

Absorption correction:
by integration (Siemens,
1996a)
 $T_{\min} = 0.750$, $T_{\max} = 0.905$
11 014 measured reflections
4038 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.059$
 $S = 0.995$
4038 reflections
282 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0153P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$R_{\text{int}} = 0.043$
 $\theta_{\max} = 25.93^\circ$
 $h = -11 \rightarrow 11$
 $k = -13 \rightarrow 13$
 $l = -13 \rightarrow 13$

$\Delta\rho_{\max} = 0.228 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.201 \text{ e } \text{\AA}^{-3}$

Extinction correction:
SHELXL97

Extinction coefficient:
0.0105 (5)

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu—O1	1.8994 (16)	Cu—N2	2.004 (2)
Cu—N1	1.938 (2)	Cu—N4	2.461 (2)
Cu—O2	1.9624 (15)		
O1—Cu—N1	92.86 (8)	O2—Cu—N2	89.35 (8)
O1—Cu—O2	169.81 (8)	O1—Cu—N4	101.52 (7)
N1—Cu—O2	83.21 (8)	N1—Cu—N4	93.37 (7)
O1—Cu—N2	92.95 (8)	O2—Cu—N4	88.14 (6)
N1—Cu—N2	168.28 (7)	N2—Cu—N4	95.43 (7)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N3—H31...O2	0.92 (1)	2.39 (1)	2.876 (3)	113 (1)
N3—H31...O3 ⁱ	0.92 (1)	2.15 (1)	3.027 (3)	159 (1)
N5—H51...O3 ⁱ	0.91 (1)	1.91 (1)	2.776 (3)	159 (1)

Symmetry code: (i) $1 - x, 2 - y, 2 - z$.

All H atoms except those on N atoms were included at calculated positions using *SHELXL97* (Sheldrick, 1997) and refined using a riding model. The U_{iso} values for the H atoms of CH and NH groups, and of the methyl groups were taken as $1.2U_{\text{eq}}$ and $1.5U_{\text{eq}}$, respectively, of the carrier atoms. The methyl groups of the pyrazole ligands were refined as rigid groups. The H31 and H51 atoms were found from difference Fourier syntheses and N—H distances were restrained to be equal. The analytical absorption correction based on face-indexing was carried out with the following faces and distances (mm): $\bar{1}00$ 0.0385, 100 0.0847, $01\bar{1}$ 0.1347, $0\bar{1}1$ 0.1540, 121 0.0770, 112 0.0847, $\bar{1}2\bar{1}$ 0.1193 and $1\bar{1}2$ 0.1540.

Data collection: *EXPOSE* (Stoe, 1997a). Cell refinement: *CELL* (Stoe, 1997b). Data reduction: *INTEGRATE* (Stoe, 1997c). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *XP* in *SHELXTL* (Siemens, 1996b). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1275). Services for accessing these data are described at the back of the journal.

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Bis(μ -3,4-dimethylphosphol-1-yl)bis(tetra-carbonylmanganese)

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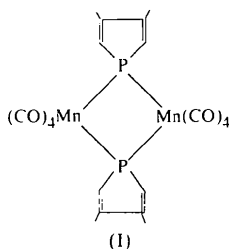
Abstract

In the title compound, $[\text{Mn}_2(\text{C}_6\text{H}_8\text{P})_2(\text{CO})_8]$, the μ_2 -bridging 3,4-dimethylphosphol-1-yl ligands show distinct localization of the C=C double bonds. The central Mn_2P_2 ring fragment is planar, with Mn—P bond lengths of 2.3586 (8) \AA .

Comment

The phospholyl ring ligand (phosphacyclopentadienyl) and its derivatives, e.g. 3,4-dimethylphospholyl, are well known to form various transition metal complexes and the ability of the ligand to act as different electron donors in different environments has been discussed thoroughly (Abel & Towers, 1979; Mathey *et al.*, 1983). In connection with our interest in bis(phosphido)-bridged transition metal carbonyl complexes (Flörke & Haupt, 1994, 1997), we investigated the structure of the title compound, (I). Only a few examples of complexes containing two phospholyl rings as three-electron bridging ligands are known. These include $(\mu\text{-L}')_2\text{M}_2(\text{CO})_8$,

with $M = \text{Mn}$, Re , and $L' = 2,3,4,5$ -tetraphenylphospholyl (Abel & Towers, 1979), and $(\mu-L)_2\text{Fe}_2(\text{CO})_6$, with $L = 3,4$ -dimethylphospholyl (Holand *et al.*, 1983). $(\mu-L)_2\text{Cr}_2(\text{CO})_{10}$ is described as a two-electron μ_2 -bridging-ligand complex (Holand *et al.*, 1984). The Mn and Re compounds have been identified by means of their IR spectra only. For the Fe and Cr compounds, IR, ^1H and ^{31}P NMR, and mass spectrometric data were recorded. Thus, the title compound is the first structurally characterized example of a doubly phospholyl-bridged dinuclear carbonyl complex.



The centre of the molecule lies on a special site with $2/m$ point symmetry. Both the Mn atoms and the axial carbonyl groups lie on the crystallographic mirror plane; the twofold axis runs through the P atoms and the centres of the opposite phospholyl C—C bonds. The Mn atoms have geometrically identical ligand environments, imposed by this symmetry. They show slightly distorted octahedral coordination with four CO ligands and two P atoms from the two bridging phospholyl rings. The CO groups display an eclipsed arrangement with C—Mn—Mn—C torsion angles of $0(2)^\circ$ for the axial ligands and $0.7(2)^\circ$ for the equatorial ones. The latter are almost coplanar with the Mn_2P_2 ring; the deviation of the C atoms from the plane is $0.008(3)$ Å. All axial C—Mn bond lengths are equal within experimental error, with an average value of $1.843(4)$ Å, but the equatorial C—Mn distances, $1.826(3)$ Å *trans* to the μ -P ligand, tend to be somewhat shorter.

The central Mn_2P_2 ring is planar with Mn1—P1 bond lengths of $2.3586(8)$ Å, and enclosed endocyclic angles Mn1—P—Mn1ⁱⁱ $101.75(4)$ and P1—Mn1—P1ⁱⁱ $78.26(4)^\circ$ [symmetry code: (ii) $-x, -y, -z$]. These are common structural features for such Mn_2P_2 ring complexes (Flörke & Haupt, 1993). The planar phospholyl ring and the Mn_2P_2 plane intersect at an angle of $89.5(1)^\circ$. The phospholyl bond lengths P—C4 $1.785(3)$, C4—C5 $1.338(4)$, C5—C5' $1.466(6)$ and C5—C6 $1.507(4)$ Å show almost entire localization of the C4—C5 double bonds [symmetry code: (i) $x, -y, -z$]. In contrast, crystallographically characterized complexes with η^5 -coordinating phospholyl groups exhibit delocalization effects to a large extent. For these structures, the phospholyl C—C bond lengths are almost equal, with average values ranging from $1.40(1)$ to $1.418(7)$ Å (Rosalky *et al.*, 1977; Holand *et al.*,

1986, 1983). Even for the osmium complex $[\text{Os}_3(\mu\text{-H})(\mu\text{-PC}_4\text{H}_2\text{Me}_2)(\mu_3\text{-C}_6\text{H}_4)(\text{CO})_9]$, likewise displaying a three-electron bridging pattern of the phospholyl group, distinctive π -electron delocalization is found, with an average C—C bond length of $1.35(6)$ Å (Deeming *et al.*, 1991). An example of localization of the phospholyl π -electrons is known: in the η^5 -coordinated complex $[(\text{CO})_5\text{W}(\text{PC}_4\text{H}_2\text{Me}_2)\{\eta^5\text{-W}(\text{CO})_5\}]$, the phospholyl ligand has a C=C double bond of $1.21(2)$ Å at the 3,4 position, with an average C—C single-bond length of $1.51(2)$ Å (Holand *et al.*, 1984).

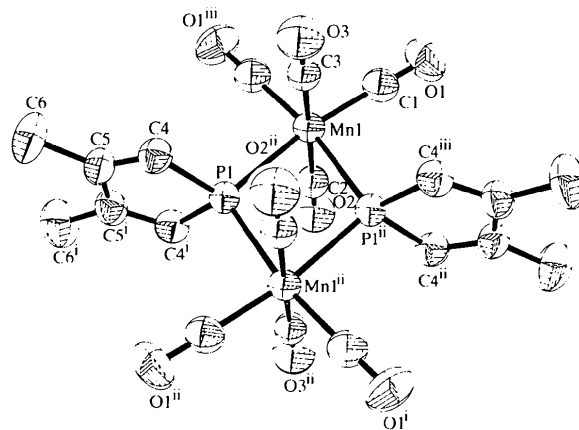


Fig. 1. The molecular structure of the title compound with H atoms omitted. Displacement ellipsoids are plotted at the 50% probability level. [Symmetry codes: (i) $x, -y, -z$; (ii) $-x, -y, -z$; (iii) $-x, y, z$.]

Experimental

The precursor complex $\text{Li}[(\text{CO})_5\text{WL}]$, (1), was synthesized according to literature methods (Holand *et al.*, 1986). $\text{Mn}_2(\text{CO})_9(\text{NCCH}_3)$ (403 mg) and (1) (404 mg), molar ratio 1:1 in THF solution, were reacted for 3 h at 323 K. After removing the volatiles *in vacuo*, the solid yellow residue was separated by TLC with *n*-hexane— CH_2Cl_2 (5:1), yielding 108.7 mg of the title compound. Yellow crystals were grown from CH_2Cl_2 solution. FT-IR, ^1H and ^{31}P NMR data for the title compound were measured. The four ν_{CO} stretching modes (cm^{-1} , cyclohexane) were as expected for a molecule with local C_2 symmetry: 2052 (*m*), 1988 (*vs*), 1973 (*s*), 1942 (*m*). ^1H NMR (CDCl_3): δ 6.3 p.p.m. (*m*, vinylic H), $^2\text{J}(\text{P-H}) = 31$ Hz. ^{31}P NMR (CDCl_3): δ -78.5 p.p.m.

Crystal data

$[\text{Mn}_2(\text{C}_6\text{H}_8\text{P})_2(\text{CO})_8]$
 $M_r = 556.15$
 Orthorhombic
Cmca
 $a = 16.886(3)$ Å
 $b = 12.481(2)$ Å
 $c = 11.521(2)$ Å
 $V = 2428.1(7)$ Å³
 $Z = 4$
 $D_x = 1.521$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 7\text{--}23^\circ$
 $\mu = 1.212$ mm⁻¹
 $T = 293(2)$ K
 Prism
 $0.27 \times 0.25 \times 0.20$ mm
 Yellow

Data collection

Siemens R3m/V diffractometer

 $\omega/2\theta$ scans

Absorption correction:

 ψ scans (North *et al.*, 1968) $T_{\min} = 0.731$, $T_{\max} = 0.761$

2902 measured reflections

1451 independent reflections

1034 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$ $\theta_{\text{max}} = 27.55^\circ$ $h = 0 \rightarrow 21$ $k = 0 \rightarrow 16$ $l = 0 \rightarrow 15$

(and some Friedel

equivalents)

4 standard reflections

every 400 reflections

intensity decay: <1%

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.075$ $S = 1.017$

1451 reflections

83 parameters

H-atom parameters

constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0378P)^2$ $+ 0.4082P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.320 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.385 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXTL (Siemens, 1995)

Extinction coefficient:

0.0003 (4)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a'_i a'_j$$

	x	y	z	U_{eq}
Mn1	0	0.08388 (4)	0.13025 (5)	0.0386 (2)
P1	-0.08814 (6)	0	0	0.0385 (3)
C1	0.0815 (2)	0.1395 (2)	0.2153 (2)	0.0532 (7)
O1	0.1337 (2)	0.1722 (2)	0.2672 (2)	0.0794 (7)
C2	0	0.2018 (3)	0.0331 (3)	0.0462 (9)
O2	0	0.2743 (2)	-0.0268 (3)	0.0672 (9)
C3	0	-0.0400 (3)	0.2165 (3)	0.0451 (9)
O3	0	-0.1167 (3)	0.2691 (3)	0.0715 (9)
C4	-0.1628 (2)	-0.0834 (2)	0.0623 (2)	0.0478 (6)
C5	-0.2355 (2)	-0.0481 (2)	0.0364 (2)	0.0540 (7)
C6	-0.3111 (2)	-0.1010 (3)	0.0756 (4)	0.0911 (13)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mn1—C1	1.826 (3)	P1—C4	1.785 (3)
Mn1—C3	1.838 (4)	C4—C5	1.338 (4)
Mn1—C2	1.849 (4)	C5—C5'	1.466 (6)
Mn1—P1	2.3586 (8)	C5—C6	1.507 (4)
P1—Mn1—P1 ⁱⁱ	78.26 (4)	C4—C5—C5'	113.4 (2)
C4—P1—C4'	90.2 (2)	C4—C5—C6	124.5 (3)
Mn1—P1—Mn1 ⁱⁱ	101.75 (4)	C5'—C5—C6	122.0 (2)
C5—C4—P1	111.5 (2)		

Symmetry codes: (i) $x, -y, -z$; (ii) $-x, -y, -z$.

Program(s) used to solve structure: SHELXTL (Siemens, 1995). Program(s) used to refine structure: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1530). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C54, 920–923[Ph₄P]₂[Sb₂S₁₅]

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Abstract

The reaction of antimony chloride, sulfur and tetraphenylphosphonium bromide in an aqueous ammonia solution under hydrothermal conditions yields orange crystals of bis(tetraphenylphosphonium) μ -sulfido- μ -tetrasulfido- $S^1:S^4$ -bis[(pentasulfido- S^1,S^5)antimonate], [(C₆H₅)₄P]₂[Sb₂S₁₅]. The structure contains tricyclic molecular Sb₂S₁₅²⁻ anions built up of two distorted ψ -trigonal bipyramidally coordinated antimony centres which are connected by two S_x²⁻ units ($x = 1, 4$) and bound to an additional S₅²⁻ ligand.

Comment

The structure of the title compound, (I), was determined as part of a project on the synthesis of new chalcogenide compounds using mild solvothermal conditions. Compared to the 'classical' high-temperature route, the low reaction temperatures applied in hydro- or solvothermal synthesis retaining thiometallate or polychalcogenide building blocks enable the construction of molecular or extended structures. Because of the variable coordina-