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Dithioformate Fe(η^2-HC(SR)S) complexes, and cleavage of the coordinated C–S bond by alkynes. A route to $\overline{\text{FeCH(SR)COC(CO}_2\text{Me)=C(CO}_2\text{Me)S}}\text{(CO)(PR}_3)_2$ complexes

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Abstract

The complexes [Fe(η^2-HCS$_2$R)(CO)$_2$(PMe$_3$)$_2$] and [Fe(η^2-CH$_2$S)(CO)$_2$(PMe$_3$)$_2$] have been obtained by reaction of borohydride with the cations [Fe(η^2-CS$_2$R)(CO)$_2$(PMe$_3$)$_2$]$^+$. The complexes Fe(η^2-HCS$_2$R)(CO)$_2$(PMe$_3$)$_2$ react with electrophilic alkynes with cleavage of the coordinated C=S bond and the insertion of both the C≡C bond and carbon monoxide into the C–S bond to give six-membered metallacyclic species.

Introduction

Reported examples of transition metal complexes, formally containing an η^2-coordinated carbon–sulphur double bond include those with η^2-thioformaldehyde attached to osmium [1], rhodium [2], and ruthenium [3], η^2-thioformaldehyde as a bridging group in cluster [4] or bimetallic derivatives [5], η^2-thioketone coordinated to vanadium [6], cobalt [7] or molybdenum [8], and η^2-dithioformate coordinated to niobium [9], iron [10], or tungsten [11]. Although there is evidence for cleavage of the η^2-coordinated carbon–sulphur bond upon hydrogenation [6] or following alkylation of the coordinated sulphur atom [12,13], to our knowledge the only examples of insertion of a C≡C bond into a coordinated C–S bond of a (X)(Y)C=S ligand, are those reported in our preliminary communication [10]. However, the insertion of an ynamine derivative into the C=S bond of thioaldehyde and ketone, η^1-coordinated through the sulphur atom, is well-documented, and proceeds via a [2 + 2] cycloaddition [14]. Alkynes are also known to insert into the RS–C bond of η^2-vinyl RSC(R′)=C(R′) ligands [15].

We now report the syntheses and characterization of η^2-dithioformate- and η^2-thioformaldehyde-iron(0) complexes obtained by borohydride reduction of $[Fe(\eta^2\text{-}CS_2R)(CO)_2(PR_3)_2]^+$ cations [16,17], and demonstrated these to be new metallacyclic iron derivatives via insertion of C≡C bond and carbonomonoxide into the coordinated carbon–sulphur bond of the $Fe(\eta^2\text{-}HC(SR)S)$ complexes.

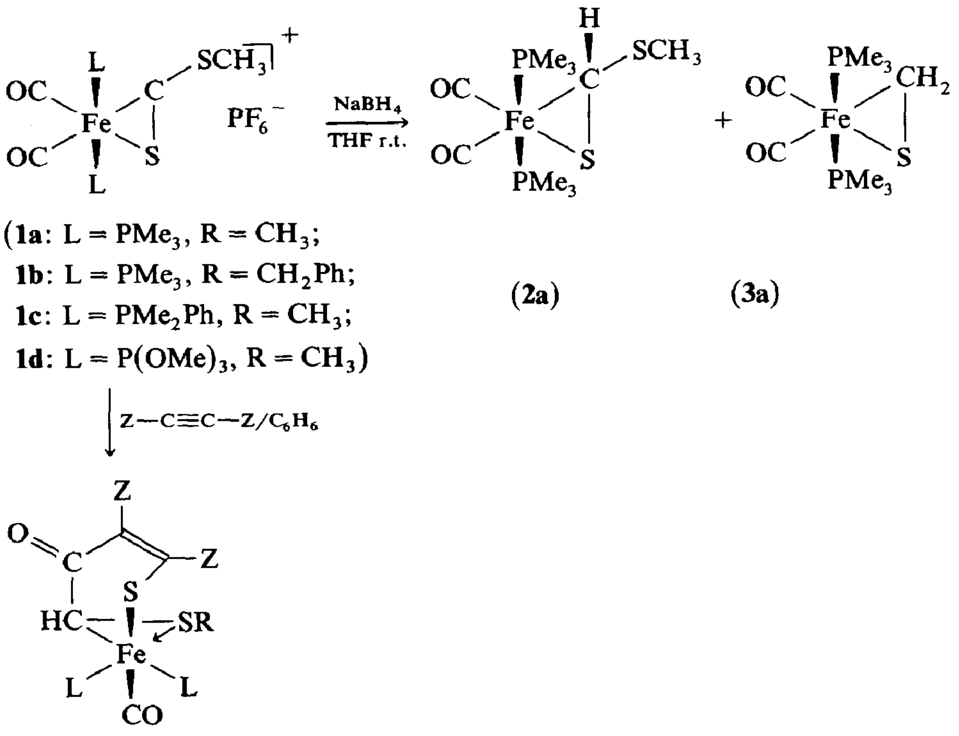
Results and discussion

Reaction of borohydride with $Fe(\eta^2\text{-}CS_2R)^+$ cations

The reaction of borohydride with $L_nM(\eta^2\text{-}CS_2R)^+$ cationic complexes has been shown to proceed in many different ways depending on the metal and the ancillary ligands. The reaction was first shown to provide a route to thiocarbonylmetal complexes $[Os(CS)(CO)_2(PPh_3)_2]$ [18] and $[Co(CS)\{N(CH_2CH_2PPh_2)_3\}]^+\ BPh_4^-$ [19]. This reaction does not lead to analogous $[Fe(CS)(CO)_2(PR_3)_2]$ complexes, which can, however, be obtained from the $[Fe(CS_2R)(CO)_2(PR_3)_2]^+$ cations by reduction either with sodium amalgam when PR_3 is PMe_3 or PMe_2Ph [20] or with tributylphosphine, when PR_3 is PPh_3 [21]. With $[Nb(\eta^2\text{-}CS_2Me)(Bu)(\eta^5\text{-}C_5H_5)_2]^+$ $NaBH_4$ forms an uncharacterized intermediate borohydride adduct that eventually gives $[Nb(\eta^2\text{-}S{=}C(SMe)H)(Bu)(\eta^5\text{-}C_5H_5)]$ [9]. The reaction of $NaBH_4$ with $Fe(\eta^2\text{-}CS_2R)$ derivatives is influenced by the other ligands bonded to the iron atom. A BH_3-adduct, $Fe(\eta^3\text{-}HC(SMe)S \rightarrow BH_3)(CO)(PR_3)_2$, with intramolecular B–H–Fe interaction is formed from the neutral $Fe(\eta^2\text{-}CS_2R)(I)(CO)(PR_3)_2$ derivative [22]. Borohydride transfers one electron to readily reducible $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]^+$ cations containing weak-electron releasing L groups (L = PPh_3) [23]. In the case of complexes containing the more basic ligands PMe_3 or PMe_2Ph, the reaction proceeds in a quite different way.

Reaction of the $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PMe_3)_2]^+PF_6^-$ complex **1a** with $NaBH_4$ in THF at room temperature rapidly gave two species **2a** and **3a**. The major product, the air-sensitive dithioformate-iron complex **2a**, was obtained in 51% yield, and the minor product, the more stable yellow thioformaldehyde-iron compound **3a** was isolated by thick layer chromatography in 5% yield (Scheme 1). Complex **3a** is obtained in better yield (25%) when the reaction is carried out at −30 °C for 16 h with subsequent heating at 40 °C for 1 h. Both of the complexes **2a** and **3a** have *cis*-carbonyl and *trans*-phosphine ligands. The ^1H NMR spectrum of **2a** shows a doublet at δ 4.57 ppm for the HCS_2R proton, which is coupled to only one phosphorus nucleus. The *trans*-PMe_3 groups ($^2J(PP)$ 185.5 Hz) are inequivalent owing to their different locations with respect to either the hydrogen or the SMe group on the two sides of the Fe–C–S plane. The two equivalent methylene protons of the CH_2S group of **3a** give rise to a triplet (δ 2.82 ppm) owing to the coupling with two equivalent ^{31}P nuclei.

*Formation of **2a**.* The hydride transfer from borohydride to the (CS_2R) carbon atom of **1a**, is not modified by the nature of the counter cation, since $[Ph_3PNPPh_3]^+$ BH_4^- ($PPN^+BH_4^-$) gives similar results to $Na^+\ BH_4^-$ in THF. The reaction of **1a** with a one molar proportion of $[Ph_3PNPPh_3]^+\ BH_4^-$ in CD_3CN was monitored by ^1H NMR spectroscopy at various temperatures. At room temperature, no BH_4^- signal was observed, but the doublet at δ 4.70 ppm ($^3J(PH)$ 7 Hz), characteristic of the HCS_2R proton of **2a**, appeared immediately. The reaction was complete within 5 min. At −30 °C the four signals in the range δ 1.36 to −1.73 ppm from the BH_4^-



(**1a**: L = PMe$_3$, R = CH$_3$;
1b: L = PMe$_3$, R = CH$_2$Ph;
1c: L = PMe$_2$Ph, R = CH$_3$;
1d: L = P(OMe)$_3$, R = CH$_3$)

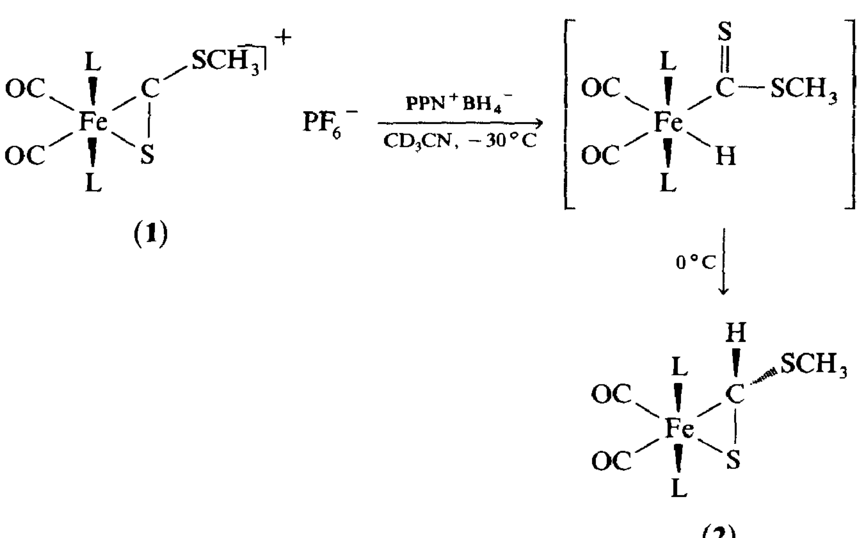
(**2a**)

(**3a**)

(**4a**: L = PMe$_3$, R = CH$_3$, Z = CO$_2$CH$_3$;
4b: L = PMe$_3$, R = CH$_2$Ph, Z = CO$_2$CH$_3$;
4c: L = PMe$_2$Ph, R = CH$_3$, Z = CO$_2$CH$_3$;
4d: L = P(OMe)$_3$, R = CH$_3$, Z = CO$_2$CH$_3$;
4e: L = PMe$_3$, R = CH$_3$, Z = CO$_2$C$_2$H$_5$)

Scheme 1

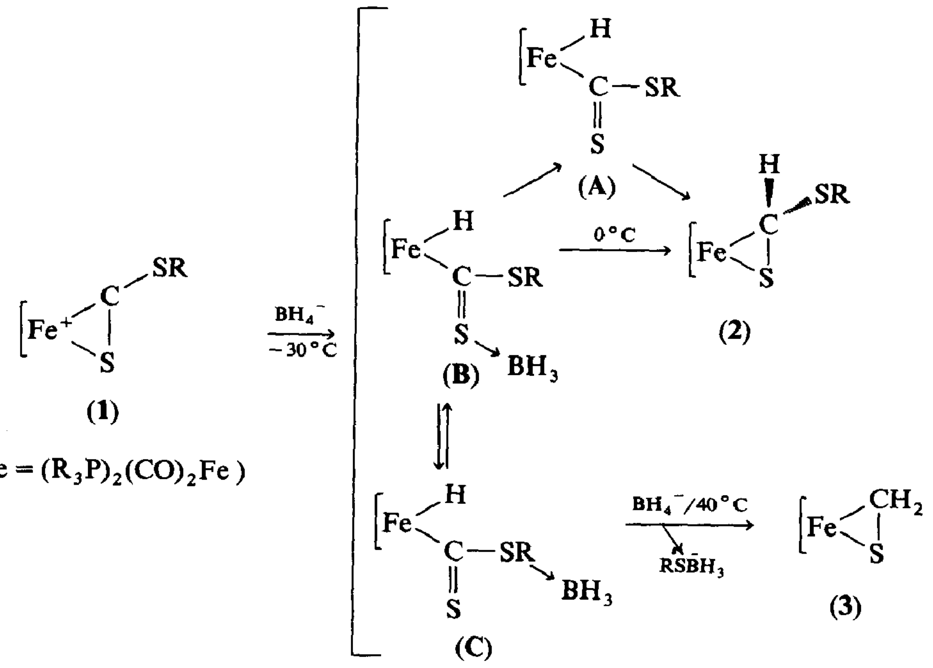
anion were observed, indicating that the reaction is slow at this temperature. A triplet grew progressively at high field (δ −7.4 ppm, ^2J(PH) 48 Hz), a position consistent with a hydride-iron intermediate containing two equivalent phosphorus nuclei. After 1 h at −30 °C the BH$_4^-$ signal had disappeared, and the temperature of the sample was then gradually increased. The signal at −7.4 ppm was still visible up to 0 °C, at which it disappeared and was replaced by the δ 4.7 ppm doublet characteristic of **2a**. The reaction involves the initial formation of a Fe(H)(η^1-CS$_2$Me) intermediate at −30 °C by hydride transfer to the metal followed by a 1,2-hydrogen shift at 0 °C from the metal to the carbon atom (Scheme 2). Such a hydride transfer to the metal was observed in the case of the isolable [Os(H)(η^2-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$] complex which on heating gave Os(CS)(CO)$_2$(PPh$_3$)$_2$ with elimination of MeSH [18]. Complex **2a** does not give Fe(CS)(CO)$_2$(PMe$_3$)$_2$ on heating, and its formation via a metal–carbon 1,2-hydrogen shift, a process not observed into the case of the osmium analogues, is probably associated with the weakness of the Fe–H relative to the Os–H bond. In Fe(η^2-CS$_2$R)$^+$ cations, the Fe–C bond has a (carbene) carbon–metal bond character, and we have previously observed a 1,2-hydrogen shift from an iron atom to a (carbene)-carbon atom [24].



Scheme 2

The ox-red potential of **1a** ($E_{1/2}$ −1.04 V vs. SCE) is much lower than that of $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+ PF_6^-$ ($E_{1/2}$ −0.74 V vs. SCE) as determined by cyclic voltammetry in acetonitrile [23]. The difference in the reduction potential accounts for the fact that electron transfer, such as occurs with $[Fe(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2]^+ PF_6^-$ [23], does not take place between BH_4^- and **1a**.

Formation of 3a. The formation of the η^2-thioformaldehyde iron complex **3a** is not fully understood. Complex **3a** was not formed by further reactions of **2a** or $Fe(CS)(CO)_2(PMe_3)_2$ with sodium borohydride or molecular hydrogen. Both hydrogen atoms of the $\eta^2\text{-}CH_2S$ ligand of **3a** come from $NaBH_4$, reaction of **1a** with $NaBD_4$ in THF giving $Fe(\eta^2\text{-}CD_2S)(CO)_2(PMe_3)_2$ (**3e**). Reaction of **1a** with an excess of $NaBH_4$ in THF at −30 °C for 16 h and then at 40 °C for 1 h gave a 25% yield of $Fe(\eta^2\text{-}CH_2S)(CO)_2(PMe_3)_2$ (**3a**). The best yields of **3a** or **3e** were obtained at the expenses of **2a** when the reaction was carried out at −30 °C for 16 h to complete the hydride transfer from BH_4^- followed by rapid heating to 40 °C. The intermediate may be a BH_3-adduct. Thus reaction of $NaBH_4$ with $Fe(\eta^2\text{-}CSR)(X)(CO)(PMe_3)_2$ gives the $[Fe(\eta^2\text{-}CH(SR)S \rightarrow BH_2(H))]$ complex [22]. Closely related BH_3-adducts such as **B** and **C** are possible (Scheme 3). Adduct **B** would account for the ease of 1,2-hydrogen migration from iron to a carbene-like carbon [24] to give **2**. Adduct **C** would account for the fact that there is an assisted elimination of the SMe group give **3**, whereas such an elimination is not observed in the reaction of **2a**. The formation of **3a** provides a new route to $M(\eta^2\text{-}CH_2S)$ complexes. Other $M(\eta^2\text{-}CH_2S)$ complexes have been reported, namely $Os(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$ [1] formed by intramolecular hydrogen migrations to the CS ligand, $Rh(\eta^2\text{-}CH_2S)(PMe_3)(C_5H_5)$ [2] made by nucleophilic addition of NaSH to $Rh(CH_2I)(I)(PMe_3)(C_5H_5)$, and $[Re(\eta^2\text{-}CH_2S)(NO)(PPh_3)(C_5H_5)]PF_6$ [3] made by addition of cyclohexane sulphide to the corresponding methilydeneruthenium complex. Calculations on the model compound $Fe(\eta^2\text{-}CH_2S)(CO)_2(PPh_3)_2$ have shown



([Fe = $(R_3P)_2(CO)_2Fe$)

Scheme 3

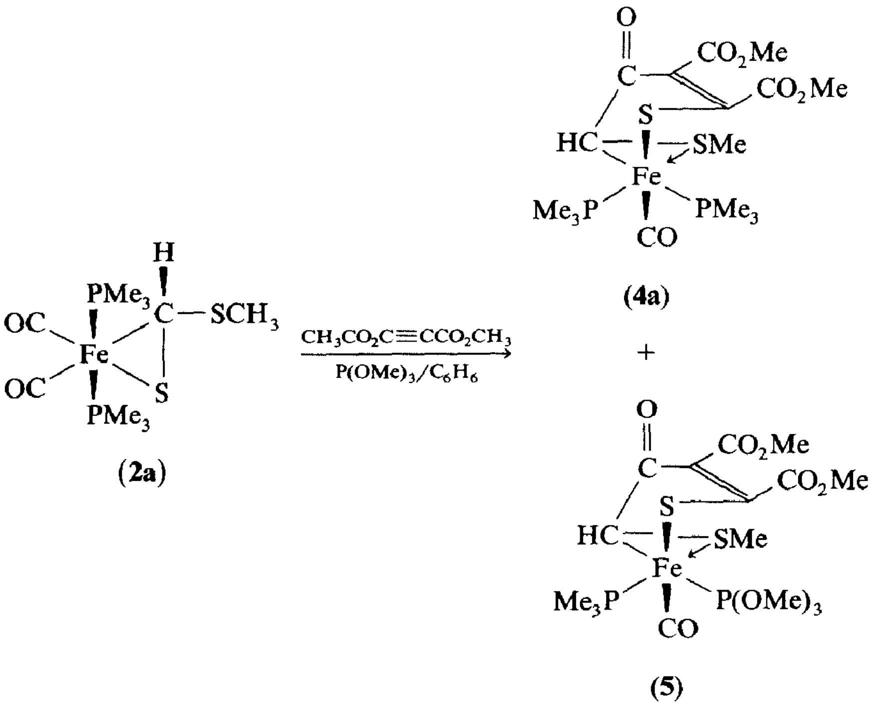
that the (η^2-CH_2S) ligand is a better π-acceptor and a better σ-donor than a (η^2-CH_2O) ligand coordinated to the same iron(0) moiety [25].

*Formation of complexes **2b–2d**.* Complexes **1b**, **1c** and **1d**, containing PMe_2Ph and $P(OMe)_3$ ligands, were treated with $NaBH_4$ in THF at room temperature under the conditions used with **1a** (Scheme 1). The formed complexes **2** were not stable, and were not characterized. They were prepared in situ for further reaction with alkynes, and this confirmed that they had been formed. No formation of complexes **3** was observed. It is noteworthy that monitoring of reactions of **1c** and **1d** with $(Ph_3PNPPh_3)^+$ BH_4^- in CD_3CN at −30 °C, in an NMR tube, gave spectra which showed a triplet, at δ −6.97 and −6.68 ppm, respectively, characteristic of the Fe-hydride intermediate.

Reaction of Fe(η^2-SCH(SMe)) complexes 2 with alkynes

*Preparation of complexes **4**.* Complex **2a** results from two successive addition reactions of electrophile (Me^+) and nucleophile (H^-) to the carbon disulphide ligand of the parent $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ complexes. The η^2-coordinated CS_2 ligands in the latter complexes are known to have 1,3-dipolar character [16]. This has been demonstrated by the cycloaddition of activated alkynes to $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ complexes to give iron-carbene complexes which can isomerize to their iron(II) metallacyclic derivatives when PR_3 is basic [26]. It thus seemed to be of interest to study the interaction of similar activated alkynes with the neutral S=C(SMe)H ligand η^2-coordinated to an iron(0) moiety. Such a reaction gave unexpected results.

The yellow complex **2a** was treated in benzene with one equivalent of dimethylacetylene dicarboxylate (DMAD) at room temperature. After 1 h the red complex



Scheme 4

4a was isolated in 70% yield by thick layer chromatography. The analogous complex 4e was obtained in 65% yield by reaction of 2a with diethylacetylene dicarboxylate (DEAD) (Scheme 1). Because of the instability of intermediates 2b–2d they were made in situ and treated directly with one equivalent of DMAD. Complexes 1b, 1c and 1d were treated with an excess of $NaBH_4$ in THF at room temperature, and after replacement of the THF solvent by benzene, the crude product was treated with one equivalent of DMAD. The derivatives 4b (35%), 4c (40%) and 4d (10%) were isolated.

The reaction of 2a at 25 ° C with one equivalent of DMAD in the presence of an excess of $P(OMe)_3$ allowed the isolation of complex 5 in 12% yield beside that of 4a (47%). It is noteworthy that complex 4a does not give 5 when heated with $P(OMe)_3$ at 40 ° C (Scheme 4).

The infrared spectrum of complexes 4 indicates that incorporation of the alkyne has occurred, as shown by the presence of CO_2R absorption bands. Only one terminal carbonyl absorption was observed. The NMR spectra of complexes 4 reveal that incorporation of the alkyne and the insertion of one carbon monoxide have occurred. The NMR spectra of complex 5 indicate the presence of one $P(OMe)_3$ group and one remaining PMe_3 group. The spectroscopic data are all consistent with both alkyne and carbon monoxide insertion. The X-ray structure of 4a was determined.

The structure of 4a. The structure of 4a is depicted in an ORTEP plot in Fig. 1. It shows that the reaction of dimethylacetylene dicarboxylate with the η^2-coordinated methyldithioformate ligand in 2a results in fragmentation of the coordinated carbon–sulphur double bond and formation of a sulphur-containing metallacycle by

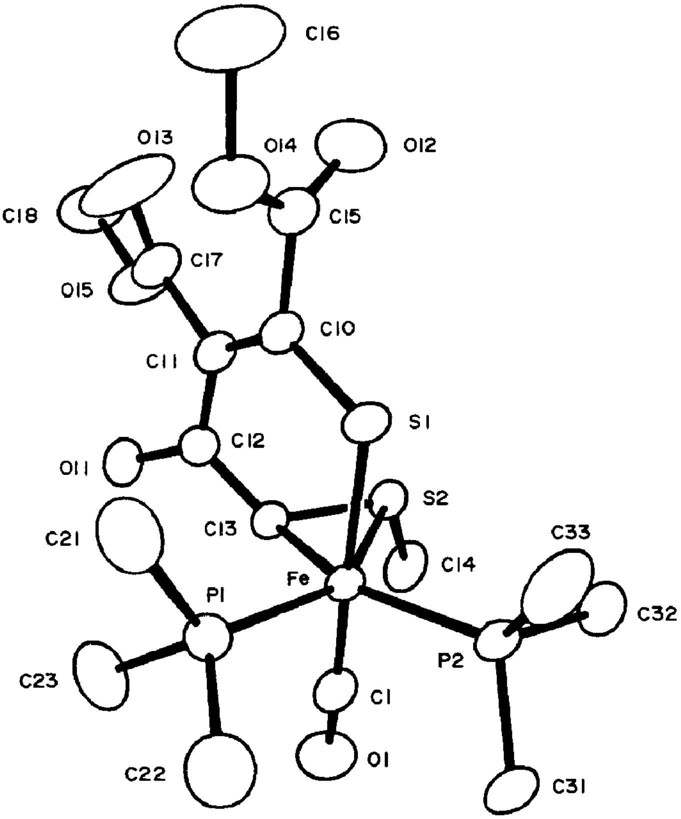
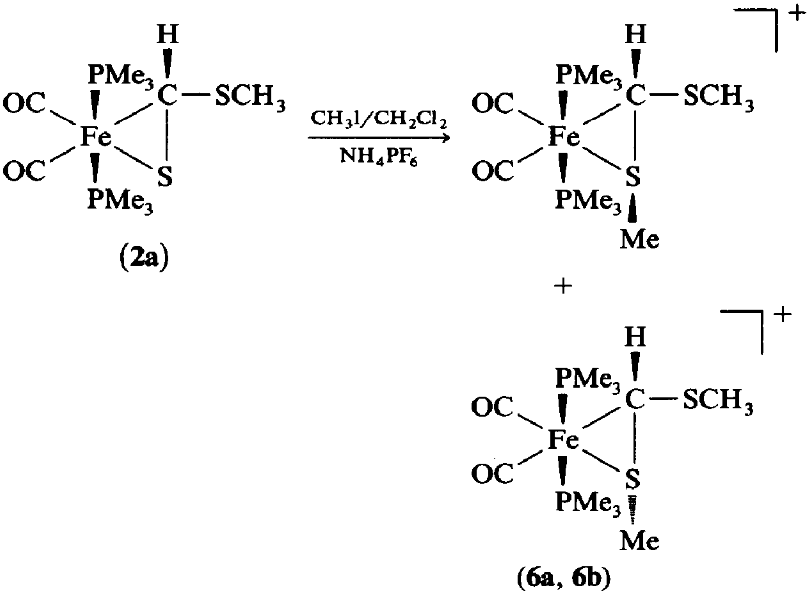


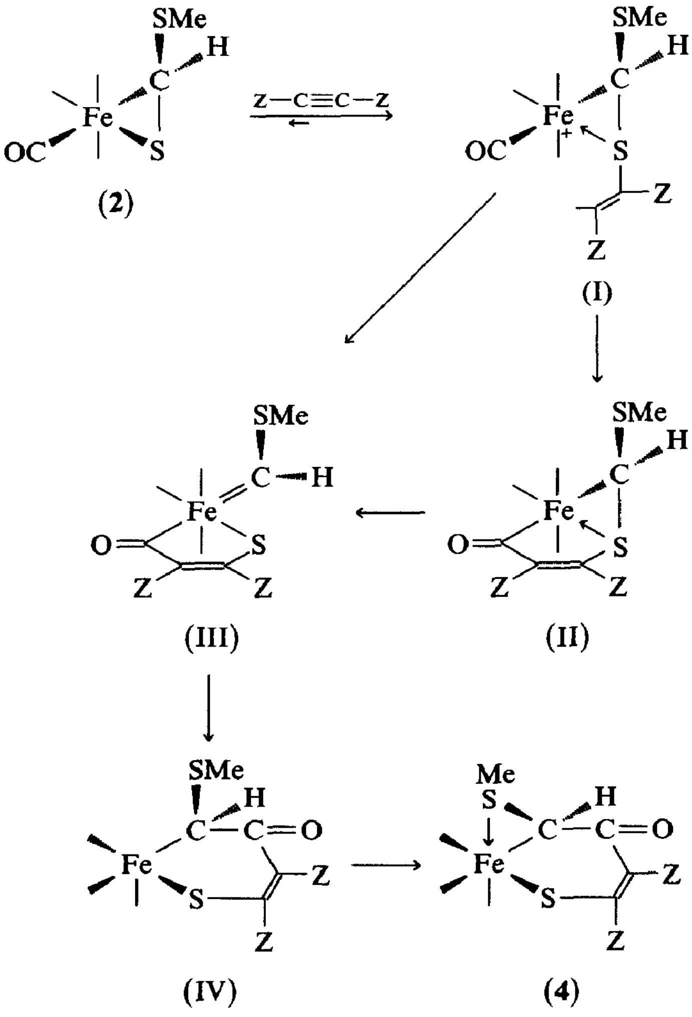
Fig. 1. ORTEP view of **4a**.



Scheme 5

insertion of the alkyne and one carbonyl group into the coordinated fragment. The "MeS" sulphur atom has now become coordinated to the metal. The equatorial sites of the distorted triangular bipyramidal molecule are occupied by the trimethylphosphine groups and the carbon–sulphur ($C_{13}S_2$) single bond. The axial positions are occupied by the remaining carbonyl ligand and the sulphido group of the novel chelating ligand (C(1)–Fe–S(1): 175.5(6)°).

The sp^3 C(13) atom [Fe–C(13)–C(12): 121.3(1)°; C(12)–C(13)–S(2): 123.6(1)°) is linked by a CO–C=C chain to the axial sulphido group, and the SMe methyl group is oriented toward the axial carbonyl. The C(10)–C(11) distance (1.271(2) Å) is typical of a C=C double bond. The bond Fe–C(13) between the carbon atom of the CHSMe group and Fe has a length (2.067(2) Å), corresponding to a single bond but the Fe–S(2) distance (2.272(1) Å) is much shorter than the Fe–S(1) distance (2.305(1) Å), and the length of the coordinated C(13)–S(2) bond (1.732(2) Å) is



Scheme 6

much shorter than that of the single C(14)–S(2) bond (1.820(2) Å). The distances between the Fe, C(13) and S(2) atoms can be compared with the corresponding distances in Fe(η^2-CS_2)$(CO)_2$$(PPh_3)$$(PMe_3)$ [16] (Fe–C 1.983(8); C–S 1.676(7); Fe–S 2.334(2) Å) and in [Fe(η^2-CS_2CH_2Ph)$(CO)_2$$(PMe_3)_2$]$PF_6$ [16] (Fe–C 1.890(3); C–S 1.634(3); Fe–S 2.322(1) Å). The data for the latter species reveal a metal–carbene carbon character and a marked shortening of the coordinated C–S bond with sp^2 carbon ligands.

Mechanism. The transformation **2** → **4** appears to be specific for electrophilic alkynes; for example, diphenylacetylene does not react with **2a**. Complex **2a** readily reacts with methyl iodide to give a mixture of the stereoisomers **6a** and **6b**, resulting from alkylation of the coordinated sulphur atom (Scheme 5). It is likely that the first step of the transformation involves the interaction of the electrophilic alkyne with the same coordinated sulphur atom (I) (Scheme 6). This coupling of the alkyne with the sulphur atom should enhance the electrophilicity of coordinated carbonyls and favor formation of the FeCOC(Z)=C(Z)S metallacycle. This cyclisation would be accompanied by the cleavage of coordinated C–S bond to afford the metal-carbene intermediate (III), either via II, or directly. Both processes have precedents thus Angelici et al. [27] have observed 1,2-migration of a SPh group from a bridging $C(SPh)_2$ group to the iron site, and both Roper [12] and Angelici [13] have presented evidence for cleavage of the coordinated C–S bond with formation of a carbene ligand on alkylation of the sulphur atom followed by reaction with a nucleophile. The insertion of the carbene ligand of III into the Fe–acyl bond is expected to give the 16 electron intermediate IV, which on coordination of the SMe sulphur atom would give complex **4**. The intermediate IV is also expected to take up the $P(OMe)_3$ ligand in the transformation **2a** → **5** before PMe_3 elimination.

Conclusion

The above results suggest that when the coordination of a (R)(Y)C=S ligand via its C,S atoms is favored, cleavage of the coordinated C–S bond by electrophiles is also favored. This reaction may be relevant to the desulphurization of thiocarbonyl derivatives and their use in carbon–carbon formation.

Experimental

Syntheses. All reactions were carried out under nitrogen by Schlenk techniques. NMR spectra were recorded on a Bruker WP80(FT) (^1H, ^{31}P, ^{13}C) or Bruker AM300WB(FT) (^{13}C) spectrometer and mass spectra were obtained with a Varian MAT 311 spectrometer at the "Centre de Mesures Physiques de l'Ouest", University of Rennes. Elemental analyses were performed by CNRS, Villeurbanne (France).

Materials. Solvents were dried by reflux over appropriate drying agents and stored under an inert atmosphere. Tetrahydrofuran and diethyl ether were distilled over benzophenone ketyl; pentane and hexane over calcium hydride; and dichloromethane first over phosphorous pentoxide and then over calcium hydride. The complexes $FeCS_2(CO)_2L_2$ and $[Fe(CS_2R)(CO)_2L_2]^+PF_6^-$ were prepared by published methods [15,16].

Synthesis of complexes 2 and 3

Only complexes **2a** and **3a**, resulting from the addition of $NaBH_4$ to the cationic dithioester precursor **1a** ($L = PMe_3$) were isolated. In other cases reactions were carried out with the crude products **2b–2d** obtained by reaction of complexes **1b–1d** with $NaBH_4$ in THF under the conditions used for conversion of **1a** into **2a** and **3a**.

Complex $Fe(\eta^2\text{-}SCH(SMe))(CO)_2(PMe_3)_2$ *(2a).* The salt **1a** (2 g, 4 mmol) was dissolved in 40 ml of dry THF in a Schlenk tube. An excess of $NaBH_4$ (0.19 g, 5 mmol) was added, and after 1 h at room temperature the solvent was distilled off. The residue was dissolved in warm pentane and the solution was filtered and concentrated, and cooled, to give 0.72 g (51%) of unstable yellow crystals of **2a**. Thick layer chromatography (eluent: pentane/ether) of the crystallisation solution followed by recrystallisation from pentane gave 0.064 g of **3a** (5%).

2a: yellow, m.p. 101–102 °C, 51% yield. IR (nujol): ν(CO) 1962, 1892, ν(CS) 942 cm^{-1}. Anal. Found: C, 34.23; H, 5.97; S, 17.63; P, 17.38. $C_{10}H_{22}O_2P_2S_2Fe$ calcd.: C, 33.72; H, 6.22; S, 18.00; P, 17.39%. Mass spectrum: *m/e* 355.990 (calcd. for $[M^+]$ ($C_{10}H_{22}O_2P_2S_2Fe$): 355.989); 328 $[M - CO]^+$; 300 $[M - 2CO]^+$. ^1H NMR (CD_2Cl_2, 306 K, 80 MHz): δ 4.57 (d, CH, ^3J(PH) 7 Hz), 2.37 (s, Me), 1.35 and 1.22 (d, PMe_3, ^2J(PH) 8.0 Hz). ^{31}P NMR (C_6D_6, 309 K, 32.38 MHz): δ 20.98 and 8.18 (d, ^2J(PP) 185.5 Hz). ^{13}C and ^{13}C $\{^1H\}$ NMR (C_6D_6, 306 K, 20.115 MHz): δ 218.4 (t, CO, ^2J(PC) 28.0 Hz), 215.9 (t, CO, ^2J(PC) 28.7 Hz), 60.9 (dt, CH, ^1J(CH) 56.1 Hz, ^2J(PC) 9.9 Hz), 24.5 (s, Me).

Complex $Fe(\eta^2\text{-}CH_2S)(CO)_2(PMe_3)_2$ *(3a).* The salt **1a** (2 g, 4 mmol) was dissolved in 40 ml of dry THF in a Schlenk tube. The solution was cooled to −30 °C and an excess of $NaBH_4$ (0.3 g, 8 mmol) was added. The mixture was stirred at −30 °C for 16 h and then kept at 40 °C for 1 h. The complex **3a** was isolated by thick layer chromatography (eluent: pentane/ether) and obtained after recrystallisation in 25% yield (300 mg).

3a: yellow, m.p. 81–82 °C, 25% yield. IR (nujol): ν(CO) 1955 and 1887, ν(CS) 940 cm^{-1}. Anal. Found: C, 34.93; H, 6.64; S, 10.18. $C_9H_{20}O_2P_2SFe$ calcd.: C, 34.85; H, 6.50; S, 10.30%. Mass spectrum: *m/e* 310.002 (calcd. for $[M^+]$ ($C_9H_{20}O_2P_2SFe$): 310.001). ^1H NMR (C_6D_6, 306 K, 60 MHz): δ 2.82 (t, CH_2S, ^3J(PH) 5.2 Hz), 0.87 (t, PMe_3, $|^2J(PH) + ^4J(PH)| = 8.4$ Hz). ^{31}P NMR (C_7D_8, 273 K, 32.38 MHz): δ 37.48 (s, PMe_3). ^{13}C NMR (C_7D_8, 273 K, 75.469 MHz): δ 219.2 (t, CO, ^2J(PC) 25 Hz), 215.0 (t, CO, ^2J(PC) 30 Hz), 37.4 (t, CH_2S, ^2J(PC) 8.0 Hz), 20.9 (m, PMe_3).

Complex $Fe(\eta^2\text{-}CD_2S)(CO)_2(PMe_3)_2$ *(3e).* The reaction of **1a** (0.5 g, 1 mmol) with $NaBD_4$ (0.6 g, 1.2 mmol) was carried out as described for the preparation of **3a**.

3e: yellow, m.p. 81–82 °C, 25% yield. IR (nujol): 1995, 1887, 940 cm^{-1}. Mass spectrum: *m/e* 312.012 (calcd. for $[M^+]$ ($C_9H_{18}D_2O_2P_2SFe$): 312.013). ^1H NMR (C_7D_8, 273 K, 300 MHz) δ 0.87 (t, PMe, $|^2J(PH) + ^4J(PH)| = 8.4$ Hz). ^2D NMR (C_7D_8, 273 K, 300 Mhz) δ 2.82 (broad triplet, CD_2S).

Preparation of complexes $Fe[\eta^3\text{-}CH(SR)COC(CO_2R)=C(CO_2R)S](CO)(PR_3)_2$ *(4)*

Complexes 4a and 4e. To a solution of **2a** (0.53 g, 1.5 mmol) in 20 ml of dry benzene 0.2 ml of dimethyl acetylene-dicarboxylate (DMAD) was added from a syringe. The mixture was stirred for 1 h at room temperature, the yellow solution rapidly turning red. The solvent was evaporated off and, the residue purified by thick layer chromatography (eluent: ether/THF). After recrystallisation from a dichloromethane/ether mixture, 527 mg of **4a** were obtained. Similarly, addition of 0.2 ml of diethyl acetylenedicarboxylate (DEAD) gave 512 mg of **4e**.

4a: red, m.p. 172–174°C, 70% yield. IR (nujol): 1895 (C≡O), 1715 and 1685 (CO_2Me), 1565 (C=O) cm^{-1}. Anal. Found: C, 38.51; H, 5.64; S, 13.09. $C_{16}H_{28}O_6P_2S_2Fe$ calcd.: C, 38.57; H, 5.66; S, 12.87%. Mass spectrum: *m/e* 470.018 (calcd. for $[M-CO^+]$ ($C_{15}H_{28}O_5P_2S_2Fe$): 470.020]. ^1H NMR ($CDCl_3$, 309 K, 100 MHz) δ 3.79 and 3.71 (s, CO_2Me), 2.00 and 1.98 (s, SME), 1.60 and 1.37 (d, PMe_3, $^2J(PH)$ 9.7 Hz), (the CH signal was masked by the CO_2Me signals). ^{31}P NMR ($CDCl_3$, 309 K, 32.38 MHz): δ 25.7 and 16.6 (dd, $^2J(PP)$ 15.1 Hz). ^{13}C NMR (CD_2Cl_2, 308 K, 20.115 MHz): δ 215.8 (dd, CO, $^2J(PC)$ 25.6 and 32.3 Hz), 199.1 (s, C=O) 168.1 and 166.4 (s, CO_2Me), 164.2 (d, S–C=, $^3J(PC)$ 16.6 Hz), 123.4 (s, CO*C*=), 53. and 52.2 (s, CO_2*Me*), 52.5 (the CH signal was in part masked by the other signal), 23.6 (s, SMe).

4e: red, m.p. 158–160°C, 65% yield. IR (nujol): 1900 (C≡O), 1715 and 1690 (CO_2Et), 1560 (C=O) cm^{-1}. Anal. Found: C, 40.79; H, 5.85. $C_{18}H_{32}O_6P_2S_2Fe$ calcd.: C, 41.07; H, 6.12%. Mass spectrum: *m/e* 498.051 (calcd. for $[M-CO]^+$ ($C_{17}H_{32}O_5P_2S_2Fe$): 498.051). ^1H NMR ($CDCl_3$, 309 K, 100 MHz): δ 4.23 and 4.17 (q, CO_2Et, $^3J(HH)$ 7.7 Hz), 3.68 (dd, CHS, $^3J(PH)$ 2.9 and 1.2 Hz), 2.00 and 1.97 (s, SMe), 1.60 and 1.38 (d, PMe_3, $^2J(PH)$ 9.7 Hz), 1.01 and 0.98 (t, CO_2Et, $^3J(HH)$ 7.7 Hz). ^{31}P NMR ($CDCl_3$, 309 K, 32.38 MHz): δ 25.5 and 15.6 (d, $^2J(PP)$ 15.1 Hz). ^{13}C NMR (CD_2Cl_2, 308 K, 20.115 MHz): δ 216.1 (dd, CO, $^2J(PC)$ 26.8 and 33.0 Hz), 199.5 (s, C=O), 167.7 and 165.5 (s, *C*O_2Et), 164.5 (d, S–C=, $^3J(PC)$ 17.9 Hz), 125.6 (s, CO*C*=), 61.5 and 60.6 (s, CO_2CH_2), 52.8 (dd, CH, $^2J(PC)$ 6.1 and 4.9 Hz), 23.7 (s, SMe), 14.2 and 14.0 (s, CH_2CH_3).

Complexes 4b, 4c and 4d. 2 mmol of **1b**, **1c** or **1d** were dissolved in 20 ml of dry THF. An excess of $NaBH_4$ was added and the mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the residue was dissolved in 20 ml of benzene. The solution was filtered and 1.5 mmol of DMAD was added, the mixture rapidly turning red. After 1 h the solvent was evaporated and the product purified by thick layer chromatography on silica gel (eluent: ether).

4b: red, m.p. 160–162°C, 409 mg 35% yield. IR (nujol): 1920 (C≡O), 1730 and 1710 (CO_2Me), 1590 (C=O) cm^{-1}. Anal. Found: C, 45.56; H, 5.60; S, 11.07. $C_{22}H_{32}O_6P_2S_2Fe$ calcd.: C, 46.00; H, 5.62; S, 11.16%. Mass spectrum: *m/e* 546.05 (calcd. for $[M-CO]^+$ ($C_{21}H_{32}O_5P_2S_2Fe$): 546.051). ^1H NMR ($CDCl_3$, 309 K, 80 MHz): δ 7.35 and 7.29 (Ph), 4.11 (dd) and 2.85 (d) (CH_2, $^2J(HH)$ 12.2 Hz, $^4J(PH)$ 2.9 Hz), 3.77 and 3.71 (s, CO_2Me), 3.48 (dd, CH, $^3J(PH)$ 14.2 and 7.1 Hz), 1.39 (d, PMe_3, $^2J(PH)$ 9.8 Hz); 1.28 (d, PMe_3, $^2J(PH)$ 8.8 Hz). ^{31}P NMR ($CDCl_3$, 309 K, 32.38 MHz): δ 27.6 and 14.9 (d, $^2J(PP)$ 15.6 Hz). ^{13}C NMR ($CDCl_3$, 309 K, 20.115 MHz): δ 215.9 (dd, CO, $^2J(PC)$ 25.6 and 32.9 Hz), 199.3 (s, C=O), 168.1 and 165.8 (s, CO_2Me), 165.6 (d, S–C=, $^3J(PC)$ 17.1 Hz), 122.3 (s, CO*C*=), 52.5 and 51.7 (s, O*Me*), 50.3 (dd, CH, $J(PC)$ 4.9 and 7.3 Hz), 46.0 (s, SCH_2), 19.1 and 18.8 (d, PMe_3, $J(PC)$ 28 Hz).

4c: red, m.p. 165–167°C, 497 mg, 40% yield. IR (nujol): 1900 (C≡O), 1715 and 1685 (CO_2Me), 1580 (C=O) cm^{-1}. Anal. Found: C, 49.98; H, 5.45; P, 9.92. $C_{26}H_{32}O_6P_2S_2Fe$ calcd.: C, 50.01; H, 5.16; P, 9.95%. ^1H NMR (C_6D_6, 309 K, 80 MHz): δ 7.40 (m, Ph), 3.87 and 3.71 (s, CO_2Me), 1.88 and 1.77 (s, SMe), 1.54 (d, PMe, ^2J(PH) 9 Hz), 1.31 (d, PMe, ^2J(PH) 8.7 Hz) (CH signal masked by the CO_2Me signals). ^{31}P NMR ($CDCl_3$, 309 K, 32.38 MHz): δ 33.6 and 22.5 (d, ^2J(PP) 10.7 Hz).

4d: red, m.p. 160–162° C (dec), 120 mg, 10% yield. IR (nujol): 1965 (C≡O), 1720 and 1690 (CO_2Me), 1590 (C=O) cm^{-1}. Mass spectrum: *m/e* 593.981 (calcd. for $[M]^+$ ($C_{16}H_{28}O_{12}P_2S_2Fe$): 593.985). ^{1}H NMR ($CDCl_3$, 303 K, 80 MHz): δ 3.79 and 3.69 (d, $P(OMe)_3$, ^3J(PH) 11 Hz), 3.77 and 3.72 (s, CO_2Me), 2.08 and 2.04 (s, SMe), CH signal masked by CO_2Me and $P(OMe)_3$ signals.

Synthesis of complex $Fe[\eta^3\text{-}CH(SCH_3(CO)C(CO_2CH_3)=C(CO_2CH_3)S](CO)(PMe_3)(P(OMe)_3)$ *(5).* To a solution of 0.267 g (0.75 mmol) of **2a** in 10 ml of dry benzene was added trimethylphosphite (0.245 ml, 2 mmol). When the solution was stirred at room temperature no reaction was observed. After 1 h, 0.25 ml of DMAD was added and the solution turned red. Formation of two different red compounds was observed. After 1 h the mixture was subjected to thick layer chromatography (eluent: ether). The separate products were recrystallised from CH_2Cl_2/ether to give 0.16 g of **4a** and 0.05 g of **5**.

4a: 156 mg, 47% yield. IR (nujol): 1895 (C≡O), 1715 and 1685 (CO_2Me) 1565 (C=O) cm^{-1}.

5: red, m.p. 150–152° C, 49 mg, 12% yield. IR (nujol): 1940 (C≡O), 1715 and 1685 (CO_2Me), 1565 (C=O) cm^{-1}. Anal. Found: C, 35.07; H, 5.27. $C_{16}H_{28}O_9P_2S_2Fe$ calcd.: C, 35.17; H, 5.16%. Mass spectrum: *m/e* 518.006 (calcd. for $[M-CO]^+$ ($C_{15}H_{28}O_8P_2S_2Fe$): 518.006). ^{1}H NMR (CD_2Cl_2, 305 K, 80 MHz) two isomers: δ 3.87 and 3.72 (s, CO_2Me), 3.68 and 3.63 (d, $P(OMe)_3$, ^3J(PH) 8.5 Hz), 2.10, 2.07, 2.06 and 2.00 (s, SMe), 1.60 and 1.39 (d, PMe_3; ^2J(PH) 9.7 Hz), (CH signal was masked by the CO_2Me signals. ^{31}P NMR ($CDCl_3$, 309 K, 32.38 MHz) two isomers: δ 174.4 (d) and 171.4 (d) [$P(OMe)_3$], 23.8 (d) and 16.4 (d) (PMe_3) (^2J(PP) 41.2 Hz).

Synthesis of complex 6. To a solution of 0.356 g (1.18 mmol) of **2a** in 20 ml of dichloromethane where added 0.282 g (2 mmol) of CH_3I and 0.326 g (2 mmol) of NH_4PF_6. The mixture was stirred for 1 h at room temperature then filtered. The filtrate was shaken with water, then separated and dried. The solvent was evaporated

Table 1

Summary of crystal data

Compound	**4a**
Formula	$C_{16}H_{28}O_6P_2S_2Fe$
Mol. Weight	498.32
System	triclinic
Space Group	$P_{\bar{1}}$, N° 2
a, Å	8.957(2)
b, Å	10.440(2)
c, Å	14.005(2)
α, deg.	70.60(1)
β, deg.	83.40(2)
γ, deg.	67.96(2)
Z	2
d_{calcd}, g cm^{-3}	1.45
μ(Mo-K_α), cm^{-1}	9.97
R	0.033
R_W	0.041

off and the residue recrystallised from a dichloromethane/pentane mixture to give 227 mg of **6a–6b**.

6a, 6b: yellow, m.p. 161–162° C, 44% yield. IR (nujol): 2030, 2020, 1950 cm^{-1}. Anal. Found: C, 25.70; H, 4.88; S, 12.52. $C_{11}H_{25}O_2P_3S_2F_6Fe$ calcd.: C, 25.60; H, 4.88; S, 12.42%. ^{1}H NMR (CD_2Cl_2, 309 K, 80 MHz); two isomers **A**/**B**: 60/40. δ 4.15 (**A**) and 3.96 (**B**) (m, CH) 2.55 (**B**), 2.39 (**A**), 2.21 (**A**) and 2.19 (**B**) (s, SMe), 1.76

Table 2

Interatomic distances (Å) and angles (deg) with esds for **4a**

Atoms		Atoms	
Bond distances			
Fe–S(1)	2.305(1)	P(2)–C(33)	1.816(2)
Fe–S(2)	2.272(1)	C(10)–C(11)	1.371(2)
Fe–P(1)	2.224(1)	C(10)–C(15)	1.511(2)
Fe–P(2)	2.252(1)	C(11)–C(12)	1.472(2)
Fe–C(1)	1.742(2)	C(11)–C(17)	1.503(2)
Fe–C(13)	2.067(2)	C(12)–O(11)	1.238(2)
S(1)–C(10)	1.718(2)	C(12)–C(13)	1.477(2)
S(2)–C(13)	1.783(2)	C(15)–O(12)	1.192(2)
S(2)–C(14)	1.820(2)	C(15)–O(14)	1.337(2)
P(1)–C(21)	1.804(2)	O(14)–C(16)	1.428(2)
P(1)–C(22)	1.814(2)	C(17)–O(13)	1.186(2)
P(1)–C(23)	1.815(2)	C(17)–O(15)	1.322(2)
P(2)–C(31)	1.828(2)	O(15)–C(18)	1.449(2)
P(2)–C(32)	1.813(2)	C(1)–O(1)	1.161(2)
Bond angles			
S(1)–Fe–S(2)	84.05(2)	Fe–P(2)–C(32)	112.47(6)
S(1)–Fe–P(1)	91.57(2)	Fe–P(2)–C(33)	119.00(7)
S(1)–Fe–P(2)	86.86(2)	C(31)–P(2)–C(32)	103.4(1)
S(1)–Fe–C(1)	176.50(6)	C(31)–P(2)–C(33)	101.0(1)
S(1)–Fe–C(13)	92.43(4)	C(32)–P(2)–C(33)	102.0(1)
S(2)–Fe–P(1)	147.91(2)	Fe–C(13)–S(2)	71.90(6)
S(2)–Fe–P(2)	107.79(2)	Fe–C(13)–C(12)	121.3(1)
S(2)–Fe–C(1)	98.14(6)	S(2)–C(13)–C(12)	123.6(1)
S(2)–Fe–C(13)	48.24(4)	C(13)–C(12)–C(11)	122.7(1)
P(1)–Fe–P(2)	103.67(2)	C(13)–C(12)–O(11)	117.2(2)
P(1)–Fe–C(1)	88.00(6)	C(11)–C(12)–O(11)	120.0(2)
P(1)–Fe–C(13)	100.47(5)	C(12)–C(11)–C(10)	124.9(2)
P(2)–Fe–C(1)	89.87(6)	C(12)–C(11)–C(17)	118.0(1)
P(2)–Fe–C(13)	155.86(5)	C(10)–C(11)–C(17)	116.9(2)
C(1)–Fe–C(13)	91.06(7)	S(1)–C(10)–C(11)	129.7(1)
Fe–S(1)–C(10)	112.42(6)	S(1)–C(10)–C(15)	110.2(1)
Fe–S(2)–C(13)	59.86(5)	C(11)–C(10)–C(15)	120.1(1)
Fe–S(2)–C(14)	113.30(7)	C(10)–C(15)–O(12)	125.2(2)
C(13)–S(2)–C(14)	102.66(8)	C(10)–C(15)–O(14)	110.7(1)
Fe–P(1)–C(21)	118.38(7)	O(12)–C(15)–C(14)	124.0(2)
Fe–P(1)–C(22)	118.87(8)	C(15)–O(14)–C(16)	115.5(2)
Fe–P(1)–C(23)	112.61(7)	C(11)–C(17)–O(13)	124.6(2)
C(21)–P(1)–C(22)	101.5(1)	C(11)–C(17)–O(15)	113.0(1)
C(21)–P(1)–C(23)	101.8(1)	O(13)–C(17)–O(15)	122.3(2)
C(22)–P(1)–C(23)	100.9(1)	C(17)–O(15)–C(18)	116.5(2)
Fe–P(2)–C(31)	116.76(6)	Fe–C(1)–O(1)	178.0(2)

(9.5 Hz); 1.73 (9.5 Hz); 1.72 (10.2 Hz); 1.70 (10.2 Hz) (d, PMe$_3$). ^{31}P NMR (CDCl$_3$, 306 K, 32.38 MHz): δ 23.75 (**A**), 23.07 (**B**), 8.67 (**A**) and 8.52 (**B**) (PMe$_3$); −144.53 (PF$_6^-$, J(PF): 710 Hz).

*X-ray diffraction study of complex **4a***

The crystal was mounted in a thin-walled glass capillary. All diffraction measurements were carried out with an Enraf–Nonius CAD-4 fully automated four cycle diffractometer using graphite-monochromatized Mo-K_α radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index and least squares routines. The space group $P\bar{1}$ was assumed and confirmed by the successful structure solution and refinement. Crystal data and details of the data are listed in Table 1. All data processing was performed on a digital PDP 11/45 computer by use of the Enraf–Nonius SPD program library (version 18). Since the absorption coefficient is only 9.97 cm^{-1}, no absorption correction was performed. Neutral atom scattering factors were calculated by the standard procedures. Anomalous dispersion corrections were applied for all non-hydrogen atoms.

The structure was solved by a combination of Patterson and difference Fourier techniques. Hydrogen atom positions were either obtained from difference Fourier

Table 3

Atomic coordinates for non-hydrogen atoms in Fe[S(MeO$_2$C)C=C(CO$_2$Me)COCHSMe](CO)(PMe$_3$)$_2$

Atom	x	y	z
Fe	0.31496(4)	0.14542(4)	0.18533(3)
S(1)	0.37687(8)	−0.09840(7)	0.20951(6)
S(2)	0.52490(8)	0.12184(7)	0.07654(5)
P(1)	0.23158(9)	0.12071(8)	0.34400(6)
P(2)	0.09398(9)	0.18663(8)	0.10057(6)
O(1)	0.2202(3)	0.4545(2)	0.1546(2)
O(11)	0.7247(3)	0.0090(2)	0.3416(2)
O(12)	0.6711(3)	−0.4260(2)	0.2166(2)
O(13)	0.8470(3)	−0.4042(3)	0.3764(3)
O(14)	0.5298(3)	−0.4185(2)	0.3582(2)
O(15)	0.9605(2)	−0.2402(2)	0.3153(2)
C(1)	0.2560(3)	0.3315(3)	0.1657(2)
C(10)	0.5675(3)	−0.2031(3)	0.2585(2)
C(11)	0.6819(3)	−0.1625(3)	0.2846(2)
C(12)	0.6600(3)	−0.0128(3)	0.2780(2)
C(13)	0.5529(3)	0.1165(3)	0.2020(2)
C(14)	0.5407(4)	0.2952(4)	−0.0001(3)
C(15)	0.6008(3)	−0.3617(3)	0.2742(2)
C(16)	0.5565(5)	−0.5695(4)	0.3818(4)
C(17)	0.8353(3)	−0.2824(3)	0.3317(2)
C(18)	1.1140(4)	−0.3504(4)	0.3562(3)
C(21)	0.2740(5)	−0.0607(4)	0.4314(3)
C(22)	0.0195(5)	0.2073(5)	0.3666(3)
C(23)	0.3215(5)	0.1989(4)	0.4088(3)
C(31)	−0.0838(4)	0.3447(4)	0.1057(3)
C(32)	0.1285(4)	0.2179(4)	−0.0340(2)
C(33)	0.0072(4)	0.0460(3)	0.1328(3)

syntheses or calculated. Hydrogen atoms were included in structure factor calculations but their positions were not refined. Full-matrix least squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$ where $\omega = 1/(\sigma(F))^2$, $\sigma(F) = (F_o^2)/2F_o$ and $\sigma(F_o)^2 = [(\sigma(I_{raw}))^2 + (PF_o^2)^2]^{1/2}$.

The final atomic coordinates for non-hydrogen atoms are listed in Table 3, and interatomic distances and angles, with errors obtained from the inverse matrix calculated on the final cycle of least squares refinements, are listed in Table 2. Tables of hydrogen atom coordinates, thermal parameters, and a list of structure factors are available from the authors.

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