

SULFUR-CONTAINING CARBENE-METAL COMPOUNDS: GENERAL ROUTE FROM CARBON DISULFIDE MANGANESE COMPLEXES; X-RAY STRUCTURE OF 1,3-DITHIOL-2-YLIDENEMANGANESE(I) DERIVATIVE *

J.Y. LE MAROUILLE **, C. LELAY *, A. BENOIT **, D. GRANDJEAN **, D. TOUCHARD *, H. LE BOZEC * and P. DIXNEUF **

*Université de Rennes, Laboratoires de Chimie des Organométalliques * et de Cristallographie **, Campus de Beaulieu, 35042 Rennes Cedex (France)*

(Received October 12th, 1979)

Summary

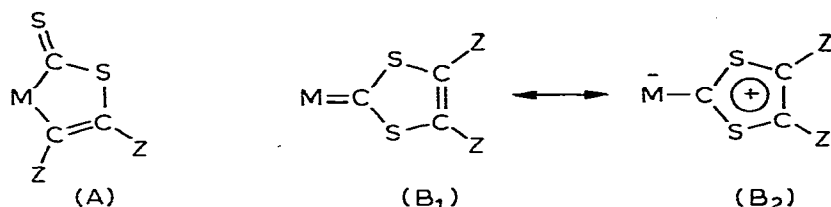
Chiral carbene-manganese(I) complexes have been synthesized by the cycloaddition of dimethyl acetylenedicarboxylate to the coordinated CS₂ ligand in Mn(η^2 -CS₂)(CO)(L)C₅H₄R (L = P(OMe)₃; PMe₂Ph; PMe₃). Irrespective of the nature of the ligand L, these 1,3-dithiol-2-ylidenemanganese(I) complexes are stable towards isomerisation into heterometallobicycles and exhibit low frequency carbonyl absorption bands in the infrared consistent with a strong electron releasing effect of the carbene ligand. The structure of Mn(CS₂C₂(CO₂Me)₂)(CO)(P(OMe)₃)(C₅H₅) has been determined by X-ray analysis of a suitable crystal. The molecule shows a carbene carbon–manganese bond C(7)–Mn of length 1.876 Å and a planar carbene which does not adopt the 1,3-dithiolium aromatic-ring geometry but contains a carbon–carbon double bond, C(8)–C(9), of length of 1.341 Å. The CO₂Me groups are out of the plane of the carbene ligand and two positions with equal occupancy are found for each oxygen atom O(3) and O(5) belonging to the C=O groups.

Introduction

The addition of dimethyl acetylene dicarboxylate to the Rh(η^2 -CS₂)(PPh₃)(C₅H₅) derivative yields a heterometallobicyclic complex of type A [1]. In contrast it was reported recently that activated alkynes reacted with Fe(η^2 -CS₂)(CO)₂L₂ compounds to give carbene-iron complexes of type B [2].

It was not clear whether the isolated carbene-metal complexes were closer to the canonical form B₁ or to B₂, but it was shown that the kinetic products

* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday on May 30th, 1980.



B could isomerise into heterometallobicyclics of type A when electron-releasing phosphorus ligands L, such as PMe_3 or PMe_2Ph , were bonded to the iron [3].

In order to examine whether the carbene-metal complex formation, resulting from the cycloaddition of electrophilic alkynes to a coordinated carbon disulphide, was a general reaction, we have studied the behaviour towards activated alkynes of $(\eta^2\text{-CS}_2)$ manganese(I) complexes. In addition, the structure of a carbene-metal derivative of type B, namely $\text{Mn}[\text{CS}_2\text{C}_2(\text{CO}_2\text{Me})_2](\text{CO})(\text{P}(\text{OMe})_3)(\text{C}_5\text{H}_5)$ (2a), has been determined for the first time to assess the relative contribution of forms B₁ and B₂ in this type of compound.

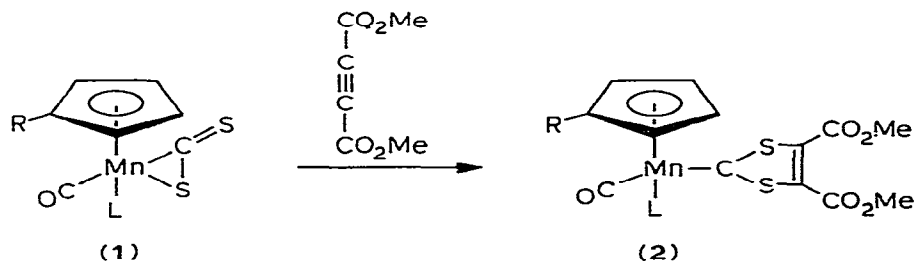
Results and discussion

Synthesis of sulfur-containing carbene-manganese complexes

Carbon disulphide manganese(I) complexes of type 1 were prepared, according to the procedure established by Herberhold et al. [4] for the preparation of 1c, by successive photochemical displacement of two carbonyls of $\text{Mn}(\text{CO})_3\text{-C}_5\text{H}_4\text{R}$ derivatives. The reactions were carried out in THF first of all in the presence of the phosphorus ligand L and then in the presence of carbon disulphide.

Addition of one equivalent of dimethyl acetylenedicarboxylate to a benzene solution of 1a, 1b and 1c at room temperature led readily to the formation of the red adducts 2a, 2b and 2c, respectively [5] (Scheme 1). Whereas the corresponding carbene-iron complexes were very air sensitive [2] the new chiral derivatives 2 were found to be air-stable and could be isolated using silica gel thick-layer chromatography. A small amount of the tetrathiafulvalene result-

SCHEME 1



- a. $\text{R} = \text{H}$; $\text{L} = \text{P}(\text{OMe})_3$
- b. $\text{R} = \text{CH}_3$; $\text{L} = \text{PMe}_2\text{Ph}$
- c. $\text{R} = \text{H}$; $\text{L} = \text{PMe}_3$

TABLE 1
¹H NMR DATA FOR COMPOUNDS 2 (δ, ppm)

	Cp	L	CO ₂ Me
2a (C ₆ D ₆) ^a	4.48	OCH ₃ : 3.23 (³ J(PH) 11.2 Hz)	3.32 (s)
2a (CDCl ₃) ^b	4.83	OCH ₃ : 3.67 (³ J(PH) 11.5 Hz)	3.97 (s)
2b (C ₆ D ₆) ^b	4.33 (m)	C ₆ H ₅ : 7.17	3.37 (s)
	4.07 (m)	CH ₃ (A): 1.43 (² J(PH) 10.0 Hz)	
		CH ₃ (B): 1.33 (² J(PH) 10.4 Hz)	
2c (CDCl ₃) ^a	4.58	CH ₃ : 1.40 (² J(PH) 9 Hz)	3.80 (s)

^a (100 MHz); ^b (60 MHz).

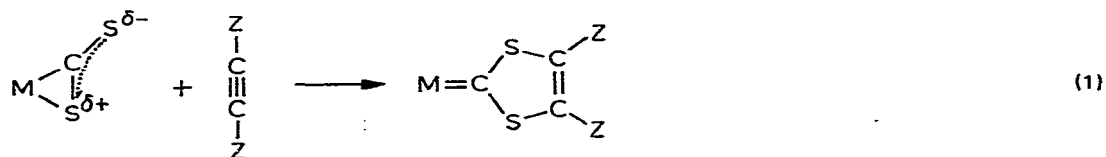
ing from the dimerisation of the carbene ligand was also isolated along with 1c.

The carbene-manganese complexes 2a–2c were fully characterised by their mass spectra, chemical analysis and by IR and NMR spectroscopy. The IR spectra of chloroform solutions of the complexes 2a, 2b and 2c showed one very low frequency carbonyl absorption band, at 1870 cm⁻¹, 1850 cm⁻¹ and 1850 cm⁻¹ respectively, compared with a band at 1914 cm⁻¹ (THF) reported for the precursor 1c [4]. This is consistent with the strong electron-releasing character of a carbene ligand.

The ¹H NMR spectra (Table 1) showed equivalent carboxylate methyl groups indicating the new ligands to be carbenes rather than heterometallobicycles of type A. Furthermore this equivalence, observed for chiral complexes 2, is supporting evidence for the rotation of the carbene ligand.

Of special interest is the ¹H NMR spectrum of derivative 2b which shows the non-equivalence of methyl groups bonded to the phosphorus atom. The diastereotopy of these methyl groups clearly shows the chirality of the complex which has four different groups bonded to the manganese atom.

It may be noted that the 1,3-dithiol-2-ylidenemanganese complexes 2 do not isomerise into the heterometallobicyclic compounds of type A, even when electron donating groups, such as PMe₂Ph or PMe₃, are bonded to the manganese. This difference of behaviour, compared with carbene-iron(0) complexes [3], probably results from a smaller electron transfer from the metal to the CS₂ ligand in the manganese derivatives 1 than in the iron complexes Fe(η²-CS₂)(CO)₂L₂: the frequency of the uncoordinated C=S bond absorption decreases with increasing electron transfer and is at a higher frequency for (η²-CS₂)manganese(I) complexes 1 [4] than for (η²-CS₂)iron(0) derivatives [6]. Moreover, we observed for the Fe(η²-CS₂)(CO)₂L₂ compounds that the ¹³CS₂ chemical shift is at lower field when donating groups L are bonded to the iron [7] (i.e. δ¹³C(CS₂) (ppm): 288.0 (L = PMe₃) and 274.5 (L = P(OMe)₃). The corresponding chemical shift for derivative 1 (L = CO; R = H) has been reported at much higher field (δ 252.7 ppm) (8). A weak metal → CS₂ electron transfer is expected to maintain an electron deficiency on the coordinated sulfur atom and hence to favour the 1,3-cycloaddition, according to eq. 1, and the stability of the carbene-metal complex [3].



The addition reactions of dimethylacetylenedicarboxylate to the coordinated carbon disulfide in manganese complexes **1**, which are quite different from the previously studied $\text{Fe}(\eta^2\text{-CS}_2)(\text{CO})_2\text{L}_2$ derivatives, show that the route to sulfur-containing carbene-metal complexes formation is quite general. The stability towards isomerisation of derivative **2** allowed us to undertake an X-ray structure determination which was performed with compound **2a**.

X-ray structure determination of 2a

The molecular structure of derivative **2a** is shown in Fig. 1. The unit cell is centrosymmetric and contains four chiral molecules. According to the sum of the Van der Waals radii there are no strong intermolecular contacts. However, there is a repulsive interaction $\text{O}(5')\cdots\text{O}(5')$ with a separation of 2.43 Å. The closest intermolecular contact of 2.89 Å is between the methyl group $\text{C}(14)$

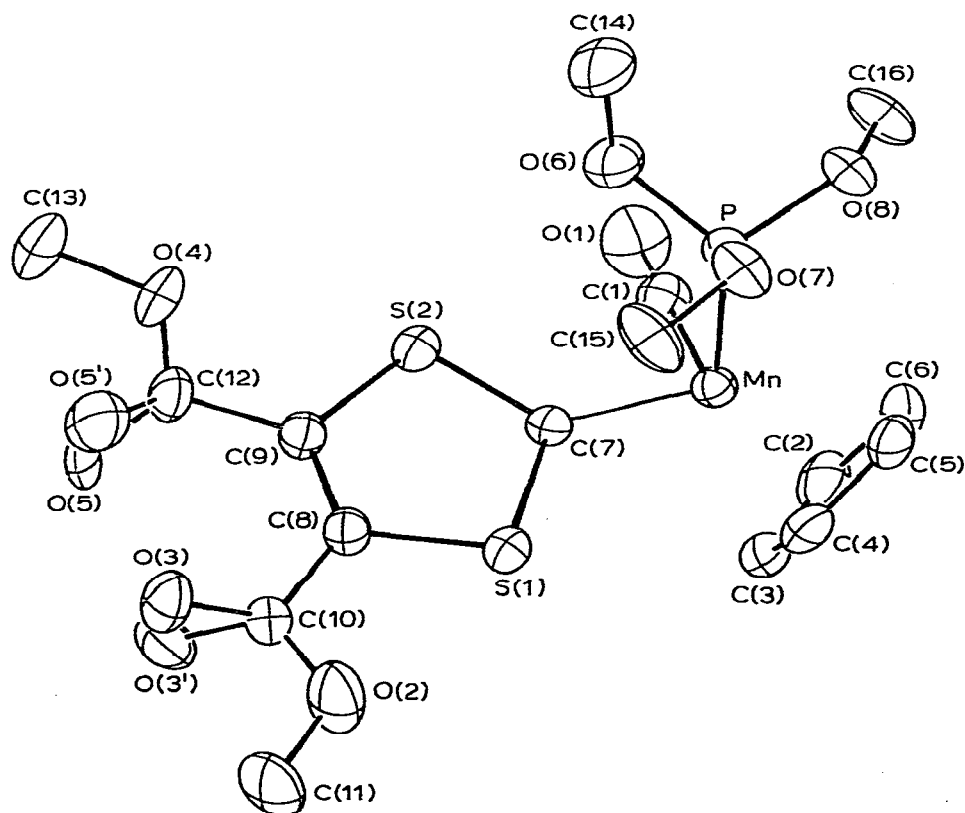


Fig. 1. ORTEP drawing of **2a** with hydrogen atoms omitted for clarity.

TABLE 2
PRINCIPAL INTRAMOLECULAR BOND LENGTHS (Å)

Mn—P	2.174(0)	O(3)—C(10)	1.302(6)
Mn—C(1)	1.754(3)	O(3')—C(10)	1.222(7)
Mn—C(2)	2.168(3)	O(4)—C(12)	1.265(3)
Mn—C(3)	2.160(3)	O(4)—C(13)	1.445(4)
Mn—C(4)	2.157(2)	O(5)—C(12)	1.246(5)
Mn—C(5)	2.134(2)	O(5')—C(12)	1.260(7)
Mn—C(6)	2.154(3)	O(6)—C(14)	1.449(3)
Mn—C(7)	1.876(2)	O(7)—C(15)	1.441(3)
S(1)—C(7)	1.732(2)	O(8)—C(16)	1.426(3)
S(1)—C(8)	1.748(3)	C(2)—C(3)	1.413(5)
S(2)—C(7)	1.753(2)	C(2)—C(6)	1.409(5)
S(2)—C(9)	1.740(2)	C(3)—C(4)	1.403(5)
P—O(6)	1.598(2)	C(4)—C(5)	1.421(5)
P—O(7)	1.603(2)	C(5)—C(6)	1.390(5)
P—O(8)	1.615(2)	C(8)—C(9)	1.343(3)
O(1)—C(1)	1.160(4)	C(8)—C(10)	1.489(3)
O(2)—C(10)	1.245(3)	C(9)—C(12)	1.498(4)
O(2)—C(11)	1.449(3)		

and O(3'). Relevant interatomic distances and angles are listed in Tables 2 and 3.

The MnC_5H_5 and $\text{MnP}(\text{OMe})_3$ groups show normal distances as previously observed with $\text{Mn}(\text{L})(\text{CO})_2(\text{C}_5\text{H}_5)$ derivatives [9–11] and the environment of the manganese atom shows expected angles close to 90° between the monodentate ligands (Table 3).

TABLE 3
SELECTED INTRAMOLECULAR BOND ANGLES ($^\circ$)

P—Mn—C(1)	90.73(9)	C(3)—C(4)—C(5)	106.92(20)
P—Mn—C(2)	109.24(9)	C(4)—C(5)—C(6)	108.40(29)
P—Mn—C(3)	87.60(9)	C(5)—C(6)—C(2)	108.71(30)
P—Mn—C(4)	103.26(9)	Mn—C(7)—S(1)	126.01(4)
P—Mn—C(5)	141.72(10)	Mn—C(7)—S(2)	125.23(5)
P—Mn—C(6)	147.14(9)	S(1)—C(7)—S(2)	108.72(15)
P—Mn—C(7)	94.88(7)	S(1)—C(8)—C(9)	115.11(21)
C(7)—S(1)—C(8)	100.56(10)	S(1)—C(8)—C(10)	117.07(22)
C(7)—S(2)—C(9)	100.16(9)	C(9)—C(8)—C(10)	127.82(27)
Mn—P—O(6)	114.18(6)	S(2)—C(9)—C(8)	115.44(22)
Mn—P—O(7)	120.41(6)	S(2)—C(9)—C(12)	118.16(16)
Mn—P—O(8)	118.83(6)	C(8)—C(9)—C(12)	126.36(20)
O(6)—P—O(7)	104.45(12)	O(2)—C(10)—O(3)	118.46(26)
O(6)—P—O(8)	103.68(12)	O(2)—C(10)—O(3')	110.40(44)
O(7)—P—O(8)	91.96(12)	O(3)—C(10)—O(3')	64.96(47)
C(10)—O(2)—C(11)	120.05(26)	O(2)—C(10)—C(8)	113.59(15)
C(12)—O(4)—C(13)	117.39(27)	O(3)—C(10)—C(8)	120.31(26)
P—O(6)—C(14)	121.84(16)	C(3')—C(10)—C(8)	120.27(33)
P—O(7)—C(15)	120.13(14)	O(4)—C(12)—O(5)	116.67(37)
P—O(8)—C(16)	119.62(15)	O(4)—C(12)—O(5')	118.13(33)
Mn—C(1)—O(1)	176.59(13)	O(5)—C(12)—O(5')	52.78(47)
O(3)—C(2)—C(6)	107.02(20)	O(4)—C(12)—C(9)	113.00(13)
C(2)—C(3)—C(4)	108.93(32)	O(5)—C(12)—C(9)	123.56(34)
		O(5')—C(12)—C(9)	120.11(29)

TABLE 4

LEAST-SQUARES PLANES IN THE ORTHONORMAL-RIGHT-HANDED REFERENCE SYSTEM

a) Equation of the C(2), C(3), C(4), C(5), C(6) plane: $-0.4030 X + 0.2484 Y - 0.8808 Z + 2.4925 = 0$ $\chi^2 = 0.4520$ Distances of atoms to the plane (Å)					
C(2)	0.0027	C(3)	0.0004	C(4)	-0.0033
C(5)	0.0050	C(6)	-0.0048		
b) Equation of the S(1), S(2), C(7), C(8), C(9) plane: $-0.9227 X - 0.3847 Y - 0.0255 Z + 6.2952 = 0$ $\chi^2 = 0.4269$ Distances of atoms of the plane (Å)					
S(1)	-0.0000	S(2)	-0.0000	C(7)	0.0003
C(8)	0.0075	C(9)	-0.0015	C(10)	0.0107
C(12)	0.0298	Mn	-0.0556		
c) Equation of the O(2), C(8), C(10), C(11) plane: $-0.7948 X - 0.6052 Y - 0.0459 Z + 9.0463 = 0$ $\chi^2 = 0.3612$ Distances of atoms to the plane (Å)					
O(2)	-0.0004	C(8)	0.0054	C(10)	-0.0046
C(11)	0.0059	O(3)	-0.5964	O(3')	0.7431
d) Equation of the O(4), C(9), C(12), C(13) plane: $-0.9456 X - 0.3137 Y - 0.0865 Z + 5.5682 = 0$ $\chi^2 = 9.3913$ Distances of atoms to the plane (Å)					
O(4)	-0.0011	C(9)	0.0194	C(12)	-0.0176
C(13)	0.0210	O(5)	0.4873	O(5')	-0.5985

Of special interest is the carbene-manganese moiety. The cyclic carbene ligand and the exocyclic C(10) and C(12) carbon atoms lie in the same plane (Table 4). Both sets of C—S bonds show slight differences: C(7)—S(1) (1.732 Å) and C(7)—S(2) (1.753 Å); C(8)—S(1) (1.748 Å) and C(9)—S(2) (1.740 Å). These differences may result from the presence of the four different ligands on the manganese leading to the chirality of the molecule, although the C—C bonds in the carbene ligand of $\text{MnC}(\text{CH}_3)_2(\text{CO})_2\text{C}_5\text{H}_5$ also have different lengths of 1.500 (14) Å and 1.527 (11) Å [11].

The C(8)—C(9) bond length of 1.343 Å is very short and corresponds exactly to the length (1.34 Å) expected for carbon—carbon double bonds (12). This is the first evidence against the aromatic nature of the ring (form A) which would have lengthened this bond.

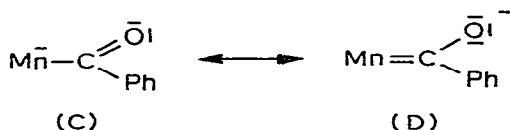
The CO_2CH_3 groups show an unusual feature in that although the methoxy groups O(2)—C(11) and O(4)—C(13), and the exocyclic C(8)—C(10) and C(9)—C(12) bonds, are slightly above the plane of the cyclic carbene ligand, the oxygen atoms O(3) and O(5) do not lie in this plane. Two positions with equal occupancy were found for each of them and these equivalent positions O(3) and O(3') or O(5) and O(5') are out of the plane of the cyclic ligand. This may result from the presence of molecules in the unit cell having different positions for these oxygen atoms which should be located in a *trans* position with respect to the mean plane of the carbene ligand for each enantiomer. Thus it is probable that either O(3) and O(5) or O(3') and O(5') belong to any particular molecule. Equal occupancy of the oxygen positions will result if two enantiomers of the same configuration differ in respect of the positions

of O(3) and O(5); i.e. in the unit cell one enantiomer of configuration R has oxygen atoms O(3) and O(5) and the other O(3') and O(5').

The absence of conjugation of the CO₂CH₃ groups with the ligand should be noted. Indeed, the C(8)—C(9) bond length is exactly that expected for a carbon—carbon double bond (1.34 Å), and both the C(8)—C(10) and C(9)—C(12) bond lengths, 1.489 Å and 1.498 Å respectively, are consistent with C(sp²)—C(sp²) single bonds (1.48 Å (12)). This bonding probably results from the position of the CO₂CH₃ groups which are not in the plane and especially from the positions of O(3) and O(5) or O(3') and O(5') which are significantly displaced out of the plane of the ligand.

The manganese atom is located slightly above the plane (0.056 Å) of the carbene ligand (Table 4). The carbene C(7)—Mn bond length is 1.876 Å in the range observed for carbene carbon—manganese bonds as in Mn[C(CH₃)₂](CO)₂C₅H₅ (1.872 Å [11]) or when the carbene carbon is linked to an unsaturated group (1.878 (1) Å [13]) or to one heteroatom such as in Mn[(C(OMe)-C₁₀H₁₇)](CO)₂C₅H₅ where the corresponding bond length is 1.89 Å [14].

The C(7)—Mn bond is, however, significantly shorter than the distance of 1.96 Å found in the anionic complex [Mn(COPh)(CO)₂(C₅H₅)]⁻NMe₄⁺ [15] for which the canonical form C is predominant over form D.



We may conclude, therefore, on the basis both of the C(7)—Mn bond length and of the absence of conjugation in the carbene ring that the carbene-manganese complexes **2** are more closely represented by an electron distribution of form B₁ than of form B₂.

Experimental

Synthesis

All reactions were carried out under nitrogen. Photochemical reactions were run in a glass vessel using a mercury lamp HANO TQ 150. IR spectra were recorded with a Unicam-SP 1100 instrument. Mass spectra were obtained with a Varian MAT 311 spectrometer. A Varian EM 360 (60 MHz) and JEOL (100 MHz) spectrometer were used for ¹H NMR.

The derivatives Mn(CO)₂(L)C₅H₄R were obtained according to the described procedure [16]. The complexes **1a**, **1b** and **1c** were prepared as reported for **1c** [4], by photolysis for 1 hour of a solution of 1 g of the derivative Mn(CO)₂(L)(C₅H₄R) in 150 ml of THF and 5 ml of CS₂. Silica gel column chromatography allowed the isolation of compounds **1** (18–25% yield) and of the unreacted starting material.

Derivatives 2a and 2b. 220–260 mg of compounds **1a** or **1b** were dissolved in 5 ml of dry benzene and one equivalent of dimethyl acetylene dicarboxylate was added with a syringe. The solution was stirred at room temperature for 0.5 hour and the red products were isolated by silica gel thick layer chromatography (eluant: hexane-ether) and crystallised from CH₂Cl₂-hexane solutions.

232 mg of 1a gave 113 mg of 2a (34%). m.p. 112°C. Analysis Found: C, 38.80; H, 4.13; Mn, 11.28; P, 6.21; S, 13.29. $C_{16}H_{20}MnO_8PS_2$ calcd.: C, 39.19; H, 4.11; Mn, 11.20; P, 6.31; S, 13.07%. Mass: 489.973 (M^+ calcd. 489.972) m/e ; 462 ($M - CO$)⁺; 338 ($M - CO - P(OMe)_3$)⁺; 120 (MnC_5H_5). IR ($CHCl_3$) (cm^{-1}): $\nu(C\equiv O)$: 1870; $\nu(C=O)$: 1735. 225 mg of 1b gave 110 mg of 2b (35%). m.p. 117°C. Mass $C_{22}H_{24}MnO_5PS_2$: Found 518.016 (M^+ calcd. 518.018) m/e ; 490 ($M - CO$)⁺; 352 ($M - CO - PMe_2Ph$)⁺; 272 [$Mn(PMe_2Ph)(C_5H_4CH_3)$]. IR ($CHCl_3$) (cm^{-1}): $\nu(C\equiv O)$: 1850; $\nu(C=O)$: 1740.

Derivative 2c. A solution of 250 mg of $Mn(CO)_2(PMe_3)C_5H_5$ in 150 ml of THF and 10 ml of CS_2 was photolyzed for 1.25 hour (cf. [4]) and then an excess (0.5 ml) of dimethyl acetylenedicarboxylate was added to the resulting solution.

After 2 hours at room temperature, the products were separated using thick layer chromatography: 2c, red (m.p. 112°C); 90 mg (20%); mass $C_{16}H_{20}MnO_5PS_2$ m/e : 442 (M)⁺; 414 ($M - CO$)⁺; 338 ($M - CO - PMe_3$)⁺; 120 (MnC_5H_5)⁺; IR- ($CHCl_3$) (cm^{-1}) $\nu(C\equiv O)$: 1850; $\nu(C=O)$: 1740. 12 mg (6%) of tetrathiafulvalene [$(MeO_2C)_2C_2S_2C$]₂ [17]. IR (Nujol) (cm^{-1}): 1743, 1717 (C=O) and 1575 (C=C); ¹H NMR ($CDCl_3$) δ (ppm): 3.86 (OCH₃).

TABLE 5

FINAL ATOMIC FRACTIONAL COORDINATES AND THEIR ESD'S ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS GIVEN BY $B_{eq} = \frac{2}{3} \sum_{ij} \beta_{ij} (a_i a_j)^2$.

Atom	X	Y	Z	B_{eq}
Mn	2751(1)	6430(0)	4117(0)	2.34
S(1)	1555(1)	6325(0)	1304(1)	3.20
S(2)	3320(1)	5341(0)	2578(1)	3.20
P	-115(1)	6454(0)	3864(1)	2.52
O(1)	2660(4)	7591(1)	3122(2)	5.62
O(2)	135(5)	6235(2)	-1175(2)	8.61
O(3)	2207(7)	5681(2)	-1487(3)	4.09
O(3')	684(10)	5400(3)	-1490(5)	7.95
O(4)	3762(5)	4335(1)	1322(2)	7.30
O(5)	2294(7)	4548(2)	-456(4)	4.10
O(5')	3656(9)	4729(3)	-338(5)	5.62
O(6)	-1292(3)	6723(1)	2634(2)	3.86
O(7)	-1163(3)	5872(1)	3997(2)	3.60
O(8)	-817(3)	6795(1)	4812(2)	3.26
C(1)	2650(4)	7125(1)	3491(2)	3.24
C(2)	3957(4)	5721(2)	5295(3)	3.92
C(3)	3117(4)	6109(2)	5870(3)	4.10
C(4)	3931(5)	6658(2)	5944(3)	4.16
C(5)	5286(4)	6608(2)	5396(3)	4.39
C(6)	5307(4)	6037(2)	5017(3)	3.98
C(7)	2518(3)	6043(1)	2700(2)	2.48
C(8)	1877(4)	5745(1)	449(2)	2.93
C(9)	2721(4)	5281(1)	1057(2)	2.89
C(10)	1202(5)	5821(1)	-849(3)	4.06
C(11)	-656(7)	6359(2)	-2415(3)	7.37
C(12)	3132(4)	4722(1)	552(3)	3.79
C(13)	4125(8)	3769(2)	919(4)	7.51
C(14)	-3235(5)	6733(2)	2276(4)	6.41
C(15)	-1047(5)	5359(2)	3333(3)	4.75
C(16)	-406(5)	7397(2)	5033(4)	4.99

X-ray data collection and reduction

Suitable crystals for X-ray diffraction were obtained by crystallisation in a dichloromethane-pentane mixture. A dark-red parallelepiped crystal measuring $0.5 \times 0.4 \times 0.4$ mm was selected for data collection at room temperature using a Nonius automatic four circle diffractometer, Mo- K_{α} radiation (λ 0.71069 Å) and a graphite monochromator. Conventional X-ray photographs established the monoclinic space group $P2_1/C$. 35 accurately centred reflections were used to refine the unit cell dimensions by the least squares method, to: a 7.852 (2) Å; b 22.962 (5) Å; c 12.002 (3) Å, β 108.42 (2)°, $Z = 4$, in agreement with the experimental density $d = 1.60$ g/cm³. Intensity data from one unique quadrant were collected with the $\theta - 2\theta$ scan technique out to $2\theta = 60^\circ$. The scan width was determined by $\Delta\theta = 1.2 + 0.35 \tan \theta$ and a constant scan time of 60 seconds was used. The intensities of 3 standard reflections monitored every 2 hours showed no significant variations during data collections. All 3511 non negative reflections were corrected for Lorentz and polarisation effects and used in the refinement. Direct methods using the Multan program [18] and Fourier maps revealed the structure. Refinement with anisotropic thermal parameters showed very high temperature factors for O(3) and O(5). A subsequent Fourier synthe-

TABLE 6

FINAL ANISOTROPIC THERMAL PARAMETERS AND THEIR ESD's ($\times 10^4$) IN THE FORM $\exp - (\sum_{ij} \beta_{ij} h_i h_j)$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	99(1)	14(0)	39(0)	1(0)	23(0)	1(0)
S(1)	182(2)	15(0)	41(0)	12(0)	21(1)	3(0)
S(2)	177(1)	16(0)	45(0)	14(0)	27(1)	3(0)
P	110(1)	13(0)	51(1)	-1(0)	32(1)	-2(0)
O(1)	341(7)	17(1)	118(3)	-11(2)	80(4)	11(1)
O(2)	466(10)	60(1)	43(2)	103(3)	37(3)	16(1)
O(3)	203(10)	28(1)	41(3)	11(3)	47(5)	2(2)
O(3')	438(21)	35(2)	90(6)	47(5)	-20(9)	-21(3)
O(4)	653(12)	19(1)	79(2)	43(2)	114(4)	4(1)
O(5)	247(12)	17(1)	55(3)	0(3)	19(5)	-6(1)
O(5')	399(15)	27(1)	93(5)	36(4)	105(8)	6(2)
O(6)	116(4)	27(1)	62(2)	10(1)	25(2)	7(1)
O(7)	175(4)	15(0)	87(2)	-16(1)	71(2)	-9(1)
O(8)	152(4)	14(0)	75(2)	-2(1)	55(2)	-8(1)
C(1)	150(6)	16(1)	60(2)	-5(1)	36(3)	2(1)
C(2)	183(7)	22(1)	55(2)	19(2)	23(3)	11(1)
C(3)	176(7)	28(1)	50(2)	12(2)	39(3)	11(1)
C(4)	203(7)	24(1)	51(2)	7(2)	25(3)	-6(1)
C(5)	147(6)	30(1)	57(2)	-9(2)	5(3)	0(1)
C(6)	126(6)	30(1)	49(2)	19(2)	17(3)	3(1)
C(7)	113(5)	13(1)	44(2)	3(1)	24(2)	2(1)
C(8)	129(5)	17(1)	45(2)	0(1)	21(2)	0(1)
C(9)	126(5)	16(1)	48(2)	1(1)	26(3)	0(1)
C(10)	244(8)	18(1)	46(2)	6(2)	13(3)	-3(1)
C(11)	363(13)	51(1)	47(3)	52(4)	17(5)	18(2)
C(12)	190(7)	20(1)	58(2)	12(2)	31(3)	-1(1)
C(13)	610(19)	20(1)	102(4)	45(3)	110(7)	1(2)
C(14)	140(7)	53(2)	90(3)	25(3)	28(4)	15(2)
C(15)	254(8)	18(1)	110(4)	-19(2)	92(5)	-18(1)
C(16)	260(9)	16(1)	128(4)	-5(2)	96(5)	-15(1)

sis then revealed two alternative positions for these oxygen atoms with equal occupancy. An electron density difference map, calculated with the reflections below $\sin \theta/\lambda = 0.3 \text{ \AA}^{-1}$ clearly revealed the positions of all hydrogen atoms. Full matrix least squares refinement of all positional parameters and anisotropic thermal coefficients (with constant isotropic coefficients ($B = 5 \text{ \AA}^2$) for the hydrogen atoms) converged to $R = 0.037$ and $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega F_o^2] = 0.046$. No significant peak remained on the final difference Fourier synthesis. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 5, the anisotropic thermal parameters expressed in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ are given in Table 6. Principal distances and angles are listed in Tables 2 and 3, and Table 4 contains a selection of relevant least-squares planes.

References

- 1 Y. Wakatsuki, H. Yamazaki and H. Iwasaki, *J. Amer. Chem. Soc.*, **95** (1973) 5781.
- 2 H. Le Bozec, A. Gorgues and P. Dixneuf, *J. Amer. Chem. Soc.*, **100** (1978) 3946.
- 3 H. Le Bozec, A. Gorgues and P. Dixneuf, *J. Chem. Soc. Chem. Commun.*, (1978) 573.
- 4 M. Herberhold and M. Süss-Fink, *Angew. Chem.*, **89** (1977) 192; *Angew. Chem. Int. Ed. Engl.*, **16** (1977) 194.
- 5 C. Lelay, D. Touchard, H. Le Bozec and P. Dixneuf, IXth International conference on Organometallic Chemistry, Dijon sept. 3-7th, 1979.
- 6 H. Le Bozec, P.H. Dixneuf, A.J. Carty and N.J. Taylor; *Inorg. Chem.*, **17** (1978) 2569.
- 7 H. Le Bozec and P. Dixneuf, unpublished results.
- 8 M. Herberhold, M. Süss-Fink and G.C. Kreiter, *Angew. Chem.*, **89** (1977) 191; *Angew. Chem. Int. Ed. Engl.* **16** (1977) 193.
- 9 C. Barbeau, K.S. Dickmann and L. Ricard, *Canad. J. Chem.*, **61** (1973) 3027.
- 10 G. Le Borgne, E. Gentric and D. Grandjean, *Acta Cryst. B*, **31** (1975) 2824.
- 11 P. Friedrich, G. Besl, E.O. Fischer and G. Huttner, *J. Organometal. Chem.*, **139** (1977) C68.
- 12 International tables for X-ray crystallography, vol. IV, Kynoch Press, Birmingham, England (1974).
- 13 W.A. Herrmann, J. Plank, M.L. Ziegler and K. Weidenhammer, *Ang. Chem. Int. Ed. Engl.*, **17** (1978) 777.
- 14 S. Fontana, U. Schubert and E.O. Fischer, *J. Organometal. Chem.*, **146** (1978) 39.
- 15 V.A. Hädicke and W. Hoppe, *Acta Cryst.*, **B**, **27** (1971) 760.
- 16 W. Strohmeier and F.J. Müller, *Chem. Ber.*, **100** (1967) 2812.
- 17 H.D. Hartzler, *J. Amer. Chem. Soc.*, **95** (1973) 4379.
- 18 G. Germain, P. Mainie and M.M. Woolson, *Acta Cryst. A*, **27** (1971) 368.