

**PHOTOCHEMICAL SYNTHESIS AND CRYSTAL
STRUCTURE OF
DIMETHYLPHOSPHINODITHIATOMANGANESE(I)
TETRACARBONYL, [Mn(CO)₄(S₂PMe₂)]**

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Abstract—The new compound [Mn(CO)₄(S₂PMe₂)] (**A**) has been prepared by the photochemical reaction of Mn₂(CO)₁₀ and Me₂P(S)P(S)Me₂ in benzene solution. A single crystal X-ray diffraction study confirms that the manganese atom in **A** is six-coordinate with a distorted octahedral array of atoms around the metal centre: the dithiophosphinate ligand adopts a chelating bidentate mode of coordination. The two P—S distances [2.008(4) and 2.004(4) Å] are equal within the limits of experimental error, as indeed are the two Mn—S distances [2.419(4) and 2.423(4) Å]. The “bite” S ··· S distance is *ca* 3.196 Å. The Mn(CO)₄ moiety adopts local C_{2v} symmetry. The crystallographic data are backed up by an IR spectroscopic study.

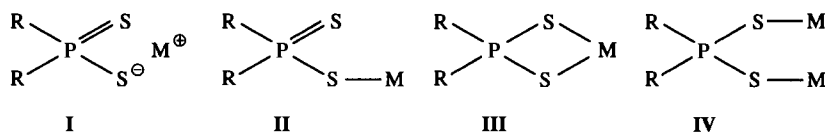
Transition metal complexes containing the dialkyldithiophosphinate (R₂PS₂[−]) or dialkyldithiophosphate [(RO)₂PS₂[−]] anions, or their diaryl analogues, form an extremely populous class of chemical compounds, which has attracted considerable attention.^{1–3} Part of this interest stems from the diverse uses which such compounds have found. Zinc dialkyldithiophosphates are used as engine oil additives to improve their extreme pressure properties. The sodium salt Na⁺[S₂P(OEt)₂][−] is used in the flotation collection of sulphide minerals, while the derivatives of (RO)₂P(S)SH (R = Me or Et) are of particular interest in the large-scale synthesis of pesticides. Such compounds also find application as antioxidants, corrosion inhibitors, detergents, catalysts (e.g. in the vul-

canization of rubber as precursors in the formation of thin layers of metal sulphides by metal organic chemical vapour deposition, and in solvent extraction processes.¹

The standard way to synthesize such derivatives is via the sodium salts Na⁺(R₂PS₂) or Na⁺[(RO)₂PS₂[−]] (R = alkyl or aryl). Four different modes of ligation of the dithiophosphinate anion have been identified. These are: ionic (**I**), monodentate (**II**), chelating bidentate (**III**) and bridging bidentate (**IV**).⁴ It has proved possible to distinguish **I**, **II** and **III** by means of either their proton-decoupled ³¹P NMR spectra⁴ or their IR spectra.^{5,6} Modes **III** and **IV** remain difficult to distinguish spectroscopically.^{4–6}

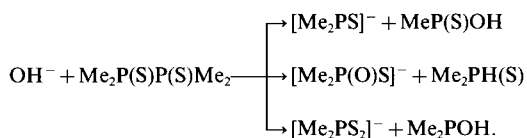
In this paper we report a novel photochemical route to the hitherto unknown manganese(I) tetracarbonyl derivative (CO)₄Mn(S₂PMe₂) (**A**). The preparation of **A** forms a part of our recent studies

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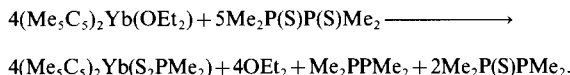


on the photochemical reactions of transition metal carbonyls with diphosphine disulphide ligands (e.g. $[\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2]$) in organic solvents.

Although the formation of a dialkyl dithiophosphinate derivative from tetramethyldiphosphine disulphide is perhaps at first sight unexpected, there are some precedents for such a reaction. The formation of, *inter alia*, $[\text{Me}_2\text{PS}_2]^-$ ions has been reported by the reaction of OH^- with $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ in the chemical ionization source of a mass spectrometer.⁷



It has also been reported that $\text{cp}^*_2\text{Yb}(\text{OEt}_2)$ ($\text{cp}^* = \text{Me}_5\text{C}_5$) reacts with $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ to yield $\text{cp}^*_2\text{Yb}(\text{S}_2\text{PMe}_2)$ (**B**) as the only metal-containing product to be isolated:⁸



Our synthesis of **A** is the first time, however, that any such reaction has been performed photochemically.

A single crystal X-ray diffraction study has been made on **A**, which has also been investigated by IR spectroscopy. It is shown that the dithiophosphinate ligand adopts a chelating bidentate mode of coordination (**III**). Thus, the molecular structure is shown to be similar to that proposed for the related species $(\text{CO})_4\text{Mn}\{\text{S}_2\text{P}(\text{OMe})_2\}$ (**C**).⁹ Compound **C** was synthesized some years ago by the reaction of $(\text{CO})_5\text{MnBr}$ and dimethyldithiophosphoric acid, $[\text{HS}_2\text{P}(\text{OMe})_2]$; its structural characterization, however, depended only upon IR spectra in the $\nu(\text{CO})$ region and upon ^1H NMR spectra.

EXPERIMENTAL

Preparation of **A**

Compound **A** was prepared by the photochemical reaction of $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ and $\text{Mn}_2(\text{CO})_{10}$. The ligand $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ was prepared via literature methods.^{10–12} A benzene solu-

tion of $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ (2 mmol, 0.372 g) and $\text{Mn}_2(\text{CO})_{10}$ (*ex. Aldrich*, 2 mmol, 0.780 g) was irradiated for 2 h using a 400 W medium pressure mercury lamp through a quartz-walled immersion well reactor. The reaction mixture was purged continually with dry nitrogen and the benzene solvent was dried and thoroughly degassed before use. An orange solution was obtained from which **A**, the major product, was separated chromatographically through a column packed with fluorisil using a 1 : 9 mixture of dichloromethane and n-pentane as eluant. Compound **A** was obtained as an orange solid. Single crystals of **A** were obtained by recrystallization from CH_2Cl_2 and slow evaporation of the solvent. A yield of approximately 18% was obtained. Elemental analyses were carried out using a Perkin–Elmer 240B microanalyser by Medac Ltd. at Brunel University. Found: C, 24.6; H, 2.22; S, 21.9. Calc: C, 24.6; H, 2.1; S, 21.9%.

Spectroscopic study

FAB mass spectra were recorded at the EPSRC Mass Spectrometry Centre at University College, Swansea on a VG Autospec instrument using caesium ion bombardment at 25 kV of the sample dissolved in 3-nitrobenzyl alcohol. IR spectra were recorded at the University of Reading on KBr discs using a Perkin–Elmer 1720-X Fourier transform spectrometer.

X-ray data collection

Crystal data are given in Table 1, together with refinement details. Data were collected with Mo-K_α radiation using the MAR research Image Plate System. The crystals were positioned at 75 mm from the Image Plate. Ninety-five frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.¹³ The structure was solved using direct methods with the SHELX86 program.¹⁴ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the methyl groups were included as components of rigid groups, each with a common thermal parameter. The structure was then refined using SHELX- ρ .¹⁵ All calculations were carried out on a Silicon Graphics R4000 work-

Table 1. Crystal data and structure refinement for **A**

Empirical formula	$\text{C}_6\text{H}_6\text{MnO}_4\text{PS}_2$
Formula weight	292.14
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system	triclinic
Space group	$P-1$
Unit cell dimensions	$a = 7.140(6)$ Å $b = 7.138(7)$ Å $c = 12.020(7)$ Å $\alpha = 99.12(1)^\circ$ $\beta = 107.98(1)^\circ$ $\gamma = 101.89(1)^\circ$
Volume	$553.69(12)$ Å ³
Z	2
Density (calculated)	1.752 Mg m ⁻³
Absorption coefficient	1.697 mm ⁻¹
$F(000)$	292
Crystal size	$0.2 \times 0.2 \times 0.2$ mm
Theta range for data collection	$1.83\text{--}25.06^\circ$
Index ranges	$0 \leq h \leq 8, -8 \leq k \leq 8, -14 \leq l \leq 13$
Reflections collected	1586
Refinement method	Full-matrix least-squares on F^2
Parameters	131
Goodness-of-fit on F^2	1.159
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.072, R_w = 0.239$
R indices (all data)	$R1 = 0.099, R_w = 0.293$
Largest diff. peak and hole	0.776 and -1.539 e Å ⁻³

station at the University of Reading. The dimensions for **A** are given in Table 2. Supplementary Publication Material includes atomic coordinates, anisotropic parameters and hydrogen positions. Coordinates have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The structure of **A** as determined by single crystal X-ray diffraction shows that the dialkyl dithiophosphate group adopts a chelating bidentate mode of ligation. The molecular structure is shown in Fig. 1, where the atom numbering scheme is also given. The sulphur atoms of the dialkyl-dithiophosphate group are bonded *trans* to CO groups, with the remaining two CO groups occupying axial sites. The manganese atom is thus six-coordinate (as is usual for manganese complexes⁹) with a somewhat distorted octahedral arrangement of the coordinating atoms.

The Mn—S [2.419(4) and 2.423(4) Å] and P—S [2.004(4) and 2.008(4) Å] distances are in line with those observed for related complexes. For example, in the molecule $[\text{Ni}(\text{S}_2\text{PPh}_2)_2]$ (**D**), the average Ni—S distance is 2.238 Å and the average P—S distance

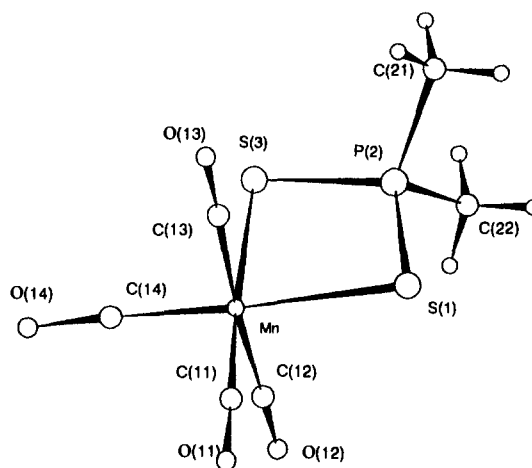


Fig. 1. Atom positions and numbering scheme for **A**.

is 2.014 Å.¹⁶ The somewhat longer metal–sulphur and rather shorter P—S distances in **A** as compared to **D** presumably reflect somewhat weaker coordination of the sulphur ligand in **A** and the increased formal oxidation state of the metal in **D**. The P—S distances in **A** are intermediate between those associated with formal single [2.122(1) Å]¹⁷ and double [range 1.923(5)–1.966(2) Å] phos-

Table 2. Bond lengths (Å) and angles (°) for **A**

Mn—C(14)	1.750(11)
Mn—C(11)	1.770(13)
Mn—C(12)	1.84(2)
Mn—C(13)	1.89(2)
Mn—S(1)	2.419(4)
Mn—S(3)	2.423(4)
S(1)—P(2)	2.008(4)
P(2)—C(21)	1.757(13)
P(2)—C(22)	1.768(13)
P(2)—S(3)	2.004(4)
C(11)—O(11)	1.16(2)
C(14)—O(14)	1.16(2)
O(12)—C(12)	1.15(2)
O(13)—C(13)	1.11(2)
C(14)—Mn—C(11)	91.3(6)
C(14)—Mn—C(12)	90.5(6)
C(11)—Mn—C(12)	92.5(6)
C(14)—Mn—C(13)	93.0(5)
C(11)—Mn—C(13)	91.1(5)
C(12)—Mn—C(13)	174.9(7)
C(14)—Mn—S(1)	175.9(4)
C(11)—Mn—S(1)	92.7(4)
C(12)—Mn—S(1)	88.4(4)
C(13)—Mn—S(1)	87.9(4)
C(14)—Mn—S(3)	93.5(4)
C(11)—Mn—S(3)	175.3(4)
C(12)—Mn—S(3)	87.7(5)
C(13)—Mn—S(3)	88.5(4)
S(1)—Mn—S(3)	82.57(12)
P(2)—S(1)—Mn	85.94(14)
C(21)—P(2)—C(22)	104.4(7)
C(21)—P(2)—S(3)	112.2(4)
C(22)—P(2)—S(3)	111.0(5)
C(21)—P(2)—S(1)	111.6(5)
C(22)—P(2)—S(1)	112.2(5)
S(3)—P(2)—S(1)	105.6(2)
P(2)—S(3)—Mn	85.93(14)
O(11)—C(11)—Mn	176.2(12)
O(14)—C(14)—Mn	178.2(11)
O(13)—C(13)—Mn	178.9(14)
O(12)—C(12)—Mn	178.8(12)

phorus–sulphur bonds.¹⁸ This finding suggests some delocalization of electrons and is in keeping with the observation that the two P—S distances in **A** are identical within the limits of experimental uncertainty. The S—P—S bond angle of 105.6 (2)° is somewhat larger than that found in **D** [101.3 (3)°].¹⁶ This angle for **A** gives a “bite” (S···S) distance of *ca* 3.196 Å.

The spectroscopic study of **A** is entirely in keeping with the single crystal X-ray diffraction study. The FAB mass spectrum shows fragmentation via successive loss of CO groups and fragmentation of the dialkyl dithiophosphinate ligand. Although the

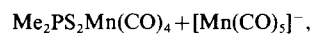
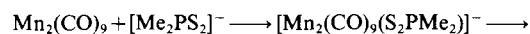
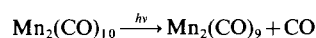
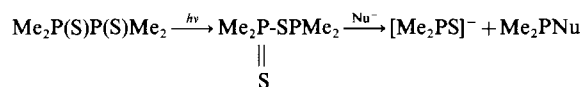
parent ion $[(\text{CO})_4\text{Mn}(\text{S}_2\text{PMe}_2)]^+$ (A^+) is seen with only very weak intensity, peaks due to other fragments are clearly observed at *m/z* values as listed below (N.B. only major features are listed, relative intensities are given in parentheses): 292 (12), A^+ ; 264 (30), $\text{A}^+ - \text{CO}$; 236 (100), $\text{A}^+ - 2\text{CO}$; 221 (50), $\text{A}^+ - (2\text{CO} + \text{Me})$; 203 (20), $\text{A}^+ - (\text{CO} + \text{Me}_2\text{P})$; 165 (25), $\text{A}^+ - (4\text{CO} + \text{Me})$; 119 (25) $\text{A}^+ - (4\text{CO} + \text{Me}_2\text{P})$. The ion giving rise to the feature at *m/z* = 119 is thus presumed to be $[\text{MnS}_2]^+$.

Compound **A** shows IR absorptions at the following positions (wavenumbers/cm⁻¹, relative intensities in parentheses): 2990 (vw), 2965 (w), 2860 (w), 2086 (wm), 2015 (vs), 1978 (s), 1936 (s), 1432 (wm), 1420 (w), 1300 (w), 1291 (wm), 942 (s), 847 (m), 726 (ms), 659 (ms), 635 (s), 618 (s), 581 (m), 546 (w), 503 (m), 479 (w), 427 (wm), 405 (m). These bands may all be assigned to vibrations of the dialkyl dithiophosphinate group^{5,6} or of the $\text{Mn}(\text{CO})_4$ moiety.¹⁹ We could obtain no reliable data in the spectral region 220–330 cm⁻¹, where complexes containing bidentate dithiophosphate ligands are reported to show one or two bands arising from $\nu(\text{M—S})$ (M = metal).⁶ Two regions of the IR spectrum are of particular interest and are worthy of further comment. In the region 540–670 cm⁻¹, bands are seen at 581 (medium intensity) and 546 (weak intensity) cm⁻¹ which may be assigned to antisymmetric and symmetric stretching modes of the PS_2 unit, respectively. The observation of two closely spaced bands arising from $\nu(\text{PS}_2)$ vibrations is entirely typical for bidentate chelating dithiophosphinate units (**III**), although for many such complexes only the more intense higher frequency band resulting from $\nu_{\text{as}}(\text{PS}_2)$ is reported. Thus, for example, **B** shows $\nu_{\text{as}}(\text{PS}_2)$ at 590 cm⁻¹,¹⁶ while a wide range of dithiophosphinate complexes are reported to show $\nu_{\text{as}}(\text{PS}_2)$ at 585 ± 5 cm⁻¹.² By contrast, monodentate dithiophosphinate complexes (**II**) show two well-separated bands in this region of the IR spectrum at *ca* 650 cm⁻¹ arising from $\nu(\text{P=S})$ and at *ca* 500 cm⁻¹ arising from $\nu(\text{P—S—M})$ (M = metal).^{5,6}

Bands arising from $\nu(\text{CO})$ vibrations are seen in the region 1950–2100 cm⁻¹. The $\text{Mn}(\text{CO})_4$ moiety has local C_{2v} symmetry. In this point group, the $\nu(\text{CO})$ vibrations transform as $a_1 + a_2 + b_1 + b_2$. All are IR active. Thus, it is expected that four IR bands should be observed in this region. They are seen at 2086 (weak-to-medium intensity), 2015 (very strong), 1978 (strong) and 1936 (strong) cm⁻¹. For comparison, **C** shows absorptions arising from $\nu(\text{CO})$ at 2095 (weak), 2020 (very strong), 2003 (strong) and 1965 (strong) cm⁻¹.⁹

Although the mechanism of reaction is clearly complex, it is pertinent at this point to make some

comment as to the possible reaction steps. It has been proposed that the ligand $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ may rearrange to $\text{Me}_2\text{PSP}(\text{S})\text{Me}_2$.⁷ Such a species would be prone towards nucleophilic attack to yield directly $[\text{Me}_2\text{PS}_2]^-$. There are two potential primary photolysis steps for $\text{Mn}_2(\text{CO})_{10}$ in solution. These are: (i) loss of CO; (ii) homolytic cleavage of the Mn—Mn bond to yield $\text{Mn}(\text{CO})_5$ radicals.^{20–23} In solvents of high “donicity”, products containing the 18-electron $[\text{Mn}(\text{CO})_5]^-$ ions may be formed by Mn—Mn bond heterolysis, e.g. in pyridine (py) the complex $[\text{Mn}(\text{py})_6][\text{Mn}(\text{CO})_5]_2$ is produced.²⁴ It is believed that this product is formed via the intermediacy of the complex $[\text{Mn}_2(\text{CO})_9\text{py}]$ and that heterolysis of the Mn—Mn bond occurs at a later stage.²³ Thus, a plausible mechanism which is in keeping with the known behaviour of $\text{Mn}_2(\text{CO})_{10}$ and of $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ is as follows:



A

where Nu is a nucleophile (N.B. in a reaction of this type involving phosphorus and sulphur species, many possible nucleophiles will certainly exist in solution). The mechanism is necessarily complex: the photochemistry of metal–metal bonded molecules is itself a very complicated area.²³ When a metal–metal bonded species is photolysed in the presence of a photochemically active ligand, then a complex reaction sequence is almost bound to occur.

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REFERENCES

1. N. N. Greenwood and A. Earnshaw, *The Chemistry of the Elements*. Pergamon Press, Oxford (1984).
2. D. J. Cole-Hamilton and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.* 1974, 739 and references cited therein.
3. W. R. Hills and M. Cowie, *Inorg. Chem.* 1990, **29**, 3349 and references cited therein.
4. C. Glidewell, *Inorg. Chim. Acta* 1977, **25**, 159.
5. J. Rockett, *Appl. Spectrosc.* 1962, **16**, 39.
6. M. Adams and J. B. Cornell, *J. Chem. Soc. A* 1968, 1299.
7. R. A. J. O’Hair, J. C. Sheldon and J. H. Bowie, *J. Chem. Soc., Dalton Trans.* 1988, 2837.
8. D. J. Berg, R. A. Andersen and A. Zalkin, *Organometallics* 1988, **7**, 1858.
9. F. A. Hartman and A. Wojcicki, *Inorg. Nucl. Chem. Lett.* 1966, **2**, 303.
10. T. Moeller, H. J. Birch and N. C. Nielson, *Inorg. Synth.* 1953, **4**, 71.
11. A. I. Vogel, *Practical Organic Chemistry*, 3rd edn. Longman, London (1977).
12. S. A. Butter and J. Chatt, *Inorg. Synth.* 1974, **15**, 186.
13. W. Kabsch, *J. Appl. Cryst.* 1988, **21**, 916.
14. G. M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467.
15. G. M. Sheldrick, *SHELXp, Program for Crystallographic Refinement*. University of Göttingen (1993).
16. P. Porta, A. Sgamellotti and N. Vinciguerra, *Inorg. Chem.* 1968, **7**, 2625.
17. E. Fluc, G. Gonzalez, K. Peers and G. H. von Schnerring, *Z. Anorg. Allg. Chem.* 1981, **473**, 51.
18. A. K. Kerr, P. M. Boorman, B. S. Misener and G. A. Van Roode, *Can. J. Chem.* 1977, **55**, 3081; T. S. Cameron and B. Dahlen, *J. Chem. Soc., Perkin II* 1975, 1737.
19. P. S. Braterman, *Metal Carbonyl Spectra*. Academic Press, London (1975).
20. M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.* 1975, **97**, 2065.
21. H. Yesaka, T. Kobayashi, K. Yasufuku and S. Nagakura, *J. Am. Chem. Soc.* 1983, **105**, 6249.
22. S. P. Church, H. Hermann, F.-W. Grevels and K. Schaffner, *J. Chem. Soc., Chem. Commun.* 1984, 785.
23. T. J. Meyer and J. V. Caspar, *Chem. Rev.* 1985, **85**, 187.
24. D. M. Allen, A. Cox, T. J. Kemp, Q. Sutana and R. B. Pitts, *J. Chem. Soc., Dalton Trans.* 1976, 1189.