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Chemistry of η^2-CS_2 Complexes. Mononuclear Iron Compounds Containing Alkoxythiocarbonyl and Chelating $Ph_2PCH{=}C(R)S$ Ligands via Coupling of Coordinated CS_2 and Phosphinoacetylenes: X-ray Structure of $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(\textit{t}\text{-}Bu)S][CS(OMe)]$

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Intramolecular coupling reactions involving the ligands CS_2 and $Ph_2PC{\equiv}CR$ held proximate in the coordination sphere of a mononuclear iron carbonyl complex have been explored. Reaction of $Fe_2(CO)_9$ with the phosphinoacetylene $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$ in CS_2 solution affords *trans*-$Fe(\eta^2\text{-}CS_2)(CO)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$. In MeOH under reflux $Fe(\eta^2\text{-}CS_2)(CO)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ is converted to the complex $Fe(CO)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)[Ph_2PCH{=}CS(t\text{-}Bu)][CS(OMe)]$ which contains novel, chelating $Ph_2PCH{=}CS(t\text{-}Bu)$ and $\eta^2\text{-}CS(OMe)$ ligands. Similarly *trans*-$Fe(\eta^2\text{-}CS_2)(CO)_2(L^1)(L^2)$ (L^1, L^2 = tertiary phosphine or phosphite) in the presence of phosphinoalkyne $Ph_2PC{\equiv}CR$ (R = Ph, *t*-Bu) in methanol are converted to $Fe(CO)(L^1)[Ph_2PCH{=}CS(R)][CS(OMe)]$. Correspondingly $Fe(\eta^2\text{-}CS_2)(CO)_2(PPh_3)(PMe_2Ph)$ in CH_2Cl_2 reacts with EtSH and $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$ to afford $Fe(CO)(PMe_2Ph)[Ph_2PCH{=}C(S)\text{-}t\text{-}Bu][CS(SEt)]$. These compounds were characterized by microanalysis, ^1H, ^{31}P, and ^{13}C NMR spectroscopy, and mass spectroscopy. Single crystals of the title compound $Fe(CO)[P(OMe)_3][Ph_2PCH{=}CS(t\text{-}Bu)][CS(OMe)]$ are triclinic of space group $P\bar{1}$ with $a = 11.115$ (1) Å, $b = 11.347$ (1) Å, $c = 12.882$ (1) Å, $\alpha = 97.80$ (1)°, $\beta = 64.90$ (1)°, $\gamma = 83.97$ (1)°, and $Z = 2$. The structure was solved and refined to $R = 0.042$ and $R_w = 0.051$ on the basis of 2647 independent Syntex $P2_1$ measured reflections (Mo $K\alpha$ radiation). The stereochemistry of the iron atom is pseudo square pyramidal with an axial CO group, the phosphorus, and sulfur atoms of the chelating PS ligand, the phosphite phosphorus atom, and the carbon atom of the $\eta^2\text{-}CS(OMe)$ group forming an approximate square plane. The sulfur atom S(2) of the C(S)OMe group also interacts with the iron atom. Likely mechanisms for these novel reactions are discussed. The synthetic route has potential for the generation of rigid, chelating PS ligands.

Introduction

In η^2-CS_2 complexes of iron, notably $Fe(\eta^2\text{-}CS_2)(CO)_2(L^1)(L^2)$ (L^1, L^2 = tertiary phosphines or phosphites), charge transfer from the donor ligands through the metal atom to the coordinated CS_2 molecule reinforces the nucleophilic character of the uncoordinated sulfur atom.[2] As a direct consequence this sulfur atom can be readily alkylated by alkyl halides[3] or used as a ligating atom in the formation of binuclear or polynuclear complexes with CS_2 bridges.[4] Moreover the η^2-CS_2 moiety has 1,3 dipolar character, as illustrated by the formation of (dithiocarbene)metal complexes via the addition of electrophilic alkynes across the coordinated CS_2 moiety.[5] We were intrigued by the possibility of exploiting these properties to accomplish the intramolecular coupling of an acetylene held proximate to a coordinated CS_2 molecule within the same molecule since such a strategy would have potential not only for the elaboration of CS_2 but also for the generation of new ligands. An attractive method of accomplishing such a goal is to use an acetylene with an appropriate heteroatom substituent capable of coordinating to the metal atom in such a fashion as to place the "free" acetylene adjacent to the η^2-CS_2 ligand. Obvious candidates of choice for such a sequence are the phosphinoacetylenes since these ligands are known to act as strong phosphine σ donors to a variety of metals.[6] Moreover, the uncoordinated triple bonds of P-coordinated phosphinoalkynes are sensitive both to nucleophilic attack[6,7] and to acetylene coupling.[8] Thus we initiated a program of studies to synthesise mixed CS_2/phosphinoalkyne compounds and to examine their chemistry. In this paper we describe the synthesis of compounds *trans*-$Fe(\eta^2\text{-}CS_2)(CO)_2(Ph_2PC{\equiv}CR)_2$ (R = *t*-Bu, Ph), intramolecular coupling reactions leading to compounds containing $\eta^2\text{-}CS(OR')$ and chelating $Ph_2PCH{=}C(R)S$ ligands and chemistry derived therefrom. The novel derivatives $Fe(CO)(L^1)[Ph_2PCH{=}C(R)S][C(OR')S]$ result from coupling of the phosphinoacetylene with CS_2, fragmentation of the latter, and trapping of both CS_2 fragments in the monomer. This reaction is of considerable current interest in view of recent papers describing the cleavage of CS_2 by cobalt[9]

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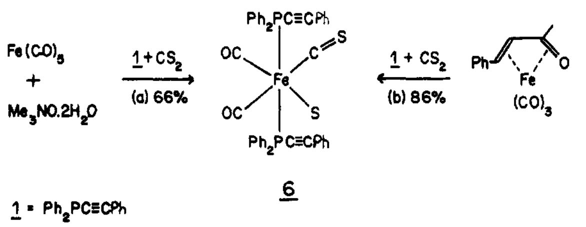
Scheme I



and osmium[10] clusters in which fragments of the CS_2 molecule are trapped by multisite bonding within the cluster framework.

Experimental Section

Synthesis. General Procedures. All reactions were carried out under nitrogen. Phosphinoalkynes were prepared according to described procedures.[11] Infrared spectra were recorded with a Pye-Unicam SP 1100 spectrometer. A Bruker WP-80 spectrometer was used for ^{31}P and ^{13}C NMR spectroscopy. Shifts are reported relative to external 85% H_3PO_4 and Me_4Si, respectively. The mass spectra were obtained at 70 eV with a Varian MAT 311 (Centre de Mêsures Physiques, Rennes). Analyses were determined at the Centre de Microanalyse du CNRS (Villeurbanne).

Derivative Fe(η^2-CS_2)(CO)$_2$(Ph$_2$PC≡CPh)$_2$ (6). Method a. To a stirred solution of 1.12 g (4 mmol) of Ph$_2$PC≡CPh (1; Scheme I) in 10 mL of ethanol were added successively 0.27 mL of Fe(CO)$_5$, 3 mL of CS_2, and then slowly with a syringe a solution of 0.45 g of $Me_3NO{\cdot}2H_2O$ (4 mmol) in 10 mL of ethanol. A red compound, **6**, precipitated at room temperature, was isolated by filtration and washed successively with ether, ethanol, and ether: yield 66% (1 g); mp 168–170 °C; IR (Nujol) ν(C≡C) 2190, ν(C≡O) 2000, 1930 cm^{-1}, ν(C=S) 1150 cm^{-1}. Anal. Calcd for $C_{43}H_{30}FeO_2P_2S_2$: C, 67.89; H, 3.95; S, 8.42; P, 8.16. Found: C, 65.19; H, 4.00; S, 8.15; P, 8.11.

Method b. To 1 g of **1** (3.5 mmol) and 0.5 g (1.75 mmol) of (benzylideneacetone)iron tricarbonyl[12] in a Schlenk tube was added 10 mL of CS_2. The mixture was stirred overnight at room temperature. The carbon disulfide was then evaporated, and the precipitate was washed with ether and ethanol and dried under vacuum. A 1.15-g (86%) sample of a red product, which was identified as **6**, was obtained.

Derivative Fe(η^2-CS_2)(CO)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$ (7). A mixture of 0.36 g (1 mmol) of Fe$_2$(CO)$_9$ and 0.53 g (2 mmol) of **2** in 20 mL of CS_2 was refluxed for 15 min. The excess of CS_2 was evaporated, and 20 mL of pentane was added to the red solid which was then filtered. A 0.38-g (53%) sample of **7** was obtained: mp 122–125 °C; IR (Nujol) ν(C≡C) 2220–2180, ν(CO) 1995, 1940, ν(C=S) 1150 cm^{-1}; ^1H NMR (CDCl$_3$) δ 1.20 (s, *t*-Bu). Anal. Calcd for $C_{39}H_{38}FeO_2P_2S_2$: C, 65.00; H, 5.30; P, 8.61; S, 8.88. Found: C, 64.60; H, 5.79; P, 8.18; S, 8.53.

Derivative Fe[=$\overline{\text{CSC(CO}_2\text{Me)=C(CO}_2\text{Me)S}}$](CO)$_2$(Ph$_2$PC≡C-*t*-Bu)$_2$ (8). The reaction was performed in an ^1H NMR tube. One equivalent (10 mg) of dimethyl acetylenedicarboxylate was added under nitrogen to 50 mg of **7** in 0.6 mL of C_6D_6. The red solution turned immediately to a brown solution of a very air-sensitive complex of the (1,3-dithiol-2-ylidene)iron derivative.[5] The reaction was quantitative as indicated by the following: ^1H NMR δ 3.36 (s, CO$_2$Me), 1.23 (s, *t*-Bu); IR (C_6D_6) ν(C≡C) 2220–2180, ν(C≡O) 1915, 1855, ν(C=O) 1735 cm^{-1}.

Derivative Fe(CO)(Ph$_2$PC≡C-*t*-Bu)[Ph$_2$PCH=C(*t*-Bu)S][η^2-CS(OMe)] (9). A solution of 0.35 g (0.48 mmol) of **7** in 30 mL of methanol was refluxed for 2 h. After removal of the solvent and chromatography on silica gel thick-layer plates (hexane–ether), red crystals of **9** were isolated: yield 77% (0.27 g); mp 145–147 °C; IR (Nujol) 2180, 1925, 1520, 1290 cm^{-1}. ^1H NMR (CDCl$_3$) δ 6.30 (d, $^2J_{PH}$ = 10 Hz, PCH=), 3.80 (s, OMe), 1.50 (s, *t*-Bu), 1.33 (s, *t*-Bu). Anal. Calcd for $C_{39}H_{42}FeO_2P_2S_2$: C, 64.64; H, 5.80; P, 8.56. Found: C, 64.69; H, 6.07; P, 7.91.

Derivatives Fe(CO)(L^1)[Ph$_2$PCH=C(R)S][η^2-CS(OR^1)] (10–12). A 1-equiv sample, of an η^2-CS_2 iron derivative, **3–5**,[2] and 1 equiv of the phosphinoalkyne **1** or **2** were dissolved in methanol or ethanol. The solution was refluxed for 1–2 h. The reaction was followed by thin-layer chromatography. After removal of the excess of alcohol under vacuum, the crude residue was chromatographed on a silica gel thick layer (eluant, hexane–ether).

The red complexes **10** and **11** were isolated and crystallized from hexane–dichloromethane mixtures.

10a (L^1 = P(OMe)$_3$, R = *t*-Bu, R^1 = Me): 0.12 g (17%) obtained from 0.5 g of **3**[2] (1.15 mmol) and 0.3 g of **2** in 12 mL of MeOH; mp 120–121 °C; mass spectrum, *m/e* 582 [M]$^+$, 554 [M – CO]$^+$, 430 [M – CO – P(OMe)$_3$]$^+$; IR (Nujol) 1935, 1510, 1290 cm^{-1}; ^1H NMR (CDCl$_3$) δ 6.20 (dd, $^2J_{P-H}$ = 9.5 Hz, $^4J_{P-H}$ = 2.6 Hz, PCH=), 4.33 (s, OCH$_3$), 3.83 (d, $^3J_{P-H}$ = 11 Hz, P(OMe)$_3$), 1.57 (s, *t*-Bu); ^{31}P NMR (CDCl$_3$) δ 160.4 (d, P(OMe)$_3$), 78.6 (d, Ph$_2$PCH=, $^2J_{PP}$ = 262 Hz). Anal. Calcd for $C_{24}H_{32}FeO_5P_2S_2$: C, 49.48; H, 5.50; S, 10.99. Found: C, 49.12; H, 5.74; S, 10.83.

10b (L^1 = PMe$_2$Ph, R = *t*-Bu, R^1 = Me): 0.4 g (68%) obtained from 0.57 g of **4**[2] (1 mmol) and 0.27 g of **2** in 20 mL of MeOH; mp 124–125 °C; mass spectrum, *m/e* 596 [M]$^+$, [M – CO]$^+$, calcd 568.087, found 568.087, 430 [M – CO – PMe$_2$Ph]$^+$; IR (Nujol) 1910, 1515, 1280 cm^{-1}; ^1H NMR (CDCl$_3$) δ 6.04 (d, $^2J_{P-H}$ = 10 Hz, PCH=), 3.70 (s, CH$_3$), 1.87 (d), 1.73 (d, $^2J_{P-H}$ = 9.5 Hz, PMe$_2$), 1.53 (s, *t*-Bu); ^{31}P NMR (CDCl$_3$) δ 78.9 (d, Ph$_2$PCH=), 26.7 (d, PMe$_2$Ph, $^2J_{P-P}$ = 176 Hz); ^{13}C NMR (CDCl$_3$) δ 298.7 (s, FeCS–), 211.1 (s, CO), 191.6 (s, =C(R)S), 105 (d), 66 (OCH$_3$), 40.3 (CMe$_3$), 31.7 (C(CH$_3$)$_3$). Anal. Calcd for $C_{29}H_{34}FeO_2P_2S_2$: C, 58.39; H, 5.71; S, 10.74; P, 10.40. Found: C, 59.48; H, 6.37; S, 9.58; P, 10.35.

10c (L^1 = PPh$_3$, R = *t*-Bu, R^1 = OMe): 0.39 g (47%) obtained from 0.71 g (1 mmol) of **5**[2,13] and 0.26 g of **2** in 15 mL of MeOH; mp 123–125 °C; IR (Nujol) 1935, 1530, 1290 cm^{-1}; ^1H NMR (CDCl$_3$) δ 7.50 (m, C$_6$H$_5$), 6.05 (d, $^2J_{P-H}$ = 10 Hz, PCH=), 3.57 (s, OCH$_3$), 1.52 (s, *t*-Bu).

11 (L^1 = PPh$_3$, R = Ph, R^1 = Me): 0.33 g (44%) obtained from 0.71 g (1 mmol) of **5**[2,13] and 0.29 g (1 mmol) of **1** in 10 mL of MeOH and 5 mL of CH$_2$Cl$_2$ after reflux for 1.5 h; mp 122–124 °C; IR (Nujol) 1937, 1535, 1295 cm^{-1}; ^1H NMR (CDCl$_3$) δ 7.40 (m, C$_6$H$_5$), 6.40 (d, $^2J_{P-H}$ = 9 Hz, PCH=), 3.50 (s, OMe).

12a [L^1 = P(OMe)$_3$, R = *t*-Bu, R^1 = Et]: 0.06 g (5%) obtained from 0.88 g of **3**[2] (2 mmol) and 0.34 g of **2** in 20 mL of EtOH; IR (Nujol) 1935, 1520, 1300 cm^{-1}; ^1H NMR (CDCl$_3$) δ 5.96 (dd, $^2J_{P-H}$ = 9 Hz and $^4J_{P-H}$ = 3 Hz, PCH=), 4.46 (m, OCH$_2$), 3.72 (d, $^3J_{P-H}$ = 11 Hz, P(OMe)$_3$), 1.48 (s, *t*-Bu), 1.40 (t, $^3J_{HH}$ = 7 Hz, CH$_3$).

12b (L^1 = PMe$_2$Ph, R = *t*-Bu, R^1 = Et): 0.17 g (57%) obtained from 0.28 g (0.5 mmol) of **4**[2] and 0.14 g of **2** in 10 mL of EtOH; mp 153–155 °C; mass spectrum, *m/e* 610 [M]$^+$, [M – CO], calcd 582.102, found 582.103, 444 [M – CO – PMe$_2$Ph]$^+$. IR (Nujol) 1912, 1510, 1290 cm^{-1}; ^1H NMR (CDCl$_3$) δ 6.20 (d, $^2J_{P-H}$ = 10 Hz, PCH=), 4.10 (m, OCH$_2$), 1.90 (d), 1.80 (d, $^2J_{PH}$ = 9.5 Hz, PMe$_2$), 1.57 (s, *t*-Bu), 1.07 (t, $^3J_{HH}$ = 8 Hz, CH$_3$). Anal. Calcd for $C_{30}H_{36}FeO_2P_2S_2$: C, 59.02; H, 5.90; S, 10.49; P, 10.16. Found: C, 59.31; H, 6.35; S, 9.34; P, 10.53.

Derivative Fe(CO)(PMe$_2$Ph)[Ph$_2$PCH=C(*t*-Bu)S][η^2-CS(SEt)] (13). A solution of 0.58 g (1 mmol) of **4**[2], 0.27 g of **2**, and 3 mL of EtSH in 8 mL of dichloromethane was refluxed in a Schlenk tube for 3 h. After removal of the solvents under vacuum, the residue was chromatographed on a silica gel thick-layer plate (eluant, hexane–ether). A red product **13** was crystallized in pentane: yield 13% (80 mg); mp 137–139 °C; mass spectrum, *m/e* 626 [M]$^+$, [M – CO]$^+$, calcd 598.080, found 598.079, 460 [M – CO – PMe$_2$Ph]$^+$, 299 [Ph$_2$PCH=C(*t*-Bu)S]$^+$, 105 [CS(SEt)]; IR (Nujol) 1915, 1515, 1295 cm^{-1}; ^1H NMR (CDCl$_3$) δ 7.60 (m, C$_6$H$_5$), 5.90 (d, $^2J_{PH}$ = 9 Hz, PCH=), 2.80 (q, $^3J_{HH}$ = 7 Hz, SCH$_2$), 1.80 (d, $^2J_{P-H}$ = 8 Hz, PMe$_2$), 1.50 (s, *t*-Bu), 1.00 (t, ^3J = 7 Hz, CCH$_3$).

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X-ray Data Collection. Crystals of $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(t\text{-}Bu)S][CS(OMe)]$ from hexane were irregular prisms. Preliminary Weissenberg and precession photography revealed only Laue symmetry $\bar{1}$, and the crystal system was assumed to be triclinic. Unit cell dimensions and the orientation matrix were determined from the setting angles of 15 reflections widely dispersed in reciprocal space. Crystal data: $a = 11.115$ (1) Å, $b = 11.347$ (1), Å, $c = 12.882$ (1) Å; $\alpha = 97.80$ (1)°, $\beta = 64.90$ (1)°, $\gamma = 83.97$ (1)°; $Z = 2$; d (calcd) = 1.349 g cm^{-3}, d(measd) = 1.34 g cm^{-3}; $V = 1433.5$ Å^3; $F(000) = 608$. The standard reduced cell has the following dimensions: $a = 11.115$ (1) Å, $b = 11.347$ (1) Å, $c = 12.882$ (1) Å; $\alpha = 97.80$ (1)°, $\beta = 115.10$ (1)°, $\gamma = 96.03$ (1)°.

The data crystal, of dimensions 0.20 × 0.22 × 0.28 mm, was set on a glass fiber in a brass pin with epoxy cement and mounted on a eucentric goniometer head for attachment to a Syntex $P2_1$ diffractometer. Intensity data were collected at 22 ± 1 °C by using Mo Kα ($\lambda = 0.71069$ Å) radiation monochromated via a highly oriented graphite crystal. All measurements were made in the θ-2θ stationary counter-moving crystal scan mode with $3.2° \leq 2\theta \geq 45°$. A variable scan rate (2-29.3° min^{-1}) was used with the rate determined by the reflection intensity estimated via a 2θ prescan. The scan width was from 2θ(Mo Kα_1) - 0.8° to 2θ(Mo Kα_2) + 0.8° and background measurements made at the beginning and end of each scan via the stationary counter-stationary crystal method with each background being counted for 25% of the total scan time. Three standard reflections remeasured after every 99 reflections showed no significant variation over the course of data collection. From a total of 3758 independent measurements 2647 intensities had $I \geq 3\sigma(\mathrm{I})$; these latter were used in the solution and refinement of the structure. Corrections were made for Lorentz and polarization effects, but with μ(Mo Kα) = 8.22 cm^{-1} no absorption correction was thought necessary. Apart from autoindexing, cell refinement and control of diffraction measurements when the Data General Nova computer was used, all computing was carried out on an IBM 360-75 system in the University of Waterloo Computing Centre. Programs used have been described previously.[14]

Solution and Refinement. The structure was solved by standard Patterson and Fourier techniques. The choice of space group $P\bar{1}$ was confirmed by the successful refinement of the structure. All least-squares refinements were full matrix, carried out on F, with the function minimized being $w(F_o - Fc)^2$. Atomic scattering factors used were those compiled in the ref 15 with corrections for both real and imaginary components of anomalous dispersion being applied for Fe, P, and S. Hydrogen parameters however were those due to Stewart et al.[16] Refinement of the Fe, two S, and two P atom positions deduced from a Patterson map together with a scale factor gave R ($R = \sum(\|F_o| - |F_c\|)/|F_o|$) of 0.403. Non-hydrogen atoms were then located via successive Fourier maps. It rapidly became clear however that the OMe groups of the tertiary phosphite were disordered over two positions. Fortunately this disorder was relatively simple representing an occupancy ratio of 0.45:0.55 over the two sites. In later refinements this occupancy ratio was utilized. A refinement of positions and isotropic thermal parameters for non-hydrogen atoms gave $R = 0.094$. Conversion to anisotropic coefficients and two further cycles reduced R to 0.057. A difference Fourier map calculated at this stage revealed chemically reasonable positions for phenyl ring hydrogen atoms and the alkenyl hydrogen. No attempt was made to locate and include methyl group hydrogen atoms. In a final cycle of refinement hydrogen atom positions and isotropic thermal parameters were refined. The final R and R_w values ($R_w = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2}$) were 0.042 and 0.051 with the weights given by $w^{-1} = 2.0 - 0.32F + 0.0009F^2$. A final difference map had a background electron density level of 0.4 e Å^{-3} with no peak higher than 0.6 e Å^{-3}. Final positional parameters for heavy atoms are listed in Table I with hydrogen data in supplementary Table S1. Anisotropic thermal parameters are available as supplementary material (Table S2). A listing of observed and calculated structure factors is also available as supplementary material.

Table I. Fractional Atomic Coordinates ($\times 10^4$) for $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(t\text{-}Bu)S][CS(OMe)]$

atom	*x/a*	*y/b*	*z/c*
Fe	1785.9 (7)	2361.9 (6)	1465.6 (6)
S(1)	3383 (1)	2631 (1)	2133 (1)
S(2)	6 (2)	4235 (1)	2195 (1)
P(1)	3048 (1)	3024 (1)	−102 (1)
P(2)	782 (1)	1543 (1)	3054 (1)
O(1)	2538 (4)	17 (3)	33 (3)
O(2)	−505 (4)	2434 (4)	905 (4)
O(3A)*	2567 (8)	2864 (7)	−1019 (6)
O(3B)*	2261 (9)	3360 (8)	−884 (9)
O(4A)*	4619 (8)	2811 (8)	−614 (7)
O(4B)*	3851 (7)	4030 (6)	−90 (6)
O(5A)*	2853 (9)	4550 (8)	49 (8)
O(5B)*	4326 (6)	1990 (6)	−1171 (5)
C(1)	2285 (5)	908 (5)	580 (5)
C(2)	250 (5)	2880 (5)	1380 (5)
C(3)	1898 (5)	1355 (5)	3696 (4)
C(4)	3012 (5)	1860 (4)	3302 (4)
C(5)	4008 (5)	1832 (5)	3847 (5)
C(6)	3587 (8)	1126 (8)	4852 (7)
C(7)	3951 (13)	3119 (8)	4418 (10)
C(8)	5411 (7)	1257 (11)	2912 (7)
C(9)	−1714 (7)	3218 (8)	1047 (8)
C(10)	3113 (8)	3408 (9)	−2118 (6)
C(11)	3123 (7)	5238 (6)	842 (7)
C(12)	5415 (6)	1513 (6)	−921 (7)
C(13)	348 (5)	64 (4)	2766 (4)
C(14)	−423 (6)	−65 (5)	2152 (5)
C(15)	−724 (7)	−1196 (6)	1882 (6)
C(16)	−261 (7)	−2182 (5)	2198 (6)
C(17)	490 (7)	−2056 (5)	2807 (6)
C(18)	795 (6)	−933 (5)	3109 (5)
C(19)	−781 (5)	2399 (4)	4272 (4)
C(20)	−714 (5)	3505 (5)	4846 (5)
C(21)	−1854 (6)	4207 (5)	5802 (5)
C(22)	−3038 (6)	3792 (6)	6163 (5)
C(23)	−3120 (6)	2692 (7)	5603 (6)
C(24)	−1991 (5)	1992 (5)	4655 (5)

Results and Discussion

Synthetic Aspects. Synthesis of $Fe(\eta^2\text{-}CS_2)(CO)_2(Ph_2PC{\equiv}CR)_2$ Complexes. Although a variety of electrophilic alkynes add readily to the η^2-CS_2 ligand in complexes of the type $Fe(\eta^2\text{-}CS_2)(CO)_2L^1L^2$, **3** ($L^1 = L^2 = P(OMe)_3$); **4** ($L^1$, L^2 = PMe_2Ph, PPh_3), and **5** ($L^1 = L^2 = PPh_3$), in benzene solution to afford the carbene iron derivatives, (1,3-dithiol-2-ylidene)iron,[5] the phosphinoalkynes $Ph_2PC{\equiv}CR$ (**1**, R = Ph; **2**, R = *t*-Bu) are inert toward the η^2-CS_2 iron complexes **3**–**5** under the same conditions, probably because of their lack of electrophilicity. To examine the possibility of the intramolecular coupling between a coordinated phosphinoalkyne and a carbon disulfide ligand, we tried to make carbon disulfide iron complexes containing phosphinoalkyne ligands.

The formation of derivatives **6** and **7** could not be achieved by simple displacement of the PPh_3 ligands of compound **5** in an inert solvent as was previously shown for the preparation of compounds **3** or **4**.[2] However, complex **6** could be formed by using two independent routes that we elaborated for the preparation of $Fe(\eta^2\text{-}CS_2)(CO)_2(Ph_3P)_2$ (**5**).[2,13] The red derivative **6** was obtained (a) in 66% yield, directly from $Fe(CO)_5$ in CS_2 with phosphinoalkyne, $Ph_2PC{\equiv}CPh$, **1** and in the presence of Me_3NO, $2H_2O$, a carbonyl displacing reagent and (b) in 86% yield by reaction of (benzylideneacetone)iron tricarbonyl[12] with CS_2 in the presence of the phosphinoalkyne **1** (Scheme I).

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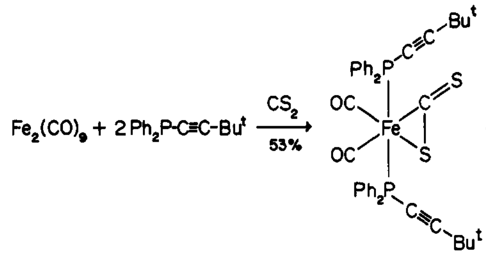
(14) Carty, A. J.; Mott, G. N.; Taylor, N. J.; Yule, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3051.

(15) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

With the phosphinoalkyne, $Ph_2PC{\equiv}C$-*t*-Bu, **2**, the reaction (a) led to the expected complex **7** but in 10% yield and the reaction (b) gave instead of **7** the addition product $Fe(CO)_3(\eta^2\text{-}PhCH{=}CHCOCH_3)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$ which is usually formed with electron-donating phosphorus ligands.[17] However, the derivative **7** was isolated in 53% yield after $Fe_2(CO)_9$ was refluxed with 2 equiv of **2** in carbon disulfide (eq 1) as with triarylphosphines.[18]

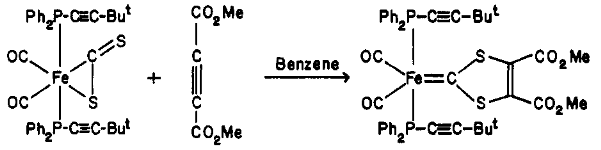


(1)

7

These derivatives **6** and **7** were characterized on the basis of their analyses and infrared spectra.[2] They show absorption bands corresponding to uncoordinated C≡C bonds, two terminal carbonyls and an uncoordinated C=S bond [IR (Nujol): **6**, 2190, 2000–1930, 1150 cm^{-1}; **7**, 2220–2180, 1995–1940, 1150 cm^{-1}]. In addition the *t*-Bu groups in **7** appeared equivalent in the ^1H NMR spectra. These data indicate the absence of intra- or intermolecular interaction between the C≡C bonds of the coordinated phosphinoalkynes and the η^2-CS_2 ligand in these compounds.

However , the η^2-CS_2 ligand is still reactive toward external electrophilic alkynes. Thus dimethyl acetylenedicarboxylate reacts, within a few seconds at room temperature, with the complex **7** in benzene solution to afford the air-sensitive, cycloaddition product **8** (eq 2) which was identified by comparison of its IR and ^1H NMR data with those of (1,3-dithiol-2-ylidene)iron complexes.[5,19]

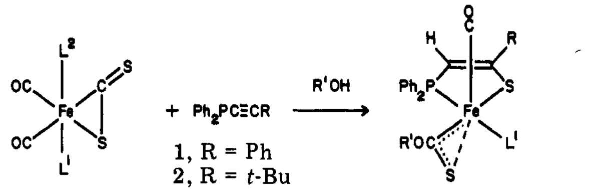


(2)

7 8

Coupling Reactions of Coordinated CS_2 and Phosphinoalkynes. Although we did not observe any interaction between the alkyne bonds and the coordinated CS_2 in complex **6** and **7** either in the solid state (IR) or in benzene or chloroform solution (^1H NMR), compound **7** reacts in methanol and heating of the solution leads to the almost complete transformation of **7**. Thus after 2 h under reflux we isolated by chromatography 77% of a red compound (mp 145–147 °C) which showed in the infrared one uncoordinated C≡C absorption band and one carbonyl absorption band [IR (Nujol) 2180, 1925, 1520, 1290 cm^{-1}] and in the ^1H NMR ($CDCl_3$) two *t*-Bu groups (δ 1.33 and 1.50), one methoxy group (δ 3.80), and one ethylenic proton coupled with a phosphorus nucleus [δ 6.30 ($^3J_{P\text{-}H}$ = 10 Hz)] consistent with formulation **9** (eq 3).

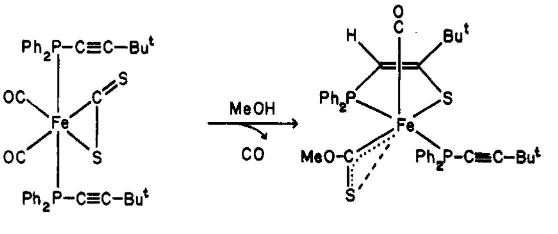
Scheme II



1, R = Ph
2, R = *t*-Bu

3, $L^1 = L^2 = P(OMe)_3$
4, $L^1 = PPh_3$, $L^2 = PMe_2Ph$
5, $L^1 = L^2 = PPh_3$
6, $L^1 = L^2 = Ph_2PC{\equiv}CPh$
7, $L^1 = L^2 = Ph_2P\text{-}C{\equiv}C\text{-}t\text{-}Bu$

9
10a, $L^1 = P(OMe)_3$, R = Bu, OR^1 = OMe (17%)
10b, $L^1 = PMe_2Ph$, (68%)
10c, $L^1 = PPh_3$, (47%)
11, $L^1 = PPh_3$, R = Ph, (44%)
12a, $L^1 = P(OMe)_3$, R = *t*-Bu, OR^1 = OEt (5%)
12b, $L^1 = PMe_2Ph$, (57%)



(3)

7 9

To examine the generality of the intramolecular coupling reaction, we tried to prepare other η^2-CS_2 iron complexes containing one phosphinoalkyne group, without any success. Thus, whereas the direct formation of **6** and **7** is facile, the substitution of one PPh_3 ligand of complexes **4** or **5**, which proceeds readily in an inert solvent such as benzene or dichloromethane with some phosphines[2] is not a useful route to mixed phosphine/phosphinoalkyne complexes. In addition, the reaction of **7** with 1 equiv of PMe_2Ph or $P(OMe)_3$ led to the formation of 50% of $Fe(\eta^2\text{-}CS_2)(CO)_2(PMe_2Ph)_2$ or $Fe(\eta^2\text{-}CS_2)(CO)_2[P(OMe)_3]_2$.[2]

However, when equimolecular amounts of the phosphinoalkyne **2** and of the η^2-CS_2 iron complex **3**, **4**, or **5** were refluxed in methanol, thick-layer chromatography of the reaction products allowed the isolation of red products **10a** (17%), **10b** (68%), and **10c** (47%), respectively (Scheme II). A similar product **11** was obtained in 44% yield by the reaction of **5** with 1 equivalent of the phosphinoalkyne, $Ph_2PC{\equiv}CPh$, **1** in refluxing methanol. In addition to the formation of **10c** and **11** an unidentified yellow product was formed.

^1H NMR spectra indicated the loss of one phosphorus ligand L^2 of precursors **3–5**, the retention of the ligand L^1, incorporation of a methoxy group and the presence of Ph_2P and R (*t*-Bu or Ph) groups arising from the phosphinoalkyne, $Ph_2PC{\equiv}CR$, **1** or **2**. In addition a doublet corresponding to an ethylenic proton coupled with one phosphorus nucleus was observed (see Experimental Section).

Infrared spectra showed the presence of one carbonyl group, the absence of the uncoordinated C≡C bond of the phosphinoalkyne and an absorption band at 1510–1530 cm^{-1} corresponding to an olefinic C=C bond absorption. In addition a strong absorption close to 1290 cm^{-1} may be due to a η^2-CS(OMe) group (vide infra) [IR (Nujol): **10a**, 1935, 1510, 1290 cm^{-1}; **10b**, 1910, 1515, 1280 cm^{-1}; **10c**, 1935, 1530, 1290 cm^{-1}; **11**, 1937, 1535, 1295 cm^{-1}].

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[17] Vessieres, A.; Touchard, D.; Dixneuf, P. *J. Organomet. Chem.* **1976**, *118*, 93.

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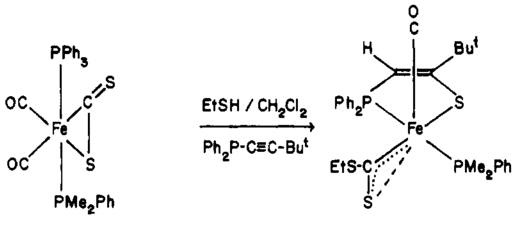
[19] Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486.

[20] Carty, A. J.; Hartstock, F.; Taylor, N. J.; Le Bozec, H.; Robert, P.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1980**, 361.

The mass spectra of the volatile complexes **10a** and **10b** showed molecular ions and fragments corresponding to the successive loss of one carbonyl and the phosphorus group $P(OMe)_3$ and PMe_3Ph, respectively. The mass of the $[M - CO]^+$ ion of complex **10b** was accurately determined (*m/e* 568.087, calcd 568.087). These data for derivatives **9–11** are entirely consistent with the structure established for **10a** by single-crystal X-ray diffraction.

The coupling reaction of a phosphinoalkyne and carbon disulfide, in the coordination sphere of only one metal center and in the presence of methanol, therefore takes place with the cleavage of the η^2-CS_2 ligand to afford, in one step, two sulfurated ligands, the chelating 1-phosphino-2-sulfidoalkene, and the η^2-alkoxythiocarbonyl group. The coupling reaction was extended to other solvents. Thus complexes **3** and **4** with 1 equiv of **2** in refluxing ethanol led to the red derivatives **12a** and **12b** which were isolated in 5% and 57% yield respectively [IR (Nujol) for **12a**, 1935, 1520, 1300 cm^{-1}, and for **12b**, 1912, 1510, 1290 cm^{-1}; mass spectrum, **12b** $[M - CO]^+$ *m/e* 582.103, calcd 582.102] (Scheme II). However no reaction was observed on heating complexes **3** and **4** with **2** in *tert*-butyl alcohol.

An analogous coupling reaction was observed in the presence of ethanethiol instead of an alcohol, but in this case the thiol was not used as the sole solvent. When complex **4** was heated with 1 equiv of **2** in a dichloromethane–ethanethiol mixture, the red complex **13** was formed and isolated in 13% yield [IR (Nujol) 1915, 1515, 1295 cm^{-1}; *m/e* $[M - CO]^+$ 598.080, calcd 598.079].



(4)

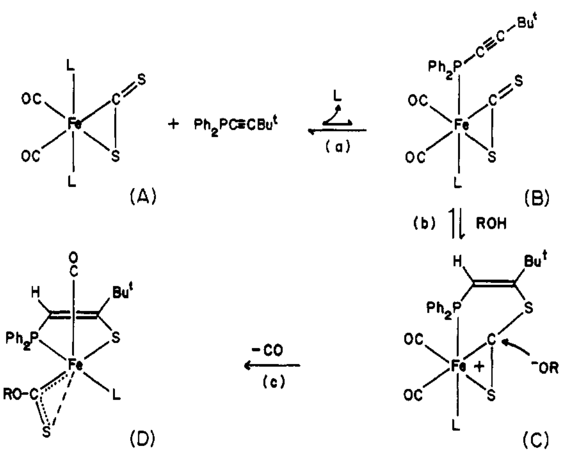
3 13

Spectroscopic Characteristics. Among the spectroscopic data we may point out that (i) the nature of the remaining ligand L^1 strongly influences the carbonyl absorption frequency which is lower for the electron-donating group $L^1 = PMe_2Ph$ (**10b**, **12b**, **13**) than for $L^1 = P(OMe)_3$ (**10a**, **12a**) or $L^1 = PPh_3$ (**10c**, **11**), (ii) the chirality of the complexes is indicated by the ^1H NMR spectra of the PMe_2Ph ligand in **10b**, **12b**, and **13** which showed two diastereotopic methyl groups, (iii) the P–P coupling constant is large and consistent with the mutual trans arrangement of the phosphorus nuclei. The $^2J_{PP}$ value is higher with $P(OMe)_3$ in **10a** (262 Hz) than with PMe_2Ph in **10b** (176 Hz), as is observed for $Fe(CS_2)(CO)_2(PR^1{}_3)(PR^2{}_3)$ complexes and increases with the electronegativity of the substituents bonded to phosphorus, and (iv) the ^{13}C NMR spectrum of **10b** in $CDCl_3$ at 30 °C showed one singlet for the carbon bonded to iron in the Fe[CS(OMe)] group, but at a very low field (δ 298.7); this observation is consistent with a carbon iron bond similar to that in (carbene)iron complexes.

Discussion of the Mechanism of Formation. The coupling of a phosphinoacetylene with CS_2 in the presence of alcohol, as shown in Scheme III, can be visualized as proceeding in three steps.

In the first step (a) activation of the phosphinoacetylene accompanies coordination.[6,7] In support of this, the reaction proceeds smoothly and in high yield (77% for **9**) when the phosphinoalkyne is already coordinated to iron as in **7**. Moreover starting with **4** the more labile ligand PPh_3 is always displaced (**10b**, **12b**, **13**) and in **3** which has $P(OMe)_3$ ligands and the strongest Fe–P bonds, the yields of chelate complex are lowest (**10a**, **12a**). Unfortunately attempts to isolate intermediate (B) from **4** or **5** with ligand **2** in toluene, dichloromethane, or acetone were unsuccessful although low-temperature ^{31}P NMR spectra of **5** with **2** in CD_2Cl_2 at −51 °C provided unequivocal evidence for the mixed complex $Fe(\eta^2\text{-}CS_2)(CO)_2(PPh_3)(PPh_2C{\equiv}C\text{-}t\text{-}Bu)$ (AB quartet, δ 60.0 (PPh_3), 35.6 ($Ph_2PC{\equiv}C$-*t*-Bu), $J_{P-P'} = 165$ Hz).

Scheme III



Step b consists of a nucleophilic addition of the uncoordinated sulfur atom at the β-alkyne carbon of the coordinated phosphinoalkyne and in the protonation of the α-alkyne carbon by the alcohol. This reaction has a close analogy in the addition of secondary phosphines to phosphinoalkynes coordinated to platinum[6] and in the addition of the nucleophilic, uncoordinated sulfur atom of the η^2-CS_2 iron complexes to an activated double bond in acid media.[21] This step is inhibited by stronger acids than alcohols. No reaction was observed with **5** and **2** in an acetic acid–methanol mixture or with **4** and **2** in a HBF_4–MeOH mixture. In the latter case a salt was isolated which did not include the $Ph_2PC{\equiv}C$-*t*-Bu fragment but corresponded to the protonation of the uncoordinated sulfur atom of **4** (IR (Nujol) ν(CO) 2045, 1965 cm^{-1}).

Step c corresponds to nucleophilic attack of the alkoxide anion on the salt **C**. With cleavage of the alkylated CS_2 this step is expected to be irreversible driving the successive equilibria a and b toward the formation of complexes of type D. The reaction appears to be influenced by the nature of the alcohol, formation of D being disfavored in the sequence MeOH > EtOH > *t*-BuOH as the size of the conjugate anion increases.

Description and Discussion of the Structure of 10a. Bond lengths and angles are listed in Tables II and III, and selected planes pertinent to the discussion are shown in Table S3. The crystal structure consists of two well separated monomer units related by a crystallographic inversion centre in the unit cell. An ORTEP II plot of the structure is illustrated (Figure 1). The molecule is one of a very small number of iron carbonyl derivatives having a square-based pyramidal rather than trigonal-bipyramidal structure. Within the coordination sphere of iron the basal positions are occupied by the phosphorus and sulfur atoms of a synthesized (de novo) chelating 1-(diphenylphosphino)-2-sulfido-3,3-dimethylbut-2-ene ligand, by a

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[21] Plusquellec, D.; Dixneuf, P. H., unpublished results.

Table II. Bond Lengths (Å) for $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(t\text{-}Bu)S][CS(OMe)]$

Fe–S(1)	2.307 (2)	O(4A)–C(11)	1.36 (1)
Fe–S(2)	2.512 (2)	O(4B)–C(11)	1.57 (1)
Fe–P(1)	2.200 (2)	O(5A)–C(12)	1.560 (9)
Fe–P(2)	2.256 (1)	O(5B)–C(12)	1.45 (1)
Fe–C(1)	1.758 (6)	C(3)–C(4)	1.346 (8)
Fe–C(2)	1.800 (6)	C(4)–C(5)	1.542 (9)
S(1)–C(4)	1.764 (5)	C(5)–C(6)	1.54 (1)
S(2)–C(2)	1.665 (6)	C(5)–C(7)	1.53 (1)
P(1)–O(3A)	1.487 (8)	C(5)–C(8)	1.51 (1)
P(1)–O(3B)	1.65 (1)	C(13)–C(14)	1.397 (9)
P(1)–O(4A)	1.560 (9)	C(14)–C(15)	1.394 (9)
P(1)–O(4B)	1.524 (8)	C(15)–C(16)	1.36 (1)
P(1)–O(5A)	1.697 (9)	C(16)–C(17)	1.37 (1)
P(1)–O(5B)	1.686 (7)	C(17)–C(18)	1.399 (9)
P(2)–C(3)	1.770 (6)	C(18)–C(13)	1.388 (8)
P(2)–C(13)	1.828 (5)	C(19)–C(20)	1.394 (8)
P(2)–C(19)	1.828 (5)	C(20)–C(21)	1.398 (8)
O(1)–C(1)	1.085 (7)	C(21)–C(22)	1.36 (1)
O(2)–C(2)	1.332 (8)	C(22)–C(23)	1.39 (1)
O(2)–C(9)	1.46 (1)	C(23)–C(24)	1.387 (9)
O(3A)–C(10)	1.53 (1)	C(24)–C(19)	1.377 (8)
O(3B)–C(10)	1.48 (1)		

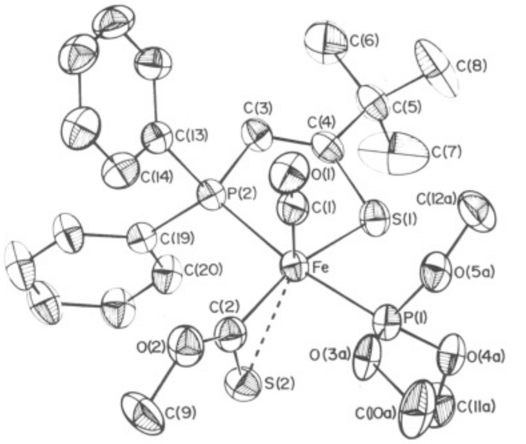

Figure 1. A perspective view of the molecular structure of $Fe(CO)[P(OMe)_3][Ph_2PCH{=}C(t\text{-}Bu)S][CS(OMe)]$. The dashed line represents a weak bonding interaction between Fe and S(2).

trimethyl phosphite ligand trans to phosphorus, and a novel methoxythiocarbonyl group trans to sulfur. A carbonyl group is situated at the remaining apical site of the pyramid. A least-squares plane through the basal atoms shows that the metal lies only 0.165 Å below the mean plane. There are however significant angular distortions within the base of the pyramid: in particular the angle S(1)–Fe–C(2) = 151.9 (1)° deviates considerably from the ideal value of 180° with C(2) tipped down from the basal plane probably as a result (vide infra) of the Fe–S(2) bonding interaction. Figure 1 shows that the net effect of these deviations from idealized geometry is a distortion toward a trigonal bipyramid with P(1) and P(2) axial and C(1), S(1), and C(2) equatorial. The $FePC_2S$ chelate ring is planar (the maximum deviation is +0.088 Å for P(2)) (Table S3) as might be expected for a rigid olefinic PS ligand. The C(3)–C(4) bond length (1.346 (8) Å) is entirely typical of a $C(sp^2)$–$C(sp^2)$[22] distance, and the C(4)–S(1) length (1.764 (5) Å) compares very favorably with the standard $C(sp^2)$–S single-bond length.[22] There are significant differences between the Fe–P bond lengths, with the metal–phosphite bond (Fe–P(1) = 2.200 (2) Å being 0.05 Å shorter than the metal–phosphine (Fe–P(2) = 2.256 (1) Å) bond. Several possible explanations can be advanced to account for this observation: (a) in competition with the trans phosphine for Fe dπ electrons, the $P(OMe)_3$, being a stronger π acceptor, forms a shorter Fe–P bond with greater dπ–dπ character: (b) $P(OMe)_3$, with a smaller ligand cone angle,[23] can approach closer to the iron atom without suffering steric repulsion from the remaining ligands; (c) the presence of electronegative substituents on phosphorus directs greater "s" character into the phosphorus lone-pair orbital (isovalent hybridization) and hence into the M–P bond, causing M–P foreshortening.[24] Although explanation (a) has been used to rationalize the difference (Δ = 0.113 Å) in Cr–P bond lengths in $Cr(CO)_5L$ [L = PPh_3, $P(OPh)_3$],[25] there is now a substantial body of information suggesting that in comparable stereochemical situations M–P(phosphite) bonds are consistently shorter than their M–P(phosphine) counterparts even in compounds where the metal is present in a normal (as opposed to low) oxidation state[26] where dπ–dπ bonding is less likely to be of significance. In the present case the Fe–P(1) bond length is short and comparable with the Fe–P distances (average 2.190 (4) Å) in the five-coordinate complex *trans*-$Fe(CO)_3[P(OCH_2)_3P]_2$[27] containing a constrained nonbulky phosphite. We thus believe that while factor (c) is largely responsible for the shorter Fe–phosphite distance, smaller contributions to bond shortening from (a) and (b) may be present.

It is notable that the Fe–S(1) bond (2.301 (2) Å) is long in comparison with the Fe–P distances particularly when considering that the chelating ligand is formally anionic and that the covalent radius of S (1.04 Å) is *smaller* than that of P (1.10 Å).[28] For comparison the Fe–S bond lengths in the dithiolate complex $Fe[S_2C(COMe)C(C_6H_4NO_2)](CO)[P(OMe)_3]_2$ average 2.175 Å.[29] A major factor contributing to the lengthening of the Fe–S(1) bond may be a high trans bond-lengthening influence of the carbon atom C(2) of the methoxythiocarbonyl group. A high trans influence for such a ligand can be anticipated from the known positions of R, C(O)R, and carbenes in the trans influence series.[30]

The nature of the interaction between the novel methoxythiocarbonyl group and the metal atom is of interest not only because this ligand per se has not previously been synthesized but also because it is clear from the X-ray analysis that the CS(OMe) group is η^2 coordinated to the metal. This is substantiated by the acuteness of the angle Fe–C(2)–S(2) (92.9(0)°) as well as the Fe–S(2) distance (2.512 (2) Å) which, while longer than Fe–S(1) (2.301 (2) Å), is only ~0.22-Å outside the sum of covalent radii for Fe (≃1.25 Å) and sulfur (≃1.04 Å).[28] Additional confirmation of an η^2 interaction with the metal arises from the

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(26) Notable examples of this are as follows: $Pd(PPh_3)_2(NCS)_2$ vs. $Pd(SCN)_2[P(OPh)_3]_2$ (Δ(Pd–P) = 0.028 Å) (Carty, A. J.; Taylor, N. J.; Wong, Y. S.; Chieh, P. C. *J. Chem. Soc., Dalton Trans.* **1976**, 572); $Au(PPh_3)Cl$ vs. $Au[P(OPh)_3]Cl$ (Δ(Au–P) = 0.033 Å) (Hitchcock, P. B.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1457; $Rh_2(OAc)_4(PPh_3)_2$ vs. $Rh_2(OAc)_4[P(OPh)_3]_2$ (Δ(Rh–P) = 0.067 Å) (Christoph, G. G.; Halpern, J.; Khare, G. P.; Koh, Y. B.; Romanowski, C. *Inorg. Chem.* **1981**, *20*, 3029.

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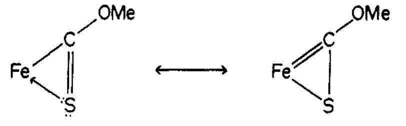
Table III. Bond Angles (Deg) for Fe(CO)[P(OMe)$_3$][Ph$_2$PCH=C(*t*-Bu)S][CS(OMe)]

S(1)-Fe-S(2)	110.4 (0)	Fe-P(1)-O(4B)*	123.9 (2)	S(1)-C(4)-C(5)	116.2 (2)
S(1)-Fe-P(1)	88.3 (0)	Fe-P(1)-O(5B)*	115.8 (2)	C(3)-C(4)-C(5)	123.0 (3)
S(1)-Fe-P(2)	85.1 (0)	O(3B)-P(1)-O(4B)*	105.3 (4)	C(4)-C(5)-C(6)	111.5 (3)
S(1)-Fe-C(1)	107.3 (1)	O(3B)-P(1)-O(5B)*	96.7 (4)	C(4)-C(5)-C(7)	108.9 (4)
S(1)-Fe-C(2)	151.9 (1)	O(4B)-P(1)-O(5B)*	97.4 (3)	C(4)-C(5)-C(8)	109.4 (4)
S(2)-Fe-P(1)	91.8 (0)	Fe-P(2)-C(3)	108.4 (1)	C(6)-C(5)-C(7)	105.0 (5)
S(2)-Fe-P(2)	95.4 (0)	Fe-P(2)-C(13)	115.3 (1)	C(6)-C(5)-C(8)	109.7 (5)
S(2)-Fe-C(1)	142.2 (1)	Fe-P(2)-C(19)	118.7 (1)	C(7)-C(5)-C(8)	112.2 (5)
S(2)-Fe-C(2)	41.4 (1)	C(3)-P(2)-C(13)	106.9 (2)	P(2)-C(13)-C(14)	118.5 (2)
P(1)-Fe-P(2)	171.5 (0)	C(3)-P(2)-C(19)	103.3 (2)	P(2)-C(13)-C(18)	121.9 (2)
P(1)-Fe-C(1)	87.7 (1)	C(13)-P(2)-C(19)	103.1 (2)	C(18)-C(13)-C(14)	119.5 (3)
P(1)-Fe-C(2)	93.0 (1)	Fe-C(1)-O(1)	176.7 (2)	C(13)-C(14)-C(15)	119.5 (3)
P(2)-Fe-C(1)	89.2 (1)	Fe-C(2)-S(2)	92.9 (0)	C(14)-C(15)-C(16)	121.2 (4)
P(2)-Fe-C(2)	95.3 (1)	Fe-C(2)-O(2)	137.4 (1)	C(15)-C(16)-C(17)	119.4 (4)
C(1)-Fe-C(2)	100.9 (2)	S(2)-C(2)-O(2)	129.8 (1)	C(16)-C(17)-C(18)	121.2 (3)
Fe-S(1)-C(4)	106.3 (1)	C(2)-O(2)-C(9)	118.5 (4)	C(17)-C(18)-C(13)	119.1 (3)
Fe-S(2)-C(2)	45.7 (1)	P(1)-O(3A)-C(10)*	123.9 (3)	P(2)-C(19)-C(20)	117.3 (2)
Fe-P(1)-O(3A)*	112.5 (3)	P(1)-O(4A)-C(11)*	119.5 (2)	P(2)-C(19)-C(24)	123.3 (2)
Fe-P(1)-O(4A)*	121.9 (3)	P(1)-O(5A)-C(12)*	121.2 (3)	C(24)-C(19)-C(20)	119.4 (3)
Fe-P(1)-O(5A)*	115.3 (3)	P(1)-O(3B)-C(10)*	117.0 (3)	C(19)-C(20)-C(21)	121.1 (3)
O(3A)-P(1)-O(4A)*	113.2 (4)	P(1)-O(4B)-C(11)*	118.8 (2)	C(20)-C(21)-C(22)	118.6 (3)
O(3A)-P(1)-O(5A)*	94.0 (4)	P(1)-O(5B)-C(12)*	117.1 (3)	C(21)-C(22)-C(23)	120.9 (4)
O(4A)-P(1)-O(5A)*	95.2 (4)	P(2)-C(3)-C(4)	118.3 (2)	C(22)-C(23)-C(24)	120.6 (3)
Fe-P(1)-O(3B)*	113.4 (3)	S(1)-C(4)-C(3)	120.7 (2)	C(23)-C(24)-C(19)	119.3 (3)

C(2)–S(2) bond length (1.665 (1) Å) which compares very favorably with the C(3)–S(1) distance (1.676 (1) Å) in the η^2-CS$_2$ complex Fe(η^2-CS$_2$)(CO)$_2$(PMe$_3$)(PPh$_3$).[2] Although there appears to be no precedent for an η^2-C(=S)OMe group, a related ligand η^2-C(=S)NMe$_2$ has been recently found in the complex Fe(CO)$_2$(CSNMe$_2$)(S$_2$CNMe$_2$).[31] The structural paramaters for this ligand bear an overall similarity to those for η^2-C(=S)OMe in Fe(CO)[P(OMe)$_3$][Ph$_2$PCH=C-*t*-BuS][CS(OMe)]. Finally we note that there is a surprisingly small difference between the Fe–C(1) (CO) (1.758 (6) Å) and the Fe–C(2) [CS(OMe)] (1.800 (6) Å) bond lengths suggesting a considerable π component to Fe–C(2) bonding. This result implies that there is a substantial contribution to the ground state of the η^2-CS(OMe) ligand from the carbene-like canonical form B as well as the expected form A.



A B

Conclusions

Intramolecular coupling between phosphinoalkyne and CS$_2$ ligands described herein is of interest for several reasons: (i) it provides a new example of activation of an R$_2$PC≡CR′ ligand via phosphorus coordination. This principle has potential synthetic implications: (ii) trapping of *both* fragments from CS$_2$ cleavage in a mononuclear complex is demonstrated for the first time; (iii) activation and elaboration of coordinated CS$_2$ via successive, two-site, additions, namely, alkylation at uncoordinated sulfur followed by nucleophilic addition at carbon, is illustrated.

In addition the resulting sulfur-containing iron complexes **9**–**13** which can be obtained in two or three steps from commercial Fe(CO)$_5$ may have an interesting and useful chemistry. We are currently exploring the reactions of the novel η^2-alkoxythiocarbonyl ligand and the use of complexes such as **9** for the generation of otherwise inaccessible rigid, chelating anionic phosphorus–sulfur ligands.

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Registry No. **1**, 7608-17-5; **2**, 33730-51-7; **3**, 64424-66-4; **4**, 64424-60-8; **5**, 64424-68-6; **6**, 82247-25-4; **7**, 82247-26-5; **8**, 82247-27-6; **9**, 82264-87-7; **10a**, 82247-28-7; **10b**, 82264-88-8; **10c**, 82264-89-9; **11**, 82247-29-8; **12a**, 82247-30-1; **12b**, 82247-31-2; **13**, 82247-32-3; tricarbonyl(*O*,2,3,4-η-4-phenyl-3-buten-2-one)iron, 38333-35-6; dimethyl 2-butynedioate, 762-42-5; CS$_2$, 75-15-0.

Supplementary Material Available: Table S1, hydrogen atom coordinates, isotropic temperature factors, and carbon–hydrogen bond lengths, Table S2, anisotropic thermal parameters, Table S3, selected planes, and a listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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[31] Dean, W. K.; Vanderveer, D. G. *J. Organomet. Chem.* **1978**, *144*, 65.