and the carbon atom C(1) to which it was bound in the starting thioalkyne. Thus the side chain now is C(=O)SC<sub>2</sub>H<sub>5</sub>. The sulfur is not ligated to iron. The third feature is

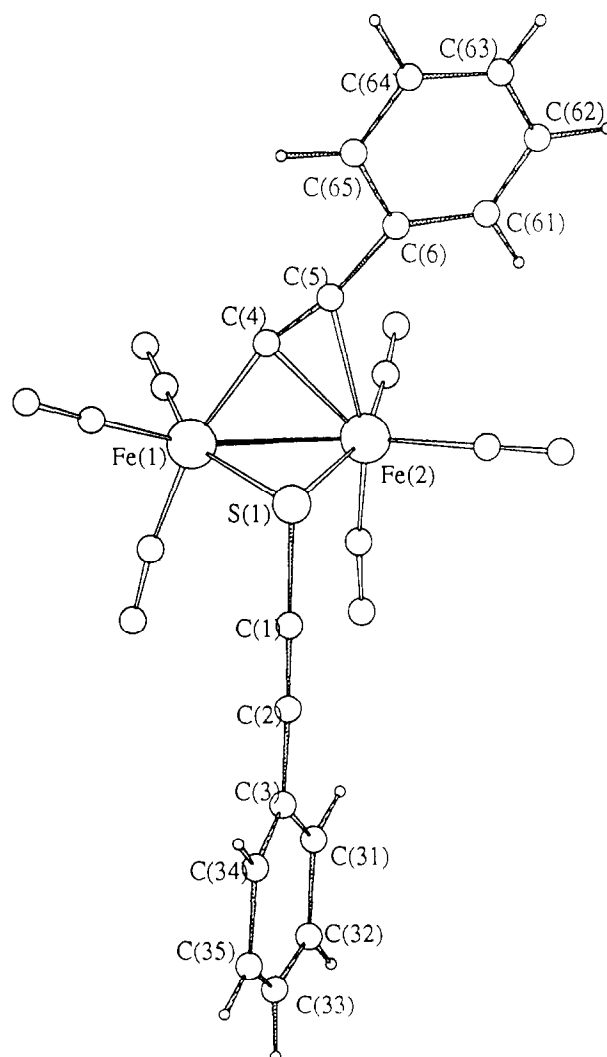


Fig. 7. Molecular structure of compound **12** [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-SCCC<sub>6</sub>H<sub>5</sub>)(μ-CCC<sub>6</sub>H<sub>5</sub>)].

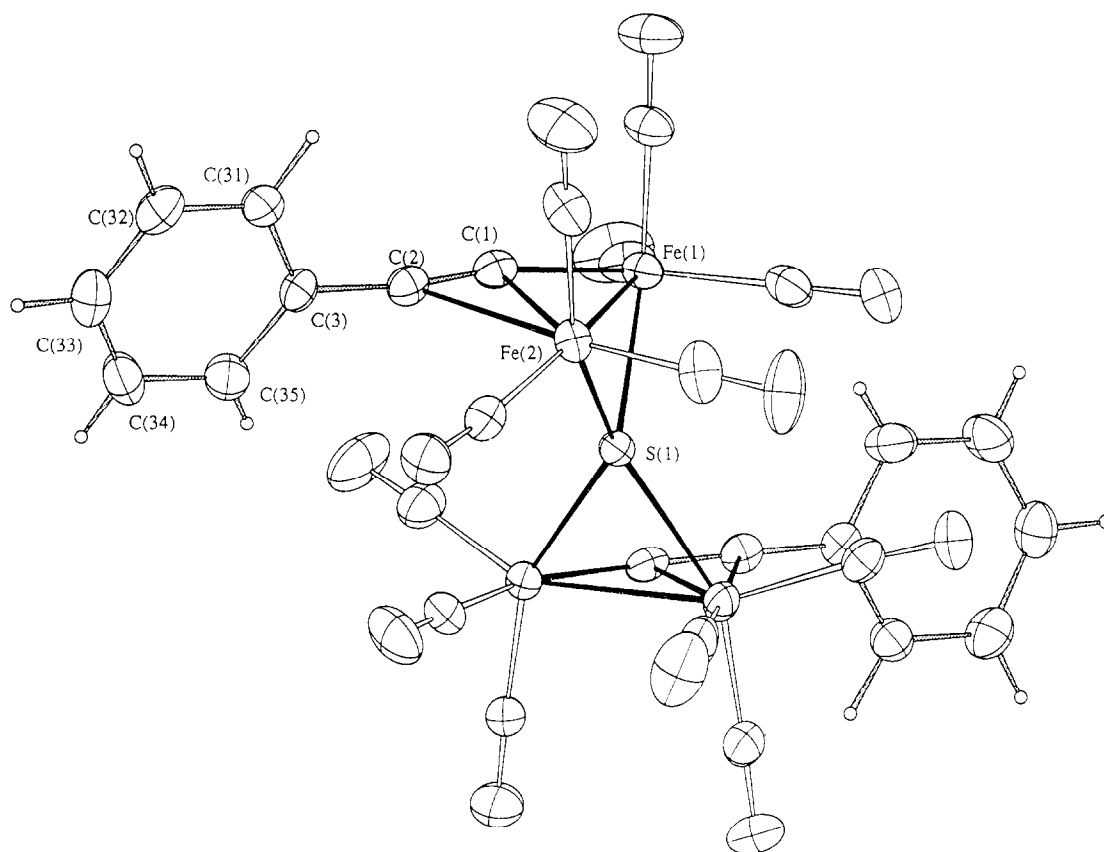
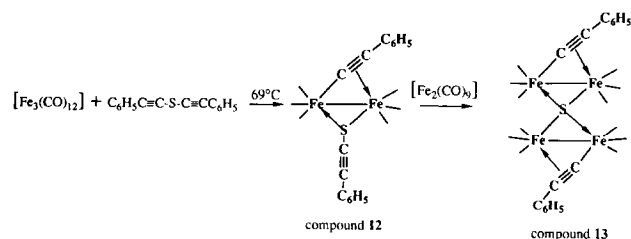


Fig. 8. Molecular structure of compound **13**  $[\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-S})(\mu\text{-CCC}_6\text{H}_5)_2]$ .

related to the link between the incoming aminoalkyne and the other alkyne, now an ethyl phenylethynylthio-carboxylate. The methyl bearing the more nucleophilic carbon C(8) of the aminoalkyne attacked at the  $C_\beta$  phenyl-bearing carbon C(2) of the acetylide of compound **2**, in contrast to the expected behaviour, described in Section 3.1.

This inverted type of attack on the less electrophilic  $C_\beta$  carbon atom has been observed by Seyferth et al. [5] as well as by Carty and co-workers [2] with a  $\text{P}(\text{C}_6\text{H}_5)_2$  bridge. Since in **11** a carbonyl has inserted between  $C_\alpha$  and  $\text{SC}_2\text{H}_5$ , one might consider that the first step of the reaction was CO insertion before the aminoalkyne attack, and that this inverted the polarity of the acetylide.

Electron book-keeping suggests 9 electron pairs. With 6 occupied vertices, this compound corresponds to an *arachno* structure.



Scheme 9.

### 3.3. Reaction of $\text{S}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$

The reaction of  $\text{RC}\equiv\text{CSC}_2\text{H}_5$  with  $[\text{Fe}_2(\text{CO})_9]$  or  $[\text{Fe}_2(\text{CO})_{12}]$  is an oxidative addition. The cleavage of the C–S bond, yielding  $\text{RC}\equiv\text{C}$  and  $\text{SC}_2\text{H}_5$  ligands is easy. It then seemed interesting to look at  $\text{RC}\equiv\text{C}-\text{S}-\text{C}\equiv\text{CR}$ , in order to make a double oxidative addition.

The compound with  $\text{R} = \text{C}_6\text{H}_5$  has been prepared by reaction of  $\text{C}_6\text{H}_5\text{C}\equiv\text{CLi}$  with  $\text{SCL}_2$  in THF (yield 70%) [8].  $\text{S}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$  was then allowed to react with  $[\text{Fe}_3(\text{CO})_{12}]$  in refluxing hexane.  $[\text{Fe}_2(\text{CO})_6(\mu\text{-S}(\text{CCCC}_6\text{H}_5))(\mu\text{-CCC}_6\text{H}_5)]$  (compound **12**) was separated by chromatography. X-ray diffraction showed that the structural type is identical to that of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-SC}_2\text{H}_5)(\mu\text{-CCR})]$  (Fig. 7) (compounds **1** and **2**) with  $\text{SC}_2\text{H}_5$  replaced by  $\text{SC}\equiv\text{CC}_6\text{H}_5$  (Tables 3, 14, 15).

The bridge  $\text{SC}\equiv\text{CC}_6\text{H}_5$  has a free triple bond which is available for further chemistry. Therefore, an excess of iron carbonyl was allowed to react with **12**. A second oxidative addition occurred and the tetranuclear compound **13**  $[\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-S})(\mu\text{-CCC}_6\text{H}_5)_2]$  was obtained (Fig. 8, Scheme 9). The four iron atoms belong to two dinuclear entities, which build a tetrahedron around a sulfur atom involving four Fe–S bonds. On each Fe–Fe group there is a  $\sigma, \pi$ -phenylacetylide, making the molecule chiral (Tables 3, 16, 17).

This structure is quite similar to that of  $[\text{Fe}_4(\text{CO})_{12}]$

( $\mu_4$ -S)( $\mu$ -SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>][18]. When it was crystallized, two kinds of non-centrosymmetrical crystals were found, with space groups  $P2_12_12_1$  ( $a = 17.003$ ,  $b = 12.934$ ,  $c = 11.874$  Å) and  $P2_1$  ( $a = 9.457$ ,  $b = 15.383$ ,  $c = 8.932$  Å,  $\beta = 94.31^\circ$ ), respectively. Although the absolute configurations, determined using anomalous scattering of iron, were not perfectly clear due to the very small size of one crystal type, a spontaneous separation of enantiomers has occurred. The spontaneous enantiomeric separation did not happen for **13** because both enantiomers cocrystallize, and are related by the inversion centre. Each molecule lies on a crystallographic twofold axis.

Examples of such structures with a tetrahedral sulfur have been described. For instance, Adams and Wang [19] studied an osmium compound [Os<sub>6</sub>(CO)<sub>20</sub>( $\mu_4$ -S)( $\mu_3$ -S)], and Raubenheimer et al. [20] studied a hexanuclear iron complex with a diethyldithiocarbamate, [Fe<sub>6</sub>(CO)<sub>18</sub>( $\mu_4$ -S)<sub>2</sub>{ $\mu_2$ -CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>].

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