Inorganica Chimica Acta, 198-200 (1992) 193-201

Activation of dithioformate by iron complexes: insertion of alkynes into the coordinated C–S bond. X-ray structures of $Fe[\eta^3\text{-}H–B(H)_2 \leftarrow S–C(SMe)H](CO)(PMe_3)_2$ and $Fe[\eta^3\text{-}S–C(Ph)=CH–CH(SMe)](CO)(PMe_3)_2$

Dilip V. Khasnis, Nadine Pirio, Daniel Touchard, Loïc Toupet and Pierre H. Dixneuf*
Unités de Recherche CNRS 415 and 804, Campus de Beaulieu, Université de Rennes I, 35042 Rennes (France)

Abstract

BH_3 containing iron complexes $Fe(\eta^3\text{-}HB(H)_2SCHSR')(CO)(PR_3)_2$ (**3**) were prepared by reduction of $Fe(\eta^2\text{-}CS_2R')(X)(CO)(PR_3)_2$ derivatives (**2**) with $NaBH_4$. The X-ray structure of **3a** ($R'=R=Me$) shows the *cis* addition of the H^- and BH_3 fragments to the coordinated dithioformate C–S bond and that one B–H bond is coordinated to the iron atom. The removal of BH_3 from **3**, on treatment with pyridine, generates a 16-electron iron moiety which can trap two-electron ligands (CO, PR_3) or react with alkynes $HC{\equiv}C–R$ ($R=Ph$, H, $C(Me)=CH_2$) to give the insertion of the alkyne into the dithioformate coordinated C–S bond and $Fe(\eta^3\text{-}S–C(R)=CH–CH–SMe)(CO)(PR_3)_2$ complexes. The latter are stable for R = Ph (**6**), for which the structure has been determined by X-ray diffraction, and R = H (**8**); the cleavage of their Fe–CH bond leads to new sulfur-containing metallacycles **7** (R = Ph) and **10** ($R=CMe=CH_2$).

Introduction

The search for substrate desulfurization processes is currently motivating the study of metal-promoted carbon–sulfur bond cleavage. Initial work has involved the desulfurization of thiocarbonates, thioketones or dithioesters [1], likely via metal–carbene intermediates. Evidence has now been given of easiness of C–S bond cleavage in bimetallacyclic systems [2], coordinated sulfur-containing alkyne [3] and complexed thiophenes [4, 5]. Moreover, the direct η^2-coordination of a carbon–sulfur bond has been shown to promote its fragmentation on hydrogenation [6] or sulfur alkylation generating transient metal carbene [7–9] or carbyne species [10].

We have previously demonstrated that the dithioformate C=S bond η^2-coordinated to a $[R_3P]_2[OC]_2Fe$ moiety in a 18-electron complex (I) can be cleaved on treatment with electrophilic alkynes and lead to the product of insertion (II) of the $C{\equiv}C$ bond and carbon monoxide ligand into the carbon–sulfur bond [8] (Scheme 1). The insertion of alkynes into a carbon–sulfur bond also occurs with sulfur η^1-coordinated thioaldehydes and thioketones via [2+2] cycloadditions [11], or with η^2-coordinated alkenyl $RSC(R')=CR'$ ligands [12]. We now wish to report (i) the full details of the preparation of η^2-dithioformate–iron/BH_3 adducts (III) for which a preliminary study has been reported [13], (ii) their use to generate 16-electron dithioformate–iron species (A), (iii) the insertion of alkynes into the coordinated dithioformate C–S bond to give IV and (iv) the X-ray diffraction studies of $Fe[\eta^3\text{-}H–B(H)_2 \leftarrow S–C(SMe)H](CO)(PMe_3)_2$ and $Fe[\eta^3\text{-}S–C(Ph)=CH–CH(SMe)](CO)(PMe_3)_2$ complexes.

Experimental

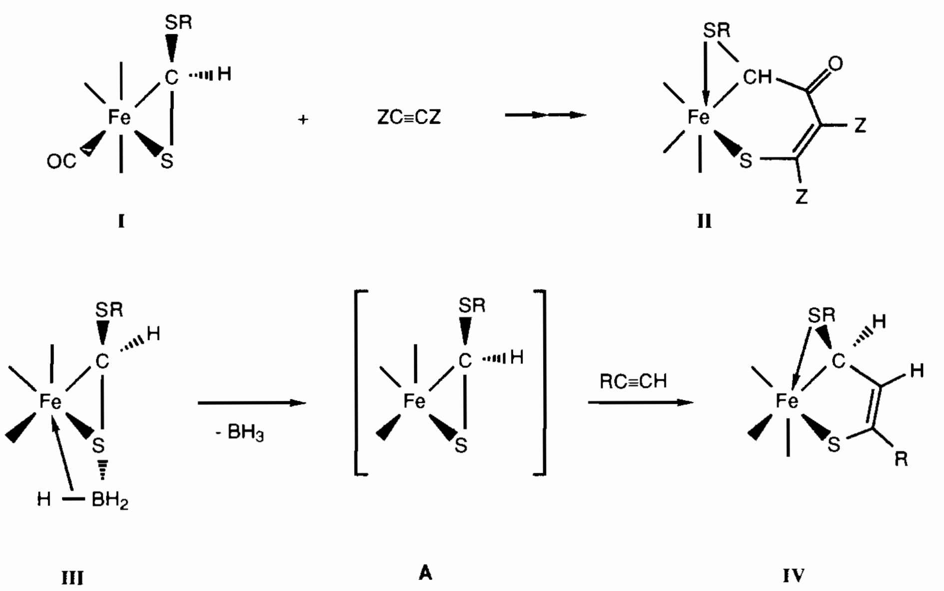
All syntheses were performed under inert atmosphere using vacuum line and Schlenk techniques. Solvents were dried over appropriate drying agents and distilled under nitrogen. Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone ketyl. Hexane and pentane were dried by reflux over calcium hydride. Pyridine was purified by distillation over KOH.

Sodium borohydride pellets (Janssen) were powdered and dried under vacuum before use. IR spectra were recorded on a Pye Unicam SP 1100 spectrometer. NMR spectra were obtained on Brucker WP 80 FT (^1H, ^{31}P) and Brucker AM 300 WB (^1H, ^{13}C) spectrometers; mass spectra were determined at 70 eV using a Varian MAT 311 double focusing spectrometer at the Centre Regional de Mesures Physiques de l'Ouest, Université de Rennes. Microanalyses were determined by the CNRS laboratory at Villeurbanne.

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00



Scheme 1.

Fe(η^2-CS$_2$R)(X)(CO)L$_2$ complexes (**2a–e**) were prepared from Fe(η^2-CS$_2$)(CO)$_2$L$_2$ derivatives (**1**) (L = PMe$_3$ and PMe$_2$Ph) [14] according to literature methods [15].

Synthesis of Fe(η^3-HB(H)$_2$SCHSR)(CO)(PMe$_3$)$_2$ (3a–c)

0.20 g (5.2 mmol) of NaBH$_4$ was added to a stirred solution of complex **2a–c** (2 mmol) in 30 ml of THF at room temperature. The reaction was monitored by thin layer chromatography. After 1 h the starting complex **2** had been completely transformed into **3**. The solvent was removed under vacuum, the complex was extracted with pentane, purified on a column of silica gel (20 g, 4×2.5 cm) under inert atmosphere (pentane:ether (20:1)) and crystallized from a hexane solution to afford a yellow crystalline solid.

3a (R = Me): 0.34 g (50%) obtained from 0.90 g of **2a**; m.p. 94–96 °C. IR (nujol): ν(B–H) 2480, 2400(m), ν(CO) 1920(s), ν(CS) 1160(m) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 297 K): δ 2.21 (s, SMe), 2.04 (d, FeCH, ^3J(PH) = 5.6 Hz), 1.15(d) and 0.99(d) ($|^2J$(PH) + ^4J(PH)$|$ = 8.45 Hz, (PMe$_3$)), −13.73 (s, broad, BH$_3$); ^{31}P NMR (C$_6$D$_6$, 32.38 MHz, 309 K): δ 29.22(s) and 13.99(s), PMe$_3$. ^{31}P NMR (C$_6$D$_6$, 121.5 MHz, 297 K): δ 30.13(d), 15.12(d) ^2J(PP) = 2.5 Hz. ^{13}C NMR (C$_6$D$_6$, 75.47 MHz, 297 K): δ 218.29 (t, ^2J(PC) = 27.1 Hz, Fe–CO), 56.43 (t, ^2J(PC) = 13.5 Hz, Fe*C*HS), 24.60 (s, SMe), 21.33 (d, ^1J(PC) = 27.8 Hz) and 19.62 (d, ^1J(PC) = 24.6 Hz) PMe$_3$. Mass spectrum, *m/e*: found: 327.994, calc. for (M-BH$_3$)$^+$: 327.993. *Anal.* Calc. for C$_9$H$_{25}$BFeOP$_2$S$_2$: C, 31.60; H, 7.36; P, 18.12; B, 3.16. Found: C, 31.80; H, 7.35; P, 17.95; B, 3.27%.

3b (R = CH$_2$–C(Me)=CH$_2$): 0.42 g (55%) obtained from 0.80 g of **2b**; m.p. 112–114 °C. IR (nujol): ν(B–H) 2460, 2400(m), ν(CO) 1930(s), ν(CS) 1160(m) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 297 K) δ 4.95 and 4.86 (=CH$_2$), 3.21 (AB, SCH$_2$, ^2J(HH) = 12.9 Hz), 2.04 (d, ^3J(PH) = 5.7 Hz, FeC*H*), 1.80 (s, CMe), 1.15(d) and 0.99 (d, ^2J(PH) = 8.5 Hz, PMe$_3$), −13.75 (broad, BH$_3$). ^{31}P NMR (C$_6$D$_6$, 32.38 MHz, 309 K): δ 28.92(s) and 14.39 (s, PMe$_3$). ^{13}C (C$_6$D$_6$, 75.47 MHz, 297 K): δ 218.20 (t, ^2J(PC) = 29.5 Hz, Fe–CO), 141.50 (s, =*C*Me), 113.59 (s, =CH$_2$), 52.10 (t, ^2J(PC) = 13.5 Hz, Fe*CH*S), 48.25 (s, S–CH$_2$), 21.16 (s, C*Me*), 21.44 (d, ^1J(PC) = 27.0 Hz) and 19.64 (d, ^1J(PC) = 24.6 Hz, PMe$_3$). *Anal.* Calc. for C$_{12}$H$_{29}$BFeOP$_2$S$_2$: C, 37.72; H, 7.65; P, 16.21. Found: C, 37.81; H, 7.58; P, 16.28%.

3c (R = CH$_2$Ph): 0.45 g (53%) obtained from 0.88 g of **2c**; m.p. 41–43 °C. IR (nujol): ν(B–H) 2460, 2410(m), ν(CO) 1920(s), ν(CS) 1160(m) cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 309 K): δ 7.14 (m, Ph), 3.76 (AB, SCH$_2$, ^2J(HH) = 12.9 Hz), 1.95 (d, CH, ^3J(PH) = 6.1 Hz), 1.14(d) and 0.99(d) (PMe$_3$, ^2J(PH) = 8.4 Hz). ^{13}C NMR (C$_6$D$_6$, 75.47 MHz, 309 K): δ 218.44 (t, CO, ^2J(PC) = 28 Hz), 51.96 (t, FeCH, ^2J(PC) = 13.5 Hz), 45.22 (s, SCH$_2$), 21.12 (d, ^1J(PC) = 28 Hz), 19.62 (d, ^1J(PC) = 24 Hz, PMe$_3$). *Anal.* Calc. for C$_{15}$H$_{29}$BFeOP$_2$S$_2$: C, 43.08; H, 6.99; P, 14.81. Found: C, 43.10; H, 6.86; P, 14.78%.

Synthesis of Fe(η^3-HB(H)$_2$SCHSR)(CO)(PMe$_2$Ph)$_2$ (3d–e)

The same procedure as for **3a–c** was used except that the reaction was carried out at room temperature for 6 h and that crystallization was performed in hexane at −30 °C.

3d (R = Me): 0.28 g (30%) obtained from 1.15 g of **2d**; m.p. 128–130 °C. IR (nujol): ν(BH) 2475, 2400(m), ν(CO) 1930(s), ν(CS) 1160(m) cm^{-1}. ^{31}P NMR (32.38

MHz, C_6D_6, 309 K): δ 38.92(s) and 22.94(s) (PMe_2Ph). ^1H NMR (300 MHz, C_6D_6, 297 K) δ 2.17 (s, SMe), 2.07 (d, Fe*CH*, ^3J(PH) = 6.1 Hz) 1.58(d) and 1.46(d) (^2J(PH) = 8.7 Hz, PMe(A)), 1.15(d) and 1.08(d) (^2J(PH) = 7.7 Hz, PMe(B)), −13.5 (broad, BH_3). ^{13}C NMR (C_6D_6, 75.47 MHz, 309 K): δ 218.53 (t, FeCO, ^2J(PC) = 26.5 Hz), 57.43 (t, FeCHS, ^3J(PC) = 13.5 Hz), 24.45 (s, SMe). *Anal.* Calc. for $C_{20}H_{31}BFeOP_2S_2$: C, 50.02; H, 6.50; P, 12.90. Found: C, 50.48; H, 6.48; P, 12.75%.

3e (R = Et): 0.27 g (28%) obtained from 1.10 g of **2e**; m.p. 138–140 °C. IR (nujol): ν(BH) 2480, 2410(m), ν(CO) 1930(s), ν(CS) 1160(m) cm^{-1}. ^{31}P NMR (32.38 MHz, C_6D_6, 309 K): δ 32.39(s), 23.80(s) (PMe_2Ph). ^1H NMR (80 MHz, C_6D_6, 309 K): δ 2.12 (d, ^3J(PH) = 6.1 Hz, FeCH), −13.29 (broad, s, BH_3). The elemental analysis of **3e** was not satisfactory due to its instability and to the presence of a small amount of Fe(η^2-CS_2Et)(X)$(CO)_2(PMe_2Ph)_2$ (**2e**) as shown by ^{31}P NMR.

Preparation of Fe(η^2-SCHSMe)$(CO)_2(PMe_3)_2$ (4)

A solution of 0.34 g of **3a** (1 mmol) in 20 ml of pentane was saturated with carbon monoxide and kept under 1 atm. of CO. 3 mmol (0.25 ml) of pyridine were added and the mixture was stirred at room temperature for 4 h. After filtration, evaporation to dryness under vacuum, the product was chromatographed under inert atmosphere (eluent: pentane/ether (25/1)) on a column of silica gel (15 g, 3×2.5 cm). 0.35 g (95%) of complex **4** [8] was obtained. IR (nujol): ν(CO) 1965, 1895 cm^{-1}. ^1H NMR (80 MHz, C_6D_6, 309 K): δ 4.68 (d, CH, ^3J(PH) = 7.5 Hz), 2.49 (s, SMe), 1.26(d) and 0.89(d) (^2J(PH) = 9 Hz, PMe_3). When the same procedure was performed without an atmosphere of CO, complex **4** was isolated in 43% yield (0.15 g).

Preparation of Fe(η^2-SCHSMe)(CO)$(PMe_3)_3$ (5)

3 mmol (0.3 ml) of PMe_3 were added to a stirred solution of 0.34 g (1 mmol) of **3a** in 20 ml of pentane. Then at room temperature 3 mmol (0.25 ml) of pyridine were added. After 4 h of stirring at room temperature, filtration through a frit and crystallization in pentane, complex **5** was obtained in 95% yield (0.385 g); m.p. 82–83 °C. IR (nujol): ν(CO) = 1870 cm^{-1}. ^1H NMR (80 MHz, C_6D_6, 309 K): δ 4.18 (m, CH), 2.59 (s, SMe), 1.33(d), 1.29(d) and 1.02(d) (PMe_3, ^2J(PH) = 6.8, 7.3 and 6.8 Hz, respectively). ^{31}P NMR (32.38 MHz, C_6D_6, 309 K): δ 25.15(dd), 13.76 (d, ^2J(PP) = 39.0 Hz), 10.97 (d, ^2J(PP) = 48.9 Hz). *Anal.* Calc. for $C_{12}H_{31}FeOS_2P_3$: C, 35.65; H, 7.72; P, 22.98. Found: C, 35.64; H, 7.62; P, 22.77%.

Reaction of complex 3a with alkynes. Formation of complexes 6 and 7 from phenylacetylene

1 mmol (0.34 g) of **3a** was dissolved in 20 ml of THF and kept in the dark. To this were added successively with a syringe 20 mmol (2.2 ml) of phenylacetylene and 10 mmol (0.8 ml) of distilled pyridine. The mixture was stirred at room temperature for 16 h. The complexes **6** and **7** were purified by chromatography on silica gel under nitrogen (eluent: hexane/ether) but could not be separated. On crystallization in hexane, air-sensitive crystals of the mixture were obtained which were stored under nitrogen at low temperature. The **6**/**7** ratio changed from one experiment to another. The overall yield was 55–60%. After crystallization in hexane complex **6** was obtained in a pure form in upto 55% yield (0.23 g) and from another experiment, complex **7** was isolated in 50% yield.

Complex 6

m.p. 66–68 °C. IR (nujol): ν(CO) 1910(s), ν(CS) 960(m) cm^{-1}. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 28.67(d), 14.08(d), ^2J(PP) = 4.8 Hz. ^1H NMR (300.13 MHz, C_6D_6): δ 8.1–7.1 (m, Ph), 6.71 (d, HC=, ^3J(HH) = 3.5 Hz), 4.49 (broad m, *HC*(SMe)), 1.26 (d, PMe_3, ^2J(PH) = 7.6 Hz), 1.21 (s, SMe), 1.09 (d, PMe_3, ^2J(PH) = 8.9 Hz). $^{13}C\{^1H\}$ NMR (75.65 MHz, C_6D_6): δ 215.35 (dd, FeCO, ^2J(PC) = 33.2 Hz and 21.5 Hz), 159.56 (d, =*C*Ph, ^3J(PC) = 20.6 Hz), 140.7 (s, =CH), 56.7 (m, *CH*SMe), 20.7 (d, PMe_3, ^1J(PC) = 23.2 Hz), 20.0 (d, PMe_3, ^1J(PC) = 27.7 Hz), 8.1 (s, SMe). *Anal.* Calc. for $C_{17}H_{28}FeOP_2S_2$: C, 47.44; H, 6.55; P, 14.39. Found: C, 47.39; H, 6.74; P. 14.10%. Mass spectrum, *m*/*e*: calc. for $(M\text{-CO-PMe}_3)^+$: 326.001, found: 326.001; calc. for M^+: 430.041, found: 430.043.

Complex 7

IR (CH_2Cl_2): ν(CO) 1920 cm^{-1}. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 23.29(d), 16.03(d), ^2J(PP) = 4.3 Hz. ^1H NMR (300.13 MHz, C_6D_6): δ 7.5–7.1 (m, Ph), 7.07 (m, =C*H*C(Ph), ^1H irradiation at δ = 6.23 ppm *and* ^{31}P irradiation at δ = 23.29 ppm give a doublet ^5J(PH) = 1.9 Hz), 6.23 (d, =C*H*(SMe), ^3J(HH) = 5.9 Hz), 1.23 (d, SMe, ^4J(PH) = 1.8 Hz), 1.18 (d, PMe_3, ^2J(PH) = 7.8 Hz), 0.91 (d, PMe_3, ^2J(PH) = 9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 215.33 (dd, FeCO, ^2J(PC) = 33.9 Hz, 24.6 Hz), 152.91 (t, S=*C*Ph, ^3J(PC) ≈ 1 Hz), 144.84 (d, =*C*HSMe, ^3J(PC) = 21.1 Hz), 131.76 (d, =CHC(Ph), ^4J(PC) = 3.3 Hz), 20.56 (d, PMe_3, ^2J(PC) = 23.2 Hz), 18.46 (d, PMe_3, ^2J(PC) = 28.0 Hz), 9.54 (s, SMe). Mass spectrum, *m*/*e*: calc. for $(M = C_{17}H_{28}FeOP_2S_2)^+$: 430.041, found: 430.042.

Synthesis of complex 8 from acetylene

Acetylene was bubbled through a solution of 1 mmol (0.34 g) of **3a** in 30 ml of THF at −50 °C until the dissolution of ≈20 mmol. Then 3 mmol (0.25 ml) of pyridine was added. The reaction mixture was stirred and left to slowly warm to room temperature. After 3 h of stirring the solvent was removed under vacuum and the product was chromatographed on a column of silica gel (20 g, 4×2.5 cm) under inert atmosphere (eluent: hexane–ether). The yellow crystalline solid **8** was obtained in 65% yield (0.22 g); m.p. 70–72 °C. IR (nujol): ν(CO) 1910 cm^{-1}. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6): δ 27.33(d), 14.20(d), $^2J(PP) = 6.2$ Hz. ^1H NMR (300.13 MHz, C_6D_6): δ 7.01 (m, =CHS), 6.20 (t, =CH–C, $^3J(HH) = 5.3$ Hz), 4.48 (m, *CH*SMe), 1.23 (d, PMe_3, $^2J(PH) = 7.6$ Hz), 1.16 (s, SMe), 1.08 (d, PMe_3, $^2J(PH) = 8.9$ Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ 215.35 (dd, FeCO, $^2J(PC) = 34$ Hz, 22 Hz), 145.5 (d, SCH=, $^3J(PC) = 21$ Hz), 129.2 (s, CCH=), 57.63 (t, HCSMe, $^2J(PC) = 14$ Hz), 8.87 (s, SMe). ^{13}C NMR: δ 145.5 (d(dt), $^1J(CH) = 161$ Hz), 129.2 (d, $^1J(CH) = 158$ Hz). *Anal.* Calc. for $C_{11}H_{24}FeOP_2$: C, 37.30; H, 6.83; Found: C, 37.62; H, 6.91%.

*Synthesis of complex **10** from isopropenylacetylene*

To a stirred solution of 1 mmol (0.34 g) of **3a** in 20 ml of THF were added 10 mmol of isopropenylacetylene and then 0.8 ml (10 mmol) of dried, distilled pyridine. After 14 h of stirring, thin layer chromatography showed the absence of **3a**. The solvent was removed and the oily products, dissolved in 50 ml of hexane, were chromatographed on a column of silica gel (30 g, diameter 2.5) (eluents: hexane and then hexane progressively enriched with ether). The orange fraction was concentrated and crystals were formed on cooling. After crystallization in hexane 0.40 g (50%) of the orange complex **10** was obtained.

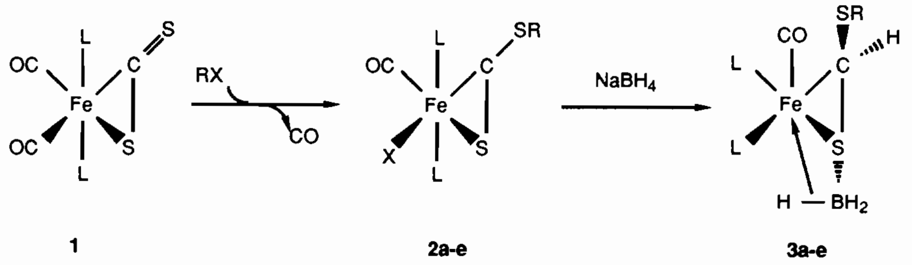
IR (KBr): ν(CO) 1881 cm^{-1}. ^{31}P NMR (C_6D_6, 121.50 MHz): δ 23.78(s), 19.10(s); ^1H NMR (C_6H_6, 300.13 MHz): δ 6.90 (d, =CH), 5.98 (d, =CH, $^3J(HH) = 10.2$ Hz), 2.26 (s, Me), 1.85 (s, Me) 1.23(d) and 1.17(d), (PMe_3, $^2J(PH) = 8$ Hz), (1.78 (s, 1H) and 0.42 (m, 1H): =CH_2). $^{13}C\ \{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 217.2 (dd, FeCO, $^2J(PC) = 16.1$, 34.8 Hz), 132.1 (d, MeS-*CH*, $^3J(PC) = 2.5$ Hz), 127.3 (d, =CHCS, $^2J(PC) = 2.5$ Hz), 103.1 (dd, =*C*Me, $^2J(PC) = 1.7$ Hz, 3.4 Hz), 100.8 (d, C=S, $^3J(PC) = 1.7$ Hz), 48.0 (dd, =CH_2, $^2J(PC) = 7.2$ Hz), 22.5 (s, Me), 21.8 (d, PMe_3, $^1J(PC) = 25.9$ Hz), 19.9 (s, Me), 19.5 (d, PMe_3, $^1J(PC) = 23.6$ Hz). ^{13}C NMR: δ 132.1 (dm, $^1J(CH) = 167.9$ Hz), 48.0 (tm, $^1J(CH) = 159.4$ Hz). Mass spectrum, *m/e*: calc. for $(M = C_{14}H_{28}FeOP_2S_2)^+$: 394.041, found: 394.041. *Anal.* Calc. for $C_{14}H_{28}FeOP_2S_2$: C, 42.64; H, 7.10; S, 15.73; P, 16.24. Found: C, 42.31; H, 7.05; S, 16.02; P, 16.02%.

*X-ray structure determination of **3a***

A yellow crystal (prism 0.28×0.37×0.40 mm) was studied on an Enraf-Nonius CAD4 automatic diffractometer with graphite monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. Crystal data: $C_9H_{25}BFeOP_2S_2$, $M_r = 342.03$, orthorhombic, space group $Pna2_1$, $a = 15.946(2)$, $b = 13.444(5)$, $c = 8.232(4)$ Å, $V = 1764.8(7)$ Å^3, $Z = 4$, $D_x = 1.29$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 12.4$ cm^{-1}, $F(000) = 720$, $T = 294$ K. The data collection ($2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range *hkl*: *h*0.19, *k*0.17, *l*0.10, intensity controls without appreciable decay (0.7%)) gave 2163 reflections from which 1578 had $I > \sigma 3(I)$. After Lorentz and polarization corrections the Fe atom was located with a Patterson map. The remaining non-hydrogen atoms were found after successive scale factor refinements and Fourier differences. After isotropic refinement ($R = 0.087$), then anisotropic refinement ($R = 0.049$), a Fourier difference allowed location of the hydrogen atoms between 0.38 and 0.18 e Å^{-3}. The whole structure was refined by the full-matrix least-square techniques (use of *F* magnitude; *x*, *y*, *z*, β_{ij} for Fe, P, S, B, O and C atoms; *x*, *y*, *z* and B_{iso} for H atoms; 220 variables and 1578 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting $R = 0.022$, $R_w = 0.025$ and $S_w = 1.067$ (residual $\Delta\rho \leqslant 0.17$ e Å^{-3}). Atomic scattering factors were obtained from the International Tables [16]. All calculations were performed on a Digital PDP 11/60 computer with the SDP package [17, 18].

*X-ray structure determination of **6***

A brown crystal (prism 0.25×0.30×0.30 mm) was studied on an Enraf-Nonius CAD4 automatic diffractometer with graphite monochromatized Mo Kα radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. Crystal data: $FeC_{17}H_{29}FeOP_2S_2$, $M_r = 431.1$, monoclinic, space group $P2_1/n$, $a = 8.591(5)$, $b = 14.558(9)$, $c = 16.470(6)$ Å, $\beta = 96.61(5)°$, $V = 2059(1)$ Å^3, $Z = 4$, $D_x = 1.388$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 10.81$ cm^{-1}, $F(000) = 904$, $T = 294$ K. The data collection ($2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range *hkl*: *h*0.10, *k*0.17, *l*19.19, intensity controls without appreciable decay (0.6%)) gave 3911 reflections from which 3114 independent ($R_{int} = 0.013$) had $I > \sigma 3(I)$. After Lorentz and polarization corrections the structure was solved with direct methods which allowed location of Fe, P and S atoms, the remaining non-hydrogen atoms being found with Fourier differences. After isotropic ($R = 0.068$), then anisotropic refinement ($R = 0.047$), the hydrogen atoms were found in a Fourier difference between 0.77 and 0.43 e Å^{-3}. The whole structure was refined by the full-matrix least-square techniques (use of *F* magnitude; *x*, *y*, *z*, β_{ij} for Fe, P, S, O and C atoms; *x*, *y*, *z* and B_{iso} for H atoms; 293 variables and 3114 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting



L = PMe$_3$: R, X : Me, I (**a**) ; CH$_2$C(Me)=CH$_2$, Cl (**b**) ; CH$_2$Ph, Cl (**c**)

L = PMe$_2$Ph : R, X : Me, I (**d**) ; Et, Br (**e**)

Scheme 2.

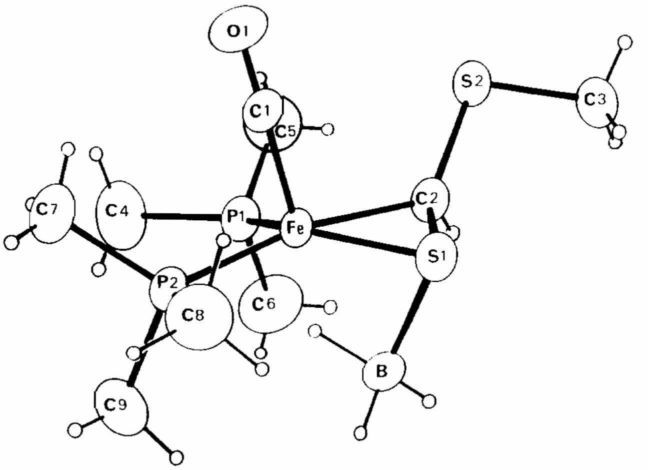


Fig. 1. Molecular structure of Fe[η^3-H–B(H)$_2$←S–C(SMe)H](CO)(PMe$_3$)$_2$ (**3a**).

$R = 0.026$, $R_w = 0.028$ and $S_w = 1.26$ (residual $\Delta\rho \leqslant 0.42$ e Å^{-3}). Atomic scattering factors were obtained from the International Tables [16]. All calculations were performed on a Digital PDP 11/60 computer with the SDP package [17, 18].

Results and discussion

Formation of Fe[η^3-HB(H)$_2$SCH(SR)] (3) complexes

The reaction of complexes **2a–e** [15] with an excess of sodium borohydride in THF at room temperature gives rise to yellow derivatives **3a** (50%), **3b** (55%), **3c** (53%), **3d** (30%) and **3e** (28%) (Scheme 2). The presence of a labile halide in the neutral complexes **2** is essential for the formation of compounds **3**, since the corresponding [Fe(η^2-CS$_2$R)(CO)$_2$L$_2$]PF$_6$ salts do not react with H$_3$B–THF, but with NaBH$_4$ give either Fe(η^2-SCHSMe)(CO)$_2$L$_2$ complexes, when L is a electron releasing ligand (L = PMe$_3$, PMe$_2$Ph) [8] or, when L is PPh$_3$, lead to the dimerization of the η^2-CS$_2$R group, via electron transfer [19].

The complexes **3** are characterized in the IR by two ν(B–H) absorptions (**3a**: 2480, 2400 cm^{-1}) and one low frequency ν(CO) absorption (1920 cm^{-1} for **3a**). ^{1}H and ^{31}P NMR data are consistent with two *cis*-phosphine ligands indicating an isomerization during the transformation **2**→**3** and ^{1}H NMR spectra show only a broad signal at high field for BH$_3$ (−13.7 for **3a**) and that the FeCHS proton ($\delta = 2.04$ ppm, ^3J(PH) = 5.6 Hz (**3a**)) is coupled with only one ^{31}P nucleus likely in the *trans* position.

An X-ray structural analysis of **3a** established the molecular structure (Fig. 1) and the *cis* addition of the H$^-$ and BH$_3$ fragments to the coordinated C=S bond of **2a**, with the halide elimination and the coordination of one H–B bond to the metal center in the *trans* position of the carbonyl ligand. The molecule can be viewed as a square pyramidal L$_2$(OC)Fe(η^2-S=CHSR) moiety complexed with BH$_3$, with the coordinated sulfur atom acting as a Lewis base toward BH$_3$ and one B–H bond acting as a 2-electron ligand for the saturation of the electron configuration of the iron atom. One B–H bond is thus acting as an agostic bond toward the iron atom, with a Fe–H distance of 1.55(4) Å and with the longer coordinated B–H(A) bond length (1.28(4) Å) with respect to the other two (Tables 1 and 2). It is noteworthy that the coordination of BH$_3$ to the sulfur atom shortens the Fe–P(1) bond in the *trans* position and the Fe–S distance (2.220(1) Å) as compared to that of a related system (2.305(1) Å) [8].

Reactivity of Fe(η^2-SCH(SR))BH$_3$ adducts

Every complex **3** can be considered as an adduct of a 16-electron L$_2$(OC)Fe(η^2-SCHSR) complex with BH$_3$, with one B–H bond acting as a 2-electron ligand. As pyridine is known to give a stable adduct with BH$_3$ we have attempted to generate the 16-electron intermediate **A** (Scheme 3) via the mild removal of the BH$_3$ unit of complexes **3**, in the presence of 2-electron ligands and of alkynes. Complex **3a** in pentane was treated with 3 equiv. of pyridine at room temperature to give complex **4** in 43% yield. When the same reaction was

TABLE 1. Positional parameters for **3a**

Atom	x	y	z	B (Å^2)
Fe	0.08400(2)	0.20406(3)	0.000	2.657(6)
S1	0.06432(6)	0.14802(7)	0.2508(1)	3.83(2)
S2	−0.08415(5)	0.29145(8)	0.2030(1)	3.99(2)
P1	0.10651(6)	0.33873(6)	−0.1404(1)	3.54(2)
P2	0.15276(5)	0.08431(6)	−0.1357(1)	3.38(2)
O1	−0.0724(2)	0.1604(2)	−0.1766(4)	5.94(7)
C1	−0.0107(2)	0.1780(2)	−0.1034(4)	3.48(7)
C2	0.0285(2)	0.2687(3)	0.1946(4)	3.46(6)
C3	−0.1008(2)	0.3073(3)	0.4177(5)	4.21(8)
C4	0.1376(4)	0.3304(4)	−0.3539(6)	6.7(1)
C5	0.0148(3)	0.4215(3)	−0.1572(6)	5.8(1)
C6	0.1895(3)	0.4186(3)	−0.0618(7)	7.0(1)
C7	0.1167(3)	0.0534(3)	−0.3406(5)	5.22(9)
C8	0.1473(3)	−0.0368(3)	−0.0365(5)	5.4(1)
C9	0.2681(2)	0.1001(3)	−0.1635(6)	5.6(1)
B	0.1806(3)	0.1863(4)	0.2199(5)	4.07(9)
H2	0.056(2)	0.316(2)	0.244(5)	4*
H3A	−0.080(2)	0.249(2)	0.470(5)	4*
H3B	−0.068(2)	0.359(2)	0.469(5)	4*
H3C	−0.158(2)	0.314(2)	0.431(5)	4*
H4A	0.136(2)	0.400(2)	−0.403(5)	4*
H4B	0.191(2)	0.297(2)	−0.351(5)	4*
H4C	0.081(2)	0.287(2)	−0.411(5)	4*
H5A	0.027(2)	0.483(2)	−0.211(4)	4*
H5B	−0.027(2)	0.391(2)	−0.197(4)	4*
H5C	0.004(2)	0.437(2)	−0.058(4)	4*
H6A	0.176(2)	0.433(2)	0.048(4)	4*
H6B	0.202(2)	0.482(2)	−0.110(4)	4*
H6C	0.236(2)	0.388(2)	−0.046(4)	4*
H7A	0.142(2)	−0.001(2)	−0.364(5)	4*
H7B	0.060(2)	0.046(2)	−0.341(4)	4*
H7C	0.124(2)	0.124(2)	−0.412(4)	4*
H8A	0.080(2)	−0.061(2)	−0.028(4)	4*
H8B	0.173(2)	−0.033(2)	0.076(4)	4*
H8C	0.182(2)	−0.084(2)	−0.098(4)	4*
H9A	0.297(2)	0.113(2)	−0.056(4)	4*
H9B	0.287(2)	0.047(2)	−0.203(4)	4*
H9C	0.273(2)	0.158(2)	−0.211(4)	4*
H10A	0.171(2)	0.223(2)	0.078(5)	4*
H10B	0.228(2)	0.121(2)	0.223(4)	4*
H10C	0.204(2)	0.246(2)	0.301(4)	4*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1.1)+b^2B(2.2)+c^2B(3.3)+ab(\cos\gamma)B(1.2)+ac(\cos\beta)B(1.3)+bc(\cos\alpha)B(2.3)]$.

TABLE 2. Selected interatomic distances (Å) and angles (°) for **3a**

Fe–S1	2.220(1)	P1–C5	1.842(5)
Fe–P1	2.178(1)	P1–C6	1.822(6)
Fe–P2	2.245(1)	P2–C7	1.830(4)
Fe–C1	1.769(3)	P2–C8	1.823(5)
Fe–C2	2.026(4)	P2–C9	1.865(5)
Fe–H10A	1.55(4)	O1–C1	1.178(4)
S1–C2	1.782(4)	C2–H2	0.87(4)
S1–B	1.941(5)	B–H10A	1.28(4)
S2–C2	1.824(4)	B–H10B	1.16(4)
S2–C3	1.800(4)	B–H10C	1.11(4)
P1–C4	1.830(5)		
S1–Fe–P1	143.02(4)	P2–Fe–C2	156.1(1)
S1–Fe–P2	106.76(4)	P2–Fe–H10A	84(1)
S1–Fe–C1	105.0(1)	C1–Fe–C2	95.3(2)
S1–Fe–C2	49.4(1)	C1–Fe–H10A	175(1)
S1–Fe–H10A	78(1)	C2–Fe–H10A	89(1)
P1–Fe–P2	104.58(4)	Fe–S1–C2	59.6(1)
P1–Fe–C1	92.9(1)	Fe–S1–B	69.7(1)
P1–Fe–C2	97.7(1)	C2–S1–B	91.7(2)
P1–Fe–H10A	86(1)	C2–S2–C3	101.7(2)
P2–Fe–C1	92.0(1)		

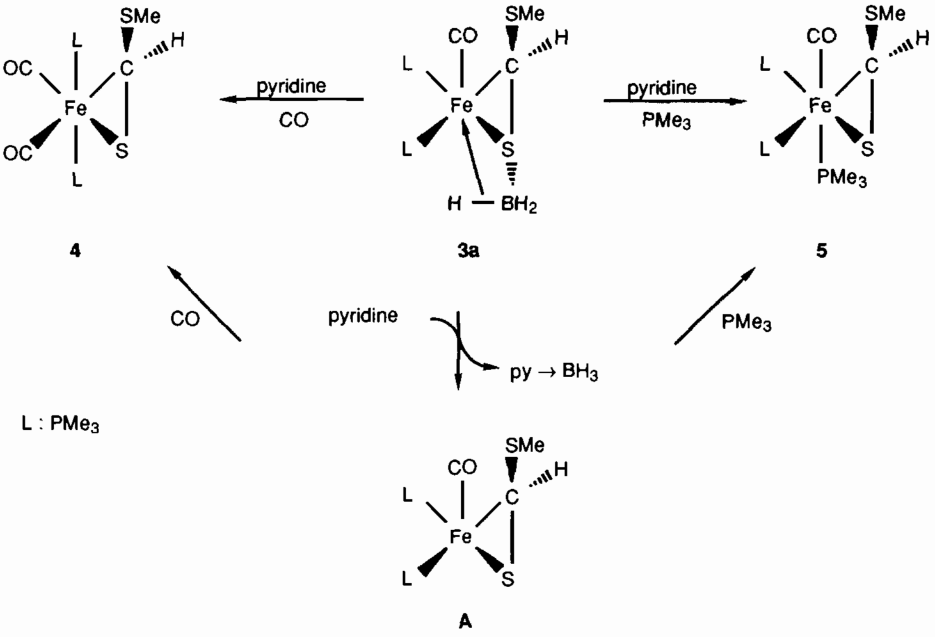
performed in carbon monoxide saturated pentane complex **4** was obtained in 95% yield (Scheme 3). The transformation **3a**→**4** corresponds to the elimination of BH_3 and the addition of one CO ligand. It takes place with the *cis*→*trans* isomerization of the phosphine ligands which corresponds to the more stable molecule: complex **4** was previously made by addition of hydride from $NaBH_4$ to the cation $Fe[(\eta^2\text{-}CS_2Me)(CO)_2(PMe_3)_2]^+$ [8].

Complex **3a** does not react with an excess of PMe_3 in pentane, but on further addition of pyridine transformation into **5** (95%) was achieved. This reaction allows the introduction of an additional PMe_3 ligand to the $Fe[\eta^2\text{-}SCH(SMe)]$ moiety whereas the corresponding cation $Fe(\eta^2\text{-}CS_2Me)(CO)L_3^+$ was not accessible [15].

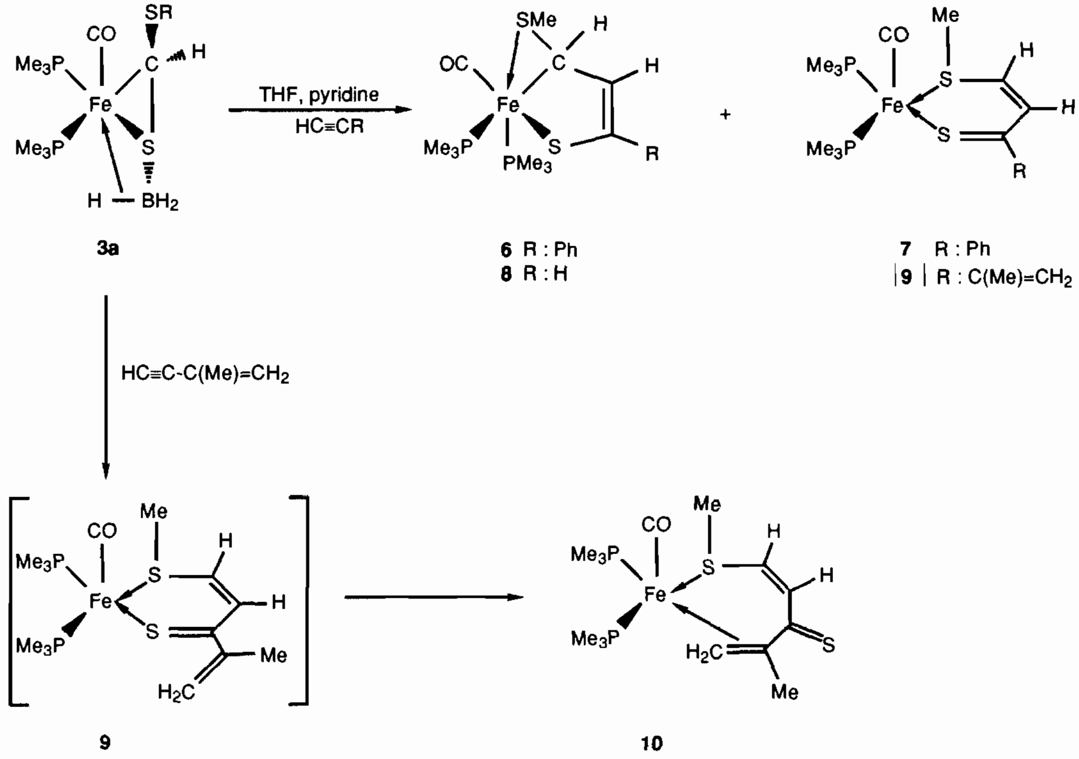
Reaction with alkynes

By contrast to $Fe(\eta^2\text{-}SCHSR)(CO)_2L_2$ derivatives which add electrophilic alkynes [8] complexes **3** do not react with these alkynes or phenylacetylene. Thus, the coordination of the sulfur atom to BH_3 inhibits the initial coupling of this sulfur with the alkyne. The alkyne does not insert into BH bonds of **3a** which thus behaves in a similar way to Me_2SBH_3. When the 16-electron species was generated from **3a** on treatment with pyridine in the presence of phenylacetylene a new reaction took place at room temperature and complexes **6** and **7** were formed (Scheme 4). The ratio of these two complexes changed from one experiment to another but both complexes were isolated in their pure form. Complexes **6** and **7** have the same formula and the main differences are observed in NMR. From the FeS*CH* resonances (^1H: δ ppm, 4.49(m) (**6**), 6.23(d) (**7**); ^{13}C: δ ppm, 56.7(m) (**6**), 144.8(d) (**7**)) it is obvious that the CH carbon is no longer sp^3 but olefinic in **7**, as compared to that of **6**. The spectroscopic data of **7** are consistent with its formation from **6** via the only cleavage of the Fe–CH bond.

The molecular structure of complex **6** (Fig. 2) was established by an X-ray diffraction study and demonstrated the insertion of the alkyne into the coordinated carbon–sulfur bond of the dithioformate ligand, and the coordination of the MeS group sulfur led to the



Scheme 3.



Scheme 4.

18-electron configuration of the iron atom. The Fe–C(2)–C(3)–C(4)–S(1) cycle is almost planar with a short C(3)–C(4) double bond (1.350(2) Å) and Fe–C(2) (2.020(1) Å) distances. By contrast the Fe–S(1) (2.307(1) Å) distance is significantly lengthened as compared to that of **3a** (2.220(1) Å) which is coordinated to BH_3 (Tables 3 and 4).

When a similar reaction was performed with acetylene the only observed product was complex **8**, isolated in 65% yield, which has a similar structure to that of **6**.

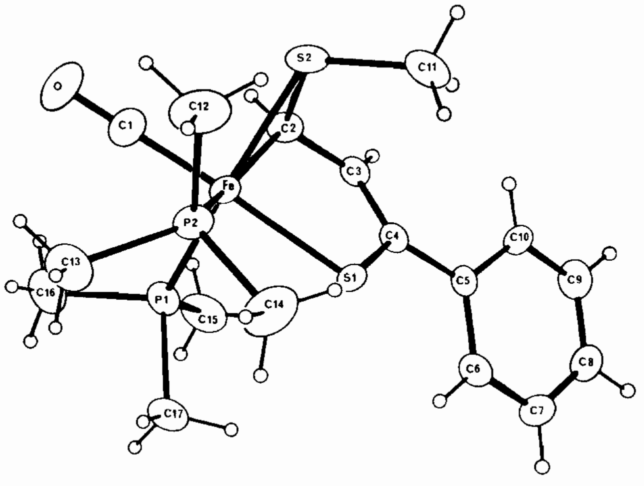


Fig. 2. Molecular structure of Fe[η^3-S–C(Ph)=CH–CH(SMe)](CO)(PMe$_3$)$_2$ (**6**).

TABLE 3. Positional parameters for **6**

Atom	*x*	*y*	*z*	*B* (Å^2)
Fe	0.07221(3)	0.21606(2)	0.05767(1)	1.364(5)
S1	0.19120(5)	0.35139(3)	0.02735(3)	1.533(8)
S2	−0.16471(5)	0.25864(4)	−0.00564(3)	2.212(9)
P1	0.30570(6)	0.15882(3)	0.05620(3)	1.880(9)
P2	0.07164(6)	0.25517(4)	0.18735(3)	1.873(9)
O	−0.0560(2)	0.0381(1)	0.08861(9)	3.71(3)
C1	−0.0044(2)	0.1097(1)	0.0768(1)	2.20(4)
C2	−0.0090(2)	0.2154(1)	−0.0621(1)	1.67(3)
C3	0.0653(2)	0.2796(1)	−0.1129(1)	1.62(3)
C4	0.1560(2)	0.3482(1)	−0.0790(1)	1.59(3)
C5	0.2322(2)	0.4166(1)	−0.1271(1)	1.66(3)
C6	0.3765(2)	0.4546(1)	−0.0982(1)	1.92(3)
C7	0.4524(2)	0.5150(1)	−0.1453(1)	2.30(4)
C8	0.3851(3)	0.5383(1)	−0.2227(1)	2.61(4)
C9	0.2414(3)	0.5015(1)	−0.2521(1)	2.84(4)
C10	0.1646(2)	0.4427(1)	−0.2047(1)	2.28(4)
C11	−0.1855(2)	0.3797(2)	−0.0244(1)	3.00(4)
C12	−0.1254(3)	0.2661(2)	0.2163(1)	3.39(5)
C13	0.1556(3)	0.1753(2)	0.2650(1)	3.29(5)
C14	0.1630(3)	0.3621(2)	0.2250(1)	3.35(5)
C15	0.3785(3)	0.1551(2)	−0.0427(1)	3.44(5)
C16	0.3323(3)	0.0400(2)	0.0893(2)	3.76(5)
C17	0.4717(2)	0.2124(2)	0.1176(1)	2.51(4)
H2	−0.044(3)	0.159(2)	−0.087(2)	4*
H3	0.053(3)	0.273(2)	−0.169(2)	4*
H6	0.420(3)	0.437(2)	−0.045(1)	4*
H7	0.544(3)	0.537(2)	−0.122(1)	4*
H8	0.436(3)	0.582(2)	−0.254(1)	4*
H9	0.195(3)	0.520(2)	−0.302(1)	4*
H10	0.067(3)	0.416(2)	−0.223(1)	4*
H11A	−0.129(3)	0.418(2)	0.016(1)	4*
H11B	−0.287(3)	0.397(2)	−0.038(1)	4*
H11C	−0.150(3)	0.390(2)	−0.072(1)	4*
H12A	−0.119(3)	0.287(2)	0.274(1)	4*
H12B	−0.179(3)	0.203(2)	0.209(1)	4*
H12C	−0.183(3)	0.305(2)	0.184(1)	4*
H13A	0.106(3)	0.111(2)	0.253(1)	4*
H13B	0.138(3)	0.197(2)	0.318(1)	4*
H13C	0.265(3)	0.164(2)	0.263(2)	4*
H14A	0.146(3)	0.366(2)	0.281(1)	4*
H14B	0.275(3)	0.358(2)	0.221(1)	4*
H14C	0.117(3)	0.409(2)	0.198(1)	4*
H15A	0.307(3)	0.116(2)	−0.077(1)	4*
H15B	0.375(3)	0.221(2)	−0.071(1)	4*
H15C	0.472(3)	0.134(2)	−0.038(2)	4*
H16A	0.440(3)	0.021(2)	0.087(1)	4*
H16B	0.261(3)	0.001(2)	0.052(2)	4*
H16C	0.301(3)	0.033(2)	0.145(1)	4*
H17A	0.456(3)	0.216(2)	0.172(2)	4*
H17B	0.559(3)	0.176(2)	0.116(2)	4*
H17C	0.482(3)	0.274(2)	0.099(1)	4*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1.1)+b^2B(2.2)+c^2B(3.3)+ab(\cos\gamma)B(1.2)+ac(\cos\beta)B(1.3)+bc(\cos\alpha)B(2.3)]$.

TABLE 4. Selected interatomic distances (Å) and angles (°) for **6**

Fe–S1	2.307(1)	P1–C17	1.827(2)
Fe–S2	2.265(1)	P2–C12	1.820(2)
Fe–P1	2.177(1)	P2–C13	1.819(2)
Fe–P2	2.218(1)	P2–C14	1.824(2)
Fe–C1	1.731(2)	O–C1	1.161(2)
Fe–C2	2.020(1)	C2–C3	1.455(2)
S1–C4	1.749(1)	C2–H2	0.96(2)
S2–C2	1.831(2)	C3–C4	1.350(2)
S2–C11	1.800(2)	C3–H3	0.92(2)
P1–C15	1.818(2)	C4–C5	1.475(2)
P1–C16	1.826(2)		
S1–Fe–S2	93.56(2)	F2–Fe–C2	155.23(5)
S1–Fe–P1	83.90(2)	C1–Fe–C2	94.55(6)
S1–Fe–P2	92.30(1)	Fe–S1–C4	99.59(5)
S1–Fe–C1	175.09(6)	Fe–S2–C2	57.96(5)
S1–Fe–C2	84.41(4)	Fe–S2–C11	114.50(6)
S2–Fe–P1	151.72(2)	C2–S2–C11	108.34(8)
S2–Fe–P2	105.79(2)	Fe–C1–O	179.2(1)
S2–Fe–C1	89.43(5)	Fe–C2–S2	71.86(5)
S2–Fe–C2	50.18(4)	Fe–C2–C3	115.9(1)
P1–Fe–P2	102.46(2)	Fe–C2–H2	119.2(1)
P1–Fe–C1	91.62(6)	S2–C2–C3	117.9(1)
P1–Fe–C2	101.59(4)	S1–C4–C3	117.4(1)
P2–Fe–C1	90.63(5)	S1–C4–C5	119.2(1)

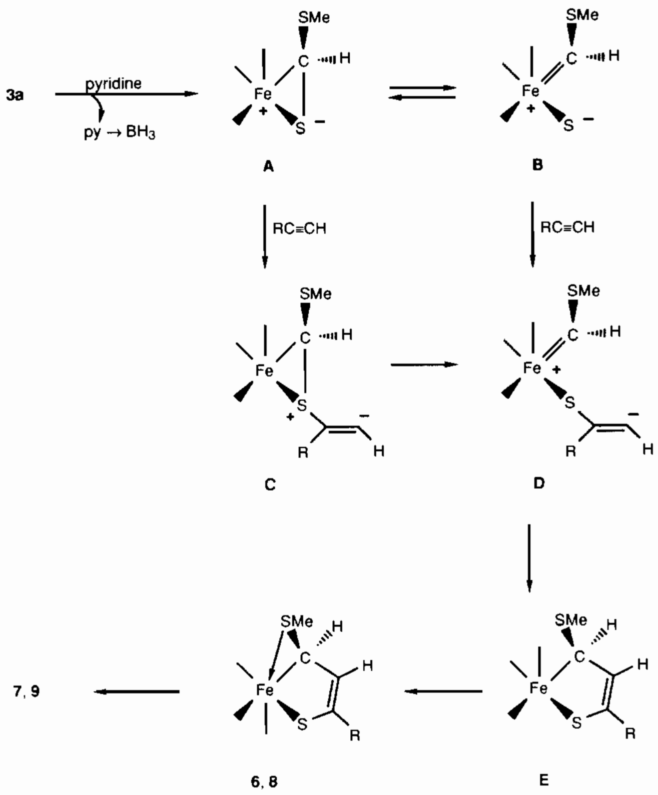
From isopropenylacetylene the reaction leads to complex **10** (50%) which results from the incorporation of the alkyne but has a coordinated CH$_2$=C bond and a free CH=CH bond. Complex **10** is thus expected to result via insertion of the C≡C bond as in **6**, cleavage of the Fe–CH bond to give an intermediate **9** analogous to **7** and simple displacement of the coordinated S=C bond by the CH$_2$=C bond to give the more stable adduct **10**.

Mechanism of the reaction 3 → 6

The insertion of C≡C bond of the alkyne into the coordinated C–S bond of **3a** can be explained as in the Scheme 5 by initial addition of the nucleophilic sulfur atom of intermediate **A** to the C≡C bond, cleavage of the C–S bond giving a carbene type intermediate **D**. The latter can also be obtained via initial cleavage of the C–S bond from intermediate **A** to give **B**, followed by addition of the alkyne. Analogous carbene species have already been postulated [8, 9]. Carbon–carbon bond formation via nucleophilic addition to the carbene carbon is expected to give the 16-electron intermediate (**E**) giving the stable complex **6** or **8** upon coordination of the MeS sulfur.

Supplementary material

Tables of anisotropic thermal parameters and structure factors may be obtained from the authors.



Scheme 5.

Acknowledgement

The authors thank A. Daridor for technical assistance.

References

1 (a) J. Daub, G. Endress, U. Erhartlt, K. H. Jogun, J. Kappler, A. Laumer, R. Pfiz and J. J. Stezowski, *Chem. Ber., 115* (1982) 1787; (b) H. Patin, G. Mignani, A. Benoit, J. Y. Le Marouille and D. Grandjean, *Inorg. Chem., 20* (1981) 4351; (c) D. E. Laycock and H. Alper, *J. Org. Chem., 46* (1981) 289.

2 (a) L. Busetto, V. Zanotti, V. G. Albano, D. Braga and M. Monari, *J. Chem. Soc., Dalton Trans,* (1987) 1133; (b) L. Busetto, M. C. Cassani, V. Zanotti, V. G. Albano and D. Braga, *J. Organomet. Chem., 415* (1991) 395.

3 D. C. Miller and R. J. Angelici, *Organometallics, 10* (1991) 79 and 89.

4 (a) A. E. Skaugset, T. B. Rauchfuss and S. R. Wilson, *Organometallics, 9* (1990) 2875; (b) S. Luo, A. E. Ogilvy, T. B. Rauchfuss, A. L. Rheingold and S. R. Wilson, *Organometallics, 10* (1991) 1002, and refs. therein.

5 J. Chen, L. M. Daniels and R. J. Angelici, *J. Am. Chem. Soc., 113* (1991) 2544, and refs. therein.

6 M. Pasquali, P. Leoni, C. Floriani, A. Chiesi-Villa and G. Guastini, *Inorg. Chem., 22* (1983) 841.

7 C. E. L. Headford and W. R. Roper, *J. Organomet. Chem., 244* (1983) C53.

8 (a) D. Touchard, P. H. Dixneuf, R. D. Adams and B. E. Segmüller, *Organometallics, 3* (1984) 640; (b) D. Touchard, J. L. Fillaut, P. H. Dixneuf, R. D. Adams and B. E. Segmüller, *J. Organomet. Chem., 386* (1990) 95.

9 G. N. Glavee and R. J. Angelici, *J. Am. Chem. Soc., 111* (1989) 3598.

10 R. A. Doyled and R. J. Angelici, *J. Am. Chem. Soc., 112* (1990) 194.

11 H. Fischer, J. Hoffmann, U. Gerbing and A. Tiriliomis, *J. Organomet. Chem., 358* (1988) 229, and refs. therein.

12 N. M. Agh-Atabay, J. L. Davidson, G. Douglas and K. W. Muir, *J. Chem. Soc., Chem. Commun.,* (1989) 549.

13 D. V. Khasnis, L. Toupet and P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.,* (1987) 230.

14 H. Le Bozec, P. H. Dixneuf, A. J. Carty and N. J. Taylor, *Inorg. Chem., 17* (1978) 2568.

15 D. Touchard, H. Le Bozec, P. H. Dixneuf, A. J. Carty and N. J. Taylor, *Inorg. Chem., 20* (1981) 1811.

16 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, UK, 1974.

17 B. A. Frenz, *Enraf-Nonius Structure Determination Package; SDS Users Guide,* Version 1985, College Station, TX 77840, USA, and Enraf-Nonius, Delft, Netherlands, 1985.

18 C. K. Johnson, *ORTEP, Rep. ORNL-3794,* Oak Ridge National Laboratory, TN, USA, 1965.

19 D. Touchard, J. L. Fillaut, D. V. Khasnis, P. H. Dixneuf, G. Mealli, D. Masi and L. Toupet, *Organometallics, 7* (1988) 67.