

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55517 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1002]

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## Dimanganese Octacarbonyl Compounds with Bridging Cyclohexylphosphanes

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### Abstract

Octacarbonyl-bis- $\mu$ -(cyclohexylphosphanido)-dimanganese,  $[\text{Mn}_2\{\mu\text{-PH}(\text{C}_6\text{H}_{11})\}_2(\text{CO})_8]$  (I), and octacarbonyl-bis- $\mu$ -(dicyclohexylphosphanido)-dimanganese,  $[\text{Mn}_2\{\mu\text{-P}(\text{C}_6\text{H}_{11})_2\}_2(\text{CO})_8]$  (II), have as a common structural fragment two edge-sharing Mn coordination octahedra with a planar  $\text{Mn}_2\text{P}_2$  ring. In (I), the hydrido and cyclohexyl ligands adopt *anti* positions. The average Mn—P bond lengths in (I) and (II) are 2.372(1) and 2.408(1) Å, respectively. The dicyclohexyl compound (II) has already been described [Flörke & Haupt (1993). *Acta Cryst.* C49. In the press] as a triclinic structure. Here we report a monoclinic modification.

### Comment

Both compounds belong to a series which contain  $\text{Mn}_2\text{P}_2$  rings and have the formula  $[\text{Mn}_2(\mu\text{-PLL}')_2(\text{CO})_8]$  [ $L = L' = \text{phenyl}$  (Masuda, Taga, Machida & Kawamura, 1987);  $L = L' = \text{H}$  (Deppisch, Schäfer, Binder & Leske, 1984);

$L = L' = \text{methyl}$  (Vahrenkamp, 1978);  $L = \text{H}$ ,  $L' = \text{phenyl}$  (Flörke & Haupt, 1993)]. As the geometrical centres of both molecules are situated on special sites [ $\bar{1}$  for (I),  $2/m$  for (II)], the rings are planar. This is also true for the other structures with the phosphorus substituents dimethyl, dihydrido, and hydrido/phenyl; the exception is the diphenyl compound which has a dihedral angle of  $4.1^\circ$ .

Both the triclinic and the new monoclinic structure of the dicyclohexyl compound exhibit the same bonding parameters. The average Mn—P bond lengths for the triclinic and monoclinic forms are 2.411(2) and 2.408(1) Å, respectively. The Mn—P—Mn and P—Mn—P angles are  $101.0(1)$  and  $79.0(1)^\circ$ , respectively, in the triclinic structure,  $101.4(1)$  and  $78.6(1)^\circ$  in the monoclinic. On going from the dicyclohexyl (II) to the monocyclohexyl compound (I), a decrease of the average Mn—P bond from 2.408(1) to 2.372(1) Å is evident. The corresponding endocyclic ring angles are  $103.0(1)^\circ$  at P and  $77.0(1)^\circ$  at Mn. The same effects apply in the phenyl compounds in which the average Mn—P distances decrease from 2.388(2) to 2.358(1) Å from the diphenyl to the hydrido/phenyl ligands. The ring angles are  $101.2(1)$  and  $103.1(1)^\circ$  at the P atom,  $78.7(1)$  and  $76.9(1)^\circ$  at Mn. As already pointed out by Deppisch *et al.* (1984), these endocyclic angles seem not to be affected to a great extent by the kind of phosphorus ligand. Even in the dihydrido compound with the sterically least demanding ligands, these angles remain nearly the same [ $103.9(1)$  and  $76.1(1)^\circ$ ]. The Mn—P bond distances, however, are strongly affected. These related alterations are the result of the different electronic properties of the ligands which, on going from the substitution pattern H/L to  $L_2$  ( $L = \text{phenyl}$  or cyclohexyl), lead in each case to an increasing +I effect at the  $\mu$ -P atom. As a result, the Mn—P bonds in the phenyl compounds are elongated by 0.030 Å and in the cyclohexyl compounds by 0.036 Å. In addition, the substitution of the  $L_2$  compounds (phenyl *versus* cyclohexyl) increases the bonds by 0.020 Å. This electronic effect has also been observed in  $(\mu_3\text{-H})_2(\mu\text{-PL}_2)(\text{CO})_6\text{Re}_3$  ( $L = \text{phenyl}$ , cyclohexyl; Haupt, Flörke & Schnieder, 1991).

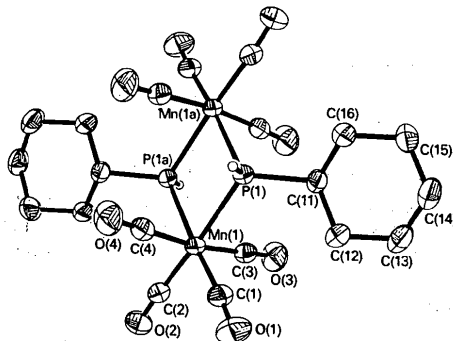


Fig. 1. Molecular structure of (I).

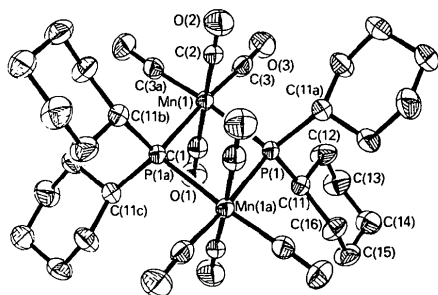


Fig. 2. Molecular structure of (II).

**Experimental****Compound (I)***Crystal data*[Mn<sub>2</sub>{PH(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>(CO)<sub>8</sub>}*M<sub>r</sub>* = 564.2

Triclinic

*P* $\bar{1}$ *a* = 8.555 (1) Å*b* = 8.604 (1) Å*c* = 9.869 (1) Å $\alpha$  = 103.12 (1)° $\beta$  = 115.15 (1)° $\gamma$  = 102.19 (1)°*V* = 600.1 (2) Å<sup>3</sup>*Z* = 1*D<sub>x</sub>* = 1.561 Mg m<sup>-3</sup>Mo *K*α radiation $\lambda$  = 0.71073 Å

Cell parameters from 30 reflections

 $\theta$  = 7–17° $\mu$  = 1.18 mm<sup>-1</sup>*T* = 293 K*F*(000) = 288

Prism

0.33 × 0.27 × 0.15 mm

Yellow

*Data collection*Siemens *R3m/V* diffractometer $\omega$ –2 $\theta$  scansAbsorption correction:  
empirical via  $\psi$  scans*T<sub>min</sub>* = 0.80, *T<sub>max</sub>* = 0.94

4273 measured reflections

2765 independent reflections

2366 observed reflections

[*F* > 4σ(*F*)]*R<sub>int</sub>* = 0.013 $\theta_{\max}$  = 27.5°*h* = 0 → 11*k* = –11 → 11*l* = –12 → 123 standard reflections  
monitored every 400

reflections

intensity variation: none

*Refinement*Refinement on *F*Final *R* = 0.024*wR* = 0.028*S* = 1.520

2366 reflections

148 parameters

Calculated weights *w* =  
1/[σ<sup>2</sup>(*F*) + 0.0001*F*<sup>2</sup>](Δ/σ)<sub>max</sub> = 0.001Δρ<sub>max</sub> = 0.23 e Å<sup>-3</sup>Δρ<sub>min</sub> = –0.22 e Å<sup>-3</sup>

The position of the phosphine H atom was located from the difference Fourier map and refined. Other H atoms were fixed at idealized positions and not refined.

**Compound (II)***Crystal data*[Mn<sub>2</sub>{P(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>(CO)<sub>8</sub>}*M<sub>r</sub>* = 728.5Mo *K*α radiation $\lambda$  = 0.71073 Å

Monoclinic

*C2/m**a* = 8.668 (4) Å*b* = 23.157 (11) Å*c* = 8.961 (4) Å $\beta$  = 107.03 (4)°*V* = 1719.8 (14) Å<sup>3</sup>*Z* = 2*D<sub>x</sub>* = 1.407 Mg m<sup>-3</sup>

Cell parameters from 25

reflections

 $\theta$  = 6–15° $\mu$  = 0.84 mm<sup>-1</sup>*T* = 293 K*F*(000) = 760

Prism

0.32 × 0.21 × 0.15 mm

Yellow

*Data collection*Siemens *R3m/V* diffractometer $\omega$ –2 $\theta$  scansAbsorption correction:  
empirical via  $\psi$  scans*T<sub>min</sub>* = 0.70, *T<sub>max</sub>* = 0.83

4212 measured reflections

2041 independent reflections

1571 observed reflections

[*F* > 4σ(*F*)]*R<sub>int</sub>* = 0.027 $\theta_{\max}$  = 27.5°*h* = –11 → 11*k* = –30 → 30*l* = 0 → 11

3 standard reflections

monitored every 400

reflections

intensity variation: none

*Refinement*Refinement on *F*<sup>2</sup>Final *R* = 0.040*wR* = 0.045*S* = 1.776

1571 reflections

108 parameters

H atoms fixed at idealized  
positions and not refinedCalculated weights *w* =1/[σ<sup>2</sup>(*F*) + 0.0001*F*<sup>2</sup>](Δ/σ)<sub>max</sub> = 0.001Δρ<sub>max</sub> = 0.55 e Å<sup>-3</sup>Δρ<sub>min</sub> = –0.28 e Å<sup>-3</sup>Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

|      | $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ |            |            | <i>U<sub>eq</sub></i> |
|------|--|------------|------------|-----------------------|
|      | <i>x</i>   | <i>y</i>   | <i>z</i>   |                       |
| (I)  |  |            |            |                       |
| Mn1  | 0.0790 (1)   | 0.9046 (1) | 0.1567 (1) | 0.032 (1)             |
| P1   | 0.1410 (1)   | 1.1671 (1) | 0.1166 (1) | 0.030 (1)             |
| C1   | 0.2469 (3)   | 0.9904 (2) | 0.3707 (2) | 0.043 (1)             |
| O1   | 0.3427 (2)   | 1.0406 (2) | 0.5062 (2) | 0.057 (1)             |
| C2   | 0.0171 (2)   | 0.6905 (2) | 0.1621 (2) | 0.039 (1)             |
| O2   | –0.0128 (2)  | 0.5589 (2) | 0.1708 (2) | 0.057 (1)             |
| C3   | 0.2430 (3)   | 0.8615 (2) | 0.0911 (2) | 0.040 (1)             |
| O3   | 0.3429 (2)   | 0.8342 (2) | 0.0493 (2) | 0.072 (1)             |
| C4   | –0.0904 (3)  | 0.9630 (2) | 0.2056 (2) | 0.041 (1)             |
| O4   | –0.1919 (2)  | 1.0031 (2) | 0.2389 (2) | 0.074 (1)             |
| C11  | 0.3840 (2)   | 1.2880 (2) | 0.1787 (2) | 0.033 (1)             |
| C12  | 0.5272 (3)   | 1.2872 (3) | 0.3376 (2) | 0.043 (1)             |
| C13  | 0.7230 (3)   | 1.3903 (3) | 0.3834 (3) | 0.049 (1)             |
| C14  | 0.7425 (3)   | 1.5706 (3) | 0.3891 (2) | 0.043 (1)             |
| C15  | 0.6028 (3)   | 1.5715 (3) | 0.2315 (3) | 0.049 (1)             |
| C16  | 0.4067 (3)   | 1.4719 (2) | 0.1874 (2) | 0.041 (1)             |
| (II) |  |            |            |                       |
| Mn1  | 0.1169 (1)   | 0.0000     | 0.3562 (1) | 0.030 (1)             |
| P1   | 0.0000   | 0.0662 (1) | 0.5000     | 0.027 (1)             |
| C1   | 0.2985 (5)   | 0.0000     | 0.5225 (5) | 0.037 (2)             |
| O1   | 0.4141 (4)   | 0.0000     | 0.6264 (4) | 0.054 (2)             |
| C2   | –0.0778 (6)  | 0.0000     | 0.2022 (5) | 0.035 (2)             |
| O2   | –0.1960 (5)  | 0.0000     | 0.1045 (4) | 0.060 (2)             |
| C3   | 0.1988 (4)   | 0.0550 (1) | 0.2556 (3) | 0.042 (2)             |
| O3   | 0.2547 (3)   | 0.0870 (1) | 0.1888 (3) | 0.067 (2)             |
| C11  | 0.1569 (3)   | 0.1140 (1) | 0.6331 (3) | 0.034 (2)             |
| C12  | 0.2447 (4)   | 0.1548 (1) | 0.5511 (3) | 0.050 (2)             |
| C13  | 0.3867 (4)   | 0.1847 (2) | 0.6656 (4) | 0.058 (2)             |
| C14  | 0.3370 (4)   | 0.2167 (2) | 0.7908 (4) | 0.050 (2)             |
| C15  | 0.2523 (4)   | 0.1762 (2) | 0.8739 (4) | 0.050 (2)             |
| C16  | 0.1083 (4)   | 0.1467 (1) | 0.7609 (3) | 0.045 (2)             |

Table 2. Selected bond lengths (Å) and angles (°)

|            |           |             |           |
|------------|-----------|-------------|-----------|
| (I)        |           |             |           |
| Mn1—P1     | 2.370 (1) | Mn1—P1A     | 2.374 (1) |
| P1—Mn1—P1A | 77.0 (1)  | Mn1—P1—Mn1A | 103.0 (1) |
| (II)       |           |             |           |
| Mn1—P1     | 2.408 (1) | Mn1—P1A     | 2.408 (1) |
| P1—Mn1—P1A | 79.0 (1)  | Mn1—P1—Mn1A | 101.0 (1) |

Compound (I) was obtained by the reaction of  $\text{Mn}_2(\text{CO})_{10}$  with cyclohexylphosphine in xylene solution in a glass tube at 443 K for 36 h and compound (II) by the reaction of  $\text{Mn}_2(\text{CO})_{10}$  with dicyclohexylphosphine dissolved in xylene in a glass tube at 433 K for 15 h. In both cases, the product was recrystallized from dichloromethane/pentane.

Scattering factors, structure solution, refinement, and all calculations for both structures: *SHELXTL-Plus* (Sheldrick, 1990). Other programs used: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55723 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1017]

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## *trans*-Dichlorobis(1,3-dihydrobenzo[*c*]thiophene-*S*)platinum(II)

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## Abstract

The asymmetric unit consists of two centrosymmetric half molecules of the title compound lying on

inversion centres. Both the Pt atoms have square-planar coordination with Pt—S distances 2.313 (2) and 2.309 (2) Å and Pt—Cl distances 2.299 (2) and 2.300 (2) Å. In both molecules, benzothiophene C atoms are almost planar [maximum deviations 0.05 (1) and 0.04 (1) Å] with S atoms lying 0.434 (7) and 0.329 (6) Å out of the planes comprising C atoms.

## Comment

Formation of coordination complexes between transition-metal species and organosulfur compounds could be employed as a means of removing sulfur compounds from effluents produced by pulp mills and other industrial facilities. Such complexes are also of intrinsic interest because of the fluxional behaviour of the sulfur ligand around the metal centre (Abel, 1990). The title compound (I) is an example of such a complex and was prepared by the interaction of 1,3-dihydrobenzo[*c*]thiophene with platinum(II) chloride in hot ethanolic solution. The crude product was purified by crystallization from ethanol. Full details of the preparative method have been published previously (Clark, Fait, Jones & Kirk, 1991).

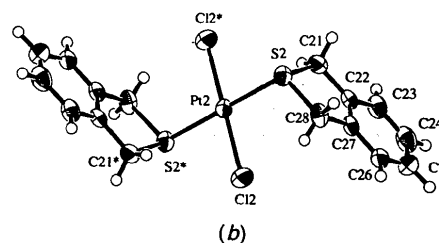
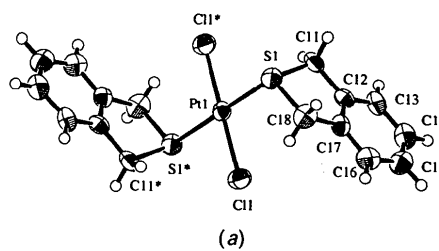
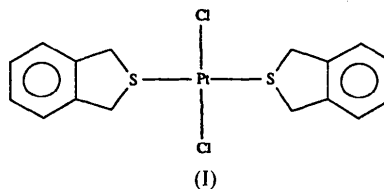


Fig. 1. Perspective views of the two independent molecules (a) and (b) of the title compound with crystallographic numbering scheme plotted by *ORTEPII* (Johnson, 1976).