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Reaction of unsymmetrical thioalkynes $RC{\equiv}CSC_2H_5$ ($R = CH_3$ or C_6H_5) with iron carbonyl: cluster nuclearity has been increased from two to five iron atoms by utilizing C–S cleavage

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Abstract

By reaction of the unsymmetrical alkylthioalkynes $RC{\equiv}C{-}SC_2H_5$ ($R = CH_3$ or C_6H_5) with iron carbonyl, the classical dinuclear compound $[Fe_2(CO)_6L]$, where L results from the coupling of two alkynes, is obtained. This compound, which contains a ferrole moiety, has a characteristic feature: a carbon–sulfur bond can be cleaved easily. This may be either the bond linking sulfur to the ferrole part if SC_2H_5 is at the α position with respect to iron, or the bond linking sulfur to the ethyl group if SC_2H_5 is at the β position with respect to iron. Utilizing these cleavages, trinuclear, tetranuclear, and pentanuclear iron clusters were prepared. Fifteen compounds corresponding to seven types of structure are described, using NMR and X-ray diffraction. Trinuclear compounds are based on an open triangle of iron atoms. Tetranuclear compounds have an iron skeleton which is either T-shaped, or planar, or made of two separate dinuclear units. The pentanuclear skeleton is composed of a triangle and a quadrangle sharing an edge.

Key words: Iron; Clusters; X-ray diffraction; Thioalkynes

1. Introduction

The classical reaction of an alkyne with iron carbonyl yields a dinuclear species containing a ferrole fragment. This structure, described by Mills and Hock in 1958 [1], has been found many times with various symmetrical alkynes, including 2,5-dithiahex-3-yne [2]. It has also been found for unsymmetrical alkynes, such as dimethylaminoalkyne [3]. This last compound contains a five-membered cycloferrapentadiene ring which is ligated to a second iron atom, σ-bonded by its iron atom and π-bonded by its butadiene part. However, building up a cyclopentadiene ring with an unsymmetrical alkyne should give three isomers, depending on the way two alkynes $RC{\equiv}CX$ couple. They will be called head-to-head (for RCCR coupling) head-to-tail (for XCCR coupling) and tail-to-tail (for XCCX coupling). During the reaction of aminoalkynes $RC{\equiv}CNR'_2$ with iron carbonyl [3a], only tail-to-tail coupling was observed for the dinuclear compound containing ferrole, and the nitrogen atoms are rather unreactive because their lone-pair electrons are coupled with the π-electron density of the ring. The two other couplings, head-to-tail and head-to-head, have been observed only in trinuclear iron compounds [4]. In the case of rhenium, Adams *et al.* [3b] observed the three possible couplings of two ynamines.

For alkylthioalkynes $RC{\equiv}CSR'$, the subject of this paper, three couplings have been found for dinuclear iron compounds; with ethylthiophenylethyne, the tail-to-tail compound was identified by X-ray diffraction. It then appeared that the carbon–sulfur bond may be cleaved by reaction of an excess of iron carbonyl. Cleavage occurs either at the bond linking sulfur to the metallacyclopentadiene fragment, or at the bond between sulfur and the R′ group.

Starting with these dinuclear complexes, and utilizing these C–S cleavages, the nuclearity of the clusters has been increased from two to five iron atoms.

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2. Experimental details

2.1. General procedure

The reactions of 1-ethylthioprop-1-yne or ethylthio (phenyl)ethyne $RC{\equiv}CSC_2H_5$ ($R = CH_3$ or C_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. The alkynes were prepared in the laboratory following previously reported methods of Pourcelot and Cadiot [5] for $R = CH_3$ and Makosza and Fedorynski [6] for $R = C_6H_5$. Nonacarbonyldiiron was synthesized from pentacarbonyliron [7]; dodecacarbonyltriiron was used as purchased from 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.

TABLE 1. Crystallographic data collection and structure refinements for compounds **5**, **14** and **15**

	5	**14**	**15**
Crystal color	brown	brown	orange
Mol. weight, g	604	826	884
Crystal size, mm	0.4 × 0.3 × 0.3	0.2 × 0.18 × 0.16	
ρ calc, g cm^{-3}	1.499	1.734	1.602
μ (Mo–Kα), cm^{-1}	12.698	20.083	17.572
Cryst. system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/a$
a, Å	10.200(2)	16.854(1)	36.613(7)
b, Å	11.317(1)	18.315(6)	9.340(1)
c, Å	14.119(8)	10.277(3)	10.474(4)
α, deg.	65.85(5)		
β, deg.	74.61(1)	99.92(2)	90.92(2)
γ, deg.	64.91(1)		
V, Å^3	1338.5	3125	3581
$F(000)$	616	1640	1776
Z	2	4	4
Diffractometer		Philips PW 1100	
Radiation (λ, Å)		Mo–Kα (0.71069)	
Scan type		θ–2θ	
Scan range, deg.	$1.1 + 0.345 \text{ tg } \theta$	$0.9 + 0.345 \text{ tg } \theta$	$0.55 + 0.345 \text{ tg } \theta$
2θ range, deg.	4–40	2–40	2–50
Reflections measured	$hkl, \bar{h}\bar{k}l, \bar{h}kl, h\bar{k}l$	$hkl, \bar{h}kl$	$hkl, \bar{h}kl$
No. of reflections collected	2626	3306	7137
No. of independent reflections merged	2467	2882	6225
No. of reflections kept for refinement	1501 ($I > 3\sigma(I)$)	932 ($I > 3\sigma(I)$)	1792 ($I > 3\sigma(I)$)
Computing programs		SHELXS and CRYSTALS [a]	
Atom form factors		[b]	
Minimized function		$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$ $[1 - (\Delta F/6\sigma F)^2]^2$	
Weighting scheme	$w = 1$	0.770, 0.0134, 0.557	$w = 1$
Secondary extinction param	–	22.3×10^{-5}	3.3×10^{-5}
Absorption corrections		DIFABS [c]	
Av. shift/esd (last cycle)	0.18	0.01	0.009
Nref./Nvar. par.	4.6	5.01	8.9
Max. height in final difference Fourier synthesis e Å^{-3}	0.3	0.8	0.65
R	0.0359	0.08	0.067
Rw	0.0396	0.07	0.076

[a] J.R. Carruthers and D.J. Watkin, CRYSTALS *An Advanced Crystallographic Computer Program*, University of Oxford, 1986.

[b] *International Table for X-ray Crystallography*, Kynoch, Birmingham, England, 1974, Vol IV.

[c] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, (1983) 3156.

IR spectra were recorded with a Perkin-Elmer 457 spectrometer using either KBr pellets or a heptane solution. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer, and chemical shifts were referenced to $Si(CH_3)_4$. Mass spectra were recorded with a Nermag R1010, usually by chemical ionisation with NH_3.

2.2. *X-ray structure analysis*

All measurements were carried out at room temperature using a Philips PW 1100 diffractometer, except for compound **9** for which an Enraf Nonius CAD4 diffractometer was used. Details of the crystallographic data collection and structure determinations are given in Tables 1, 2 and 3. Suitable crystals, sometimes very

TABLE 2. Crystallographic data collection and structure refinements for compounds **6**, **10**, **12** and **13**

	6	**10**	**12**	**13**
Cryst. color	dark red	red	brown	brown
Mol. weight, g	592	704	788	704
Cryst. size, mm	0.4 × 0.06 × 0.2	0.5 × 0.04 × 0.18		0.1 × 0.26 × 0.16
ρ calc, g cm^{-3}	1.654	1.68	1.832	1.771
μ (Mo–Kα), cm^{-1}	20.696	22.85	27.28	24.112
Cryst. system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	16.505(3)	9.052(8)	16.734(13)	8.827(3)
b, Å	15.547(6)	12.488(4)	14.856(6)	9.291(3)
c, Å	9.143(3)	24.197(8)	11.303(4)	16.415(5)
α, deg.		90.51(4)		102.89(1)
β, deg.	97.68(1)	95.93(3)	95.28(4)	90.40(1)
γ, deg.		90.18(3)		100.38(2)
V, Å^3	2325	2720.5	2798	1291
$F(000)$	1192	1408	1568	704
Z	4	4	4	2
Diffractometer			Philips PW 1100	
Radiation (λ, Å)			Mo–Kα (0.71069)	
Scan type			θ–2θ	
Scan range, deg.	0.8 + 0.345 tg θ	0.9 + 0.345 tg θ	1.1 + 0.345 tg θ	1.2 + 0.345 tg θ
2θ range, deg.	4–50	4–46	4–40	4–40
Reflections measured	hkl, $\bar{h}kl$	hkl, $\bar{h}\bar{k}l$, $\bar{h}kl$, $h\bar{k}l$	hkl, $\bar{h}kl$	hkl, $\bar{h}\bar{k}l$, $\bar{h}kl$, $h\bar{k}l$
No. of reflections collected	4908	7833	3201	2517
No. of independent reflections merged	4024	7366	2527	2382
No. of reflections kept for refinement	1005 ($I > 3\sigma(I)$)	2488 ($I > 3\sigma(I)$)	784 ($I > 3\sigma(I)$)	957 ($I > 3\sigma(I)$)
Computing programs			SHELXS and CRYSTALS [a]	
Atom form factors			[b]	
Minimized function			$\Sigma w(\lvert F_0 \rvert - \lvert F_c \rvert)^2$	
Weighting scheme			$w = 1$	
Secondary extinction param	–	2.8×10^{-5}	–	–
Absorption corrections			DIFABS [c]	
Av. shift/esd (last cycle)	0.02	0.07	0.017	0.05
Nref./Nvar. par.	8.04	8.5	5	6.6
Max. height in final difference Fourier synthesis e Å^{-3}	0.87	0.72	0.63	1.6
R	0.09	0.063	0.063	0.121
Rw	0.10	0.069	0.075	0.117

[a] J.R. Carruthers and D.J. Watkin, *CRYSTALS An Advanced Crystallographic Computer Program*, University of Oxford, 1986.

[b] *International Table for X-ray Crystallography*, Kynoch, Birmingham, England, 1974, Vol IV.

[c] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, (1983) 3156.

tiny, were chosen and placed in Lindeman glass capillary tubes. Cell dimensions were determined from 25 selected reflections. 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) [8] and successive Fourier maps were used to locate the positions of all atoms. Full-matrix least-squares refinement of atomic parameters and isotropic (compounds **6**, **8**, **10**, **12**, **13**, **14**, and **15**) or anisotropic (compounds **5**, **9**, and **11**) thermal parameters were carried out using CRYSTALS programs [9] and a DEC Microvax II. The size of the crystal and the number of recorded reflections for compounds **6**, **8**, **10**, **12–14**, and **15** did not allow the refinement of anisotropic thermal parameters. The scattering 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

TABLE 3. Crystallographic data collection and structure refinements for compounds **8**, **9** and **11**

	8	**9**	**11**
Cryst. color	dark red	dark red	dark red
Mol. weight, g	716	716	828
Cryst. size, mm	0.26 × 0.4 × 0.18	0.06 × 0.26 × 0.34	0.5 × 0.3 × 0.2
ρ calc, g cm^{-3}	1.543	1.607	1.651
μ (Mo–Kα), cm^{-1}	16.114	16.327	18.804
Cryst. system	orthorhombic	monoclinic	monoclinic
Space group	P cab	$P2_1/n$	$P2_1$
a, Å	17.535(3)	20.106(2)	15.99(1)
b, Å	27.549(2)	14.399(2)	8.799(2)
c, Å	12.402(2)	10.273(1)	11.859(2)
α, deg.			
β, deg.		95.61(1)	93.29(1)
γ, deg.			
V, Å^3	5991	2958	1666
F(000)	2896	1448	832
Z	8	4	2
Diffractometer	Philips PW 1100	CAD4 Enraf-Nonius	Philips PW 1100
Radiation (λ, Å)		Mo–Kα (0.71069)	
Scan type		θ–2θ	
Scan range, deg.	1 + 0.345 tg θ	0.8 + 0.345 tg θ	1.2 + 0.345 tg θ
2θ range, deg.	2–50	2–40	4–50
Reflections measured	hkl	hkl, $\bar{h}kl$	hkl, $\bar{h}kl$
No. of reflections collected	5805	5551	3317
No. of independent reflections merged	5019	5185	3151
No. of reflections kept for refinement	945 ($I > 3\sigma(I)$)	1954 ($I > 3\sigma(I)$)	2228 ($I > 3\sigma(I)$)
Computing programs		SHELXS and CRYSTALS [a]	
Atom form factors		[b]	
Minimized function		$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$	
Weighting scheme		$w = 1$	
Secondary extinction param	–	2.03×10^{-5}	2.35×10^{-5}
Absorption corrections		DIFABS [c]	
Av. shift/esd (last cycle)	0.009	0.26	0.05
Nref./Nvar. par.	5.7	5.4	5.35
Max. height in final difference Fourier synthesis e Å^{-3}	0.64	0.39	0.42
R	0.073	0.036	0.04
Rw	0.081	0.039	0.044

[a] J.R. Carruthers and D.J. Watkin, *CRYSTALS An Advanced Crystallographic Computer Program*, University of Oxford, 1986.

[b] *International Table for X-ray Crystallography*, Kynoch, Birmingham, England, 1974, Vol IV.

[c] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, (1983) 3156.

TABLE 4. Fractional parameters for compound **5**

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	0.3451(1)	0.3284(1)	0.1727(1)	0.0354
Fe(2)	0.2510(1)	0.2509(1)	0.3613(1)	0.0348
S(1)	0.0466(3)	0.0761(3)	0.3295(2)	0.0468
S(2)	−0.1234(3)	0.4181(3)	0.3337(2)	0.0435
C(1)	−0.080(1)	0.238(1)	0.142(1)	0.0828
C(2)	−0.113(1)	0.169(1)	0.2563(9)	0.0627
C(3)	0.1295(9)	0.2021(9)	0.2826(6)	0.0324
C(4)	0.279(1)	0.1694(9)	0.2461(6)	0.0336
C(5)	0.371(1)	0.030(1)	0.2356(8)	0.0390
C(6)	−0.301(1)	0.354(1)	0.5136(9)	0.0816
C(7)	−0.150(1)	0.299(1)	0.4644(8)	0.0603
C(8)	0.0586(9)	0.3437(9)	0.2830(6)	0.0327
C(9)	0.1528(9)	0.4222(9)	0.2381(6)	0.0285
C(10)	0.0894(9)	0.5730(9)	0.2175(7)	0.0321
C(51)	0.345(1)	−0.005(1)	0.1616(9)	0.0579
C(52)	0.436(1)	−0.132(1)	0.147(1)	0.0760
C(53)	0.545(1)	−0.222(1)	0.206(1)	0.0741
C(54)	0.573(1)	−0.190(1)	0.2786(9)	0.0635
C(55)	0.486(1)	−0.063(1)	0.2956(8)	0.0540
C(101)	−0.018(1)	0.657(1)	0.1519(8)	0.0460
C(102)	−0.070(1)	0.798(1)	0.1258(9)	0.0667
C(103)	−0.019(1)	0.859(1)	0.164(1)	0.0647
C(104)	0.088(1)	0.779(1)	0.232(1)	0.0698
C(105)	0.143(1)	0.635(1)	0.2564(7)	0.0489
C(11)	0.525(1)	0.223(1)	0.1363(7)	0.0478
C(12)	0.401(1)	0.475(1)	0.1285(7)	0.0490
C(13)	0.271(1)	0.369(1)	0.0597(8)	0.0469
C(21)	0.290(1)	0.089(1)	0.4634(8)	0.0568
C(22)	0.175(1)	0.336(1)	0.4564(8)	0.0509
C(23)	0.418(1)	0.277(1)	0.3387(8)	0.0530
O(11)	0.6418(8)	0.1561(8)	0.1107(6)	0.0709
O(12)	0.4421(8)	0.5642(8)	0.0989(6)	0.0691
O(13)	0.2205(9)	0.3917(8)	−0.0120(6)	0.0732
O(21)	0.313(1)	−0.0128(9)	0.5309(6)	0.0884
O(22)	0.131(1)	0.3856(9)	0.5204(7)	0.0838
O(23)	0.5205(8)	0.2915(8)	0.3479(6)	0.0676

TABLE 5. Selected distances (Å) and angles (°) for compound **5**

Fe(1)–Fe(2): 2.496(2) Fe(1)–C(23): 2.41(1) Fe(2)–C(23): 1.78(1)
O(23)–C(23)–Fe(2): 164°3(9)

isotropic thermal parameter. Fractional parameters, selected distances and bond angles are given in Tables 4–23. Supplementary material provides atomic and thermal parameters for all atoms, structure factors, and a complete list of bond distances and angles; it is available from the authors.

TABLE 6. Fractional parameters for compound **6**

Atom	*x*	*y*	*z*	U_{iso}
Fe(1)	0.0429(3)	0.3158(3)	0.1516(5)	0.038(1)
Fe(2)	0.2008(3)	0.3022(3)	0.2071(5)	0.044(1)
Fe(3)	0.0162(3)	0.1564(3)	0.1914(5)	0.036(1)
S(1)	−0.1376(6)	0.2889(6)	0.265(1)	0.053(3)
S(2)	0.1273(5)	0.2855(6)	−0.020(1)	0.045(3)
C(1)	−0.029(2)	0.261(2)	0.282(3)	0.040(9)
C(2)	0.005(2)	0.211(2)	0.400(3)	0.036(9)
C(3)	−0.039(2)	0.176(2)	0.525(4)	0.06(1)
C(4)	−0.132(2)	0.395(2)	0.363(4)	0.06(1)
C(5)	−0.223(2)	0.431(2)	0.346(4)	0.06(1)
C(6)	0.114(2)	0.237(2)	0.274(3)	0.031(9)
C(7)	0.089(2)	0.192(2)	0.397(4)	0.05(1)
C(8)	0.145(2)	0.139(2)	0.505(4)	0.05(1)
C(9)	0.145(2)	0.376(2)	−0.147(4)	0.05(1)
C(10)	0.082(2)	0.367(2)	−0.284(4)	0.07(1)
C(11)	0.066(2)	0.406(2)	0.248(3)	0.035(9)
C(12)	−0.036(2)	0.374(2)	0.033(4)	0.06(1)
C(21)	0.231(2)	0.328(2)	0.397(4)	0.05(1)
C(22)	0.273(2)	0.221(3)	0.204(4)	0.06(1)
C(23)	0.252(2)	0.392(2)	0.145(4)	0.05(1)
C(31)	0.084(2)	0.085(3)	0.132(4)	0.07(1)
C(32)	−0.035(2)	0.180(2)	0.015(4)	0.05(1)
C(33)	−0.049(2)	0.074(3)	0.223(4)	0.07(1)
O(11)	0.077(1)	0.467(2)	0.327(2)	0.059(7)
O(12)	−0.082(2)	0.415(2)	−0.034(3)	0.081(9)
O(21)	0.251(2)	0.347(2)	0.515(3)	0.088(8)
O(22)	0.316(2)	0.161(2)	0.190(3)	0.096(9)
O(23)	0.289(2)	0.450(2)	0.110(3)	0.090(9)
O(31)	0.133(2)	0.036(2)	0.095(3)	0.10(1)
O(32)	−0.069(1)	0.184(2)	−0.109(3)	0.067(7)
O(33)	−0.094(2)	0.019(2)	0.256(4)	0.12(1)

2.3. Syntheses

Only syntheses of compounds of interest for this paper are described here. These reactions also yielded compounds of other structural types; they are described elsewhere [10].

2.3.1. Dinuclear complexes

2.3.1.1. Compounds 1 and 3 (R = CH_3; head-to-head and head-to-tail). A solution of $[Fe_2(CO)_9]$ (0.9 g, 2.6 mmol), $CH_3C{\equiv}CSC_2H_5$ (0.2 g, 2 mmol), and $(CH_3)_3NO$

TABLE 7. Selected distances (Å) and angles (°) for compound **6**

Fe(1)–Fe(2): 2.589(6) Fe(1)–Fe(3): 2.548(7) S(2)–Fe(1): 2.28(1)
S(2)–Fe(2): 2.27(1) C(6)–Fe(1): 1.94(3) C(6)–Fe(2): 1.92(3)
C(6)–Fe(3): 2.09(3)
Fe(3)–Fe(1)–Fe(2): 94.6(2) Fe(1)–S(2)–Fe(2): 69.4(3)
Fe(1)–C(6)–Fe(2): 84.3(12) Fe(3)–C(6)–Fe(1): 78.2(10)
Fe(3)–C(6)–Fe(2): 140.7(16)

TABLE 8. Fractional parameters for compound **8**

Atom	x	y	z	U_{iso}
Fe(1)	0.0201(2)	0.4331(2)	0.2121(4)	0.040(1)
Fe(2)	0.1678(2)	0.4290(2)	0.2096(5)	0.041(1)
Fe(3)	0.0069(3)	0.3829(2)	0.3842(4)	0.039(1)
S(1)	−0.1443(5)	0.3741(4)	0.2116(9)	0.064(3)
S(2)	0.0998(5)	0.4889(3)	0.2880(9)	0.054(2)
C(1)	−0.232(3)	0.387(2)	0.030(4)	0.13(2)
C(2)	−0.150(2)	0.381(2)	0.072(3)	0.08(1)
C(3)	−0.043(1)	0.375(1)	0.234(2)	0.030(8)
C(4)	−0.003(2)	0.329(1)	0.260(2)	0.038(8)
C(7)	0.091(2)	0.390(1)	0.263(2)	0.033(8)
C(11)	0.034(2)	0.427(2)	0.076(3)	0.06(1)
C(12)	−0.055(2)	0.473(2)	0.189(4)	0.08(1)
C(8)	0.075(1)	0.338(1)	0.285(3)	0.029(8)
C(21)	0.212(2)	0.471(2)	0.120(4)	0.09(1)
C(22)	0.236(2)	0.425(2)	0.303(4)	0.08(1)
C(23)	0.196(2)	0.378(2)	0.131(3)	0.07(1)
C(6)	0.110(2)	0.547(1)	0.223(3)	0.07(1)
C(5)	0.060(3)	0.583(2)	0.257(4)	0.14(2)
C(31)	0.074(2)	0.397(1)	0.485(3)	0.05(1)
C(32)	−0.051(2)	0.349(1)	0.468(3)	0.05(1)
C(33)	−0.045(2)	0.433(2)	0.403(3)	0.07(1)
C(41)	−0.042(2)	0.281(1)	0.262(3)	0.036(9)
C(42)	−0.028(2)	0.247(2)	0.348(3)	0.06(1)
C(43)	−0.059(2)	0.201(2)	0.356(3)	0.07(1)
C(44)	−0.093(3)	0.185(2)	0.260(4)	0.09(1)
C(45)	−0.106(2)	0.213(2)	0.174(3)	0.08(1)
C(46)	−0.077(2)	0.260(1)	0.173(3)	0.06(1)
C(81)	0.132(1)	0.2988(9)	0.304(2)	0.011(6)
C(82)	0.183(1)	0.303(1)	0.387(3)	0.030(8)
C(83)	0.240(2)	0.266(1)	0.405(3)	0.05(1)
C(84)	0.239(2)	0.226(1)	0.335(3)	0.05(1)
C(85)	0.191(2)	0.224(1)	0.245(3)	0.06(1)
C(86)	0.134(2)	0.259(1)	0.230(3)	0.05(1)
O(11)	0.045(2)	0.417(1)	−0.015(3)	0.10(1)
O(12)	−0.105(2)	0.504(1)	0.181(3)	0.12(1)
O(21)	0.240(2)	0.495(1)	0.053(3)	0.093(9)
O(22)	0.282(1)	0.417(1)	0.373(2)	0.079(9)
O(23)	0.217(1)	0.346(1)	0.083(2)	0.09(1)
O(31)	0.119(1)	0.4084(9)	0.549(2)	0.074(9)
O(32)	−0.092(2)	0.328(1)	0.528(2)	0.091(9)
O(33)	−0.082(2)	0.468(1)	0.430(2)	0.089(9)

TABLE 10. Fractional parameters for compound **9**

Atom	x	y	z	U_{eq}
Fe(1)	0.70843(6)	0.68395(9)	0.1666(1)	0.0299
Fe(2)	0.58773(6)	0.64948(9)	0.2165(1)	0.0339
Fe(3)	0.74713(6)	0.74937(9)	0.3905(1)	0.0309
S(1)	0.8396(1)	0.5558(2)	0.5122(2)	0.0395
S(2)	0.6214(1)	0.7857(2)	0.1416(2)	0.0359
C(1)	0.8812(7)	0.569(1)	0.769(1)	0.1019
C(2)	0.8226(6)	0.5868(9)	0.682(1)	0.0573
C(3)	0.7742(4)	0.6055(6)	0.4072(8)	0.0264
C(4)	0.7870(4)	0.6428(6)	0.2838(8)	0.0282
C(5)	0.5203(6)	0.8635(8)	−0.018(1)	0.0626
C(6)	0.5862(5)	0.8147(7)	−0.0226(9)	0.0450
C(7)	0.6688(4)	0.6585(6)	0.3253(8)	0.0292
C(8)	0.7060(4)	0.6158(6)	0.4346(8)	0.0246
C(11)	0.6963(5)	0.5760(7)	0.0872(9)	0.0421
C(12)	0.7493(5)	0.7256(7)	0.0299(9)	0.0399
C(21)	0.5360(5)	0.6245(7)	0.066(1)	0.0385
C(22)	0.5261(6)	0.6964(8)	0.310(1)	0.0568
C(23)	0.5815(5)	0.5325(8)	0.274(1)	0.0463
C(31)	0.6930(5)	0.8186(7)	0.478(1)	0.0466
C(32)	0.8223(5)	0.7826(7)	0.490(1)	0.0443
C(33)	0.7581(5)	0.8367(7)	0.2703(9)	0.0348
C(41)	0.8540(4)	0.6335(6)	0.2340(8)	0.0304
C(42)	0.8767(5)	0.5442(7)	0.2101(9)	0.0393
C(43)	0.9388(5)	0.5326(8)	0.156(1)	0.0453
C(44)	0.9516(5)	0.697(1)	0.149(1)	0.0548
C(45)	0.9740(5)	0.608(1)	0.122(1)	0.0529
C(46)	0.8910(5)	0.7095(7)	0.1990(9)	0.0477
C(81)	0.6739(4)	0.5763(7)	0.5450(8)	0.0324
C(82)	0.6294(5)	0.6269(7)	0.612(1)	0.0475
C(83)	0.5958(6)	0.5864(8)	0.707(1)	0.0547
C(84)	0.6063(5)	0.4960(9)	0.741(1)	0.0523
C(85)	0.6489(6)	0.4430(8)	0.674(1)	0.0555
C(86)	0.6833(5)	0.4837(7)	0.578(1)	0.0455
O(11)	0.6933(4)	0.5061(5)	0.0357(7)	0.0594
O(12)	0.7726(4)	0.7520(6)	−0.0603(7)	0.0713
O(21)	0.5030(4)	0.6057(5)	−0.0268(7)	0.0579
O(22)	0.4880(5)	0.7298(7)	0.3695(9)	0.0911
O(23)	0.5765(4)	0.4583(6)	0.3068(8)	0.0650
O(31)	0.6574(5)	0.8640(6)	0.5310(9)	0.0755
O(32)	0.8696(4)	0.8031(6)	0.5521(8)	0.0621
O(33)	0.7693(3)	0.9000(5)	0.2108(6)	0.0475

(0.2 g, 2.6 mmol) in a hexane-dichloromethane (40–20 ml) mixture was stirred at room temperature for 2.5 h. The resulting solution was concentrated under vacuum and the residue was chromatographed on silica gel. Compounds **1** and **3** were eluted together as the second yellow fraction with a 90–10 mixture of heptane-dichloromethane (yield: 3%).

TABLE 9. Selected distances (Å) and angles (°) for compound **8**

Fe(1)–Fe(2): 2.593(5)
Fe(1)–Fe(3): 2.554(7)
S(2)–Fe(1): 2.28(1)
S(2)–Fe(2): 2.25(1)
C(7)–Fe(1): 1.83(3)
C(7)–Fe(2): 1.85(3)
C(7)–Fe(3): 2.11(3)
Fe(3)–Fe(1)–Fe(2): 94.4(2)
Fe(1)–S(2)–Fe(2): 69.7(3)
Fe(1)–C(7)–Fe(2): 89.5(13)
Fe(3)–C(7)–Fe(1): 80.4(11)
Fe(3)–C(7)–Fe(2): 144.4(16)

2.3.1.2. Mixture of compounds 1 and 3. IR (heptane solution): ν_{CO} terminal: 2080, 2040, 2000, 1980 cm^{-1} and ν_{CO} semi-bridging: 1940 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + H]^+$ $(m/z) = 481$. No evidence of a tail-to-tail isomer.

2.3.1.3. Compounds 2, 4, and 5 ($R = C_6H_5$; head-to-head, head-to-tail and tail-to-tail). A solution of $[Fe_2(CO)_9]$ (1.6 g, 4.4 mmol), $C_6H_5C{\equiv}CSC_2H_5$ (0.55 g, 3.4 mmol) and $(CH_3)_3NO$ (0.34 g, 4.5 mmol) in a hexane (40 ml)-dichloromethane (20 ml) mixture was stirred at room temperature for 3 h. After the reaction, the solution was concentrated and the residue was chromatographed on silica gel. Compounds **2**, **4** and **5** were eluted together as the third yellow fraction with a 90–10 mixture of heptane-dichloromethane (yield: 4%).

2.3.1.4. Mixture of compounds 2, 4, and 5. IR (KBr pellet): ν_{CO} terminal: 2080, 2040, 2000, 1980 cm^{-1} and ν_{CO} semi-bridging: 1930 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + H]^+$ $(m/z) = 605$. Analysis Calc.: C, 51.65; H, 3.3. Found: C, 51.69; H, 3.1%.

2.3.1.5. Mixture of compounds 2 and 4. ^1H NMR (500 MHz, C_6D_6 at 7.16 ppm): t 0.51 ppm for CH_3CH_2S, unresolved multiplet centred at 1.9 ppm for two diastereotopic H of CH_3CH_2S; t 0.74 ppm for CH_3CH_2S; two unresolved multiplets centred at 2.25 and 2.4 ppm for two diastereotopic H of CH_3CH_2; multiplets between 6.9 and 7.4 ppm for C_6H_5.

2.3.1.6. Compound 5; tail-to-tail. Only brown crystals of compound **5** crystallized from this reaction solution. The crystal structure was determined by X-ray diffraction. The ^1H NMR spectrum of pure compound **5** was recorded using selected crystals.

^1H NMR (500 MHz, C_6D_6 at 7.28 ppm): t 1 ppm 6H for two CH_3CH_2S; two unresolved multiplets centred at 2.6 and 3.0 ppm 4H for two diastereotopic H of two CH_3CH_2S; multiplets between 7 and 7.5 ppm for $2C_6H_5$.

2.3.2. Trinuclear complexes

2.3.2.1. Compounds 6 and 7 ($R = CH_3$; head-to-head and head-to-tail). A solution of $[Fe_3(CO)_{12}]$ (0.9 g, 1.8 mmol) and $CH_3C{\equiv}CSC_2H_5$ (0.18 g, 1.8 mmol) in 50 ml refluxing hexane was stirred for 24 h, until the $[Fe_3(CO)_{12}]$ completely disappeared as judged by thin-layer chromatography ($R_f = 0.50$ in hexane). The resulting solution was filtered and the filtrate was chromatographed on silica gel. Compound **7** was eluted as the third dark-red fraction with heptane (yield: 6%) and compound **6** as the fourth dark-red fraction with heptane (yield: 13%).

2.3.2.2. Compound 6; head-to-head. IR (heptane solution): ν_{CO} terminal: 2060, 2040, 2010, 1990 and 1960 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + H]^+$ $(m/z) = 593$. ^1H NMR (500 MHz, C_6D_6 at 7.16 ppm): 2s 1.90 and 1.92 ppm for two CH_3; t 1.23 ppm $^3J_{CH3CH2} = 7.4$ Hz for CH_3CH_2S bridging; two multiplets 2.35 ppm and 2.51 ppm $^2J_{H-H} = 12.9$ Hz and $^3J_{CH3CH2} = 7.4$ Hz for two diastereotopic H of CH_3CH_2S bridging; t 1.02 ppm $^3J_{CH3CH2} = 7.4$ Hz for CH_3CH_2S; two multiplets 2.73 ppm and 2.79 ppm $^2J_{H-H} = 12.1$ Hz and $^3J_{CH3CH2} = 7.4$ Hz for two diastereotopic H of CH_3CH_2S. Single crystals of compound **6** were obtained and the crystal structure was determined by X-ray diffraction.

2.3.2.3. Compound 7; head-to-tail. IR (heptane solution): ν_{CO} terminal: 2080, 2040, 2020, 1990 and 1970 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + H]^+$ $(m/z) = 593$. ^1H NMR (500 MHz, C_6D_6 at 7.16 ppm): 2s 2.27 and 2.5 ppm for two CH_3; t 1.23 ppm $^3J_{CH3CH2} = 7.4$ Hz for CH_3CH_2S bridging; two multiplets 2.38 ppm and 2.48 ppm $^2J_{H-H} = 12.8$ Hz and $^3J_{CH3CH2} = 7.4$ Hz for two diastereotopic H of CH_3CH_2S bridging; t 0.89 ppm $^3J_{CH3CH2S} = 7.4$ Hz for

TABLE 11. Selected distances (Å) and angles (°) for compound **9**

Fe(1)–Fe(2): 2.577(2)	Fe(1)–Fe(3): 2.536(2)	S(2)–Fe(1): 2.277(3)
S(2)–Fe(2): 2.236(3)	C(7)–Fe(1): 1.919(8)	C(7)–Fe(2): 1.888(8)
C(7)–Fe(3): 2.106(8)		
Fe(3)–Fe(1)–Fe(2): 95.87(6)	Fe(1)–S(2)–Fe(2): 69.64(8)	
Fe(1)–C(7)–Fe(2): 85.2(3)	Fe(3)–C(7)–Fe(1): 78.0(3)	
Fe(3)–C(7)–Fe(2): 143.7(5)		

TABLE 12. Fractional parameters for compound **10**

Atom	x	y	z	U_{iso}
First molecule				
Fe(1)	0.2447(3)	0.1788(2)	0.5999(1)	0.0384(8)
Fe(2)	0.3151(4)	0.0958(2)	0.6956(1)	0.0450(8)
Fe(3)	0.0162(3)	0.2869(2)	0.6340(1)	0.0409(8)
Fe(4)	0.3022(4)	0.3197(3)	0.5283(1)	0.0478(9)
S(1)	0.1597(6)	0.1712(5)	0.5081(2)	0.047(2)
S(2)	0.1506(6)	0.0236(4)	0.6282(2)	0.044(1)
C(1)	0.206(2)	0.332(2)	0.5932(9)	0.043(6)
C(2)	0.191(2)	0.395(2)	0.6407(9)	0.048(6)
C(3)	0.187(2)	0.518(2)	0.6383(9)	0.051(6)
C(4)	0.257(3)	0.069(2)	0.470(1)	0.063(7)
C(5)	0.237(3)	0.096(2)	0.407(1)	0.067(7)
C(6)	0.219(2)	0.225(2)	0.6732(8)	0.044(6)
C(7)	0.201(2)	0.335(2)	0.6898(9)	0.045(6)
C(8)	0.202(3)	0.378(2)	0.749(1)	0.060(7)
C(9)	0.230(2)	−0.089(2)	0.5929(8)	0.042(6)
C(10)	0.198(3)	−0.196(2)	0.623(1)	0.071(8)
C(11)	0.432(3)	0.147(2)	0.595(1)	0.066(7)
C(21)	0.433(3)	−0.020(2)	0.696(1)	0.074(8)
C(22)	0.227(3)	0.066(2)	0.755(1)	0.065(7)
C(23)	0.456(3)	0.174(2)	0.728(1)	0.076(8)
C(31)	−0.072(3)	0.185(2)	0.668(1)	0.067(7)
C(32)	−0.106(3)	0.383(2)	0.652(1)	0.055(6)
C(33)	−0.084(3)	0.265(2)	0.570(1)	0.068(8)
C(41)	0.436(3)	0.279(2)	0.486(1)	0.089(9)
C(42)	0.199(3)	0.410(2)	0.487(1)	0.061(7)
C(43)	0.426(3)	0.411(2)	0.558(1)	0.085(9)
O(11)	0.558(2)	0.135(1)	0.5924(7)	0.086(6)
O(21)	0.508(2)	−0.095(2)	0.6962(8)	0.098(6)
O(22)	0.170(2)	0.055(1)	0.7948(8)	0.084(6)
O(23)	0.546(3)	0.229(2)	0.7518(9)	0.118(8)
O(31)	−0.136(2)	0.126(1)	0.6914(8)	0.084(6)
O(32)	−0.188(2)	0.450(1)	0.6664(7)	0.087(6)
O(33)	−0.162(2)	0.257(2)	0.5289(9)	0.102(7)
O(41)	0.528(2)	0.262(2)	0.4555(9)	0.108(7)
O(42)	0.123(2)	0.468(2)	0.4579(9)	0.105(7)
O(43)	0.511(3)	0.474(2)	0.580(1)	0.127(8)
Second molecule				
Fe(101)	0.7651(3)	−0.3226(2)	0.8989(1)	0.0402(8)
Fe(102)	0.6966(4)	−0.4834(3)	0.8351(1)	0.0463(9)
Fe(103)	1.0003(4)	−0.2665(3)	0.8473(1)	0.0450(8)
Fe(104)	0.7094(4)	−0.1307(3)	0.9275(1)	0.0535(9)
S(101)	0.8645(6)	−0.2422(5)	0.9783(2)	0.047(2)
S(102)	0.8367(6)	−0.4929(5)	0.9181(2)	0.046(2)
C(101)	0.802(2)	−0.185(2)	0.8669(9)	0.047(6)
C(102)	0.829(2)	−0.173(2)	0.8119(9)	0.044(6)
C(103)	0.840(3)	−0.065(2)	0.783(1)	0.067(7)
C(104)	0.790(3)	−0.297(2)	1.041(1)	0.061(7)
C(105)	0.821(3)	−0.216(2)	1.091(1)	0.091(9)
C(106)	0.802(2)	−0.355(2)	0.8235(8)	0.039(6)
C(107)	0.825(2)	−0.275(2)	0.7840(9)	0.047(6)
C(108)	0.833(3)	−0.295(2)	0.722(1)	0.059(7)
C(109)	0.735(3)	−0.557(2)	0.9728(9)	0.056(7)
C(110)	0.737(3)	−0.676(2)	0.967(1)	0.073(8)
C(111)	0.577(3)	−0.331(2)	0.909(1)	0.060(7)
C(121)	0.546(3)	−0.557(2)	0.858(1)	0.069(8)
C(122)	0.790(3)	−0.585(2)	0.805(1)	0.089(9)
C(123)	0.585(3)	−0.448(2)	0.779(1)	0.086(9)
C(131)	1.088(3)	−0.383(2)	0.866(1)	0.063(7)
C(132)	1.120(3)	−0.237(2)	0.799(1)	0.076(8)
C(133)	1.095(3)	−0.186(2)	0.897(1)	0.070(8)
C(141)	0.586(3)	−0.123(2)	0.981(1)	0.073(8)
C(142)	0.813(3)	−0.010(2)	0.942(1)	0.072(8)
C(143)	0.581(3)	−0.078(2)	0.880(1)	0.088(9)
O(111)	0.450(2)	−0.337(1)	0.9117(8)	0.090(6)
O(121)	0.450(2)	−0.611(1)	0.8705(7)	0.085(6)
O(122)	0.858(2)	−0.655(2)	0.7882(8)	0.099(6)
O(123)	0.503(3)	−0.420(2)	0.738(1)	0.120(8)
O(131)	1.153(2)	−0.464(1)	0.8758(7)	0.081(5)
O(132)	1.209(3)	−0.221(2)	0.767(1)	0.122(8)
O(133)	1.164(2)	−0.123(1)	0.9274(8)	0.085(6)
O(141)	0.503(2)	−0.119(2)	1.0132(9)	0.104(7)
O(142)	0.881(3)	0.066(2)	0.9467(9)	0.115(7)
O(143)	0.492(3)	−0.043(2)	0.845(1)	0.131(8)

CH_3CH_2S; two multiplets 2.30 ppm and 2.21 ppm $^2J_{H-H} = 13$ Hz and $^3J_{CH3CH2} = 7.4$ Hz for two diastereotopic H of CH_3CH_2S.

Compound **6** and **7** may also be obtained by reaction of a mixture of compounds **1** and **3** with an excess of $[Fe_2(CO)_9]$ in refluxing hexane for 8 h.

*2.3.2.4. Compounds **8** and **9** (R = C_6H_5; head-to-head and head-to-tail.* A solution of $[Fe_3(CO)_{12}]$ (1 g, 1.9 mmol) and $C_6H_5C{\equiv}CSC_2H_5$ (0.308 g, 1.9 mmol) was stirred in refluxing hexane for 24 h, until $[Fe_3(CO)_{12}]$ disappeared as judged by thin-layer chromatography. After the solution was filtered and concentrated under vacuum, the filtrate was chromatographed on silica gel. Compounds **8** and **9** were eluted together as the third dark-red fraction with a 90–10 mixture of heptane-dichloromethane (total yield: 16%). Compounds **8** and **9** were not separated on the column, but they crystallized in two different crystalline types. They were separated under a microscope, and their crystal structures were determined by X-ray diffraction.

Compounds **8** and **9** can also be prepared by reaction of a mixture of compounds **2** and **4** with an excess of $[Fe_2(CO)_9]$ for 5 h in refluxing hexane.

*2.3.2.5. Compound **8**; head-to-head.* IR (heptane solution): ν_{CO} terminal: 2080, 2050, 2000, 1990 and 1960 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + H]^+$ $(m/z) = 717$. ^1H NMR (500 MHz, C_6D_6 at 7.16 ppm): t 1.25 ppm for CH_3CH_2S bridging; two unresolved multiplets centred at 2.35 ppm and 2.55 ppm for two diastereotopic H of CH_3CH_2S bridging; t 0.8 ppm CH_3CH_2S; two unresolved multiplets centred at 2.28 ppm and 2.38 ppm for two diastereotopic H of CH_3CH_2S; multiplets between 6.9 and 7.5 ppm for two C_6H_5.

TABLE 13. Selected distances (Å) and angles (°) for compound **10**

Fe(1)–Fe(2): 2.564(4)	Fe(1)–Fe(3): 2.670(4)	Fe(1)–Fe(4): 2.572(4)
S(1)–Fe(1): 2.277(6)	S(1)–Fe(4): 2.277(6)	S(2)–Fe(1): 2.255(6)
S(2)–Fe(2): 2.269(6)	C(1)–Fe(1): 1.95(2)	C(1)–Fe(3): 2.14(2)
C(1)–Fe(4): 1.88(2)	C(6)–Fe(1): 1.90(2)	C(6)–Fe(2): 1.89(2)
C(6)–Fe(3): 2.13(2)		
Fe(4)–Fe(1)–Fe(3): 94.4(1)	Fe(3)–Fe(1)–Fe(2): 93.4(1)	
Fe(4)–S(1)–Fe(1): 68.8(2)	Fe(1)–S(2)–Fe(2): 69.0(2)	
Fe(4)–C(1)–Fe(1): 84.3(9)	Fe(3)–C(1)–Fe(1): 81.4(8)	
Fe(2)–C(6)–Fe(1): 85.2(9)	Fe(3)–C(6)–Fe(1): 82.9(8)	
Fe(4)–C(1)–Fe(3): 146.0(11)	Fe(3)–C(6)–Fe(2): 142.4(11)	

2.3.2.6. Compound 9; head-to-tail. IR (heptane solution): ν_{CO} terminal: 2070, 2040, 2010, 1990 and 1980 cm^{-1}. Mass spectrometry (chemical ionisation): $[M+H]^+$ $(m/z) = 717$. ^1H NMR (500 MHz, C_6D_6 at 7.16 ppm): t 1.19 ppm for $\mathrm{C}H_3\mathrm{CH}_2\mathrm{S}$ bridging; two unresolved multiplets centred at 2.3 ppm and 2.5 ppm for two diastereotopic H of $\mathrm{CH}_3\mathrm{C}H_2\mathrm{S}$ bridging; t 0.64 ppm for $\mathrm{C}H_3\mathrm{CH}_2\mathrm{S}$; one unresolved multiplet centred at 2.08 ppm for two diastereotopic H of $\mathrm{CH}_3\mathrm{C}H_2\mathrm{S}$; multiplets between 6.9 and 7.5 ppm for $2\mathrm{C}_6H_5$.

2.3.3. Tetra and pentanuclear complexes

2.3.3.1. Compounds 10 (tetranuclear) and 12 (pentanuclear) ($R = CH_3$; head-to-head). A solution of compound **6** (0.085 g, 0.14 mmol) with an excess of $[Fe_2(CO)_9]$ in 15 ml heptane was stirred at 60°C for 4 h. $[Fe_2(CO)_9]$ was added progressively to the solution. The reaction solution was chromatographed on silica gel. The first fraction eluted with heptane was $[Fe_3(CO)_{12}]$ formed during the reaction; then compound **10** was eluted as the second red fraction (yield: 55%). Compound **12** was eluted as the third brown fraction with a 95–5 mixture of heptane-dichloromethane (yield: 5%). Both compounds **10** and **12** crystallized at −20°C and their structures were determined by X-ray diffraction.

2.3.3.2. Compound 10; tetranuclear complex. IR (heptane solution): ν_{CO} terminal: 2080, 2050, 2010 and 1990 cm^{-1}. Mass spectrometry (chemical ionisation): $[M+H]^+$ $(m/z) = 705$ and $[M+H]^+ - 1CO = 677$. ^1H NMR (500 MHz, C_6D_6 at 7.28 ppm): s 2 ppm for $2CH_3$; t 1.46 ppm for two $\mathrm{C}H_3\mathrm{CH}_2\mathrm{S}$ bridging; two unresolved multiplets centred at 2.48 ppm and 2.65 ppm for two diastereotopic H of two $\mathrm{CH}_3\mathrm{C}H_2\mathrm{S}$ bridging.

2.3.3.3. Compound 12; pentanuclear complex. IR (KBr pellet): ν_{CO} terminal: 2020, 1980, 1970, 1950 and

TABLE 14. Fractional parameters for compound **11**

Atom	x	y	z	U_{eq}
Fe(1)	0.19772(9)	0.3318(3)	0.1563(1)	0.0326
Fe(2)	0.3366(1)	0.3973(3)	0.0695(1)	0.0457
Fe(3)	0.24904(9)	0.0583(3)	0.2243(1)	0.0360
Fe(4)	0.10108(9)	0.3706(3)	0.3194(1)	0.0395
S(1)	0.0587(2)	0.2789(4)	0.1471(2)	0.0441
S(2)	0.2254(2)	0.2825(4)	−0.0249(2)	0.0485
C(1)	−0.0956(7)	0.409(2)	0.093(1)	0.0719
C(2)	−0.0052(7)	0.420(2)	0.066(1)	0.0629
C(3)	0.1985(6)	0.251(1)	0.3058(8)	0.0333
C(4)	0.2696(7)	0.191(1)	0.3672(9)	0.0344
C(5)	0.187(2)	0.402(3)	−0.237(1)	0.1029
C(6)	0.165(1)	0.407(2)	−0.121(1)	0.0734
C(7)	0.3113(6)	0.268(1)	0.1910(9)	0.0329
C(8)	0.3398(7)	0.205(1)	0.2954(9)	0.0347
C(81)	0.4313(7)	0.174(2)	0.324(1)	0.0454
C(82)	0.4737(7)	0.048(2)	0.287(1)	0.0587
C(83)	0.5574(9)	0.029(2)	0.315(1)	0.0754
C(84)	0.6006(8)	0.130(3)	0.379(2)	0.0682
C(85)	0.5620(9)	0.256(2)	0.416(1)	0.0702
C(86)	0.4787(7)	0.281(2)	0.391(1)	0.0586
C(91)	0.2708(7)	0.131(1)	0.4861(9)	0.0372
C(92)	0.3334(8)	0.165(2)	0.568(1)	0.0571
C(93)	0.3318(9)	0.106(2)	0.674(1)	0.0622
C(94)	0.273(1)	0.007(2)	0.702(1)	0.0704
C(95)	0.2079(9)	−0.028(2)	0.622(1)	0.0689
C(96)	0.2079(8)	0.029(2)	0.516(1)	0.0580
C(11)	0.1923(7)	0.534(1)	0.1492(9)	0.0379
C(21)	0.4006(9)	0.509(2)	0.169(1)	0.0589
C(22)	0.420(1)	0.291(2)	0.012(1)	0.0777
C(23)	0.331(1)	0.557(2)	−0.029(1)	0.0646
C(31)	0.2860(7)	−0.007(1)	0.092(1)	0.0465
C(32)	0.2855(8)	−0.109(2)	0.300(1)	0.0516
C(33)	0.1446(7)	−0.015(1)	0.210(1)	0.0433
C(41)	0.0345(8)	0.540(2)	0.301(1)	0.0555
C(42)	0.0347(8)	0.253(2)	0.396(1)	0.0592
C(43)	0.1589(8)	0.459(2)	0.434(1)	0.0578
O(11)	0.1868(6)	0.661(1)	0.1433(8)	0.0585
O(21)	0.4404(7)	0.581(2)	0.230(1)	0.0870
O(22)	0.4713(8)	0.222(2)	−0.024(1)	0.1073
O(23)	0.3301(9)	0.656(1)	−0.091(1)	0.0871
O(31)	0.3136(6)	−0.052(1)	0.0127(8)	0.0693
O(32)	0.3050(7)	−0.216(1)	0.3474(8)	0.0719
O(33)	0.0788(5)	−0.068(1)	0.2091(9)	0.0592
O(41)	−0.0016(7)	0.648(1)	0.297(1)	0.0800
O(42)	−0.0086(8)	0.177(2)	0.442(1)	0.1012
O(43)	0.1965(6)	0.516(1)	0.5066(9)	0.0789

TABLE 15. Selected distances (Å) and angles (°) for compound **11**

Fe(1)–Fe(2): 2.566(2) Fe(1)–Fe(3): 2.652(2) Fe(1)–Fe(4): 2.567(2)
S(1)–Fe(1): 2.268(3) S(1)–Fe(4): 2.264(3) S(2)–Fe(1): 2.260(3)
S(2)–Fe(2): 2.282(4) C(3)–Fe(1): 1.91(3) C(3)–Fe(3): 2.13(1)
C(3)–Fe(4): 1.90(1) C(7)–Fe(1): 1.92(1) C(7)–Fe(2): 1.90(1)
C(7)–Fe(3): 2.14(1)
Fe(4)–Fe(1)–Fe(3): 93.63(7) Fe(3)–Fe(1)–Fe(2): 93.78(7)
Fe(4)–S(1)–Fe(1): 69.01(9) Fe(1)–S(2)–Fe(2): 68.8(1)
Fe(4)–C(3)–Fe(1): 84.8(4) Fe(3)–C(3)–Fe(1): 81.9(4)
Fe(2)–C(7)–Fe(1): 84.4(4) Fe(3)–C(7)–Fe(1): 81.2(4)
Fe(4)–C(3)–Fe(3): 144.6(5) Fe(3)–C(7)–Fe(2): 141.0(5)

1920 cm^{-1}. Mass spectrometry (electronic impact): $[M]^+$ $(m/z) = 788$; $[M]^+ - 1CO = 760$; $[M]^+ - 2CO = 732$; $[M]^+ - 3CO = 704$; $[M]^+ - 4CO = 676$; $[M]^+ - 5CO = 648$; $[M]^+ - 6CO = 620$; $[M]^+ - 7CO = 592$; $[M]^+ - 8CO = 564$; $[M]^+ - 9CO = 536$; $[M]^+ - 10CO = 508$; $[M]^+ - 11CO = 480$. ^{1}H NMR (500 MHz, C_6D_6 at 7.29 ppm): 2s 1.90 and 2.17 ppm for two CH_3; t 0.64 ppm for CH_3CH_2S (H of CH_3 italic); unresolved multiplet, apparently a quadruplet 1.64 ppm for CH_3CH_2S; t 1.1 ppm for CH_3CH_2S; unresolved multiplet under the singlet at 1.90 ppm for two diastereotopic H of CH_3CH_2S.

2.3.3.4. Compound 11 (R = C_6H_5; tetranuclear, head-to-head). Selected crystals of compound **8** (0.015 g, 0.02 mmol) were allowed to react with an excess of $[Fe_2(CO)_9]$ in 20 ml heptane. The solution was stirred at 60°C for 4 h and chromatographed on silica gel $[Fe_3(CO)_{12}]$ was first eluted with heptane and then compound **11** was eluted as a red fraction with a 50–50 mixture of heptane-dichloromethane (yield: 70%). IR (KBr pellet): ν_{CO} terminal: 2090, 2080, 2010 and 1990 cm^{-1}. Mass spectrometry (chemical ionisation): $[M+H]^+$ $(m/z) = 829$; $[M+H]^+ - 1CO = 801$; $[M+H]^+ - 2CO = 773$; $[M+H]^+ - 3CO = 745$; $[M+H]^+ - 4CO = 717$. ^{1}H NMR (500 MHz, C_6D_6 at 7.29 ppm): t 1.5 ppm for CH_3CH_2S; two unresolved multiplets centred at 2.5 and 2.7 ppm for two diastereotopic H of CH_3CH_2S; unresolved multiplets between 7 and 7.8 ppm for $2C_6H_5$.

2.3.3.5. Compound 13 (R = CH_3; tetranuclear, head-to-tail). A solution of compound **7** (0.023 g, 0.04 mmol) with an excess of $[Fe_2(CO)_9]$ in 15 ml heptane was stirred at 60°C for 4 h. The solution was then chromatographed on silica gel. $[Fe_3(CO)_{12}]$ was eluted as a second fraction, and four other fractions were eluted with heptane. Only the fourth fraction, compound **13**, has been identified and its crystal structure was determined by X-ray diffraction (yield: 30%).

IR (KBr pellet): ν_{CO} terminal: 2080, 2020, 1980, 1970, 1960 and 1940, ν_{CO} bridging: 1810 cm^{-1}. Mass spectrometry (chemical ionisation): $[M+H]^+$ $(m/z) = 705$. ^{1}H NMR (500 MHz, C_6D_6 at 7.29 ppm): 2s 2.70

TABLE 16. Fractional parameters for compound **12**

Atom	x	y	z	U_{iso}
Fe(1)	0.6672(3)	0.7529(5)	−0.0389(5)	0.030(2)
Fe(2)	0.6847(3)	0.8072(5)	0.1824(5)	0.035(2)
Fe(3)	0.8032(3)	0.7328(4)	0.0761(5)	0.028(2)
Fe(4)	0.8118(3)	0.6036(4)	−0.0923(5)	0.029(2)
Fe(5)	0.7171(3)	0.6896(5)	−0.2384(5)	0.035(2)
S(1)	0.7860(7)	0.5670(8)	−0.2840(9)	0.036(3)
S(2)	0.6758(6)	0.6059(8)	−0.0906(9)	0.031(3)
C(1)	0.776(2)	0.741(3)	−0.098(3)	0.02(1)
C(2)	0.834(2)	0.811(3)	−0.072(3)	0.03(1)
C(3)	0.914(2)	0.828(3)	−0.122(3)	0.03(1)
C(4)	0.870(3)	0.604(4)	−0.364(4)	0.06(1)
C(5)	0.842(3)	0.595(4)	−0.506(4)	0.06(2)
C(6)	0.734(2)	0.841(3)	0.050(3)	0.04(1)
C(7)	0.809(2)	0.866(3)	0.017(3)	0.03(1)
C(8)	0.854(2)	0.949(3)	0.068(3)	0.02(1)
C(9)	0.607(3)	0.512(3)	−0.121(4)	0.05(1)
C(10)	0.519(3)	0.543(3)	−0.161(4)	0.06(2)
C(11)	0.578(3)	0.747(4)	0.035(4)	0.07(2)
C(12)	0.625(2)	0.827(3)	−0.149(4)	0.05(1)
C(21)	0.617(3)	0.893(4)	0.198(4)	0.07(2)
C(22)	0.643(2)	0.728(3)	0.271(4)	0.05(1)
C(23)	0.762(2)	0.846(3)	0.286(3)	0.03(1)
C(31)	0.895(3)	0.741(3)	0.170(4)	0.05(1)
C(32)	0.773(3)	0.639(4)	0.154(4)	0.06(2)
C(41)	0.918(3)	0.623(3)	−0.091(4)	0.04(1)
C(42)	0.830(2)	0.499(3)	−0.022(4)	0.03(1)
C(51)	0.629(3)	0.681(4)	−0.342(5)	0.08(2)
C(52)	0.758(2)	0.766(3)	−0.319(4)	0.05(1)
O(11)	0.511(2)	0.732(2)	0.052(3)	0.07(1)
O(12)	0.599(2)	0.882(2)	−0.213(3)	0.07(1)
O(21)	0.575(2)	0.954(2)	0.213(3)	0.06(1)
O(22)	0.617(2)	0.667(3)	0.326(3)	0.11(1)
O(23)	0.813(2)	0.869(2)	0.356(3)	0.07(1)
O(31)	0.953(2)	0.740(3)	0.232(3)	0.08(1)
O(32)	0.752(2)	0.569(2)	0.197(3)	0.06(1)
O(41)	0.984(2)	0.630(2)	−0.076(3)	0.07(1)
O(42)	0.840(2)	0.429(2)	0.010(3)	0.07(1)
O(51)	0.579(2)	0.667(3)	−0.416(3)	0.09(1)
O(52)	0.791(2)	0.818(2)	−0.379(3)	0.063(9)

TABLE 17. Selected distances (Å) and angles (°) for compound **12**

Fe(1)–Fe(2): 2.619(8)
Fe(1)–Fe(3): 2.533(8)
Fe(1)–Fe(5): 2.649(8)
Fe(2)–Fe(3): 2.652(8)
Fe(3)–Fe(4): 2.717(8)
Fe(4)–Fe(5): 2.528(9)
S(1)–Fe(4): 2.24(1)
S(1)–Fe(5): 2.24(1)
S(2)–Fe(1): 2.27(2)
S(2)–Fe(4): 2.28(1)
S(2)–Fe(5): 2.24(1)
C(1)–Fe(1): 2.00(3)
C(1)–Fe(3): 1.98(3)
C(1)–Fe(4): 2.13(4)
C(1)–Fe(5): 1.94(4)
C(6)–Fe(1): 1.94(4)
C(6)–Fe(2): 1.84(4)
C(6)–Fe(3): 1.99(4)
Fe(5)–Fe(1)–Fe(3): 93.2(3)
Fe(3)–Fe(1)–Fe(2): 61.9(2)
Fe(3)–Fe(2)–Fe(1): 57.4(2)
Fe(2)–Fe(3)–Fe(1): 60.6(2)
Fe(4)–Fe(3)–Fe(1): 80.0(2)
Fe(3)–Fe(4)–Fe(5): 91.7(3)
Fe(4)–Fe(5)–Fe(1): 81.5(3)
Fe(4)–S(1)–Fe(5): 68.7(4)
Fe(1)–S(2)–Fe(5): 71.9(4)
Fe(1)–S(2)–Fe(4): 96.0(5)
Fe(4)–S(2)–Fe(5): 68.0(5)
Fe(3)–C(1)–Fe(1): 79.1(12)
Fe(1)–C(1)–Fe(5): 84.5(13)
Fe(3)–C(1)–Fe(4): 82.6(14)
Fe(4)–C(1)–Fe(5): 76.5(14)
Fe(2)–C(6)–Fe(1): 87.4(18)
Fe(3)–C(6)–Fe(1): 80.2(16)
Fe(5)–C(1)–Fe(3): 147.2(22)
Fe(3)–C(6)–Fe(2): 87.4(17)

and 2.32 ppm for two CH_3; t 1.04 ppm for CH_3CH_2S; two unresolved multiplets centred at 2.41 and 2.32 ppm for two diastereotopic H of CH_3CH_2S; t 0.58 ppm for CH_3CH_2S; one large unresolved multiplet centred at 1.53 ppm for two diastereotopic H of CH_3CH_2S.

*2.3.3.6. Compounds **14** and **15** ($R = C_6H_5$; tail-to-tail).* Selected crystals of compound **5** (0.016 g, 0.026 mmol) were allowed to react with an excess of $[Fe_2(CO)_9]$ in 5 ml hexane. The solution was stirred under reflux for 5 h, until compound **5** disappeared as judged by thin layer chromatography ($R_f = 0.71$ in a 50–50 heptane-dichloromethane mixture). Column separation with heptane led to $[Fe_3(CO)_{12}]$ as the first fraction. Compound **14** was eluted as the second yellow fraction (yield 30%). Compound **15** was eluted as the third orange fraction (yield 35%). Both compounds **14** and **15** crystallized at -20°C from a heptane solution. Crystal structures were determined by X-ray diffraction.

*2.3.3.7. Compound **14** ($R = C_6H_5$; tail-to-tail).* IR (KBr pellet): ν_{CO} terminal: 2090, 2070, 2050, 2030, 2000 and 1990; ν_{CO} semi-bridging: 1930 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + NH_4]^+$ $(m/z) = 844$.

*2.3.3.8. Compound **15** ($R = C_6H_5$, tail-to-tail).* IR (KBr pellet): ν_{CO} terminal: 2060, 2010, 1990, 1970, 1960 and 1950; ν_{CO} semi-bridging: 1930; $\nu_{C=O}$: 1640 cm^{-1}. Mass spectrometry (chemical ionisation): $[M + H]^+$ $(m/z) = 885$; $[M + NH_4]^+$ $(m/z) = 902$. ^1H NMR (500 MHz, C_6D_6 at 7.28 ppm): t 0.42 ppm 3H for

TABLE 18. Fractional parameters for compound **13**

Atom	x	y	z	U_{iso}
Fe(1)	0.2498(7)	0.0504(6)	0.6992(4)	0.031(2)
Fe(2)	0.3491(6)	0.0814(6)	0.8543(4)	0.029(2)
Fe(3)	0.2025(7)	0.3183(6)	0.7175(4)	0.029(2)
Fe(4)	0.1702(6)	0.2769(6)	0.8719(4)	0.032(2)
S(1)	0.518(1)	0.459(1)	0.6161(8)	0.057(4)
S(2)	0.105(1)	0.036(1)	0.8063(7)	0.032(3)
C(1)	0.423(5)	0.319(4)	0.663(3)	0.04(1)
C(2)	0.332(4)	0.195(4)	0.634(2)	0.011(8)
C(3)	0.310(5)	0.164(5)	0.534(3)	0.05(1)
C(4)	0.683(6)	0.369(6)	0.581(3)	0.08(2)
C(5)	0.808(8)	0.478(8)	0.560(5)	0.12(2)
C(6)	0.350(4)	0.233(4)	0.792(2)	0.04(1)
C(7)	0.437(5)	0.346(5)	0.751(3)	0.05(1)
C(8)	0.553(5)	0.478(5)	0.815(3)	0.06(1)
C(9)	−0.179(8)	−0.170(8)	0.770(4)	0.12(2)
C(10)	−0.039(6)	−0.135(6)	0.833(3)	0.07(1)
C(11)	0.402(6)	−0.036(6)	0.676(3)	0.07(2)
C(12)	0.138(7)	−0.089(6)	0.621(4)	0.08(2)
C(23)	0.336(5)	0.138(5)	0.970(3)	0.05(1)
C(21)	0.546(5)	0.138(4)	0.853(2)	0.03(1)
C(22)	0.345(6)	−0.101(6)	0.856(3)	0.07(2)
C(31)	0.190(5)	0.494(5)	0.699(3)	0.06(1)
C(32)	0.050(4)	0.226(4)	0.657(2)	0.03(1)
C(34)	0.061(5)	0.380(5)	0.825(3)	0.05(1)
C(42)	0.272(4)	0.432(4)	0.938(2)	0.02(1)
C(41)	0.031(7)	0.267(7)	0.950(4)	0.10(2)
O(11)	0.499(4)	−0.111(4)	0.661(2)	0.09(1)
O(12)	0.052(4)	−0.161(4)	0.575(2)	0.07(1)
O(21)	0.685(4)	0.171(3)	0.857(2)	0.062(9)
O(22)	0.336(4)	−0.240(4)	0.853(2)	0.09(1)
O(23)	0.328(4)	0.174(3)	1.036(2)	0.058(9)
O(31)	0.180(4)	0.608(4)	0.681(2)	0.07(1)
O(32)	−0.083(4)	0.158(3)	0.622(2)	0.061(9)
O(34)	−0.037(4)	0.439(4)	0.817(2)	0.08(1)
O(41)	−0.057(6)	0.258(5)	1.003(3)	0.13(2)
O(42)	0.331(4)	0.553(4)	0.979(2)	0.07(1)

TABLE 19. Selected distances (Å) and angles (°) for compound **13**

Fe(1)–Fe(2): 2.623(8)	Fe(1)–Fe(3): 2.549(8)	Fe(2)–Fe(4): 2.585(8)
Fe(3)–Fe(4): 2.656(8)	S(2)–Fe(1): 2.20(1)	S(2)–Fe(2): 2.23(1)
S(2)–Fe(4): 2.23(1)	C(6)–Fe(1): 2.07(4)	C(6)–Fe(2): 1.91(4)
C(6)–Fe(3): 2.14(4)	C(6)–Fe(4): 2.10(4)	C(34)–Fe(3): 2.20(4)
C(34)–Fe(4): 1.77(5)		
Fe(3)–Fe(1)–Fe(2): 95.9(3)	Fe(4)–Fe(2)–Fe(1): 78.5(2)	
Fe(4)–Fe(3)–Fe(1): 78.5(2)	Fe(3)–Fe(4)–Fe(2): 94.2(3)	
Fe(2)–S(2)–Fe(1): 72.8(4)	Fe(1)–S(2)–Fe(4): 96.3(4)	
Fe(4)–S(2)–Fe(2): 71.0(4)	Fe(2)–C(6)–Fe(1): 82.4(15)	
Fe(3)–C(6)–Fe(1): 74.5(13)	Fe(3)–C(6)–Fe(2): 142.2(21)	
Fe(4)–C(6)–Fe(1): 104.5(17)	Fe(4)–C(6)–Fe(2): 80.0(14)	
Fe(4)–C(6)–Fe(3): 77.4(13)	Fe(4)–C(34)–Fe(3): 83.4(18)	
O(34)–C(34)–Fe(3): 118.8(36)	O(34)–C(34)–Fe(4): 156.8(42)	

$C\mathit{H}_3\mathrm{CH}_2\mathrm{S}$; two unresolved multiplets centred at 2.05 and 2.4 ppm 2H for two diastereotopic H of $\mathrm{CH}_3\mathrm{C}\mathit{H}_2\mathrm{S}$; t 0.94 ppm 3H for $\mathrm{C}\mathit{H}_3\mathrm{CH}_2\mathrm{S}$; two unresolved multiplets centred at 2.55 ppm and 2.32 ppm 2H for two diastereotopic H of $\mathrm{CH}_3\mathrm{C}\mathit{H}_2\mathrm{S}$; multiplets between 7 ppm and 7.9 ppm for two C_6H_5.

3. Results and discussion

3.1. Dinuclear complexes (compounds 1 to 5)

The reaction of $[Fe_2(CO)_9]$ with $RC{\equiv}CSC_2H_5$ (R = CH_3 or C_6H_5) and with $(CH_3)_3NO$ as an activator, yielded at room temperature a mixture of dinuclear isomers (Scheme 1). They were not separated by chromatography. The IR spectra of all these solutions showed the occurrence of a semi-bridging CO, ν_{CO} at 1940 cm^{-1} (R = CH_3) and at 1930 cm^{-1} (R = C_6H_5). This is a normal feature for dinuclear compounds containing a cyclopentadiene fragment resulting from the coupling of two alkyne molecules.

For R = CH_3, head-to-head (compound **1**, R = CH_3) and head-to-tail (compound **3**, R = CH_3) isomers were assumed to occur in solution because the action of an excess of $[Fe_2(CO)_9]$ gave the corresponding trinuclear compounds which were separated and crystallized (see below).

For R = C_6H_5, the solution also contained the isomers tail-to-tail (compound **5**), head-to-tail (compound **4**), and a small amount of the head-to-head isomer (compound **2**). The tail-to-tail isomer (compound **5**) was separated as single crystals under a microscope and the crystal structure was determined by X-ray diffraction (Fig. 1).

The ^1H NMR spectrum of the $[Fe_2(CO)_6\{C_6H_5C(SC_2H_5)C(SC_2H_5)CC_6H_5\}]$ tail-to-tail compound **5** is clear. It shows only one triplet at 1 ppm ($^3J_{CH3CH2} = 7.4$ Hz) indicating two equivalent CH_3 groups. At 2.6 and

TABLE 20. Fractional parameters for compound **14**

Atom	x	y	z	U_{iso}
Fe(1)	0.3744(3)	0.8475(3)	−0.0165(4)	0.061(2)
Fe(2)	0.3300(3)	0.7853(3)	0.1721(4)	0.056(2)
Fe(3)	0.1513(3)	0.9922(3)	0.2235(4)	0.063(2)
Fe(4)	0.1634(3)	0.8877(3)	0.3762(4)	0.058(2)
S(1)	0.1399(4)	0.8727(4)	0.1539(7)	0.042(2)
S(2)	0.2724(5)	0.9478(6)	0.3316(8)	0.068(3)
C(3)	0.236(1)	0.864(2)	0.106(2)	0.032(8)
C(4)	0.263(1)	0.824(2)	0.005(3)	0.034(8)
C(5)	0.199(2)	0.794(2)	−0.104(3)	0.045(9)
C(8)	0.300(2)	0.900(2)	0.199(3)	0.055(9)
C(9)	0.378(2)	0.891(2)	0.160(3)	0.046(8)
C(10)	0.451(2)	0.931(2)	0.243(3)	0.046(8)
C(51)	0.131(1)	0.835(2)	−0.161(2)	0.033(8)
C(52)	0.071(2)	0.808(2)	−0.268(3)	0.06(1)
C(53)	0.086(2)	0.740(2)	−0.307(3)	0.049(9)
C(54)	0.152(2)	0.695(2)	−0.253(3)	0.07(1)
C(55)	0.210(2)	0.722(2)	−0.146(3)	0.07(1)
C(101)	0.444(2)	1.008(2)	0.245(3)	0.07(1)
C(102)	0.512(2)	1.045(2)	0.322(3)	0.07(1)
C(103)	0.578(2)	1.005(2)	0.381(3)	0.08(1)
C(104)	0.584(2)	0.931(2)	0.370(3)	0.08(1)
C(105)	0.516(2)	0.885(2)	0.299(3)	0.08(1)
C(11)	0.372(2)	0.806(2)	−0.165(4)	0.08(1)
C(12)	0.483(2)	0.853(2)	−0.007(3)	0.09(1)
C(13)	0.355(2)	0.928(2)	−0.079(3)	0.07(1)
C(21)	0.268(2)	0.715(2)	0.189(3)	0.08(1)
C(22)	0.377(2)	0.779(2)	0.334(4)	0.09(1)
C(23)	0.401(2)	0.732(2)	0.106(3)	0.07(1)
C(31)	0.161(2)	1.065(3)	0.337(4)	0.12(2)
C(32)	0.047(2)	1.001(2)	0.186(3)	0.09(1)
C(33)	0.177(2)	1.038(2)	0.087(3)	0.07(1)
C(41)	0.175(2)	0.929(2)	0.526(4)	0.10(1)
C(42)	0.058(2)	0.872(2)	0.379(3)	0.08(1)
C(43)	0.202(3)	0.804(3)	0.444(4)	0.12(2)
O(11)	0.366(1)	0.772(2)	−0.266(3)	0.120(9)
O(12)	0.551(2)	0.864(1)	−0.005(2)	0.101(8)
O(13)	0.332(1)	0.992(2)	−0.119(2)	0.105(9)
O(21)	0.217(1)	0.668(1)	0.191(2)	0.085(8)
O(22)	0.403(1)	0.768(1)	0.448(2)	0.090(8)
O(23)	0.443(1)	0.687(1)	0.070(2)	0.097(8)
O(31)	0.163(2)	1.113(2)	0.410(3)	0.14(1)
O(32)	−0.024(2)	1.011(1)	0.159(2)	0.109(9)
O(33)	0.193(1)	1.062(1)	−0.012(2)	0.106(9)
O(41)	0.189(2)	0.960(2)	0.629(3)	0.119(9)
O(42)	−0.008(1)	0.872(1)	0.389(2)	0.096(8)
O(43)	0.212(1)	0.741(2)	0.463(2)	0.101(9)

TABLE 21. Selected distances (Å) and angles (°) for compound **14**

Fe(1)–Fe(2): 2.473(6)
S(2)–Fe(4): 2.26(1)
C(23)–Fe(1): 2.46(3)
S(1)–Fe(3)–S(2): 80.4(3)
S(1)–Fe(3)–Fe(4): 56.8(2)
S(1)–Fe(4)–Fe(3): 58.0(3)
Fe(4)–S(2)–C(8): 104.6(11)
Fe(3)–S(1)–Fe(4): 65.2(3)
Fe(3)–S(1)–C(3): 98.2(10)
Fe(3)–Fe(4): 2.461(7)
S(1)–Fe(3): 2.301(9)
C(23)–Fe(2): 1.76(3)
S(1)–Fe(4)–S(2): 82.0(3)
S(2)–Fe(3)–Fe(4): 56.41(3)
S(2)–Fe(4)–Fe(3): 58.1(3)
Fe(3)–S(2)–Fe(4): 65.5(3)
Fe(3)–S(2)–C(8): 97.7(10)
Fe(4)–S(1)–C(3): 106.4(9)
O(23)–C(23)–Fe(2): 169.7(30)
S(2)–Fe(3): 2.30(1)
S(1)–Fe(4): 2.267(8)

3 ppm are two multiplets of two diastereotopic hydrogens belonging to two equivalent CH_2 groups (Fig. 2).

These peaks are also found in the ^1H NMR spectrum of the reaction mixture ($R = C_6H_5$). In addition, one can see peaks corresponding to the head-to-tail compound **4**, which contains two non-equivalent CH_3CH_2S groups (Fig. 2). The first CH_3CH_2S group has a triplet at 0.51 ppm for CH_3 and a multiplet centred at 1.9 ppm for the two non-equivalent H of CH_2; the second CH_3CH_2S group has a triplet at 0.74 ppm for CH_3 and two 2.25, 2.4 ppm multiplets for the two non-equivalent H of CH_2. In the same spectrum, one can see a weak triplet at the edge of the triplet at 0.74 ppm, but no multiplet for the corresponding CH_2 of a supposed CH_3CH_2S group; this multiplet may be hidden by the other peaks. This is interpreted as showing a small amount of the head-to-head compound **2**. Actually, the occurrence of the three isomers was subsequently proved since an excess of $[Fe_2(CO)_9]$ reacted with this solution and yielded structurally related polynuclear compounds (tri-, tetra- and penta-nuclear) displaying the three possible couplings (see below).

3.2. Trinuclear complexes (compounds 6 to 9)

From the mixture of dinuclear compounds of formula $[Fe_2(CO)_6\{R_2C_4(SC_2H_5)_2\}]$, one should be able to form trinuclear clusters. These dinuclear compounds may be described as *nido* structures following the PSEP rule [11] because they have six vertices and seven pairs of skeletal electrons. *Closo* compounds might be obtained by adding a $Fe(CO)_2$ group without additional electrons. Indeed, such a cluster transformation has been observed previously after reaction of $[Fe_2(CO)_6\{C_6H_5C[N(C_2H_5)_2]C[N(C_2H_5)_2]CC_6H_5\}]$ with an excess of iron carbonyl [12]. Crystal structures of starting materials and products were determined by X-ray (Scheme 2).

A similar reaction was carried out with the mixture of dinuclear compounds $[Fe_2(CO)_6\{R_2C_4(SC_2H_5)_2\}]$ and an excess of iron carbonyl. Trinuclear compounds were obtained with the expected mass (mass spec-

TABLE 22. Fractional parameters for compound **15**

Atom	x	y	z	U_{iso}
Fe(1)	0.80989(8)	0.9473(3)	0.3772(3)	0.0327(8)
Fe(2)	0.82957(8)	0.6944(3)	0.4086(3)	0.0264(8)
Fe(3)	0.96210(8)	0.8395(4)	0.2245(3)	0.0326(8)
Fe(4)	0.93350(8)	0.5891(3)	0.2075(3)	0.0279(8)
S(1)	0.8790(1)	0.6606(6)	0.1135(5)	0.030(1)
S(2)	0.9238(1)	0.7392(6)	0.3687(5)	0.027(1)
C(1)	1.0431(6)	0.464(3)	0.346(2)	0.052(7)
C(2)	1.0025(6)	0.440(3)	0.307(2)	0.047(6)
C(3)	0.8774(5)	0.799(2)	0.347(2)	0.021(4)
C(4)	0.8596(5)	0.884(2)	0.431(2)	0.035(6)
C(5)	0.8794(5)	0.943(2)	0.549(2)	0.029(5)
C(6)	0.8603(8)	0.436(4)	−0.042(3)	0.10(1)
C(7)	0.8487(6)	0.508(3)	0.082(2)	0.047(6)
C(8)	0.8562(5)	0.758(2)	0.237(2)	0.024(5)
C(9)	0.8209(5)	0.807(2)	0.238(2)	0.028(5)
C(10)	0.7958(5)	0.790(2)	0.122(2)	0.026(5)
C(51)	0.9047(6)	1.053(3)	0.532(2)	0.050(6)
C(52)	0.9234(8)	1.116(3)	0.638(3)	0.076(9)
C(53)	0.9163(8)	1.070(3)	0.753(3)	0.078(9)
C(54)	0.8913(8)	0.965(3)	0.777(3)	0.073(8)
C(55)	0.8710(6)	0.898(3)	0.673(2)	0.053(7)
C(101)	0.8065(6)	0.848(3)	0.009(2)	0.043(6)
C(102)	0.7840(6)	0.839(3)	−0.100(2)	0.043(6)
C(103)	0.7514(6)	0.766(3)	−0.092(2)	0.052(7)
C(104)	0.7385(6)	0.707(3)	0.021(2)	0.053(7)
C(105)	0.7618(5)	0.716(2)	0.135(2)	0.036(5)
C(11)	0.7613(6)	0.959(3)	0.338(2)	0.045(6)
C(12)	0.8027(7)	1.054(3)	0.513(3)	0.066(8)
C(13)	0.8266(6)	1.084(2)	0.281(2)	0.039(6)
C(21)	0.8539(7)	0.586(3)	0.523(2)	0.060(7)
C(22)	0.8081(6)	0.536(3)	0.362(2)	0.040(6)
C(23)	0.7932(6)	0.751(3)	0.505(2)	0.047(6)
C(31)	0.9840(7)	0.830(3)	0.081(3)	0.072(8)
C(32)	0.9835(7)	0.988(3)	0.305(2)	0.052(7)
C(33)	0.9298(6)	0.949(3)	0.151(2)	0.040(6)
C(41)	0.9516(7)	0.530(3)	0.063(2)	0.057(7)
C(42)	0.9196(6)	0.425(3)	0.264(2)	0.054(7)
C(43)	0.9824(5)	0.576(2)	0.281(2)	0.026(5)
O(11)	0.7311(5)	0.966(2)	0.313(2)	0.063(5)
O(12)	0.7984(5)	1.126(2)	0.604(2)	0.079(6)
O(13)	0.8376(5)	1.168(2)	0.211(2)	0.069(5)
O(21)	0.8677(5)	0.522(2)	0.605(2)	0.094(7)
O(22)	0.7913(5)	0.432(2)	0.335(2)	0.074(5)
O(23)	0.7702(4)	0.755(2)	0.582(1)	0.056(4)
O(31)	0.9994(5)	0.826(2)	−0.018(2)	0.081(6)
O(32)	0.9952(5)	1.090(2)	0.352(2)	0.079(6)
O(33)	0.9058(5)	1.016(2)	0.105(2)	0.066(5)
O(41)	0.9613(5)	0.476(2)	−0.032(2)	0.078(6)
O(42)	0.9115(6)	0.315(3)	0.310(2)	0.097(7)
O(43)	0.9971(4)	0.695(2)	0.299(1)	0.040(4)

TABLE 23. Selected distances (Å) and angles (°) for compound **15**

Fe(1)–Fe(2): 2.491(5)
Fe(3)–Fe(4): 2.568(5)
S(2)–Fe(3): 2.278(6)
S(2)–Fe(4): 2.228(6)
S(1)–Fe(4): 2.311(6)
C(23)–Fe(2): 1.76(2)
C(23)–Fe(1): 2.36(2)
Fe(4)–S(2)–C(3): 105.1(6)
Fe(3)–S(2)–C(3): 112.2(6)
Fe(3)–S(2)–Fe(4): 69.5(2)
Fe(4)–S(1)–C(8): 104.2(6)
O(23)–C(23)–Fe(2): 163.2(22)

troscopy: $m/z = 592$, $R = CH_3$, and $m/z = 716$, $R = C_6H_5$).

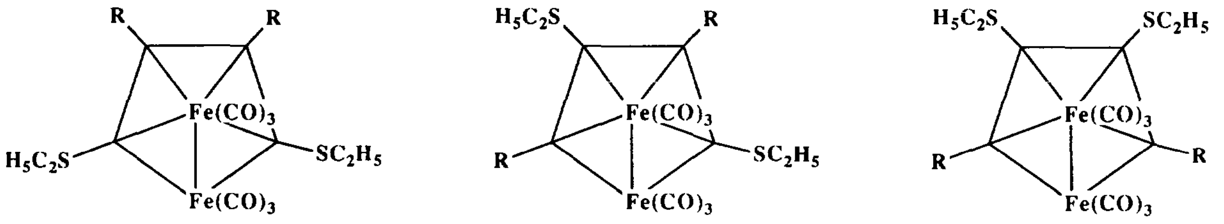
As stated above, the starting solution was actually a mixture of head-to-head and head-to-tail compounds for $R = CH_3$ and of head-to-head, head-to-tail, and tail-to-tail compounds for $R = C_6H_5$. In the case of $R = CH_3$, chromatography led to the head-to-head trinuclear compound **6** and the head-to-tail trinuclear compound **7**. When $R = C_6H_5$, separation by chromatography was not successful, but single crystals of head-to-head compound **8** and head-to-tail compound **9** were separated under a microscope from the same fraction.

The trinuclear compounds **6–9**, were also obtained directly from the reaction of $[Fe_3(CO)_{12}]$ with $RC{\equiv}CSC_2H_5$ in refluxing hexane. In the case of compounds **6** and **7** ($R = CH_3$) yields were 15% and 6% respectively, and the total yield for the unseparated **8** and **9** ($R = C_6H_5$) was 18%.

The structures of **6–9** were not the expected *closo structure* (Scheme 3). Both trinuclear head-to-head compounds (**6** $R = CH_3$, and **8** $R = C_6H_5$) were crystallized and their crystal structures were determined (Figs. 3 and 4), whereas for the head-to-tail coupling, only compound **9**, $R = C_6H_5$, crystallized and its structure was determined by X-ray diffraction (Fig. 5). Head-to-tail compound **7**, $R = CH_3$, was identified by mass and ^1H NMR spectroscopy, and by its reactivity. In particular, the ^1H NMR spectra of both **6** and **7** (Fig. 6) featured two SC_2H_5 groups. For each of them, there is strong diastereotopy. Considering the structure of compound **6** discussed below, it is clear that both compounds have the same SC_2H_5 bridge (triplet 3H of CH_3CH_2S at 1.23 ppm), with the same $^3J = 7.4$ Hz. The 3H of the other CH_3CH_2S do not have exactly the same chemical shifts (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.

X-ray structure determinations showed that trinuclear compounds **6**, **8**, and **9** are built upon a metallacycle, the ferracyclopentadiene fragment of which results from the head-to-head coupling of two thioalkyne molecules for compounds **6** and **8** and from the head-to-tail coupling for compound **9**.

The three iron atoms are at the vertices of an open triangle; the Fe(3)–Fe(1)–Fe(2) angle is equal to 94.6(2)° (compound **6**, $R = CH_3$), 94.4(2)° (compound **8**, $R = C_6H_5$) and 95.87(6)° (compound **9**, $R = C_6H_5$).



head-to-head
Compound 1, R = CH_3
Compound 2, R = C_6H_5

head-to-tail
Compound 3, R = CH_3
Compound 4, R = C_6H_5

tail-to-tail
Compound 5, R = C_6H_5

Scheme 1.

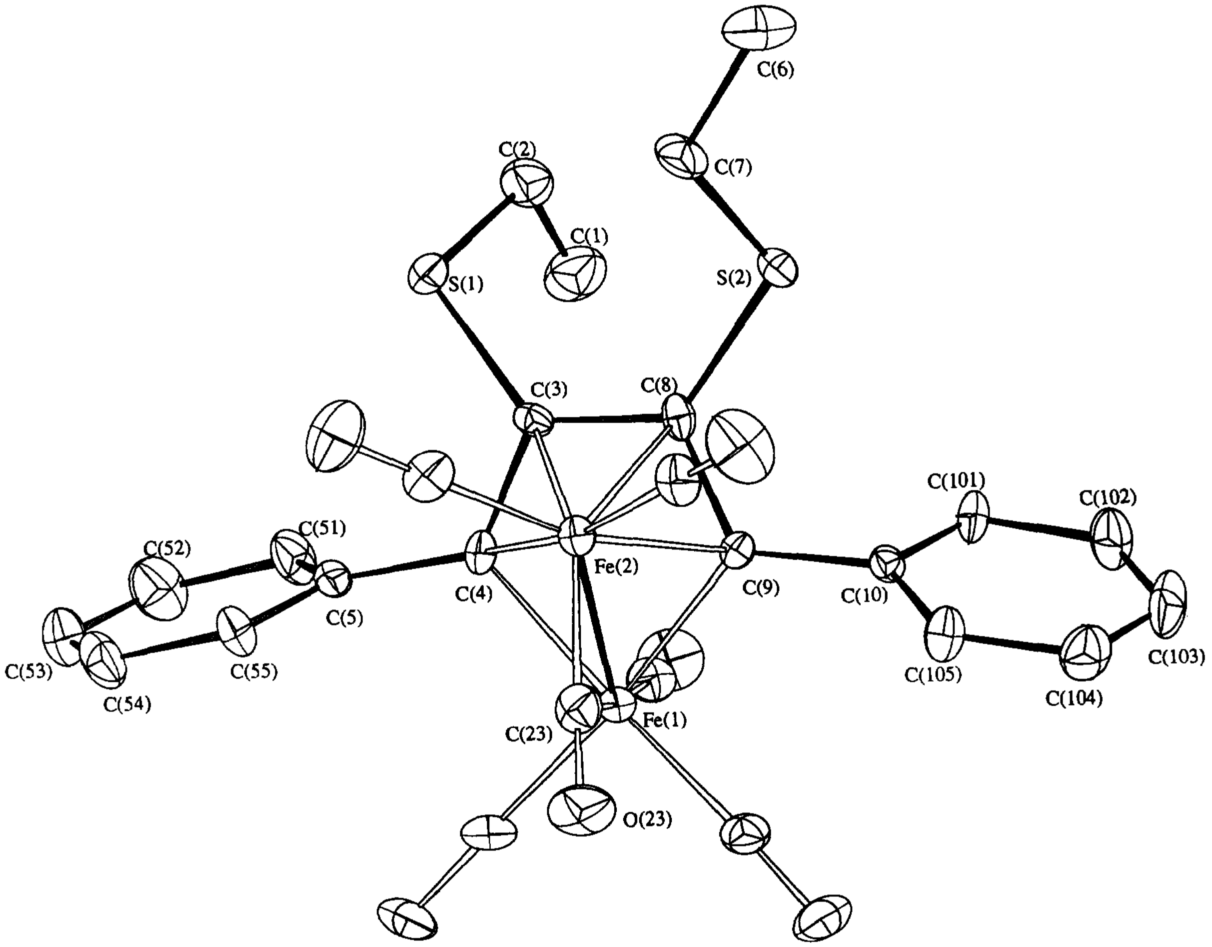
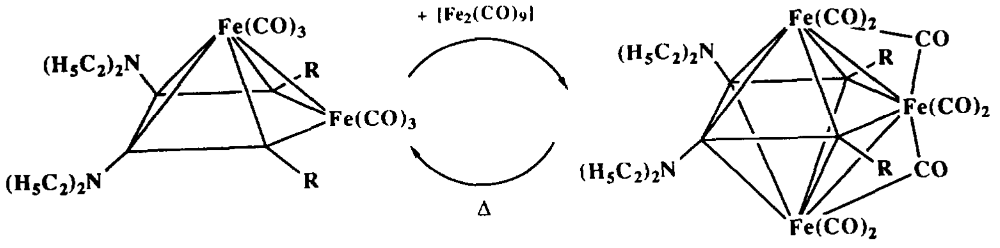


Fig. 1. Molecular structure of compound 5, $[Fe_2(CO)_6\{\mu_2\text{-}C(C_6H_5)C(SC_2H_5)C(SC_2H_5)C(C_6H_5)\}]$.

One edge is the former Fe(1)–Fe(3) bond of the dinuclear compound, and the other is formed by the Fe(1)–Fe(2) bond joining the Fe(1) atom of the cycloferrapentadiene ring to the added Fe(2) atom. Fe(1) and Fe(2) are bridged by an SC_2H_5 group which was cleaved from the ring carbon atom in the α position with



Scheme 2.

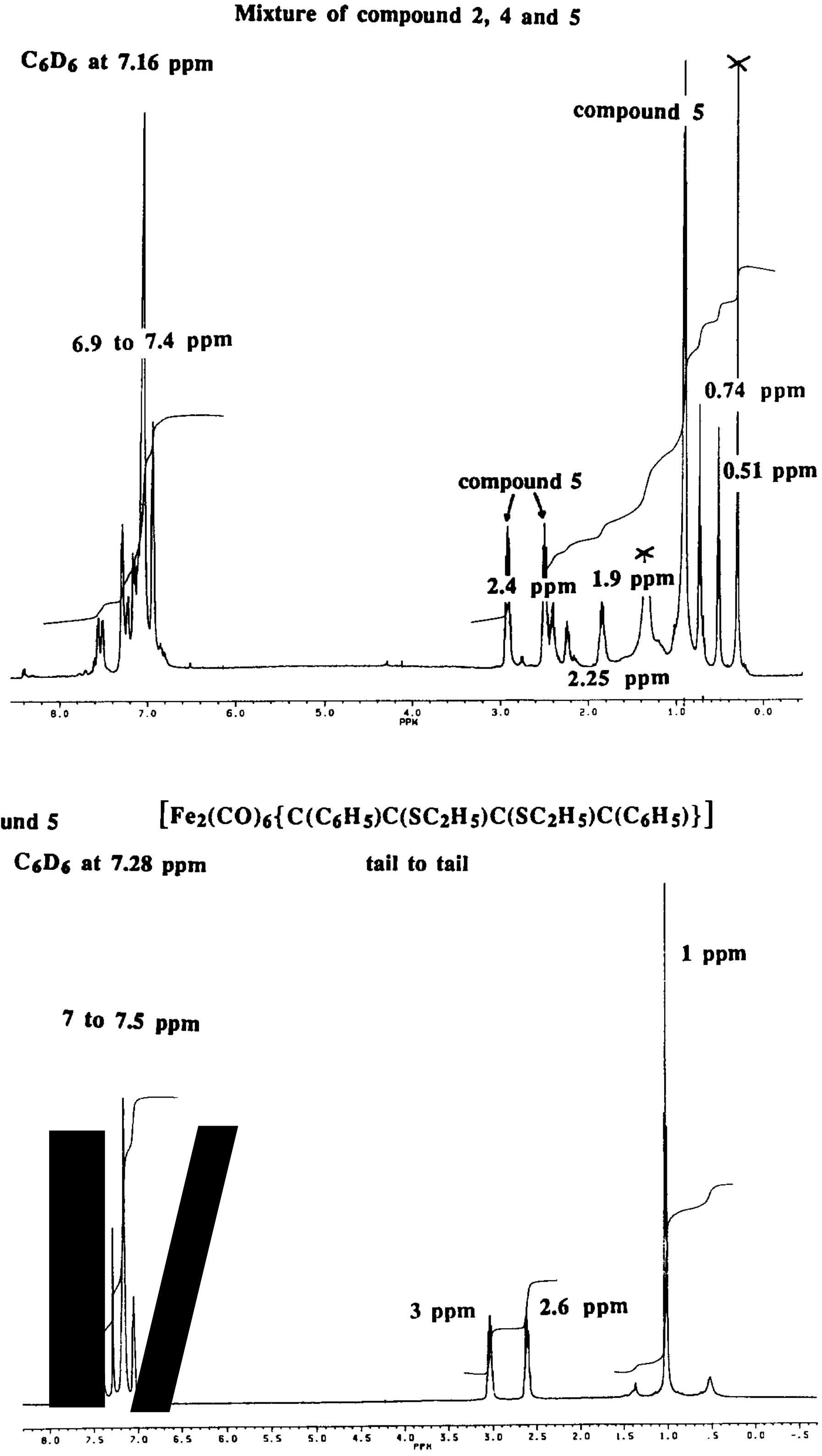
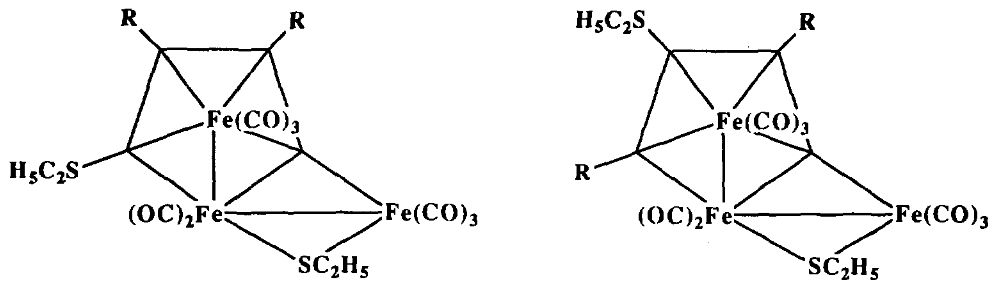


Fig. 2. ^1H NMR spectra of compound 5 and of mixture of compounds 2, 4, 5.



head-to-head

Compound 6, R = CH_3
Compound 8, R = C_6H_5

head-to-tail

Compound 7, R = CH_3
Compound 9, R = C_6H_5

Scheme 3.

respect to Fe(1), and the added iron atom Fe(2) is now bound to this carbon atom so that Fe(2) inserts into the C–SC_2H_5 bond.

As a consequence of the C–S cleavage, the four atoms Fe(1), Fe(2), Fe(3) and C(6) (compound **6**) or C(7) (compounds **8** and **9**) form a butterfly structure;

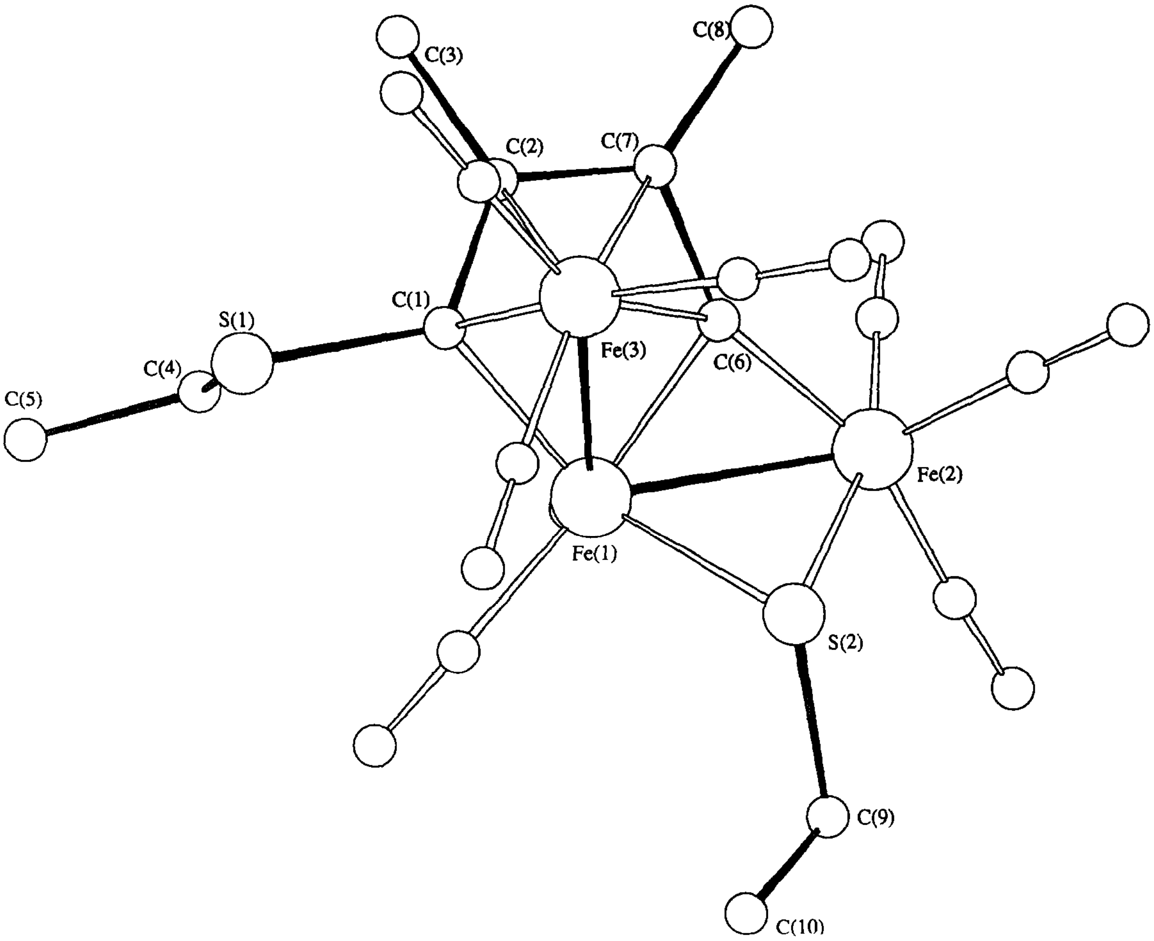


Fig. 3. Molecular structure of compound **6**, $[Fe_3(CO)_8\{\mu_3\text{-}C(SC_2H_5)C(CH_3)C(CH_3)C\}(\mu_2\text{-}SC_2H_5)]$.

the hinge is Fe(1)–C (1.94(3) Å for compound **6**, 1.83(3) Å for compound **8**, and 1.919(8) Å for compound **9**); the dihedral angles between the two planes Fe(1)–Fe(3)–C and Fe(1)–Fe(2)–C are 144.2° (compound **6**), 146.2° (compound **8**) and 147.7° (compound **9**).

These trinuclear complexes do not have the expected *closo* structure. However, another green compound was separated from the reaction solution of compound **7** with $[Fe_2(CO)_9]$. Very tiny crystals were obtained and the crystal structure determination ($R = 0.085$) revealed a *closo* compound, with an unexpected cycloferrapentadiene moiety. One could describe this compound as the result of a head-to-tail coupling of two thioalkyne molecules presumably followed by the replacement by hydrogen of the $C-SC_2H_5$ bond in the β position with respect to the iron atom. Although this hydrogen atom was not located on the Fourier difference map, its occurrence was deduced from mass spectrometry. It is difficult to explain the formation of such a compound.

3.3. Tetranuclear complexes (compounds 10 and 11; head-to-head)

Since head-to-head coupling provided a cycloferrapentadiene ring with two SC_2H_5 groups in the α position with respect to iron, and since a trinuclear compound was obtained after $C-SC_2H_5$ cleavage (compounds **6** and **8**), one SC_2H_5 group was still attached to the ring after a third iron atom was added. Thus it was tempting to add a fourth iron atom, expect-

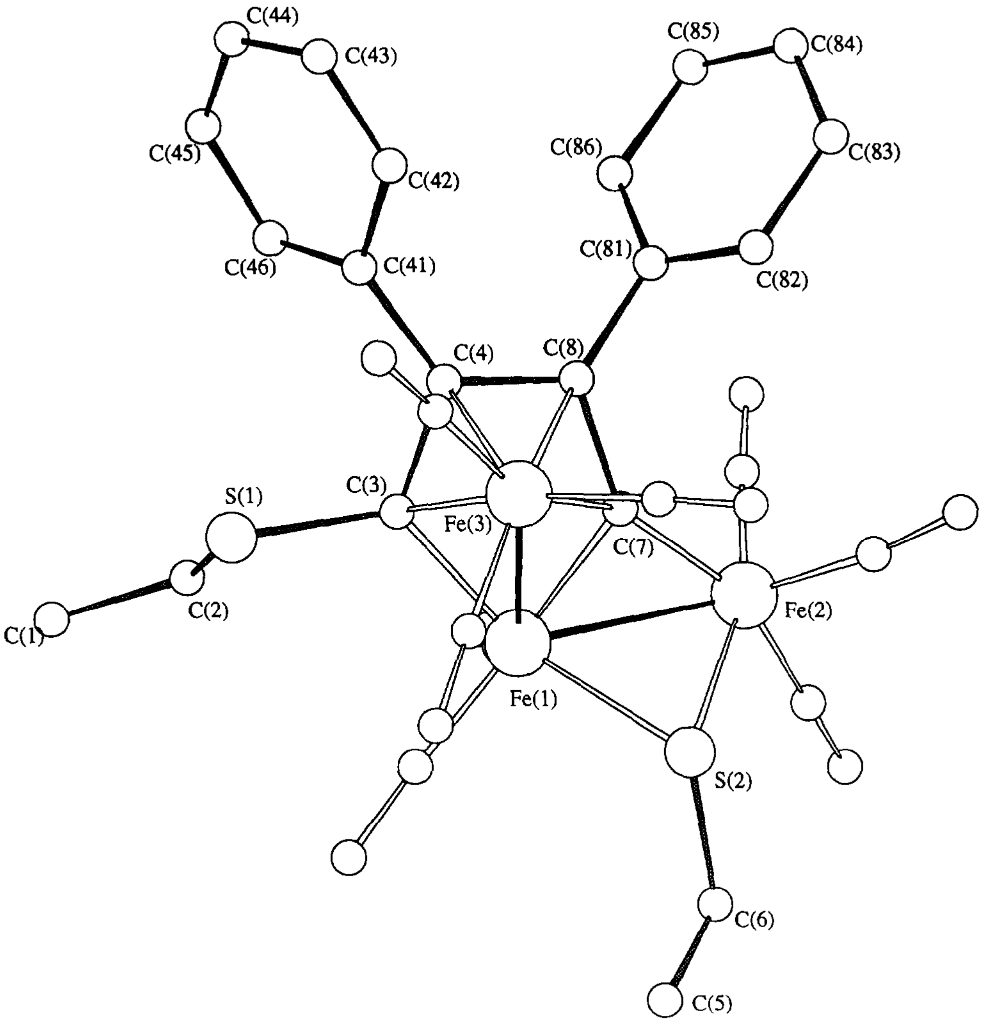


Fig. 4. Molecular structure of compound **8**, $[Fe_3(CO)_8\{\mu_3-C(SC_2H_5)C(C_6H_5)C(C_6H_5)C\}\mu_2-SC_2H_5)]$.

ing the same cleavage of the second C–CS_2H_5 bond. A further excess of $[Fe_2(CO)_9]$ was then allowed to react with trinuclear compounds **6** (R = CH_3) and **8** (R = C_6H_5). In both cases, dark red tetranuclear compounds **10** and **11** were obtained. They have the expected masses 704 and 828 corresponding to the formula $[Fe_4(CO)_{10}(\mu\text{-}SC_2H_5)_2(\mu_4\text{-}CCRCRC)]$. The crystal structure has an approximate plane of symmetry which cannot be a crystallographic plane of symmetry since the unit cells are triclinic ($P\bar{1}$) for R = CH_3 and monoclinic ($P2_1$) for R = C_6H_5 (Figs. 7 and 8). Moreover, in the latter compound, phenyl groups are not symmetrically oriented. Since the space group is non-centrosymmetric, the chirality of the molecule was checked and atomic coordinates are given accordingly. The four iron atoms are arranged in a T-shape, the horizontal being Fe(2), Fe(1), Fe(4) with Fe(2)–Fe(1)–Fe(4) equal to 147.6° for both compounds and there are two SC_2H_5 bridging groups, one spanning Fe(1) and Fe(2) and one spanning Fe(1) and Fe(4).

Each ring carbon atom remaining after the C–S cleavage (C(1) and C(6) for R = CH_3, C(3) and C(7) for R = C_6H_5) is bound to three iron atoms, making Fe_3C butterflies, one on each side of the molecule. Dihedral angles around hinges are 144.5° and 129.1° for R = CH_3, and 143.0° and 146.9° for R = C_6H_5 (Scheme 4).

3.4. Pentanuclear complex (compound 12; head-to-head)

In the reaction of trinuclear compound **6** (R = CH_3) with an excess of $[Fe_2(CO)_9]$, another brown compound was found as a minor product. It was separated by chromatography (yield 5%). The higher mass (found by mass spectrometry) is 788; the comparison with the 704 mass of the tetranuclear compound suggested a new compound containing five iron atoms. The X-ray structure determination showed that the formula

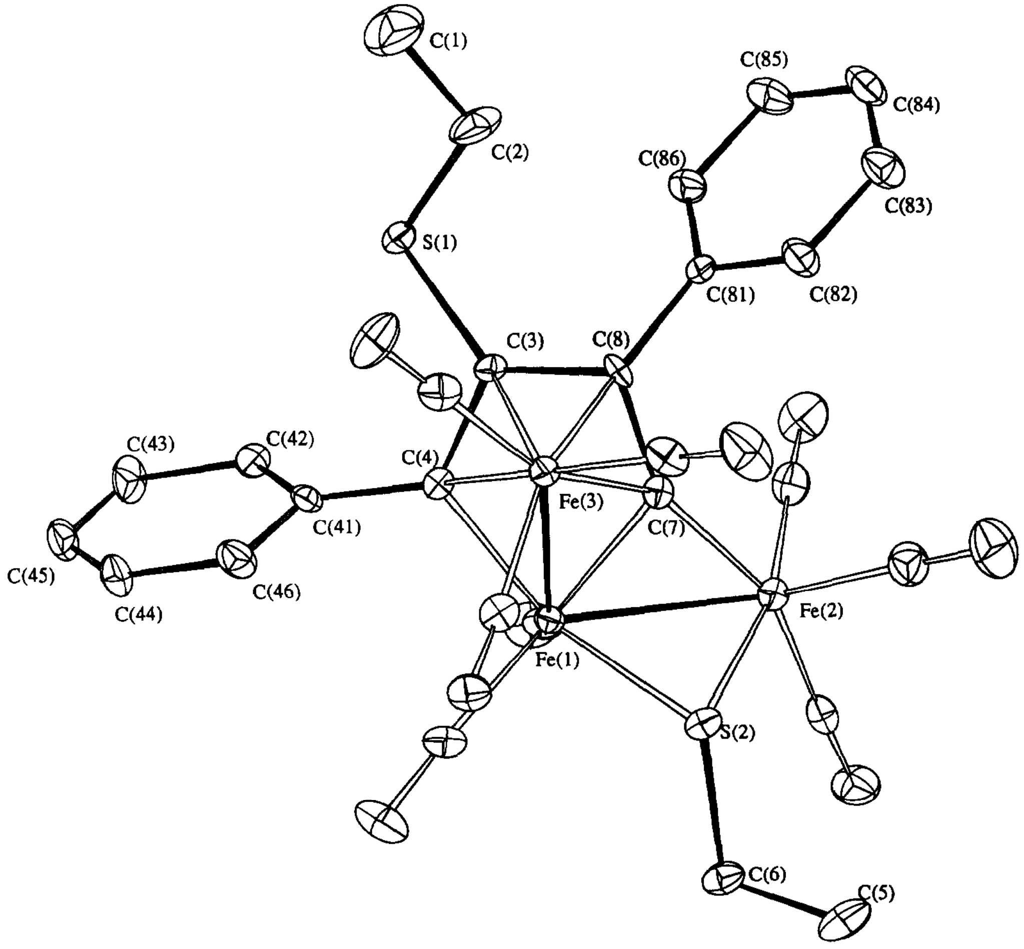


Fig. 5. Molecular structure of compound 9, $[Fe_3(CO)_8\{\mu_3\text{-}C(C_6H_5)C(SC_2H_5)C(C_6H_5)C\}(\mu_2\text{-}SC_2H_5)]$.

is $[Fe_5(CO)_{11}(\mu\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)\{\mu_5\text{-}CC(CH_3)C(CH_3)C\}]$, (compound **12**) (Fig. 9, Scheme 5). The compound is composed of an iron atom quadrilateral with a short-long edge alternation (Fe(1)–Fe(3) = 2.533(8), Fe(3)–Fe(4) = 2.717(8), Fe(4)–Fe(5) = 2.528(9) and Fe(5)–Fe(1) = 2.649(8) Å) and a triangle of iron atoms (Fe(1)–Fe(3) = 2.533(8), Fe(3)–Fe(2) = 2.652(8), and Fe(2)–Fe(1) = 2.619(8) Å), sharing the Fe(1)–Fe(3) edge. It is remarkable that both SC_2H_5 groups are bridging only iron atoms of the quadrilateral, one being μ_3 and the other one μ_2. Thus, one thiolate has migrated from one side of the molecule to the other, and consequently the open iron triangle of the starting compound now appears as a closed triangle.

The quadrilateral may be considered as the basal plane of a distorted square pyramid, the vertex of which is the C(1) carbon atom of the cycloferrapentadiene ring which has lost a SC_2H_5 group. Although the four C–Fe distances are similar within standard deviations (1.98(3), 1.94(4), 2.00(3), 2.13(4) Å), the iron atom base of the pyramid is skewed, one iron being above the mean square plane and the next one below (Fe(1): +0.32; Fe(3): −0.31; Fe(4): +0.37; Fe(5): −0.32 Å). The shortest Fe–Fe distance is doubly bridged by both SC_2H_5 groups; the next shortest is the shared edge of the quadrilateral and of the triangle. It is easy to confirm that all iron atoms are surrounded by 18 electrons.

One might then think about a symmetrical six-iron compound containing two fused quadrangles. Unfortunately, the reaction of compound **12** with an excess of $[Fe_2(CO)_9]$ did not occur even after a five days heating in refluxing toluene. Thus, the triangle of iron atoms seems to be a dead end to the cluster building route.

3.5. *Tetranuclear complex (compound 13; head-to-tail)*

Compound **13** was obtained by reaction of iron carbonyl with compound **7**, which contains two head-to-tail coupled thioalkyne molecules. Its mass, 704, is the same as for tetranuclear compound **10**. However, its structure is necessarily different for two reasons. First, the second C–SC_2H_5 bond (compound **9**) situated in the β position with respect to the iron atom cannot be broken to build a second SC_2H_5 bridge; second, the IR spectrum of compound **13** shows a semi-bridging CO group (1830 cm^{-1}) which does not exist for compound **10**.

The crystal structure determination of compound **13** (Fig. 10, Scheme 4) shows a distorted square pyramid Fe_4C. The base is a skewed quadrilateral of four iron atoms. The four Fe–Fe distances show a short-long bond alternation (Fe(1)–Fe(2) = 2.623(8), Fe(2)–Fe(4) = 2.585(8), Fe(4)–Fe(3) = 2.656(8), Fe(3)–Fe(1) = 2.549(8) Å). The vertex of the pyramid is carbon atom C(6), the terminal atom of the butadiene fragment which resulted from the head-to-tail coupling of alkynes $C(CH_3)C(SC_2H_5)C(CH_3)C$; this carbon atom lost the SC_2H_5 group as in the starting compound **7**. The butadiene fragment makes a ferracyclopentadiene ring with Fe(1); it is bonded to Fe(3) by Fe(1) and by the four carbon atoms C(2), C(1), C(7), C(6). Thus the butadiene moiety spans one side of the quadrilateral,

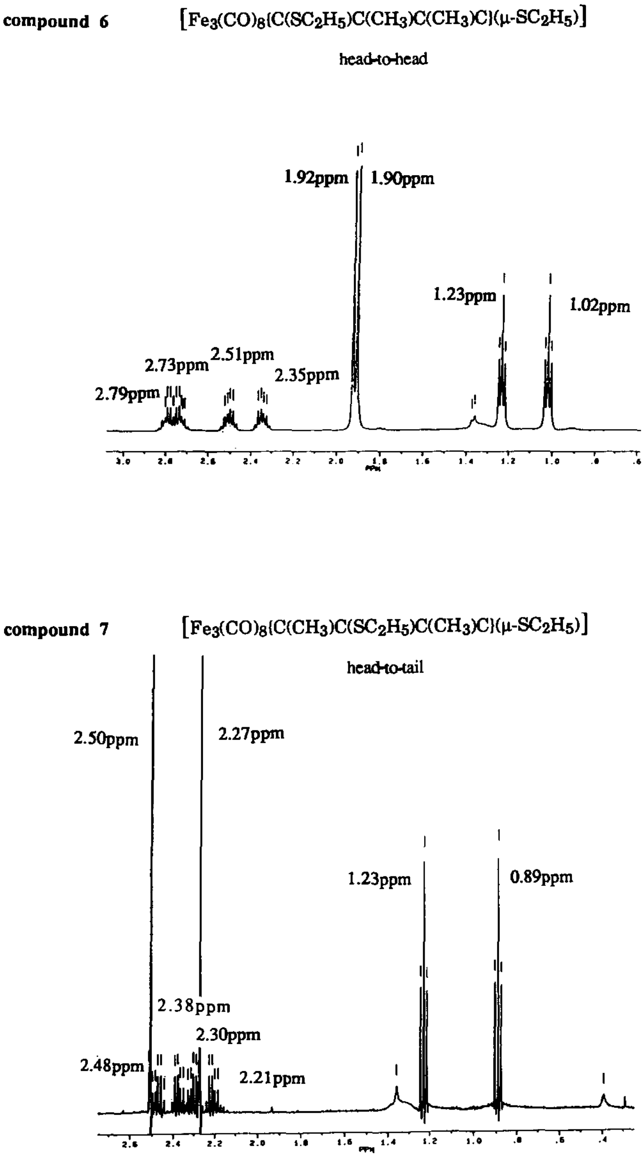


Fig. 6. ^1H NMR spectra of compounds **6** and **7**.

the other side of which is spanned by a μ_3-SC_2H_5 linked to Fe(1), Fe(2), and Fe(4).

The ferracyclopentadiene ring is bent around the C(2)–C(6) line with a dihedral angle between the planes C(2)–Fe(1)–C(6) and C(2)–C(1)–C(7)–C(6) of 28.5°. Fe(1) and Fe(3) are ligated to two carbonyls whereas Fe(2) and Fe(4) are ligated to three. One CO bound to Fe(4) has a semi-bridging character and spans the Fe(3)–Fe(4) bond: Fe(4)–C(34) = 1.77(5), Fe(3)–C(34) = 2.20(4) Å. Angles F(4)–C(34)–O(34), Fe(3)–C(34)–O(34), and Fe(4)–C(34)–Fe(3) are 157(4), 119(4), and 83(2)° respectively.

This complex is unusual since the C(6) carbon atom is involved in five bonds, *i.e.* four Fe–C bonds and one C–C bond, C(6)–Fe(1) = 2.07(4), C(6)–Fe(2) = 1.91(4), C(6)–Fe(3) = 2.14(4), and C(6)–Fe(4) = 2.10(4). The electron count fulfills the EAN rule.

3.6. Tetranuclear complexes: ($R = C_6H_5$) Compounds 14 and 15 (tail-to-tail), Scheme 6

The tail-to-tail coupling corresponds to dinuclear compound **5**, $[Fe_2(CO)_6\{C(R)C(SC_2H_5)C(SC_2H_5)C(R)\}]$, in which both cycloferrapentadiene ring carbon atoms in the α position with respect to iron atom bear a methyl or a phenyl group. We obtained a product only with $R = C_6H_5$ and this was separated by selecting crystals under a microscope and not by chromatography. As described above, this compound is a *nido*-type cluster with seven skeletal electron pairs. The question then arose: would it be possible to build a *closo* structure by adding a $Fe(CO)_2$ group because the absence of the ethylmercapto group on carbon atoms in the α position with respect to iron should prevent the cleavage of the C–S bond and the construction of either a trinuclear or a tetranuclear iron compound?

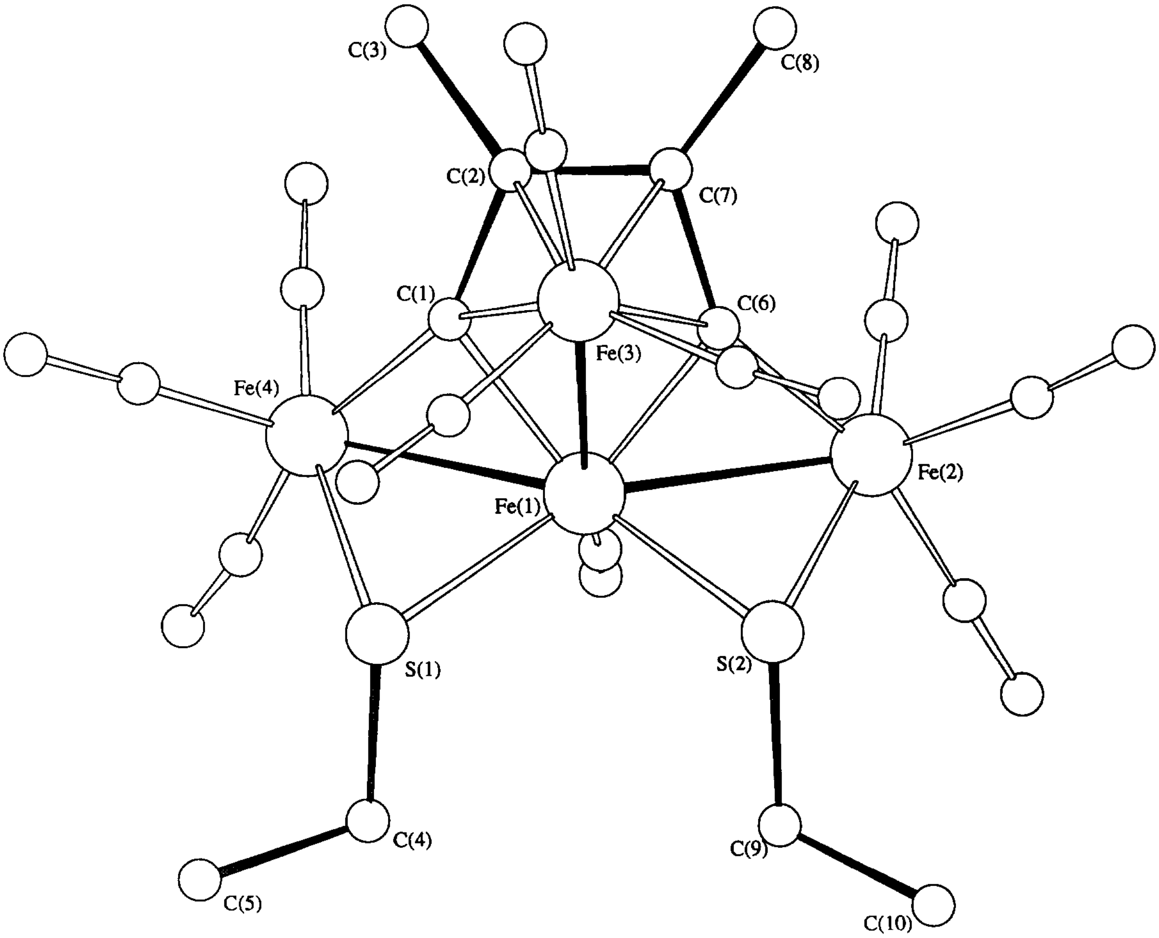


Fig. 7. Molecular structure of compound **10**, $[Fe_4(CO)_{10}\{\mu_4\text{-}CC(CH_3)C(CH_3)C\}(\mu_2\text{-}SC_2H_5)_2]$.

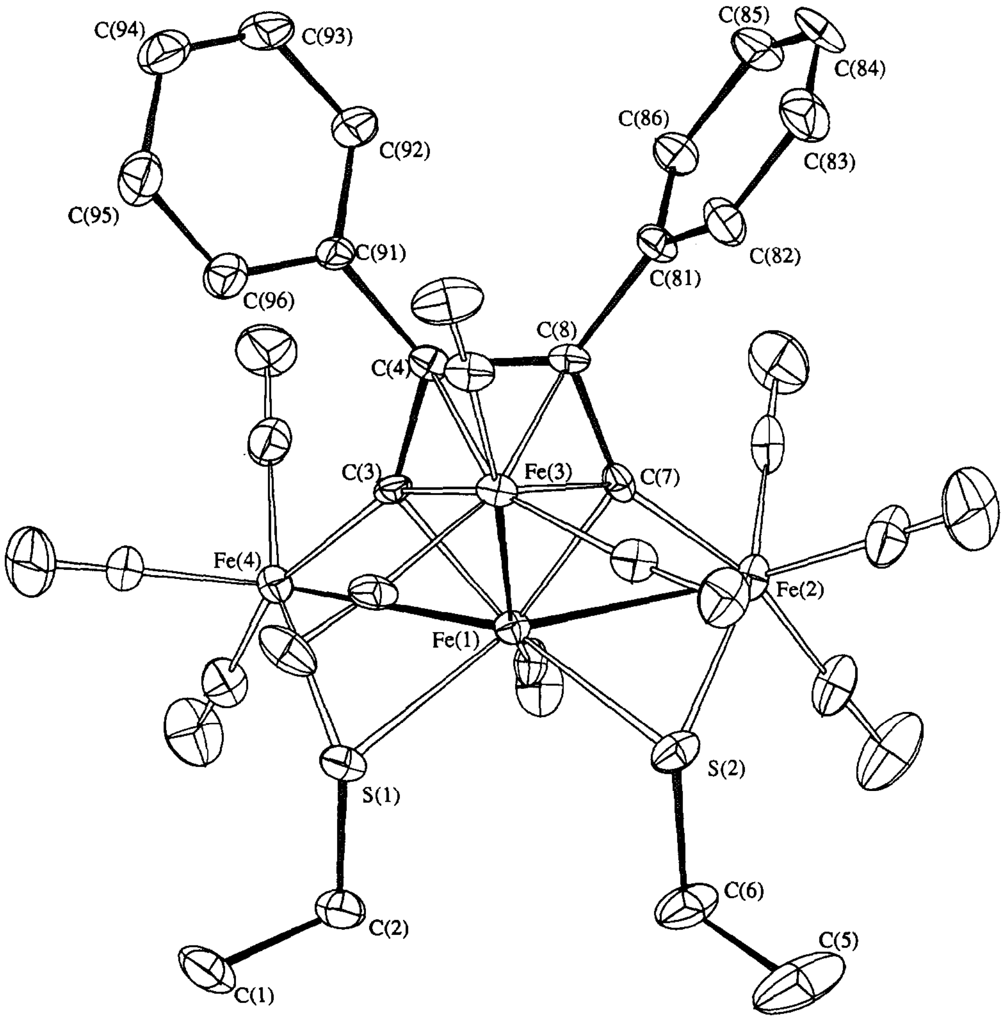
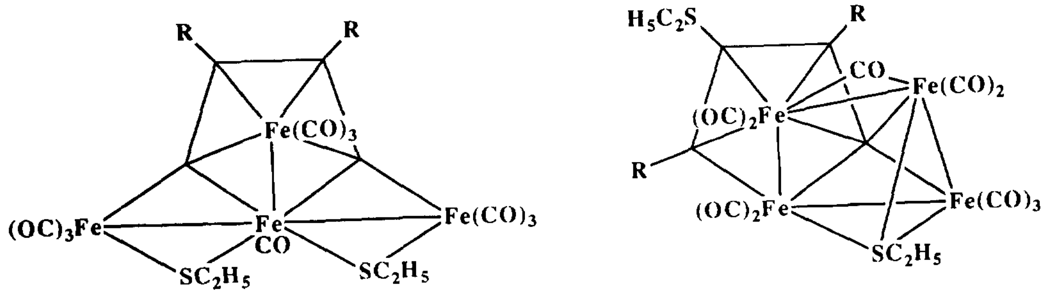


Fig. 8. Molecular structure of compound 11, $[Fe_4(CO)_{10}\{\mu_4\text{-}CC(C_6H_5)C(C_6H_5)C\}(\mu_2\text{-}SC_2H_5)_2]$.



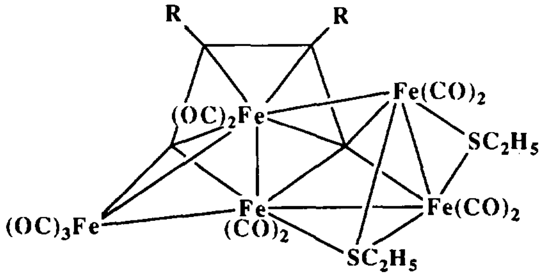
head-to-head

Compound 10, R = CH_3
Compound 11, R = C_6H_5

head-to-tail

Compound 13, R = CH_3

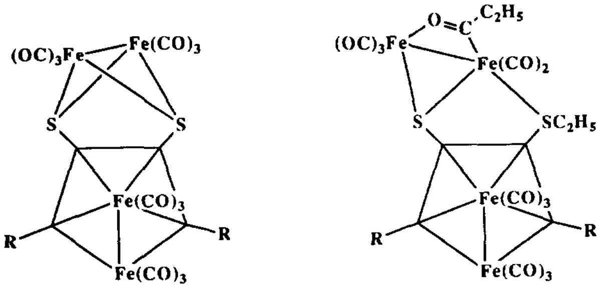
Scheme 4.



head-to-head

Compound 12, R = CH_3

Scheme 5.



tail-to-tail

Compound 14, R = C_6H_5

Compound 15, R = C_6H_5

Scheme 6.

Such a *nido-closo* transformation occurs for the aminoalkyne-containing dinuclear complex $[Fe_2(CO)_6\{C_6H_5CC[N(C_2H_5)_2]C[N(C_2H_5)_2]CC_6H_5\}]$ (Scheme 2).

The reaction was carried out by adding an excess of $[Fe_2(CO)_9]$ to selected crystals of compound **5** in refluxing hexane. Chromatography using heptane as eluent gave three fractions, two of which provided crystals. A yellow fraction gave compound **14** and an orange fraction yielded compound **15**.

The molecular mass of compound **14** measured by chemical ionisation spectrometry was 844; thus the actual molecular mass would be 826 if the highest peak is attributed to $[M + NH_4]^+$. A tetranuclear compound

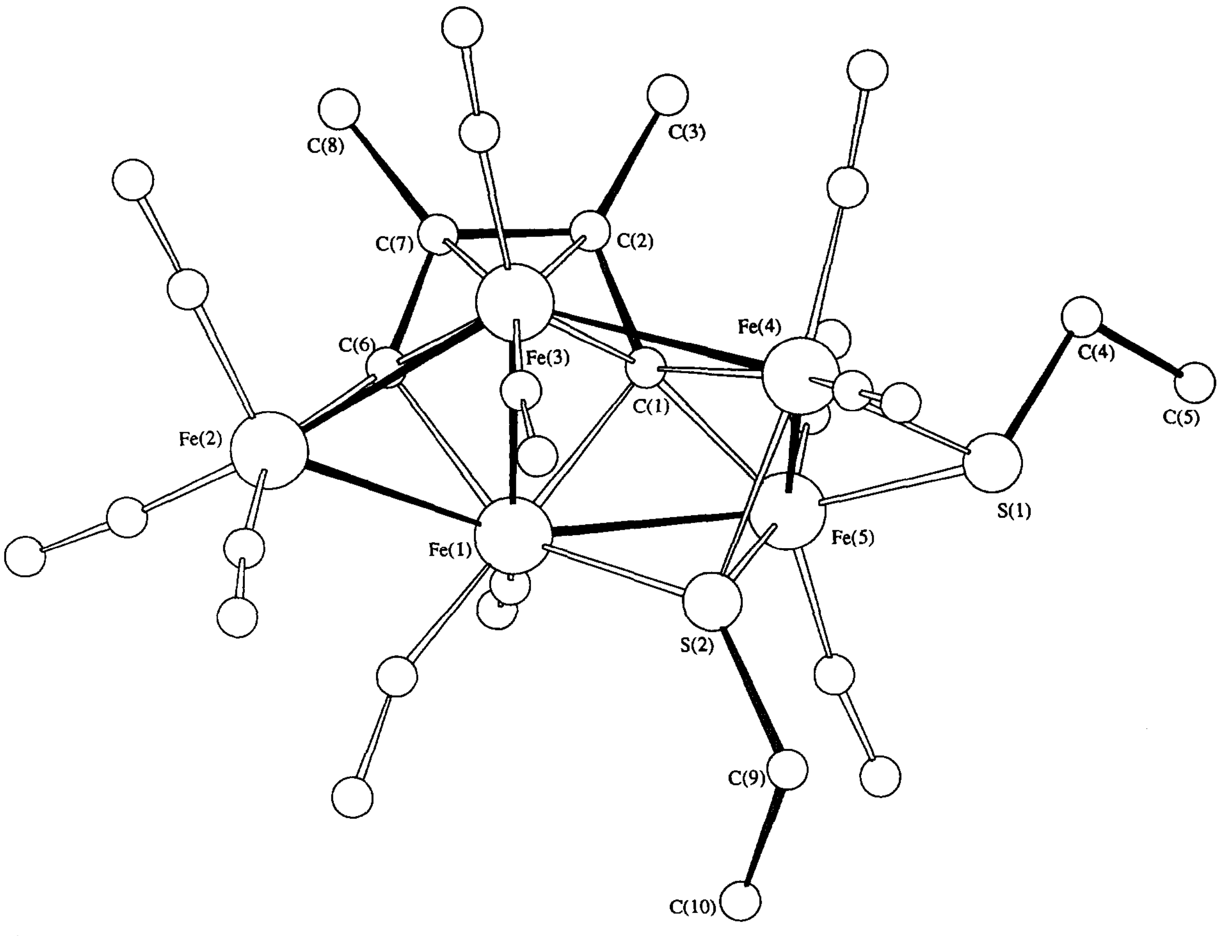


Fig. 9. Molecular structure of compound 12, $[Fe_5(CO)_{11}\{\mu_5\text{-}CC(CH_3)C(CH_3)C\}(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)]$.

for which it seemed difficult to suggest a structure, was assumed although the IR spectrum suggested the occurrence of a semi-bridging CO group ($\nu_{CO} = 1930$ cm^{-1}), as in the starting compound **5**. Fortunately, the growth of yellow single crystals allowed a crystal structure determination which showed a rare and unexpected cleavage of the S-C_2H_5 bond (Fig. 11). Both sulfur atoms which were linked to adjacent carbon atoms in the starting compound **5** lost their ethyl groups and ligated a $Fe_2(CO)_6$ fragment, each sulfur being bound to both iron atoms. The Fe-Fe distance in the $Fe_2(CO)_6$ group is 2.461(7) Å while the other Fe-Fe distance is 2.473(6) Å, *i.e.* the same values within experimental errors. The sulfur-carbon bond lengths (1.78(2) and 1.75(3) Å) did not change very much compared to those of the starting dinuclear compound **5** (1.772(9) and 1.769(9) Å).

Concerning compound **15**, the chemical ionisation spectrum showed a peak at 902; the molecular mass of compound **15** would be 884 assuming a $[M + NH_4]^+$ peak. This spectrum would correspond to another tetranuclear compound, different from compound **14**. Indeed, the IR spectrum of compound **15** suggests a semi-bridging CO group with a $\nu_{C\equiv O}$ band at 1930

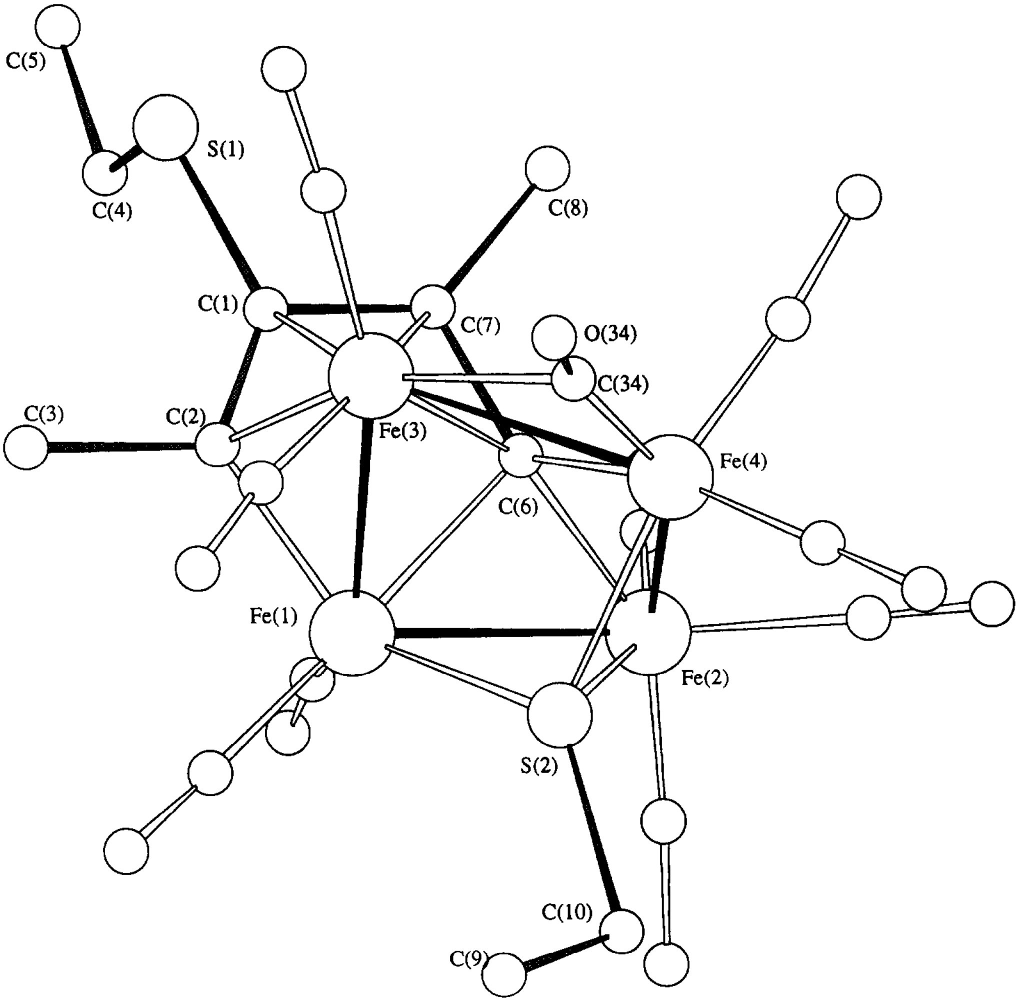


Fig. 10. Molecular structure of compound **13**, $[Fe_4(CO)_{10}\{\mu_4\text{-}C(CH_3)C(SC_2H_5)C(CH_3)C\}(\mu_3\text{-}SC_2H_5)]$.

cm^{-1} and a ketonic $\nu_{C=O}$ band at 1640 cm^{-1}. The crystal structure determination confirmed this (Fig. 12). The molecular structure of compound **15** shows some similarities with that of compound **14** but also two major differences. The first is that only one S–C_2H_5 bond was broken. Both sulfur atoms are ligated to a $Fe_2(CO)_5(\mu\text{-}C_2H_5CO)$ fragment. The sulfur atom of the SC_2H_5 group is ligated to one iron atom only (2.311(6) Å) because the Fe(3)–S distance, 3.645 Å, is non-bonding. The sulfur atom which has lost its ethyl group is ligated to both iron atoms (2.278(6), 2.228(6) Å). These Fe–S bond lengths are rather different, but the two S–C bonds between sulfur and the cycloferrapentadiene ring remain the same (1.80(2) and 1.80(3) Å). The second major difference is a propanoyl bound to iron by its carbonyl group, through C(43) to Fe(4) and through O(43) to Fe(3), thus building a four-membered ring, Fe(3)Fe(4)C(43)O(43). This ring is nearly planar (Fe(3): +0.015, Fe(4): −0.016, C(43): +0.032, O(43): −0.03 Å). The observed ketonic IR band is attributed to this C(43)O(43) group. This compound may be an intermediate between compounds **5** and **14** where both S–C_2H_5 bonds were broken.

As a consequence of the unsymmetrical ligation of the $Fe_2(CO)_5(\mu\text{-}C_2H_5CO)$ fragment, the Fe(3)–Fe(4) bond makes an angle of 58.9° with the ferracyclopentadiene ring.

As far as the ^{1}H NMR of compound **15** is con-

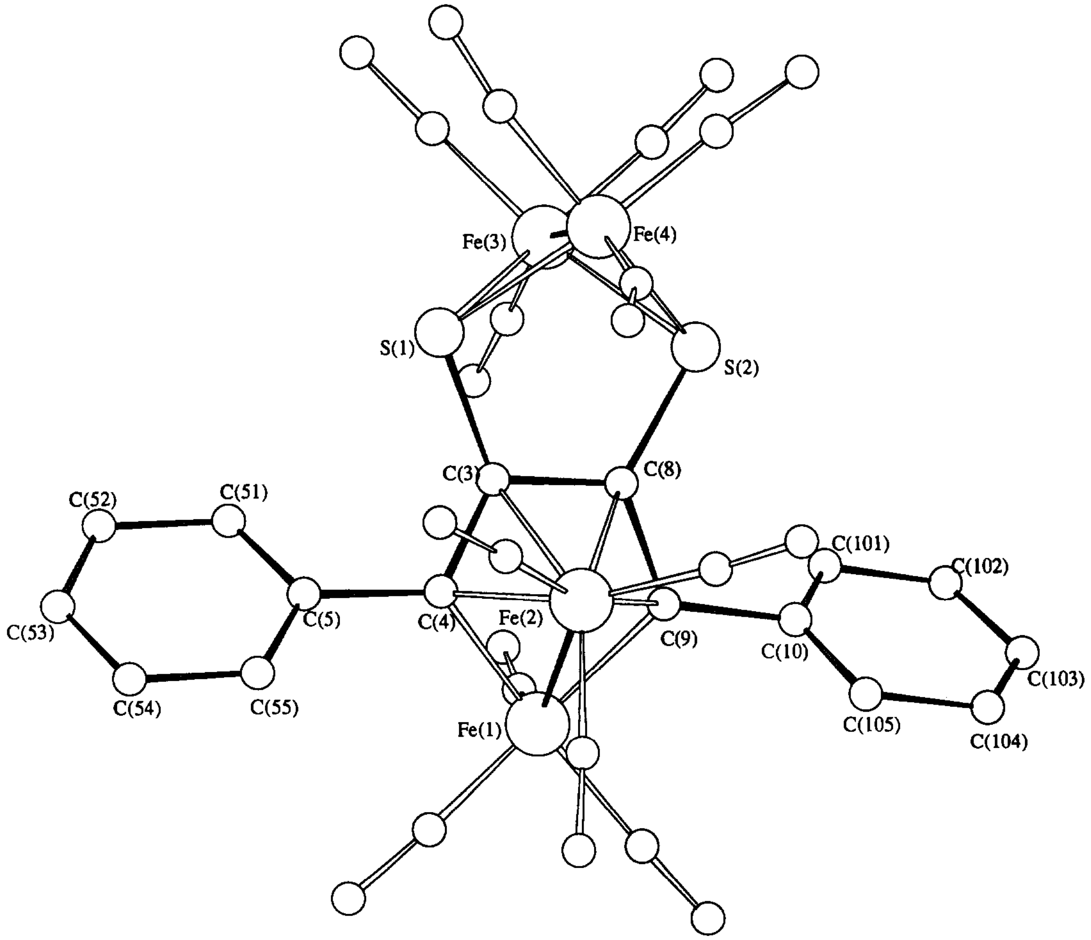
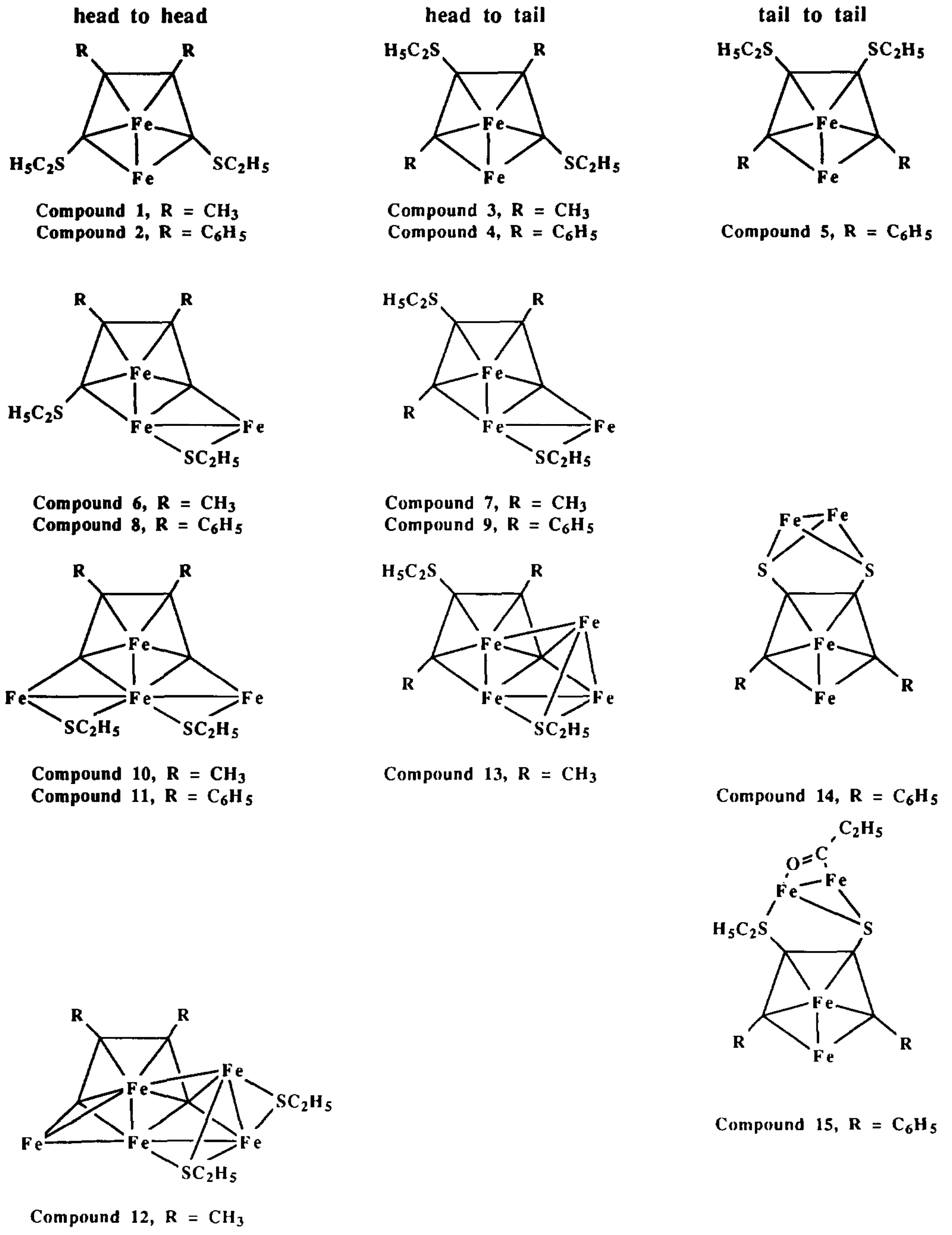


Fig. 11. Molecular structure of compound **14**, $[Fe_4(CO)_{12}\{\mu_4\text{-}C(C_6H_5)C(S)C(S)C(C_6H_5)\}]$.

cerned, there are two very distinct C_2H_5 groups, belonging to C_2H_5CO and to C_2H_5S. The first shows a triplet at 0.42 ppm and two poorly resolved quadruplets of two non-equivalent H centred at 2.05 and 2.4 ppm. The second is identified by its triplet at 0.94 ppm and two quadruplets of two non-equivalent H atoms centred at 2.32 and 2.55 ppm. If one considers the SC_2H_5 group of compound **8**, in which the sulfur atom is not ligated to the iron atom, its peaks are located at 0.89 ppm for the triplet and at 2.30 and 2.21 ppm for both quadruplets. The peaks are shifted as expected toward slightly lower fields because of removal of electrons from sulfur upon coordination.

4. Conclusion

Scheme 7 presents a summary of the compounds described here. The three columns refer to the three



Scheme 7.

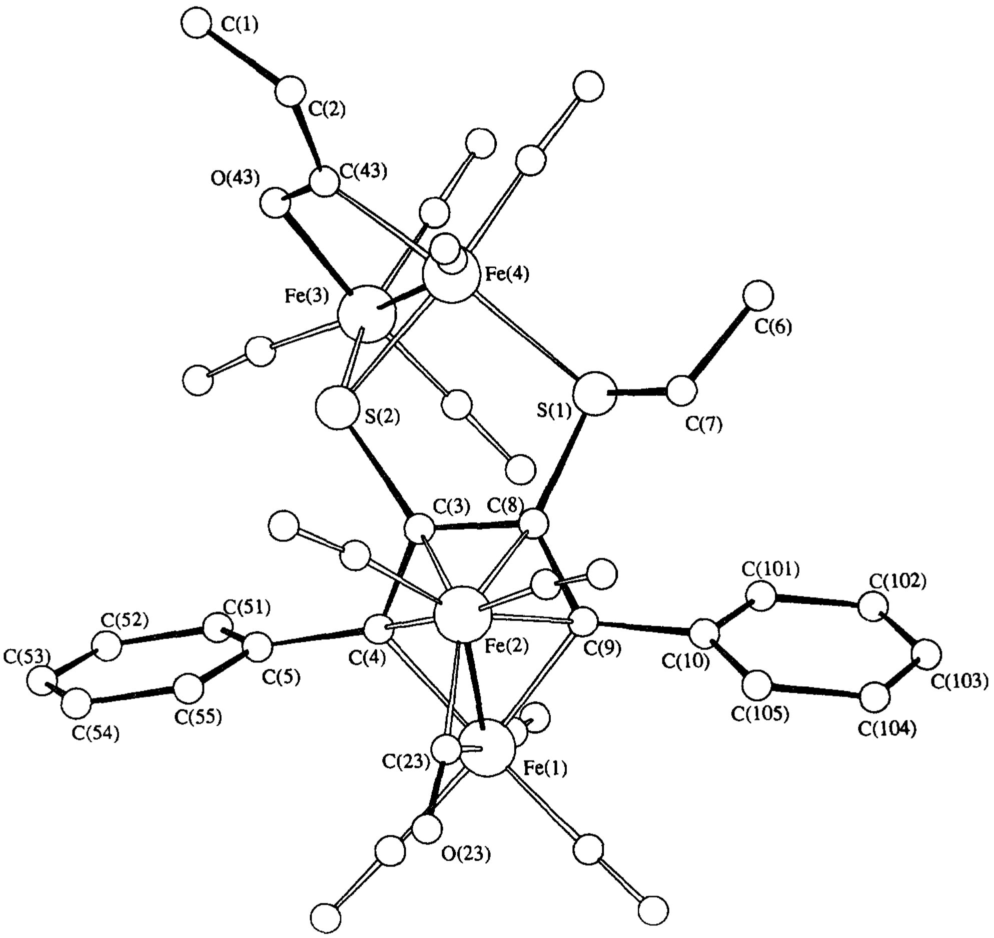


Fig. 12. Molecular structure of compound **15**, $[Fe_4(CO)_{11}(\mu_2\text{-}O{=}CC_2H_5)\{\mu_4\text{-}C(C_6H_5)C(S)C(SC_2H_5)C(C_6H_5)\}]$.

possible couplings of the starting dinuclear classical ferrole-type compounds. This Scheme shows in each case how an excess of iron carbonyl progressively led to trinuclear, tetranuclear and finally pentanuclear compounds. The number of compounds and the nature of the R radical attached to the alkyne $RC{\equiv}CSC_2H_5$ (ethyl or phenyl) are indicated.

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