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Use of Organometallic Ligands in the Synthesis of CS_2-Bridged Heterodinuclear Complexes. X-ray Structure of $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$

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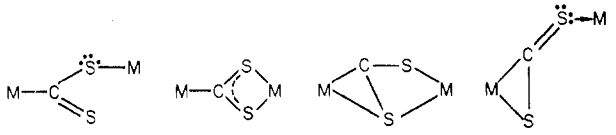
Heterodinuclear complexes $L_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$ (L = P $(OMe)_3$, PMe_2Ph, PMe_3) and $(Me_3P)_2(CO)_2FeCS_2Mo(CO)_5$ containing carbon disulfide as a bridging group have been synthesized from the corresponding (η^2-CS_2) iron derivatives. The complexes are fluxional at room temperature whereas the $FeCS_2$ precursors are rigid, but the variable-temperature ^{13}C NMR is consistent with a π-type bond between the CS_2 and the iron atom and a sulfur–manganese σ bond. The infrared spectra show that the $L_2(CO)_2FeCS_2$ ligands behave as strong electron-donating groups. The structure of $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$ has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, of space group $P2_1/c$ with $a = 10.411$ (1) Å, $b = 9.762$ (2) Å, $c = 28.194$ (5) Å, and $\beta = 93.090$ (10)°. Full-matrix least-squares methods refined the structure to $R = 0.053$ from 2685 nonzero independent reflections. The $FeCS_2Mn$ moiety is nearly planar with the CS_2 bridge η^2 coordinated to iron, through one C=S bond, and σ bonded to the manganese with the second sulfur atom only, with the Mn—S(2) bond length of 2.260 (2) Å and the C(3)—S(2)—Mn angle of 119.6 (2)°. The coordination of the manganese to the sulfur atom S(2) does not modify significantly the geometry around the iron atom but lengthens the C(3)—S(2) bond and shortens the C(3)—S(1) bond (1.658 (6) Å) and especially the Fe—C(3) bond (1.939 (6) Å).

Introduction

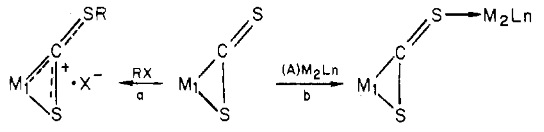
A few complexes containing the carbon disulfide group as a bridge between two identical metal atoms have been isolated such as $K_6[(NC)_5Co(CS_2)Co(CN)_5]$.[1,2] The complex $C_5H_5(CO)_2FeCS_2Fe(CO)_2C_5H_5$[3] contains a bridging CS_2 group of type A whereas recent X-ray structure determinations indicated an arrangement of type B for $[Cl(Ph_3P)_2PtCS_2Pt(PPh_3)_2]BF_4$[4] and of type C for (triphos)$CoCS_2Co$(triphos).[5]



A B C D

Recently Herberhold et al. proposed a new type of CS_2 bridge in $CS_2[Mn(CO)_2C_5H_5]_2$[6,7] and in $CS_2[Cr(CO)_2(arene)]_2$[8] for which the variable-temperature ^1H NMR spectra gave evidence for an intramolecular rearrangement resulting from the exchange of the sites of both metal atoms on the CS_2 group.[6]

The isolation of derivatives of the type $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ (**1**),[9] containing a stable iron–carbon disulfide bond, and evidence of the nucleophilicity of the CS_2 ligand, given by its reaction with electrophilic alkynes[10] and the general nucleophilic substitution of alkyl halides by the uncoordinated sulfur atom as shown in reaction a of eq 1,[11] led us to attempt the substitution of weakly bonded ligands by the uncoordinated sulfur atom of complexes I as illustrated in step b, in order to produce heterodinuclear derivatives of the type $L_2(CO)_2FeCS_2MLn$ (II) containing a bridging carbon disulfide group.



I II (1)

In parallel with our preliminary work in this field[12] other heterodinuclear derivatives having $CoCS_2Mn$[13] and $CoCS_2Cr$[13,14] moieties of type D or $FeCS_2Pt$ and $PtCS_2Pd$ moieties of type B[15] have recently been reported.

In this paper we report the general route for the synthesis of heterodinuclear complexes containing the $FeCS_2M$ unit and the X-ray structure of one of these, $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$. This structure allows the elucidation of the nature of the bonding of the CS_2 bridge with the metal atoms which corresponds to form D and can be compared directly to the reported structure of $(Me_3P)(Ph_3P)(CO)_2FeCS_2$ (**1d**)[9] to show how the coordination of the manganese to one sulfur atom modifies the ligand $L_2(CO)_2FeCS_2$.

Experimental Section

General Methods. The IR spectra were recorded on a Pye-Unicam SP 1100 spectrophotometer (accuracy ±1 cm^{-1}). The ^1H NMR spectra were obtained on a Varian EM 360 spectrometer (C_6D_6 solutions with Me_4Si internal standard unless otherwise noted). ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WH 90 spectrometer (for the ^{13}C NMR, Me_4Si is the internal standard; ^{31}P shifts are downfield (+) from external H_3PO_4). Mass spectra were measured at 70 eV by using a Varian MAT 311 double-focusing spectrometer (Centre de Mesures Physiques, Rennes, France). Microanalyses were determined by CNRS Microanalyses (Villeurbanne, France). All reactions and manipulations were carried out routinely under nitrogen. $L_2(CO)_2Fe(\eta^2\text{-}CS_2)$ complexes (**1**) were prepared as indicated in ref 9.

Synthesis. $L_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$ (2a (L = P(OMe)$_3$), 2b (L = PMe$_2$Ph), 2c (L = PMe$_3$)). To a solution of Mn(THF)(C-

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Table I. Infrared Data[a,b]

		$L_2(CO)_2FeCS_2MLn$		$L_2(CO)_2FeCS_2$ (1)[c]		
		$\nu_{C\equiv O}$, cm^{-1}	$\nu_{C=S}$, cm^{-1}		$\nu_{C\equiv O}$, cm^{-1}	$\nu_{C=S}$, cm^{-1}
$P(OMe)_3$	**2a**	*2019*, *1951*, 1910, 1860	1162	**1a**	*2020–1950*	1157
PMe_2Ph	**2b**	*1984*, *1932*, 1914, 1853	1159	**1b**	*1987–1928*	1137
PMe_3	**2c**	*1996*, *1918*, 1903, 1850	1143	**1c**	*1985–1924*	1128
PMe_3	**3c**	*1987*, *1928*, 2082, 2023, 1945, 1908, 1873	1132–1118			

[a] The frequencies in italics correspond to the carbonyl bonded to iron. [b] Suspension in Nujol. [c] Data from ref 9.

$O)_2C_5H_5$,[16] prepared by irradiation of 480 mg of $Mn(CO)_3C_5H_5$ in 80 mL of freshly distilled THF, was added complex **1a**, **1b**, or **1c** in 20 mL of THF under nitrogen. The deep red solution was stirred at room temperature for 3 h, the solvent was then removed under reduced pressure, and the recovered $Mn(CO)_3C_5H_5$ and derivative **1** were separated from complex **2** by silica gel column chromatography under an inert atmosphere using toluene as eluant. The red complexes **2a**, **2b**, and **2c** were crystallized from a hexane–ether mixture.

2a: yield 43% (0.60 g from 1 g of **1a**); mp 105–106 °C; mass spectrum, *m/e* 612 [M^+] (calcd 612), 584 [$(M - CO)^+$], 556 [$(M - 2CO)^+$], 528 [$(M - 3CO)^+$], 500 [$(M - 4CO)^+$], 404 [$[Fe(CS)(CO)_2(P(OMe)_3)_2]^+$], 348 [$[Fe(CS)(P(OMe)_3)_2]^+$], 304 [$[Fe(P(OMe)_3)_2]^+$]; ^1H NMR (C_6D_6) δ 3.33 (t, $^3J_{P-H}$ = 11.0 Hz, CH_3), 4.58 (C_5H_5). ^{31}P NMR (C_6D_6) δ 91.1. Infrared data are in Table I. Anal. Calcd for $C_{16}H_{23}FeMnO_{10}P_2S_2$: C, 31.39; H, 3.79; P, 10.12. Found: C, 31.30; H, 3.72; P, 10.11.

2b: yield 56% (0.85 g from 1.1 g of **1b**); mp 148–149 °C; mass spectrum, *m/e* 639.555 [M^+](calcd 639.556); ^1H NMR (C_6D_6) δ 1.28 (t, $^2J_{P-H}$ = 8.0 Hz, CH_3), 4.62 (C_5H_5), 7.35 (C_6H_5). Infrared data are in Table I. Anal. Calcd for $C_{26}H_{27}FeMnO_4P_2S_2$: C, 48.80; H, 4.20; P, 9.68; S, 10.02. Found: C, 48.78; H, 4.24; P, 9.42; S, 10.06.

2c: yield 68% (1 g from 1 g of **1c**); mp 136–137 °C; mass spectrum, *m/e* 515.924 [M^+] (calcd 515.924); ^1H NMR (C_6D_6) δ 0.83 (t, $^2J_{P-H}$ = 8.5 Hz, CH_3), 4.52 (C_5H_5); ^{31}P NMR (C_6D_6) δ 16.3; ^{13}C NMR (CD_2Cl_2, 216 K) δ 283.0 (t, $^2J_{P-C}$ = 14.0 Hz, CS_2), 216.4 (t, $^2J_{P-C}$ = 27.2 Hz, FeCO), 21 4.6 (t, $^2J_{P-C}$ = 23.1 Hz, FeCO), 235.7 (MnCO), 82.7 (C_5H_5), 15.3 (t, $^1J_{P-C}$ = 14.8 Hz, CH_3). Infrared data are in Table I. Anal. Calcd for $C_{16}H_{23}FeMnO_4P_2S$: C, 37.25; H, 4.49; P, 12.01; S, 12.43. Found: C, 37.30; H, 4.54; P, 12.00; S, 12.58.

$(Me_3P)_2(CO)_2FeCS_2Mo(CO)_5$ (3c). A cyclohexane solution of 77 mg of $Mo(CO)_6$ and 100 mg of complex **1c** was refluxed overnight. The solvent was removed, and the orange complex **3c** was separated from the starting material by silica gel column chromatography under nitrogen (eluant cyclohexane–ether) and crystallized from a hexane–ether mixture.

3c: yield 46% (78 mg); mp 122–124 °C; mass spectrum, *m/e* 577.837 [M^+] (calcd 577.837); ^1H NMR (C_6D_6) δ 1.33 (t, $^2J_{P-H}$ = 8.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 309 K) δ 301.9 (t, $^2J_{P-C}$ = 17.3 Hz, CS_2), 206.1 (s, MoCO), 15.5 (t, $^1J_{P-C}$ = 15.7 Hz, CH_3P). Infrared data are in Table I. Anal. calcd for $C_{14}H_{18}FeMoO_7P_2S_2$: C, 29.10; H, 3.14; P, 10.72. Found: C, 29.08; H, 3.13; P, 10.70.

X-ray Analysis. Collection and Reduction of the X-ray Data. Dark red prisms of $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$ were grown from a dichloromethane–hexane mixture. Preliminary Weissenberg and precession photographs established that the molecule crystallizes in the monoclinic space group $P2_1/c$ with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. The unit cell parameters a = 10.411 (1) Å, b = 9.762 (2) Å, c = 28.194 (5) Å, β = 93.090 (10)°, and V = 2861 $Å^3$ were obtained by least-squares refinement from 25 accurately centered-diffractometer reflections, by using Mo Kα (λ = 0.709 26 Å) graphite-monochromated radiation. The calculated density 1.487 g cm^{-3} is in good agreement with the measured density (d = 1.47 (3) g cm^{-3}) obtained by the flotation method in a mixture of 1,2-dichloroethylene and carbon tetrachloride for four empirical formulas per unit cell. A well-shaped prism crystal 0.27 × 0.18 × 0.18 mm in dimension was mounted on a Nonius CAD4 automatic four-circle diffractometer for data collection using the θ–2θ scan technique. The integrated intensities were obtained from scan angles (in degrees) calculated from $S = 1.00 + 0.35 \tan\theta$ and increased by 25% at each end for the background count. The crystal–counter distance was 173 mm, and the counter aperture was calculated by $d = 2.00 + 0.3 \tan\theta$ (in millimeters). By use of the above conditions and graphite-monochromated Mo Kα radiation, the intensities and estimated standard deviations of 2685 unique reflections were collected to $2\theta = 50°$ with a constant scan rate of 1.6°/min. Three standard reflections were monitored every 200 min of exposure, and no significant variation was observed. All the reflections were corrected for Lorentz and polarization effects by the program MAXE;[17] absorption corrections were applied by using Gaussian integration.[18] All nonzero reflections were considered as observed.

Solution and Refinement of the Structure. The positions of the heaviest atoms (Fe, Mn, S, P) confirmed from the Patterson function were found with the aid of the program MULTAN[19] in the most probable set. From three-dimensional electron density difference maps, the positions of the remaining nonhydrogen atoms were obtained. After successive full-matrix least-squares refinement[20] with anisotropic thermal parameters, the location of all the hydrogen atoms was found on electron density difference maps by using the reflections below $(\sin\theta)/\lambda = 0.3\ Å^{-1}$, but the least-squares refinement of their coordinates failed due to a high thermal motion of the phenyl groups. These hydrogen atoms were fixed in their ideal positions, with a constant isotropic thermal factor of 5 $Å^2$ and were not refined. Scattering functions were taken from ref 21 with corrections included for both the real and imaginary parts of the anomalous dispersion.[22] Further cycles of refinement with anisotropic thermal parameters for nonhydrogen atoms and ideal constrained positions for hydrogen atoms converged to $R = \sum \Delta F / \sum |F_o| = 0.053$ and $R_w = (\sum w(\Delta F)^2 / \sum w|F_o|^2)^{1/2} = 0.056$ with $\Delta F = |F_o - F_c|$. The weights were calculated as $1/w = \sigma_F^2 = (\sigma_I^2 + (0.06I)^2)/4I$.[23] The estimated standard deviation (esd) of an observation of unit weight was 1.12, no significant peak remained on a final electron density difference map, and no shift greater than 0.1 esd was observed in the final refinement. The final position parameters for nonhydrogen atoms are listed in Table II. Relevant bond lengths and angles are gathered in Tables III and IV. Table V contains a selection of least-squares planes.

Results and Discussion

Synthesis. The (η^2-CS_2) iron derivatives containing phosphites (**1a**) or phosphines (**1b** and **1c**) react smoothly at room temperature with $Mn(THF)(CO)_2C_5H_5$[16] in THF solution. The THF ligand is displaced from manganese by the uncoordinated, basic sulfur atom of derivatives **1**, and the resulting orange complexes **2a** (43%), **2b** (56%), and **2c** (68%) were separated from the starting materials by silica gel chromatography (Scheme I).

Similarly, the reaction of **1c** with molybdenum hexacarbonyl in refluxing cyclohexane proceeded with the displacement of one carbonyl bonded to the molybdenum, and the heterodinuclear compound **3c** was isolated in 43% yield.

The formulation of complexes **2a–c** and **3c** was established by their elemental analyses and their mass spectrum which shows the molecular ion and the main fragments resulting from

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Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Equivalent Thermal Parameters (Å^2)

atom	x	y	z	B_{eq}
Fe	1102 (1)	−2462 (1)	798 (0)	2.495
Mn	3679 (1)	−5069 (1)	2191 (0)	2.953
S(1)	2222 (2)	−4523 (2)	820 (1)	3.235
S(2)	2432 (2)	−3416 (2)	1853 (1)	3.033
P(1)	2930 (2)	−1364 (2)	608 (1)	2.884
P(2)	−735 (2)	−3606 (2)	936 (1)	3.409
C(1)	417 (7)	−2062 (8)	215 (3)	3.657
C(2)	615 (8)	−1082 (9)	1136 (3)	4.187
C(3)	2030 (6)	−3508 (7)	1284 (2)	2.398
C(4)	4926 (7)	−4843 (8)	1798 (3)	3.510
C(5)	3023 (7)	−6431 (8)	1840 (3)	3.795
C(6)	2747 (8)	−5193 (11)	2850 (3)	4.927
C(7)	3607 (10)	−6278 (9)	2814 (3)	5.027
C(8)	4841 (10)	−5768 (11)	2787 (3)	5.339
C(9)	4764 (10)	−4334 (12)	2816 (3)	5.940
C(10)	3473 (11)	−3992 (10)	2852 (3)	5.449
C(11)	2820 (8)	476 (8)	579 (3)	5.171
C(12)	4344 (7)	−1572 (10)	1012 (3)	5.559
C(13)	3485 (7)	−1857 (8)	27 (3)	3.572
C(14)	4351 (9)	−2885 (9)	−18 (4)	5.848
C(15)	4710 (11)	−3265 (10)	−491 (5)	7.890
C(16)	4156 (14)	−2560 (14)	−866 (5)	8.624
C(17)	3307 (12)	−1538 (14)	−824 (3)	8.420
C(18)	2962 (8)	−1168 (10)	−379 (3)	5.559
C(19)	−1204 (9)	−4855 (11)	483 (3)	6.691
C(20)	−2167 (7)	−2521 (11)	941 (3)	6.299
C(21)	−777 (6)	−4548 (7)	1489 (3)	2.974
C(22)	−1032 (8)	−3863 (9)	1896 (3)	5.073
C(23)	−1076 (10)	−4593 (13)	2333 (3)	6.388
C(24)	−857 (11)	−5972 (17)	2338 (5)	8.343
C(25)	−587 (12)	−6624 (11)	1942 (5)	7.945
C(26)	−546 (8)	−5939 (9)	1508 (3)	5.251
O(1)	−22 (6)	−1828 (8)	−152 (2)	7.076
O(2)	328 (7)	−170 (7)	1371 (2)	7.255
O(4)	5775 (6)	−4641 (7)	1552 (2)	6.577
O(5)	2642 (6)	−7368 (6)	1629 (2)	6.262

Table III. Relevant Bond Lengths (Å)

Fe-S(1)	2.325 (2)	C(1)-O(1)	1.139 (9)
Fe-P(1)	2.264 (2)	C(2)-O(2)	1.154 (10)
Fe-P(2)	2.260 (2)	C(4)-O(4)	1.160 (9)
Fe-C(1)	1.808 (7)	C(5)-O(5)	1.153 (10)
Fe-C(2)	1.736 (8)	C(6)-C(7)	1.393 (13)
Fe-C(3)	1.939 (6)	C(7)-C(8)	1.382 (14)
Mn-S(2)	2.260 (2)	C(8)-C(9)	1.405 (16)
Mn-C(4)	1.750 (7)	C(9)-C(10)	1.392 (15)
Mn-C(5)	1.779 (7)	C(10)-C(6)	1.395 (14)
Mn-C(6)	2.127 (7)	C(13)-C(14)	1.357 (11)
Mn-C(7)	2.117 (8)	C(14)-C(15)	1.447 (17)
Mn-C(8)	2.143 (9)	C(15)-C(16)	1.370 (18)
Mn-C(9)	2.177 (9)	C(16)-C(17)	1.341 (19)
Mn-C(10)	2.156 (8)	C(17)-C(18)	1.366 (13)
S(1)-C(3)	1.658 (6)	C(18)-C(13)	1.418 (11)
S(2)-C(3)	1.642 (6)	C(21)-C(22)	1.361 (11)
P(1)-C(11)	1.802 (8)	C(22)-C(23)	1.427 (13)
P(1)-C(12)	1.838 (7)	C(23)-C(24)	1.365 (20)
P(1)-C(13)	1.822 (7)	C(24)-C(25)	1.324 (19)
P(2)-C(19)	1.820 (9)	C(25)-C(26)	1.394 (16)
P(2)-C(20)	1.828 (8)	C(26)-C(21)	1.380 (11)
P(2)-C(21)	1.811 (7)		

the loss of the carbonyls. The compounds, slightly air-sensitive in solution, are air-stable in the solid state. This stability and the yields obtained indicate that the attachment of a metal atom on the uncoordinated sulfur atom of the η^2-CS_2 ligand does not labilize the Fe–CS_2 bond. In addition, it is noteworthy that the reaction does not occur with subsequent desulfuration.

Spectroscopic Studies. The D-type geometry of the CS_2 bridge, confirmed by the X-ray determination of **2b**, was first established by NMR spectroscopy. The ^{31}P NMR spectra indicated the equivalence of the phosphorus nuclei in derivatives **2a** (δ 91.1) and **2c** (δ 16.3); in addition a virtual coupling was observed for the methyl H of the phosphorus groups in

Table IV. Relevant Bond Angles (Deg)

S(1)-Fe-P(1)	89.5 (1)	Fe-P(1)-C(11)	115.5 (2)
S(1)-Fe-P(2)	89.7 (1)	Fe-P(1)-C(12)	117.5 (2)
S(1)-Fe-C(1)	113.1 (2)	Fe-P(1)-C(13)	112.6 (2)
S(1)-Fe-C(2)	144.3 (2)	Fe-P(2)-C(19)	114.6 (3)
S(1)-Fe-C(3)	44.6 (1)	Fe-P(2)-C(20)	114.2 (3)
P(1)-Fe-P(2)	176.2 (1)	Fe-P(2)-C(21)	116.5 (2)
P(1)-Fe-C(1)	89.5 (2)	C(11)-P(1)-C(12)	100.7 (4)
P(1)-Fe-C(2)	91.5 (2)	C(11)-P(1)-C(13)	104.1 (4)
P(1)-Fe-C(3)	90.9 (2)	C(12)-P(1)-C(13)	104.8 (4)
P(2)-Fe-C(1)	87.4 (2)	C(19)-P(2)-C(20)	101.3 (4)
P(2)-Fe-C(2)	91.3 (2)	C(19)-P(2)-C(21)	104.4 (4)
P(2)-Fe-C(3)	91.2 (2)	C(20)-P(2)-C(21)	104.1 (4)
C(1)-Fe-C(2)	102.6 (4)	Fe-C(1)-O(1)	179.0 (7)
C(1)-Fe-C(3)	157.7 (3)	Fe-C(2)-O(2)	177.7 (6)
C(2)-Fe-C(3)	99.7 (3)	Mn-C(4)-O(4)	176.6 (3)
Fe-S(1)-C(3)	55.2 (2)	Mn-C(5)-O(5)	175.9 (3)
Mn-S(2)-C(3)	119.6 (2)	S(1)-C(3)-S(2)	139.7 (3)

Table V. Least-Squares Planes and Atomic Displacements Therefrom (Å)

(a) Plane Defined by C(6), C(7), C(8), C(9), C(10)^a

Equation of Plane: $-0.0672x + 0.0465y - 0.9967z + 8.4075 = 0$

C(6)	0.004	C(10)	−0.000	C(5)	2.754
C(7)	−0.005	Mn	1.786	O(4)	3.449
C(8)	0.006	S(2)	2.897	O(5)	3.328
C(9)	−0.004	C(4)	2.810		

(b) Plane Defined by C(13), C(14a), C(15), C(16), C(17), C(18)^b

Equation of Plane: $-0.7478x - 0.6617y - 0.0543z + 1.5171 = 0$

C(13)	0.003	C(16)	0.003	Fe	2.190
C(14)	−0.003	C(17)	0.001	P(1)	0.073
C(15)	−0.001	C(18)	−0.004		

(c) Plane Defined by C(21), C(22), C(23), C(24), C(25), C(26)^c

Equation of Plane: $-0.9707x - 0.1724y - 0.1673z - 0.9936 = 0$

C(21)	0.004	C(24)	0.010	Fe	−1.988
C(22)	−0.005	C(25)	−0.006	P(2)	0.009
C(23)	0.001	C(26)	−0.003		

(d) Plane Defined by Fe, Mn, S(1), S(2), C(3)^d

Equation of Plane: $0.8405x + 0.4940y - 0.2225z + 0.8010 = 0$

Fe	0.002	C(3)	−0.010	C(5)	−0.898
S(1)	0.001	O(1)	−0.036	O(4)	2.576
S(2)	−0.003	O(2)	0.007	O(5)	−1.532

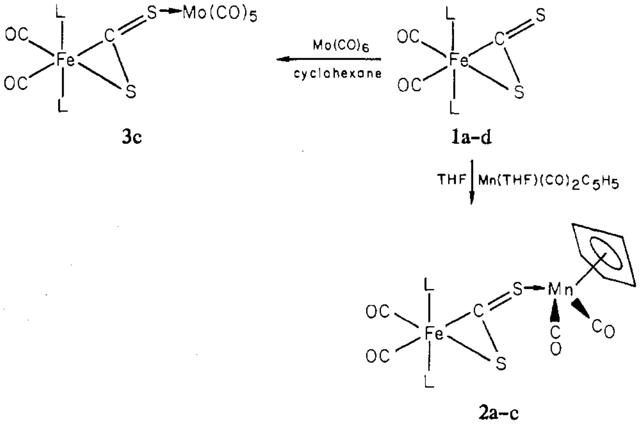
(e) Least-Squares Plane Defined by Fe, S(1), S(2), C(1), C(2), C(3), O(1), O(2)^e

Equation of Plane: $0.8484x + 0.4842y - 0.2140z + 0.7430 = 0$

Fe	0.002	C(2)	−0.009	Mn	0.083
S(1)	0.001	C(3)	−0.009	P(1)	2.265
S(2)	−0.003	C(1)	−0.036	P(2)	−2.256
C(1)	−0.012	O(2)	0.007		

[a] $\chi^2 = 1.25$. [b] $\chi^2 = 0.50$. [c] $\chi^2 = 1.77$. [d] $\chi^2 = 837.3760$. [e] $\chi^2 = 837$.

Scheme I



L: a, $P(OMe)_3$; b, PMe_2Ph; c, PMe_3; d, PPh_3 and PMe_3

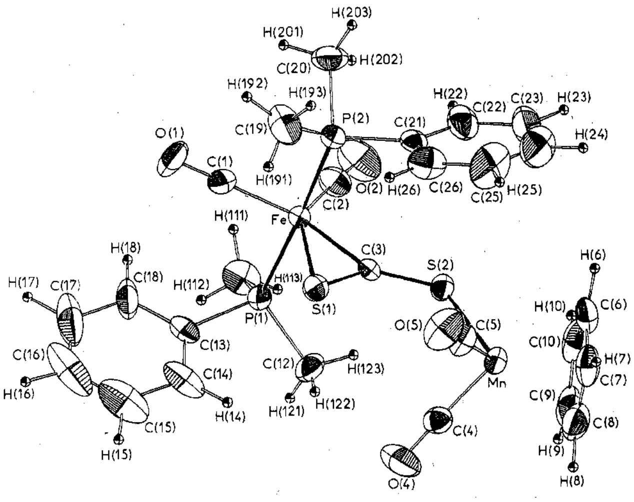


Figure 1. ORTEP drawing of $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$.

2a–c and **3c**. This information is consistent with the conservation of the trans position of the phosphorus ligands.[9] Of special interest was the variable-temperature ^{13}C NMR spectrum of compound **2c**. At 309 K, only the C_5H_5 (δ 82.17) and the CH_3P (δ 15.66, $^2J_{P-C} = 14.85$ Hz) groups could be observed; this indicated an exchange of the carbonyls bonded to the iron and manganese atoms. At 216 K, two triplets at δ 216.4 and 214.6 were observed for the carbonyls bonded to iron as indicated by the coupling with two identical phosphorus nuclei; $^2J_{P-C} = 27.2$ and 23.1 Hz, respectively. A singlet corresponding to two equivalent carbonyls bonded to manganese was exhibited at δ 235.7. These low-temperature data are consistent with a CS_2 group π bonded to the iron atom, leading to two nonequivalent carbonyls bonded to the iron atom, and σ bonded through one sulfur atom to the manganese atom. Whereas the precursor **1c** is rigid at 309 K, the exchange of the carbonyls of **2c** at the same temperature shows that the coordination of the sulfur atom nonbonded to iron facilitates the rotation of the Fe–η^2-CS_2 bond or the exchange of the π- and σ-bond types between the CS_2 bridge and the metal atoms, as shown by Herberhold et al. for $([C_5H_5(CO)_2Mn]_2CS_2)$.[6] It is also noteworthy that the chemical shift of the CS_2 group is not significantly modified by the coordination of the manganese ($\delta(^{13}CS_2)$ ($^2J_{P-C}$, Hz): **1c**, 288.0 (15.6); **2c**, 283.0 (14.0)).

In the infrared spectra, the comparison of the carbonyl absorption frequencies of derivatives **2a–c** and **3c** with those of their precursors **1** (Table I) gives some information on the behavior of the heterodinuclear complexes. Whereas the frequencies of the carbonyls bonded to the iron are not strongly modified, those of the carbonyls bonded to the manganese are lower than 1925 and 1860 cm^{-1}, the frequencies observed for $Mn(PMe_3)(CO)_2C_5H_5$.[24] These frequencies show that complexes **1** behave as strong electron-donating ligands when bonded to the manganese in complexes **2**.

In complexes **2** and **3c** the C=S frequency is surprisingly higher than in precursors **1** since it is expected that the coordination of manganese or molybdenum to the sulfur atom should decrease the C=S force constant, but, in the $FeCS_2M$ unit, the considered C=S bond which is situated between two atoms of high mass is subject to a mechanical coupling and thus a decrease of the C=S force constant in derivatives **2** and **3c**, as compared to complexes **1**, may give rise to a higher observed frequency.

Finally it is noteworthy that both in bimetallic complexes **2** and **3c** and in compounds **1** the C=S frequency decreases with the increase in the electron-donating ability of the phosphorus groups which corresponds to the sequence $P(OMe)_3 < PMe_2Ph < PMe_3$.[9] This is consistent with the increase of the electron transfer from iron toward the second metal atom through the carbon disulfide bridge.

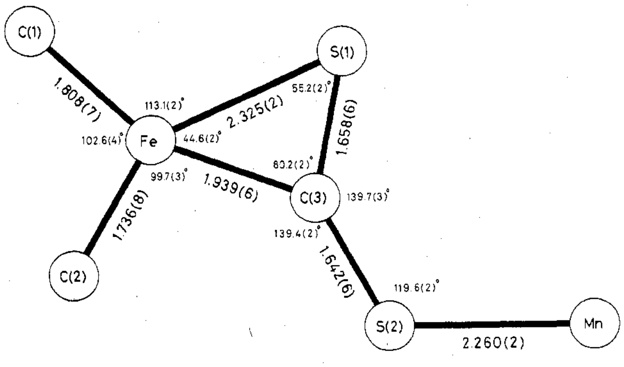
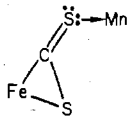


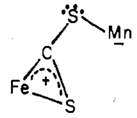
Figure 2. C_2FeCS_2Mn moiety in **2b**.

Crystal and Molecular Structure of $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$ (2b). The molecule, shown in Figure 1 along with the atomic numbering scheme used, consists of discrete entities, except for the possible interaction between O(1) (at *x*, *y*, *z*) and H(111) (at −*x*, −*y*, −*z*) as their separation is 2.37 Å, and the distance of 3.36 Å between O(1) and the atom C(11) (at −*x*, −*y*, −*z*) and the angle O(1)–H(111)–C(11) at ca. 162° are all consistent with the possible existence of a hydrogen bond.

The crystal structure determination shows that the $FeCS_2Mn$ moiety is nearly planar, the manganese atom being only 0.083 Å away from the plane of the $FeCS_2$ unit (Table V). The C(3)–S(1) linkage is π bonded to the iron atom while the S(2) atom only is coordinated to the manganese atom. The C(3)–S(2)–Mn angle is close to 120° (119.6 (2)°) and indicates that there is no significant change of hybridization of the S(2) atom by coordination to the manganese atom. Consequently representation E seems to be more consistent with this information than the other possible form F.



E



F

As the π bond, between the iron atom and the C(3)–S(1) linkage in precursors **1**, is maintained in complex **2b**, the structure of **2b** can be compared directly to the structure already reported for the derivative $Fe(\eta^2\text{-}CS_2)(CO)_2(PMe_3)(PPh_3)$ (**1d**)[9] to examine how the coordination of the sulfur atom S(2) to the manganese modifies the $Fe(CS_2)(CO)_2(PR_3)_2$ group, on the assumption that the different nature of the phosphorus ligands in **1d** and **2b** is not the determining factor. The relevant structural data of the $FeCS_2Mn$ fragment are indicated on Figure 2. The coordination of the S(2) atom leads to a slight shortening of the C(3)–S(1) bond distance (1.658 (6) Å in **2b** and 1.676 (7) Å in **1d**) and to a lengthening of the C(3)–S(2) bond distance (1.642 (6) Å in **2b** and 1.615 Å in **1d**), but the corresponding reduction of the bond order is not large enough to reach a single S–C(sp^2) bond for which a length of 1.73–1.75 Å is expected.[25] The Fe–S(1) bond distance (2.325 (2) Å in **2b** and 2.334 (2) Å in **1d**) and both angles Fe–S(1)–C(3) and S(1)–C(3)–S(2) respectively 55.2(2) and 139.7 (3)° in **2b** and 56.4 (2) and 138.9 (1)° in **1d** are not significantly modified. In contrast the Fe–C(3)

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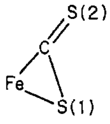
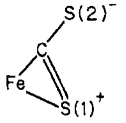
bond distance is much shorter in **2b** (1.939 (6) Å) than in **1d** (1.983 (8) Å). This Fe–C bond length is in the range of the reported data for a Fe–C(carbene) bond distance such as 1.945 Å[26] or 1.905 Å.[27] In the study of (triphos)$CoCS_2Cr(CO)_5$[14] preliminary data show a similar variation only for the C(3)–S(1) and C(3)–S(2) bonds by coordination of the S(2) atom.

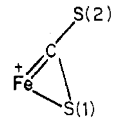
The effect of the coordination of the manganese to the S(2) atom, mainly reflected in the S(1)–C(3), S(2)–C(3), and especially C(3)–Fe bonds, can be explained by the contribution of the canonical forms III, IV, and V already taken into account to explain the electron distribution of the $FeCS_2$ unit in **1d**.[9]



III



IV



V

The reduction of the C(3)–S(2) bond order and the shortening of the C(3)–S(1) and C(3)–Fe bond lengths would then correspond to a more important contribution of the 1,3 dipolar forms IV and V in **2b** than in the precursor **1d**.

The contribution of the canonical forms IV and V also explains the electron transfer from iron to the manganese moiety, as shown by the carbonyl and C=S absorption frequencies in the infrared spectra, but the relative contribution of form III cannot be negligible for the C(3)–S(2)–Mn angle of 119.6 (2)°, indicating that rehybridization of the S(2) atom does not occur as would be the result from contribution solely of forms IV and V.

Stereochemically the iron moiety can be described in terms of a trigonal bipyramid with the two mutually trans phosphine ligands in the apical positions and the equatorial plane containing the two carbonyl and the CS_2 groups. This stereochemistry is consistent on one hand with the departures of the equatorial atoms from their mean plane (Table V) and on the other hand with the observed angles P(1)–Fe–P(2) (176.2 (1)°) and the averaged angles between the equatorial atoms and the phosphorus atoms (90.12°). As a similar stereochemistry was observed for the complex **1d**,[9] the coordination of the S(2) atom does not modify the stereochemistry around the iron atom but leads to a different conformation of the phosphorus ligands as compared to that of the equatorial ligands. From structural data of derivative **1d**[9] it can be shown that the phosphorus ligands are in the staggered conformation with respect to each other and to the equatorial ligands.[28] In contrast Figure 3 shows the eclipsed conformation of the phosphorus ligands with respect to each other but a staggered conformation with respect to the equatorial ligands in **2b**; this may be due to the steric interactions between the $C_5H_5(CO)_2Mn$ moiety and the phosphorus substituents.

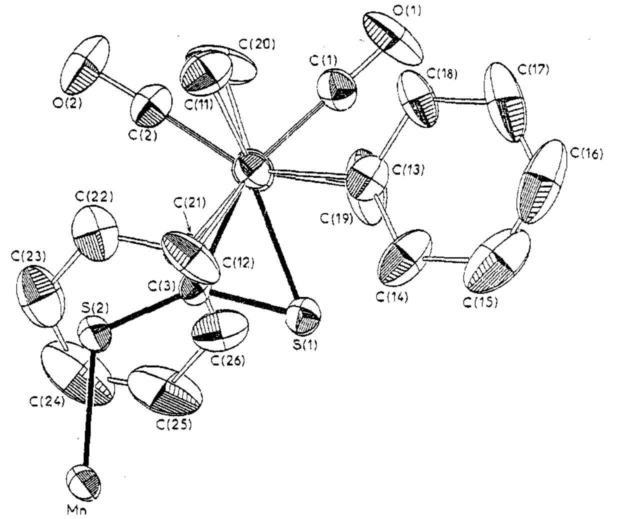


Figure 3. Side view of the $(PhMe_2P)_2(CO)_2FeCS_2Mn$ moiety in **2b**.

The coordination of the $L_2(CO)_2FeCS_2$ ligand to the manganese (i) leads to a Mn–S(2) bond length of 2.260 (2) Å which is only slightly longer than that found in the bridged alkylthio cationic complex $([CH_3C_5H_4(CO)_2Mn]_2SC_2H_5)ClO_4$ (2.256 Å[29]) and (ii) does not modify the arrangement of the ligands around the manganese atom as compared to other complexes of type $Mn(L)(CO)_2C_5H_5$[30,31] with a planar cyclopentadienyl ligand at a distance of 1.786 Å from the manganese and with a OC–Mn–CO angle of 91.2 (4)°.

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Registry No. **1a**, 64424-66-4; **1b**, 64424-57-3; **1c**, 64424-58-4; **2a**, 67848-97-9; **2b**, 67848-98-0; **2c**, 67848-99-1; **3c**, 74231-10-0; $Mn(THF)(CO)_2C_5H_5$, 12093-26-4; $Mn(CO)_3C_5H_5$, 12079-65-1; $Mo(CO)_6$, 13939-06-5.

Supplementary Material Available: Table S_1, anisotropic thermal parameters, Table S_2, fractional coordinates of hydrogen atoms, a stereoscopic view of $(PhMe_2P)_2(CO)_2FeCS_2Mn(CO)_2C_5H_5$, and a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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