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Reactions of $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$: synthesis and structures of $[\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2](\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (R = alkyl, phenyl or acyl)

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Abstract

The reaction of $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ forms $(\mu_3\text{-S})_2\text{Fe}_3(\text{CO})_9$ (**1**) and/or anionic intermediates $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ (**2**) depending on the substituents R^1 and R^2. The actions of the anionic complexes **2** with alkyl halides, PhN_2BF_4 and acid chlorides give $[\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2](\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (R = alkyl, Ph or acyl). The structures of $(\mu\text{-}\eta^2\text{-CH=CHPh})(\mu\text{-CH}_2\text{=CHCH}_2\text{S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\cdot0.5\text{C}_6\text{H}_{12}$ and $(\mu\text{-}\eta^2\text{-CH=CH-furyl-2})[\mu\text{-PhCH=CHC(O)S}][\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ were determined by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Alkenyl ligand; Bridging-sulfur ligand; Complexes; Synthesis; Structures

1. Introduction

The anionic complexes $[(\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2)(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ have shown interesting reactivity towards electrophiles and acetylenes, C–C bond formation being observed in most cases [1–5]. The anions also readily take up heteroatom-bridging ligands to give complexes of type $[(\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2)(\mu\text{-X})\text{Fe}_2(\text{CO})_6$ where X = Cl [6], SR [7] or PR_2 [8]. In a related study, we reported the reaction of $[(\mu\text{-}\eta^2\text{-CH=CHPh})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, forming a tetranuclear anionic complex $[(\mu\text{-}\eta^2\text{-CH=CHPh})(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ [9]. In an attempt to determine how general the reaction is, we have investigated the reaction of $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ ($R^1 = R^2$ = H or Ph; R^1 = Me, R^2 = H; R^1 = H, R^2 = Et or 2-furyl) with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. The reactivity of the formed anionic complexes $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-S})\{\text{Fe}_2(\text{CO})_6\}_2(\mu_4\text{-S})]^-$ toward alkyl halides, PhN_2BF_4 and acid chlorides was studied. The crystal structures of $(\mu\text{-}\eta^2\text{-CH=CHPh})(\mu\text{-CH}_2\text{=CHCH}_2\text{S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\cdot0.5\text{C}_6\text{H}_{12}$ and $(\mu\text{-}\eta^2\text{-CH=CH-furyl-2})[\mu\text{-PhCH=CHC(O)S}][\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ were determined.

2. Results and discussion

The reaction of $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and the synthesis of complexes **1**, **3a**–**3d**, **4** and **5a**–**5c** are summarized in Scheme 1. Reaction of $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ in THF with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ proceeded readily at −78°C, as indicated by gas evolution and by red–brown to red–orange color change. After treatment of the reaction mixture with an electrophile, two products were usually formed: $(\mu_3\text{-S})_2\text{Fe}_3(\text{CO})_9$ (**1**) and $[\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2](\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ [R = R^3, Ph or R^4C(O)]. When $R^1 = R^2$ = H or Ph in $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$, only complex **1** was isolated. Further experiments showed that complex **1** was formed in the step of reaction of $[\{\mu\text{-}\eta^2\text{-C(R}^1)\text{=CHR}^2\}(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$,

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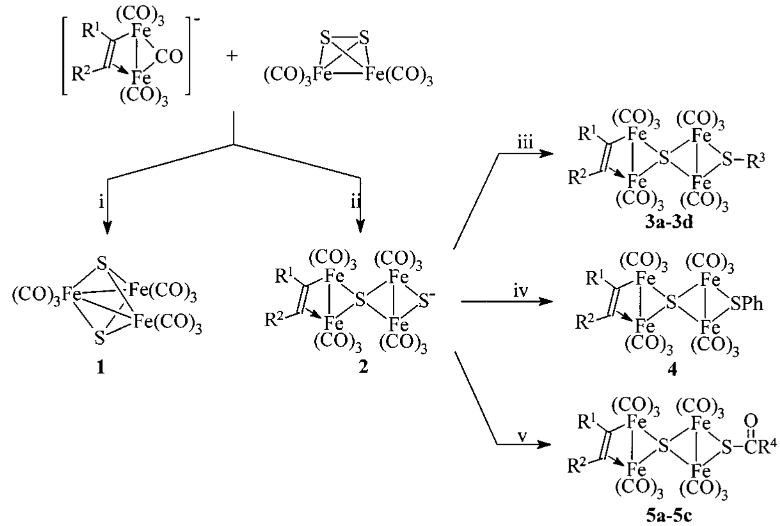
regardless of the alkyl halides added ((i) in Scheme 1). Another species formed by reaction of $[\{\mu$-η^2-C(R^1)=CHR$^2\}(\mu$-CO)Fe$_2$(CO)$_6]^-$ with (μ-S$_2$)Fe$_2$(CO)$_6$ is assumed to be an anionic complex $[\{\mu$-η^2-C(R^1)=CHR$^2\}(\mu$-S)$\{$Fe$_2$(CO)$_6\}_2(\mu_4$-S)$]^-$ (**2**) ((ii) in Scheme 1), in which the sulfur–sulfur bond of (μ-S$_2$)Fe$_2$(CO)$_6$ is cleaved by the iron-centered anions [5,8] and the μ-CO ligand of $[\{\mu$-η^2-C(R^1)=CHR$^2\}(\mu$-CO)Fe$_2$(CO)$_6]^-$ is replaced by one of the sulfur atoms of (μ-S$_2$)Fe$_2$(CO)$_6$. Treatment of the anions **2** in situ with R^{3}X (R^{3}X = EtBr, PhCH$_2$Cl or CH$_2$=CHCH$_2$Br) gave neutral complexes [μ-η^2-C(R^1)=CHR^2](μ-R^{3}S)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**3a**–**3d**) ((iii) in Scheme 1), and with PhN$_2$BF$_4$ or R^{4}C(O)Cl (R^4 = Ph, CH=CHPh or Me) yielded [μ-η^2-C(R^1)=CHR^2](μ-PhS)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**4**) (R^1 = Me, R^2 = H) ((iv) in Scheme 1) and [μ-η^2-C(R^1)=CHR^2][μ-R^{4}C(O)S][Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**5a**–**5c**) ((v) in Scheme 1), respectively. It is worth pointing out that the reaction of **2** (R^1 = Me, R^2 = H) with PhN$_2$BF$_4$ formed a complicated mixture. Only two of the components were separated and identified as **1** and the expected complex. The others were too tiny to separate. The relatively low yields of products **3a**–**3d** and **5a**–**5c** may be attributed to the extensive decomposition in the course of the reactions.

Complex **1** is known. It was characterized by elemental analysis and by comparison of its melting point and IR spectral data to those of authentic sample [10]. The complexes **3a**–**3d**, **4** and **5a**–**5c** are air stable in solid state, but decompose slowly in solution when exposed to air. They are very soluble in polar organic solvents such as methylene chloride and soluble in petroleum ether. These new compounds were characterized by elemental analyses, IR and ^{1}H-NMR spectra. The IR spectrum of each of complexes **3**–**5** showed terminal carbonyl bands, ranging from 1965 to 2087 cm^{-1}. For complexes **5a**–**5c** the absorption bands of thiocarboxylato groups were also observed. The ^{1}H-NMR spectra of complexes **3**–**5** indicated that each of them exists only as one conformer, although there are two possible conformational isomers, **A** and **B**, according to the orientations of the S–R ligand to the cluster core. Each of the complexes **3a**–**3d** and **5c** can be attributed to equatorial isomer **A** by comparing the chemical shifts of SR groups with the reported data for complexes (μ-RS)(μ-R′S)Fe$_2$(CO)$_6$ or [(μ-RS)Fe$_2$(CO)$_6$]$_2$(μ-S–S-μ) [11,12]. For example, the chemical shift of SCH$_2$ at 2.49 ppm for **3a** is very close to that of equatorial C$_2$H$_5$ (δ_{SCH_2} = 2.44 ppm) in complex [(μ-RS)Fe$_2$(CO)$_6$]$_2$(μ-S–S-μ), rather than to the axial one (δ_{SCH_2} = 1.92 ppm) [11]. For complexes **4** and **5a**–**5b**, however, the available data do not allow us to say which is present in the respective product, but it seems that isomer **B** is disfavored by repulsion between the axial R group and terminal carbonyls. This deduction was confirmed by single-crystal X-ray diffraction results of complexes **3d** and **5b** (see below). The coupling constants of ethenyl protons, ranging from 12.4 to 14.4 Hz, for **3c**, **3d**, **5b** and **5c** also indicated that the protons exist in a *trans* configuration. In addition, single-crystal X-ray diffraction analysis of **3d** also showed the presence of cyclohexane molecule in the crystal. The cyclohexane



Cluster	3a	3b	3c	3d	4	5a	5b	5c
R^1	Me	H	H	H	Me	Me	H	H
R^2	H	Et	2-furyl	Ph	H	H	2-furyl	Ph
R^3 or R^4	Et	PhCH$_2$	Et	allyl		Ph	PhCH=CH	Me

Scheme 1. Reagents and conditions: (i) THF, −78°C, 30 min then r.t., stirred 4 h; (ii) THF, −78°C, 30 min; (iii) R^{3}X (R^{3}X = EtBr for **3a** and **2c**, PhCH$_2$Cl for **3b** and CH$_2$=CHCH$_2$Br for **3d**), −78°C to r.t., stirred 6 h (16 h for **3a**); (iv) PhN$_2$BF$_4$, −78°C to r.t., stirred 16 h; (v) R^{4}C(O)Cl (R^4 = Ph for **5a**, PhCH=CH for **5b**, Me for **5c**), −78°C to r.t., stirred 6 h.

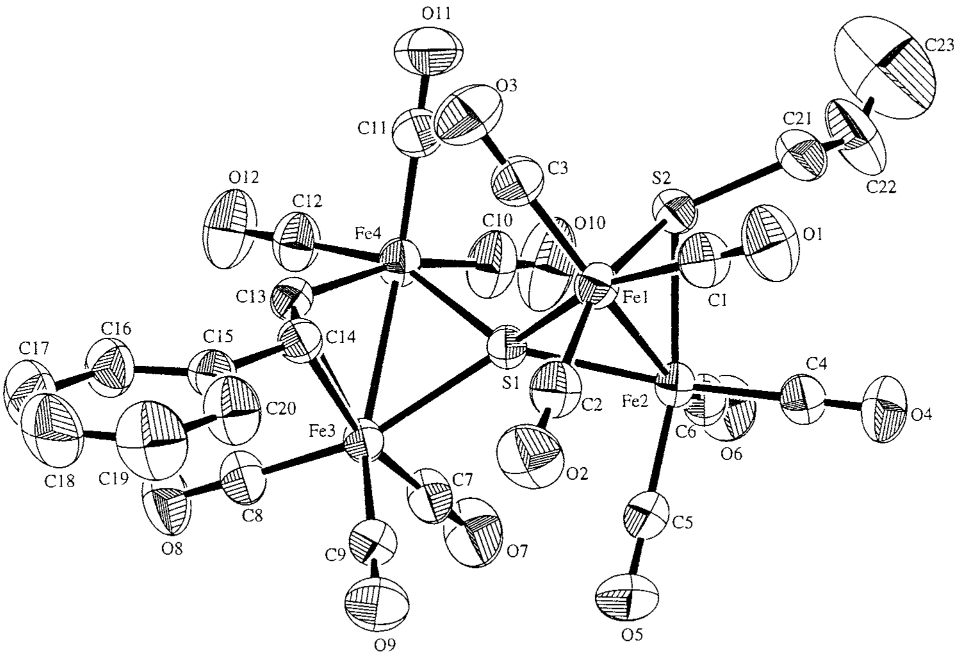
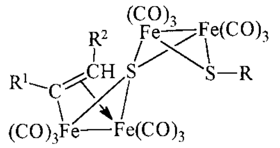
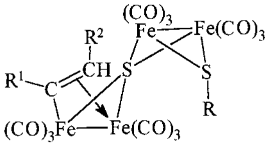


Fig. 1. ORTEP diagram of **3d** showing the 40% probability thermal ellipsoids.

molecule may come from crystallizing solvent petroleum ether.



A



B

2.1. Structure of (μ-η^2-CH=CHPh)(μ-CH$_2$=CHCH$_2$S)-[Fe$_2$(CO)$_6$]$_2$(μ_4-S)·0.5C$_6$H$_{12}$ (**3d**·0.5C$_6$H$_{12}$)

The molecular structure of the complex present in **3d**·0.5C_6H_{12} is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The crystal structure of **3d**·0.5C_6H_{12} is shown in Fig. 2. The molecule consists of two doubly bridged $Fe_2(CO)_6$ units joined to a common bridging sulfur atom ligand. One of the units is also bridged by a μ-η^2-phenylethenyl group and the other by a thioallyl group. The orientation of the allyl is equatorial. The common bridging sulfur atom is situated at the center of a distorted tetrahedron made up of four iron atoms. The dihedral angle between the Fe(1)Fe(2)S(1) plane and Fe(3)Fe(4)S(1) plane is 84.46°. The overall structure is similar to those of (μ-C_5H_4N)(μ-2-C_5H_4NS)[$Fe_2(CO)_6$]$_2$(μ$_4$-S) [13] and (μ-Me_2NCS)(μ-Me_2NC)[$Fe_2(CO)_6$]$_2$(μ$_4$-S) [14]. The Fe–S distances to the central sulfur atom [2.236(1)–2.259(1) Å, av. 2.249 Å) are about the same as those found in complexes (μ-CH_3S)$_2$[$Fe_2(CO)_6$]$_2$(μ$_4$-S) (av. 2.248 Å) [15], (μ-C_5H_4N)(μ-2-C_5H_4NS)[$Fe_2(CO)_6$]$_2$(μ$_4$-S) (av. 2.249 Å) [13] and (μ-Bu^{t}S)(μ-PhCH$_2$S)[$Fe_2(CO)_6$]$_2$(μ$_4$-S) (av. 2.247 Å) [16]. The Fe(1)–Fe(2) distance of 2.5336(9) Å is close to those in (μ-CH_3S)$_2$[$Fe_2(CO)_6$]$_2$-(μ$_4$-S) (av. 2.540 Å) [15] and (μ-PhC≡CS)(μ-EtS)-[$Fe_2(CO)_6$]$_2$(μ$_4$-S) (av. 2.536 Å) [17]. The Fe(3)–Fe(4) distance of 2.557(1) Å is also comparable to that found in (μ-PhCH$_2$S)(μ-η^2-PhC=CHPh)–$Fe_2(CO)_6$] (2.569(2) Å). The Fe–C distances to the ethenyl ligand (av. 2.102

Table 1
Selected bond distances (Å) and angles (°) for complex **3d**

Bond distances			
Fe(1)–Fe(2)	2.5336(9)	Fe(3)–C(13)	2.099(4)
Fe(1)–S(1)	2.259(1)	Fe(3)–C(14)	2.234(4)
Fe(1)–S(2)	2.268(1)	Fe(4)–S(1)	2.236(1)
Fe(2)–S(1)	2.242(1)	Fe(4)–C(13)	1.975(4)
Fe(2)–S(2)	2.256(1)	S(2)–C(21)	1.833(5)
Fe(3)–Fe(4)	2.557(1)	C(13)–C(14)	1.390(6)
Fe(3)–S(1)	2.258(1)	C(14)–C(15)	1.486(6)
Bond angles			
Fe(2)–Fe(1)–S(1)	55.44(3)	S(1)–Fe(4)–C(13)	85.8(1)
Fe(2)–Fe(1)–S(2)	55.72(4)	Fe(3)–C(13)–Fe(4)	77.7(1)
Fe(4)–Fe(3)–S(1)	54.93(3)	Fe(3)–C(13)–C(14)	76.6(2)
S(1)–Fe(1)–S(2)	76.39(4)	Fe(4)–C(13)–C(14)	130.4(3)
Fe(4)–Fe(3)–C(14)	79.2(1)	Fe(3)–C(14)–C(13)	66.1(2)
S(1)–Fe(3)–C(13)	82.4(1)	Fe(3)–C(14)–C(15)	122.1(3)
S(1)–Fe(3)–C(14)	82.7(1)	C(13)–C(14)–C(15)	125.1(4)
Fe(1)–Fe(2)–S(1)	56.05(3)	Fe(1)–S(1)–Fe(2)	68.51(4)
Fe(1)–Fe(2)–S(2)	56.16(4)	Fe(1)–S(1)–Fe(3)	138.33(5)
S(1)–Fe(2)–S(2)	76.95(4)	Fe(1)–S(1)–Fe(4)	128.44(5)
C(13)–Fe(3)–C(14)	37.3(1)	Fe(2)–S(1)–Fe(3)	132.21(5)
Fe(3)–Fe(4)–S(1)	55.72(3)	Fe(2)–S(1)–Fe(4)	132.21(5)
Fe(4)–Fe(3)–C(13)	49.0(1)	Fe(3)–S(1)–Fe(4)	69.35(4)
Fe(3)–Fe(4)–C(13)	53.3(1)	Fe(1)–S(2)–Fe(2)	68.12(4)

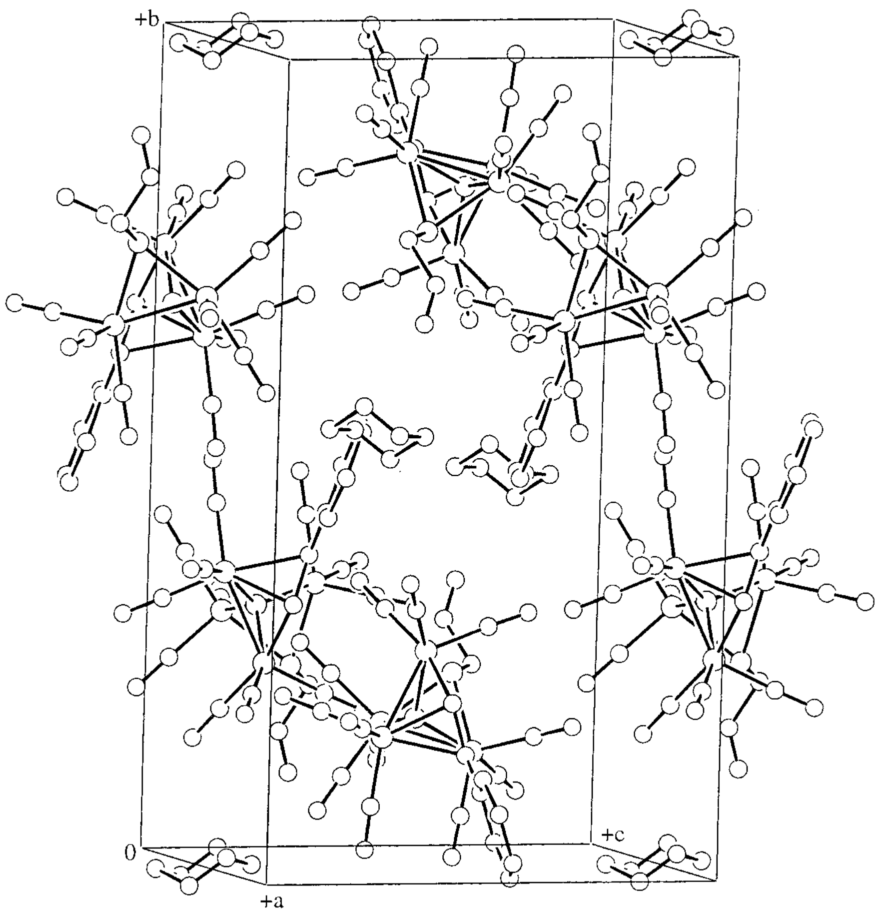


Fig. 2. The unit cell of crystalline **3d**·$0.5C_6H_{12}$.

Å) are close to those in (μ-$PhCH_2S$)(μ-η^2-PhC=CHPh)-$Fe_2(CO)_6$ (av. 2.097 Å), but the C–C distance of the ethenyl is shorter [1.390(6) vs. 1.440(10) Å in (μ-$PhCH_2S$)(μ-η^2-PhC=CHPh)$Fe_2(CO)_6$] [18]. The angles are of the expected values except Fe(4)–C(13)–C(14) [130.4(3)°], which is greater than those corresponding in complexes (μ-$PhCH_2S$)(μ-η^2-PhC=CHPh)-$Fe_2(CO)_6$] [120.9(5)°] [18] and (μ-Ph_2P)(μ-η^2-PhC=CHPh)$Fe_2(CO)_6$] [120.4(6)°] [8].

2.2. Structure of (μ-η^2-CH=CH-furyl-2)[μ-Ph-CH=CHC(O)S][$Fe_2(CO)_6$]$_2$(μ_4-S) (**5b**)

The molecular structure and the atom numbering scheme of complex **5b** is shown in Fig. 3. Selected bond distances and angles are presented in Table 2. The structure of complex **5b** is very similar to that of complex **3d**. Most of the bond lengths and angles are also comparable to those of complex **3d**. However, some differences were also noticed. For example, the dihedral angle between the Fe(1)Fe(2)S(2) plane and Fe(3)Fe(4)S(2) plane in complex **5b** is 88.9°, greater than that in complex **3d** (84.46°). In addition, as seen from Fig. 3, the substitute PhCH=CHC(O) is attached to bridged S(1) atom by an e-type of bond and the ethenyl protons of PhCH=CHC(O) group is *trans*, which is consistent with the ^{1}H-NMR spectral data.

3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. $Na_2Fe_2(CO)_8$ [19], PhN_2BF_4 [20], acid chlorides [PhCH=CHC(O)Cl, 2-furyl-CH=CHC(O)Cl, EtCH=CHC(O)Cl, CH_2=C(Me)C(O)Cl] [21], Na^+[{μ-η^2-C(R^1)=CHR^2}(μ-CO)$Fe_2(CO)_6$]$^-$ [5] and (μ-S_2)Fe_2-$(CO)_6$ [22] were prepared by published procedures. The progress of all reactions was monitored by thin-layer chromatography. Infrared spectra (KBr disc) were obtained by using a Bruker VECTOR22 spectrometer. ^{1}H-NMR spectra were recorded on either a Varian EM360L or a Bruker DMX500 spectrometer

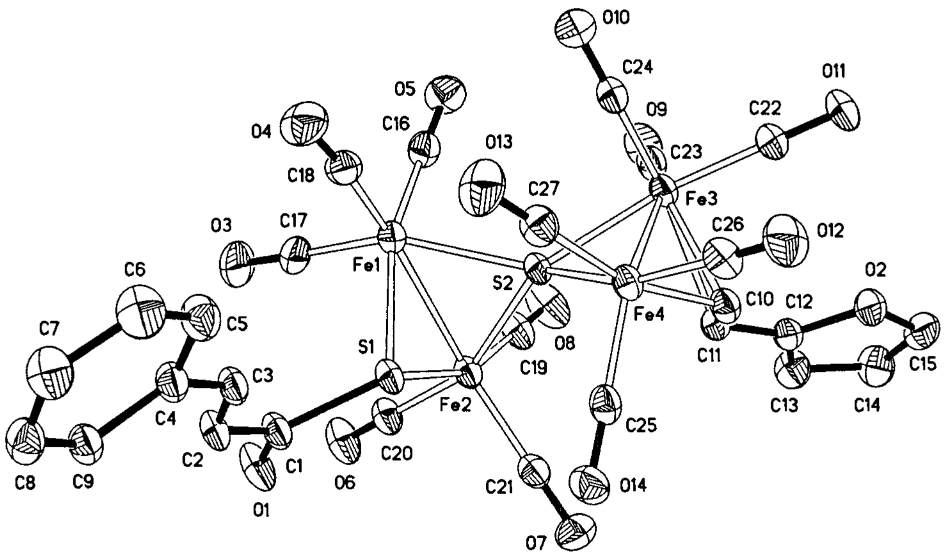


Fig. 3. ORTEP diagram of **5b** showing the 20% probability thermal ellipsoids.

with a $CDCl_3$ solvent. Elemental analyses were performed with a Perkin–Elmer 240C analyzer. Melting points were uncorrected.

3.1. Reaction of $[\{\mu\text{-}\eta^2\text{-C(R)=CHR}\}(\mu\text{-CO})Fe_2(CO)_6]^-$ (R = Ph or H) with $(\mu\text{-}S_2)Fe_2(CO)_6$

$(\mu\text{-}S_2)Fe_2(CO)_6$ (0.38 g, 1.10 mmol) was added to a cooled (−78°C) solution of $[\{\mu\text{-}\eta^2\text{-C(Ph)=CHPh}\}(\mu\text{-CO})Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (0.48 g, 1.26 mmol), PhC≡CPh (0.23 g, 1.29 mmol) and trifluoroacetic acid (0.1 ml, 1.30 mmol) in THF (30 cm^3). After stirring for 30 min at −78°C, $PhCH_2Cl$ (0.1 cm^3, 1.40 mmol) was syringed into the solution. The mixture was warmed to room temperature (r.t.) and stirred overnight. The solvent was removed at reduced pressure and the residue was extracted with petroleum ether and filtered. After removal of solvent, the mixture was purified by filtration chromatography. Petroleum ether eluted a purple–red band which gave $(\mu_3\text{-S})_2Fe_3(CO)_9$ (0.17g, 48%), m.p. 112–114°C. Anal. Found: C, 22.51. $C_9Fe_3O_9S_2$ requires: C, 22.35%. IR: ν_{max} (cm^{-1}) 2099m, 2077m, 2064s, 2040s, 2017s, 2000s, 1988s (CO).

A similar reaction was carried out by treatment of $[\{\mu\text{-}\eta^2\text{-CH=CH}_2\}(\mu\text{-CO})Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (0.29 g, 0.76 mmol), trifluoroacetic acid (0.06 cm^3, 0.77 mmol) and acetylene gas in THF (20 cm^3) with $(\mu\text{-}S_2)Fe_2(CO)_6$ (0.24 g, 0.70 mmol) and successive $PhCH_2Cl$ (0.1 cm^3, 0.87 mmol). After work-up, complex **1** (0.12 g, 49%) was obtained as needle crystals, m.p. 112–114°C.

Reaction was also carried out according to the same procedure and scale as above but in the absence of $PhCH_2Cl$. After stirring for 4 h at r.t., complex **1** was obtained.

3.2. Preparation of $[\mu\text{-}\eta^2\text{-C(Me)=CH}_2](\mu\text{-EtS})\text{-}[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (**3a**)

Addition of $(\mu\text{-}S_2)Fe_2(CO)_6$ (0.46 g, 1.34 mmol) to a cooled (−78°C) solution of $[\{\mu\text{-}\eta^2\text{-C(Me)=CH}_2\}\text{-}(\mu\text{-CO})Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (0.84 g,

Table 2
Selected bond distances (Å) and angles (°) for complex **5b**

Bond distances			
Fe(1)–S(2)	2.2486(11)	Fe(4)–C(10)	1.956(3)
Fe(1)–S(1)	2.2815(11)	Fe(4)–S(2)	2.2271(11)
Fe(1)–Fe(2)	2.5346(9)	S(1)–C(1)	1.841(3)
Fe(2)–S(2)	2.2597(11)	O(1)–C(1)	1.203(4)
Fe(2)–S(1)	2.2635(12)	C(1)–C(2)	1.468(4)
Fe(3)–C(10)	2.097(4)	C(2)–C(3)	1.299(5)
Fe(3)–C(11)	2.239(4)	C(3)–C(4)	1.479(5)
Fe(3)–S(2)	2.2592(12)	C(10)–C(11)	1.405(5)
Fe(3)–Fe(4)	2.5662(11)	C(11)–C(12)	1.459(4)
Bond angles			
S(2)–Fe(1)–S(1)	76.20(4)	C(1)–S(1)–Fe(1)	111.77(13)
S(2)–Fe(1)–Fe(2)	56.00(3)	Fe(2)–S(1)–Fe(1)	67.79(4)
S(1)–Fe(1)–Fe(2)	55.77(4)	Fe(4)–S(2)–Fe(1)	131.40(4)
S(2)–Fe(2)–S(1)	76.34(4)	Fe(4)–S(2)–Fe(3)	69.78(3)
S(2)–Fe(2)–Fe(1)	55.58(3)	Fe(1)–S(2)–Fe(3)	134.68(4)
S(1)–Fe(2)–Fe(1)	56.44(3)	Fe(4)–S(2)–Fe(2)	129.72(4)
C(10)–Fe(3)–C(11)	37.63(13)	Fe(1)–S(2)–Fe(2)	68.42(3)
C(10)–Fe(3)–S(2)	82.66(9)	Fe(3)–S(2)–Fe(2)	134.85(4)
C(11)–Fe(3)–S(2)	82.30(9)	O(1)–C(1)–C(2)	123.2(3)
C(10)–Fe(3)–Fe(4)	48.32(8)	O(1)–C(1)–S(1)	121.5(2)
C(11)–Fe(3)–Fe(4)	78.19(8)	C(2)–C(1)–S(1)	115.3(3)
S(2)–Fe(3)–Fe(4)	54.52(4)	C(11)–C(10)–Fe(4)	128.8(3)
C(10)–Fe(4)–S(2)	86.75(11)	C(11)–C(10)–Fe(3)	76.7(2)
C(10)–Fe(4)–Fe(3)	53.20(11)	Fe(4)–C(10)–Fe(3)	78.48(13)
S(2)–Fe(4)–Fe(3)	55.70(3)	C(10)–C(11)–C(12)	124.2(3)
C(1)–S(1)–Fe(2)	114.72(12)	C(10)–C(11)–Fe(3)	65.7(2)
		C(12)–C(11)–Fe(3)	122.5(2)

2.20 mmol) and $CH_2{=}C(Me)C(O)Cl$ (0.21 cm^3, 2.15 mmol) in THF (30 cm^3) gave a red–orange solution. After stirring for 30 min at −78°C, to the solution was added ethyl bromide (0.16 cm^3, 2.21 mmol) and then was allowed to warm to r.t. After a reaction period of 16 h at r.t., the solvent was removed at reduced pressure and the residue was extracted with a 9:1 (v/v) mixture of petroleum ether–CH_2Cl_2 and filtered. After removal of solvent, the residue was purified by filtration chromatography. Petroleum ether eluted a purple–red band which gave complex **1** (0.25 g, 38%). Petroleum ether–CH_2Cl_2 (9:1 v/v) eluted a red band which yielded red crystals of complex **3a** (0.13 g, 14%), m.p. 87–90°C. Anal. Found: C, 29.15; H, 1.37. $C_{17}H_{10}Fe_4O_{12}S_2$ requires: C, 29.43; H, 1.45%. ^{1}H-NMR: δ (ppm) 1.39 (t, 3H, $J = 6.2$ Hz, CH_3), 2.49 (q, 2H, $J = 6.3$ Hz, SCH_2), 2.72 (m, 4H, $=CH + CH_3$), 3.79 (s, 1H, $=CH$). IR: ν_{max} (cm^{-1}) 2083m, 2058s, 2038vs, 1997s, 1973s (CO).

3.3. Preparation of (μ-η^2-CH=CHEt)(μ-PhCH$_2$S)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**3b**)

Complex **3b** was synthesized using a similar method to that for **3a**. $[\{\mu\text{-}\eta^2\text{-}CH{=}CHEt\}(\mu\text{-}CO)Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (0.57 g, from 1.49 mmol) and $EtCH{=}CHC(O)Cl$ (0.19 g, 1.60 mmol) in THF (30 cm^3) was treated with $(\mu\text{-}S_2)Fe_2(CO)_6$ (0.34 g, 0.99 mmol) at −78°C. To the resulting mixture $PhCH_2Cl$ (0.17 cm^3, 1.48 mmol) was added and stirred at r.t. for 6 h. After similar work-up complex **1** (0.15 g, 31%) and red crystals of complex **3b** (0.12 g, 16%) were obtained. Complex **3b**, m.p. 124–127°C. Anal. Found: C, 35.80; H, 1.86. $C_{23}H_{14}Fe_4O_{12}S_2$ requires: C, 35.88; H, 1.83%. ^{1}H-NMR: δ (ppm) 1.42 (t, 3H, $J = 6.6$ Hz, CH_3), 2.25–2.74 (m, 2H, CH_2), 3.63 (s, 2H, CH_2), 3.88–4.04 (m, 1H, CH), 7.28 (s, 5H, Ph), 7.98 (d, 1H, $J = 12.5$ Hz, CH). IR: ν_{max} (cm^{-1}) 2083m, 2056s, 2037vs, 2002s, 1987s, 1975s (CO).

3.4. Preparation of (μ-η^2-CH=CH-furyl-2)(μ-EtS)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**3c**)

A similar procedure to that for **3a** was used. $[(\mu\text{-}\eta^2\text{-}CH{=}CH\text{-}furyl\text{-}2)(\mu\text{-}CO)Fe_2(CO)_6]^-$ was prepared from $Na_2Fe_2(CO)_8$ (0.53 g, 1.38 mmol) and 2-furyl-$CH{=}CHC(O)Cl$ (0.21 g, 1.35 mmol) in THF (30 cm^3). The reaction of the anion with $(\mu\text{-}S_2)Fe_2(CO)_6$ (0.30 g, 0.87 mmol) and successive ethyl bromide (0.14 cm^3, 1.87 mmol) gave, after removing the small amount of **1** by filtration chromatography, red crystals of complex **3c** (0.21 g, 46%), m.p. (dec.) 124°C. Anal. Found: C, 32.27; H, 1.53. $C_{20}H_{10}Fe_4O_{13}S_2$ requires: C, 32.21; H, 1.38%. ^{1}H-NMR: δ (ppm) 1.40 (t, 3H, $J = 6.7$ Hz, CH_3), 2.45 (q, 2H, $J = 6.8$ Hz, CH_2), 4.63 (d, 1H, $J = 14.4$ Hz, CH), 6.21 (s, 2H, furyl), 7.18 (s, 1H, furyl), 8.42 (d, 1H, $J = 14.4$ Hz, CH). IR: ν_{max} (cm^{-1}) 2085m, 2059s, 2039vs, 1995s (CO).

3.5. Preparation of (μ-η^2-CH=CHPh)(μ-CH$_2$=CH-CH$_2$S)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**3d**)

Complex **3d** was synthesized using a similar method to that for **3c**. $[\{\mu\text{-}\eta^2\text{-}CH{=}CHPh\}(\mu\text{-}CO)Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (0.89 g, 2.33 mmol) and $PhCH{=}CHC(O)Cl$ (0.38 g, 2.30 mmol) in THF (30 cm^3) was reacted with $(\mu\text{-}S_2)Fe_2(CO)_6$ (0.52 g, 1.51 mmol) and followed by $CH_2{=}CHCH_2Br$ (0.22 cm^3, 2.54 mmol). Similar work-up to that for **3c** gave red crystals of complex **3d** (0.26 g, 22%), m.p. 137–140°C. Anal. Found: C, 35.58; H, 1.62. $C_{23}H_{12}Fe_4O_{12}S_2$ requires: C, 35.98; H, 1.58%. ^{1}H-NMR: δ (ppm) 3.10 (d, 2H, $J =$ 6.6 Hz, CH_2), 4.78 (d, 1H, $J = 14.4$ Hz, CH), 5.13 (m, 2H, CH_2), 5.34 (m, 1H, CH), 7.25 (s, 5H, Ph), 8.72 (d, 1H, $J = 14.4$ Hz, CH). IR: ν_{max} (cm^{-1}) 2083m, 2032s, 2007s, 1985s (CO).

3.6. Preparation of [μ-η^2-C(Me)=CH$_2$][μ-PhS][Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**4**)

$[\{\mu\text{-}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}S)\{Fe_2(CO)_6\}_2(\mu_4\text{-}S)]^-$ was prepared by a similar procedure to that for **3a**. To the solution of $[\{\mu\text{-}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}CO)Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (0.49 g, 1.28 mmol) and $CH_2{=}C(Me)C(O)Cl$ (0.20 cm^3, 1.30 mmol) in THF (25 cm^3) at −78°C was added $(\mu\text{-}S_2)Fe_2(CO)_6$ (0.30 g, 0.87 mmol) and the mixture stirred for 30 min. The mixture was treated with PhN_2BF_4 (0.20 g, 1.04 mmol) at −78°C and stirred at r.t. for 5 h. Solvent was removed in vacuo to leave a brown residue, which was purified by column chromatography with petroleum ether–CH_2Cl_2 (20:1 v/v) as eluent. The first purple–red band gave complex **1** (0.11 g, 26%). The second red band gave red–orange crystals of complex **4** (0.13 g, 20%). The followed tiny bands were not collected. **4**: m.p. 108–111°C. Anal. Found: C, 34.13; H, 1.73. $C_{21}H_{10}Fe_4O_{12}S_2$ requires: C, 34.00; H, 1.36%. ^{1}H-NMR: δ (ppm) 2.80 (s, 4H, CH_3 and CH), 3.85 (s, 1H, CH), 5.13 (m, 2H, CH_2), 7.15–7.80 (m, 5H, Ph). IR: ν_{max} (cm^{-1}) 2085m, 2063m, 2036vs, 2002s, 1981s, 1965m (CO).

3.7. Preparation of [μ-η^2-C(Me)=CH$_2$][μ-PhC(O)S][Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**5a**)

A similar procedure to that for **3a** was used to prepare intermediate anion $[\{\mu\text{-}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}S)\{Fe_2(CO)_6\}_2(\mu_4\text{-}S)]^-$. To a cooled solution of $[\{\mu\text{-}\eta^2\text{-}C(Me){=}CH_2\}(\mu\text{-}CO)Fe_2(CO)_6]^-$ prepared from $Na_2Fe_2(CO)_8$ (1.03 g, 2.70 mmol) and $CH_2{=}C(Me)C(O)Cl$ (0.26 cm^3, 2.66 mmol) in THF (30 cm^3) was added

Table 3
Crystallographic data for complexes **3d**·0.5C_6H_{12} and **5b**

	3d·0.5C_6H_{12}	**5b**
Empirical formula	$C_{26}H_{18}O_{12}S_2Fe_4$	$C_{27}H_{12}O_{14}S_2Fe_4$
Formula weight	809.93	847.89
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$
a (Å)	12.131(2)	9.300(2)
b (Å)	21.206(4)	12.127(2)
c (Å)	12.663(7)	15.377(3)
α (°)		104.67(3)
β (°)	98.44(2)	98.16(3)
γ (°)		101.80(3)
V (Å^3)	3222(1)	1607.5(6)
Z	4	2
$D_{calc.}$ (g cm^{-3})	1.669	1.752
Crystal size (mm)	0.20 × 0.20 × 0.45	0.32 × 0.26 × 0.24
Radiation λ (Å)	0.71069	0.71073
$F(000)$	1624.00	844
μ (Mo–K$_\alpha$) (cm^{-1})	19.50	19.65
Temperature (K)	293(1)	293(2)
Total reflections	5316	5073
Independent reflections	5030	4846
Reflections with $I>3\sigma(I)$ [a] or $I>2\sigma(I)$ [b]	3799	4470
R [a] or R_1 [b]	0.034	0.0484
R_w [a] or wR_2 [b]	0.042	0.1550

[a] For complex **3d**.

[b] For complex **5b**. R or $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w = [\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, wF_o^2]^{1/2}$, $wR_2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$.

(μ-S_2)$Fe_2(CO)_6$ (0.62 g, 1.80 mmol). The resultant mixture was reacted with PhC(O)Cl (0.32 cm^3, 2.27 mmol). After a reaction period of 6 h at r.t., the solvent was removed at reduced pressure and the residue was extracted with a 9:1 (v/v) mixture of petroleum ether–CH_2Cl_2 and filtered. After removal of solvent, the residue was purified by filtration chromatography. Petroleum ether eluted a purple–red band which gave complex **1** (0.21 g, 24%). Petroleum ether–CH_2Cl_2 (7:1 v/v) eluted a red band which yielded dark red crystals of complex **5a** (0.22 g, 16%), m.p. (dec.) 164 °C. Anal. Found: C, 34.15; H, 1.39. $C_{22}H_{10}Fe_4O_{13}S_2$ requires: C, 34.32; H, 1.31%. ^{1}H-NMR: δ (ppm) 2.74 (s, 3H, CH_3), 2.86 (s, 1H, CH_2), 3.87 (s, 1H, CH_2), 7.47 (m, 3H, Ph), 8.02 (m, 2H, Ph). IR: ν_{max} (cm^{-1}) 2087s, 2060s, 2039vs, 2009s, 1996s, 1971s (Fe–CO); 1676m (CO).

*3.8. Preparation of (μ-η^2-CH=CH-furyl-2)[μ-Ph-CH=CHC(O)S][$Fe_2(CO)_6$]$_2$(μ_4-S) (**5b**)*

To the solution of Na$^+$[(μ-η^2-CH=CH-furyl-2)(μ-CO)$Fe_2(CO)_6$]$^-$ prepared from $Na_2Fe_2(CO)_8$ (0.81 g, 2.12 mmol) and 2-furyl-CH=CHC(O)Cl (0.33 g, 2.11 mmol) in THF (30 cm^3) was added at −78°C (μ-S_2)$Fe_2(CO)_6$ (0.45 g, 1.31 mmol) and the mixture stirred for 30 min. The mixture was treated with PhCH=CHC(O)Cl (0.35 g, 2.10 mmol) at −78°C and then stirred at r.t. for 6 h. After the same work-up as described above, complex **1** (0.08 g, 13%) and complex **5b** (0.47 g, 42%) were obtained. **5b**: red crystals, m.p. 134–136°C. Anal. Found: C, 37.70; H, 1.27. $C_{27}H_{12}Fe_4O_{14}S_2$ requires: C, 38.25; H, 1.43%. ^{1}H-NMR: δ (ppm) 4.73 (d, 1H, J = 13.1 Hz, CH), 6.31 (s, 2H, furyl), 6.69 (d, 1H, J = 15.9 Hz, CH), 7.18 (s, 1H, furyl), 7.30–7.49 (m, 5H, Ph), 7.83 (d, 1H, J = 15.6 Hz, CH), 8.55 (d, 1H, J = 13.1 Hz, CH). IR: ν_{max} (cm^{-1}) 2086s, 2061s, 2039vs, 2004s, 1989s (Fe–CO); 1667m (CO).

*3.9. Preparation of (μ-η^2-CH=CHPh)[μ-$CH_3C(O)S$]-[$Fe_2(CO)_6$]$_2$(μ_4-S) (**5c**)*

To the solution of Na$^+$[(μ-η^2-CH=CHPh)(μ-CO)$Fe_2(CO)_6$]$^-$ prepared from $Na_2Fe_2(CO)_8$ (0.59 g, 1.54 mmol) and PhCH=CHC(O)Cl (0.25 g, 1.51 mmol) in THF (20 cm^3) was added at −78°C (μ-S_2)$Fe_2(CO)_6$ (0.33 g, 0.96 mmol) and the mixture stirred for 30 min. The mixture was treated with $CH_3C(O)Cl$ (0.14 cm^3, 1.97 mmol) at −78°C and then stirred at r.t. for 5 h. Filtration chromatography gave, after removing a small amount of **1**, red crystals of **5c** (0.21 g, 28%), m.p. 118–120°C. Anal. Found: C, 33.97; H, 1.44. $C_{27}H_{12}Fe_4O_{14}S_2$ requires: C, 34.32; H, 1.31%. ^{1}H-NMR: δ (ppm) 2.58 (s, 3H, CH_3), 4.82 (d, 1H, J = 12.4 Hz, CH), 7.37 (s, 5H, Ph), 8.81 (d, 1H, J = 12.6 Hz, CH). IR: ν_{max} (cm^{-1}) 2086s, 2041vs, 2007br (Fe–CO); 1724m (CO).

*3.10. Crystal data and structure determination of complexes **3d** and **5b***

Details are given in Table 3. Suitable crystals of complexes **3d** and **5b** were grown from petroleum ether–CH_2Cl_2 solution at r.t. Data were collected on Rigaku AFC7R (for **3d**) or Siemens P4 (for **5b**) four-circle diffractometers using monochromated Mo–K$_\alpha$ radiation. The structures were solved by direct methods (SHELXS-86 [23] or Siemens SHELXTL) and refined by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 134592 for compound **3d** and CCDC no. 134593 for compound **5b**.

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