

Zr1—N4	2.423 (5)	Zr101—N104	2.387 (5)
Zr1—N5	2.390 (5)	Zr101—N105	2.409 (5)
N1—Zr1—N2	101.7 (2)	N101—Zr101—N102	100.5 (2)
N1—Zr1—N3	117.0 (2)	N101—Zr101—N103	118.0 (2)
N2—Zr1—N3	141.2 (2)	N102—Zr101—N103	141.4 (2)
N1—Zr1—N4	100.6 (2)	N101—Zr101—N104	101.7 (2)
N2—Zr1—N4	87.7 (2)	N102—Zr101—N104	87.9 (2)
N3—Zr1—N4	83.5 (2)	N103—Zr101—N104	82.3 (2)
N1—Zr1—N5	100.7 (2)	N101—Zr101—N105	104.9 (2)
N2—Zr1—N5	87.2 (2)	N102—Zr101—N105	86.2 (2)
N3—Zr1—N5	87.7 (2)	N103—Zr101—N105	86.3 (2)
N4—Zr1—N5	158.7 (2)	N104—Zr101—N105	153.4 (2)

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**$\mu$ -Bromo- $\mu$ -cyclohexylphosphido-bis(tetra-carbonylmanganese) and  $\mu$ -Bromo- $\mu$ -(pentacarbonylmanganese)phosphido-bis-(tetracarbonylmanganese)†**

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**Abstract**

The central molecular fragment of the first title complex, [Mn<sub>2</sub>Br(C<sub>6</sub>H<sub>12</sub>P)(CO)<sub>8</sub>], is a four-membered non-planar Mn<sub>2</sub>BrP ring with a cyclohexyl ring and a H atom attached to the bridging P atom. In the related second title complex, [Mn<sub>3</sub>Br(PH)(CO)<sub>13</sub>], the cyclohexyl ligand is substituted by an Mn(CO)<sub>5</sub> group which displays an unusual ecliptic arrangement with the axial carbonyl ligands of the ring Mn atoms.

**Comment**

There exist few structural characterizations of dinuclear metal carbonyl complexes with one phosphido and one halogeno bridging group as the central molecular fragment  $MM'(\mu-X)(\mu-P)$  ( $X = \text{halogen}$ ). Most of the complexes comprise a direct metal–metal bond and show butterfly-like structures (*e.g.* Taylor, Mott & Carty, 1980; Fischer & Vahrenkamp, 1981; Geoffroy, Rosenberg, Herlinger & Rheingold, 1986; Jungbluth, Stöckli-Evans & Süß-Fink, 1989). A nearly planar arrangement of the  $MM'(\mu-X)(\mu-P)$  core as well as a non-bonding metal–metal separation are found in the complexes  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-I})(\mu\text{-PPH}_2)\text{Mn}(\text{CO})_4]$  (Horton, Mays, Adatia, Henrick & McPartlin, 1988) and  $[\text{Ph}_3\text{P}(\text{CO})_3\text{Re}(\mu\text{-I})(\mu\text{-PPH}_2)\text{Re}(\text{CO})_4]$  (Flörke & Haupt, 1991). The recent work (Flörke, 1996) on  $[(\text{CO})_4\text{Mn}(\mu\text{-Br})(\mu\text{-PH}_2)\text{Mn}(\text{CO})_4]$ , hereafter referred to as (III), was the first X-ray structure determination of a corresponding dimanganese complex with the bridging ligand  $X = \text{Br}$ .

We present here the two related title structures,  $[(\text{CO})_4\text{Mn}(\mu\text{-Br})\{\mu\text{-PH}(\text{C}_6\text{H}_{11})\}\text{Mn}(\text{CO})_4]$ , (I), and  $[(\text{CO})_4\text{Mn}(\mu\text{-Br})\{\mu\text{-PH}[\text{Mn}(\text{CO})_5]\}\text{Mn}(\text{CO})_4]$ , (II), which may be derived formally from (III) by substitution of one H atom attached to the  $\mu\text{-P}$  atom by a cyclohexyl ligand or an Mn(CO)<sub>5</sub> group, respectively. In both complexes, each Mn atom is approximately octahedrally

† Alternative names:  $\mu$ -bromo-octacarbonyl-1 $\kappa^4$ C,2 $\kappa^4$ C- $\mu$ -cyclohexylphosphanido-1:2 $\kappa^2$ P-dimanganese and  $\mu$ -bromo-1:2 $\kappa^2$ Br-tridecacarbonyl-1 $\kappa^4$ C,2 $\kappa^4$ C,3 $\kappa^5$ C- $\mu_3$ -phosphanido-1:2:3 $\kappa^3$ P-trimanganese.

The *ortho*-, *meta*- and *para*-C atoms of one of the 2,6-diisopropylamide ligands of Zr101 were found to be disordered over two sites as indicated by examination of their anisotropic displacement parameters in the final stages of structure refinement; half-occupancy isotropic atoms were refined. Suitable restraints were applied to the displacement parameters and to the C—C distances both between the two ring fragments and within the two rings. No attempt was made to model two sites for the two *ortho*-isopropyl group substituents or the *ipso*-C atom.

Data collection: *STADIA* (Stoe & Cie, 1995a). Cell refinement: *STADIA*. Data reduction: *XRED* (Stoe & Cie, 1995b). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

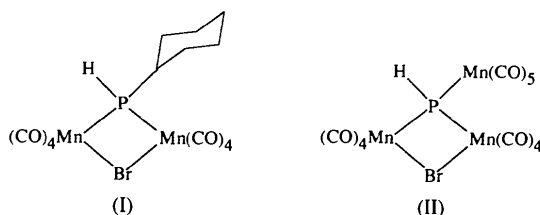
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1159). Services for accessing these data are described at the back of the journal.

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coordinated by four carbonyl groups and the bridging bromo and phosphido ligands. Both octahedra share a common edge along the P···Br vector. Thus, each molecule achieves  $C_s$  symmetry with a non-crystallographic mirror plane passing through both bridging atoms. The axial carbonyl groups show an eclipsic arrangement at the metal atoms. They are tilted 4.8 and 0.6° around the Mn···Mn vector for (I) and (II), respectively.



The Mn—Br bond lengths of both complexes are equal within experimental error, with an average value of 2.548 (1) Å for (I) and 2.545 (1) Å for (II). They are somewhat shorter than the corresponding length of 2.606 (5) Å in complex (III). The Mn—P bond lengths in (I), with an average value of 2.370 (2) Å, are shorter than the corresponding endocyclic distances for (II), with an average of 2.410 (1) Å, which is due to the different monovalent cyclohexyl and Mn(CO)<sub>5</sub> substituents, respectively. The average Mn—C bond lengths of carbonyl groups 1 and 5 for (I) [1.798 (6) Å] and 2 and 5 for (II) [1.789 (4) Å], which are *trans* to the  $\mu$ -Br ligands, are shorter than the other Mn—C bonds [1.851 (6) and 1.850 (5) Å, respectively]. Similar effects of shortened *M*—C bonds *trans* to bridging-halogen ligands are known from the literature (Lal De, 1983; Taylor *et al.*, 1980; Geoffroy *et al.*, 1986, and references therein).

The long Mn···Mn distances of 3.702 (1) Å in (I) and 3.737 (1) Å in (II) are non-bonding, as expected on the basis of the 18 valence-electron rule. They are comparable to the metal—metal separations of 3.717 Å in (III) and 3.703 Å in [(CO)<sub>4</sub>Mn( $\mu$ -PH<sub>2</sub>)<sub>2</sub>Mn(CO)<sub>4</sub>] (Deppisch, Schäfer, Binder & Leske, 1984).

The endocyclic ring angles for (I) and (II) are almost equal with Mn—P—Mn 102.68 (6) and 101.64 (4)°, Mn—Br—Mn 93.21 (4) and 94.48 (3)°, and average P—Mn—Br 81.92 (5) and 81.59 (3)°, respectively. The values for (III), in the same order, are 106.4 (2), 90.9 (1) and 81.3 (3)°. The corresponding Mn<sub>2</sub>PBr rings of both title complexes are not planar but folded with PBrMn/MnBrP dihedral angles of 5.4 (I) and 8.4° (II).

Accordingly, for (I), the axial carbonyl ligands 3 and 7 on the cyclohexyl side show a non-bonding intramolecular O3···O7 distance of 3.638 (6) Å, whereas the *trans* positioned carbonyl ligands 4 and 8, which face the H atom ligand, are only 3.310 (6) Å apart. In the symmetrically P-substituted complex (III), the separations of the axial carbonyl groups are roughly equal (O···O 3.57 and 3.48 Å). For complex (II), however, the

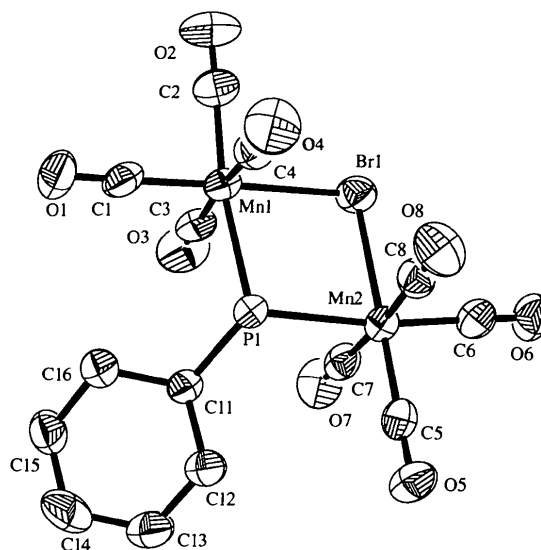


Fig. 1. The molecular structure of (I) with H atoms omitted. Displacement ellipsoids are plotted at the 50% probability level.

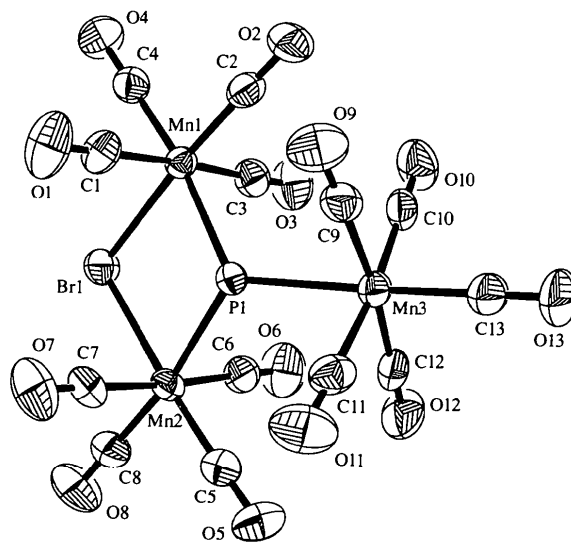


Fig. 2. The molecular structure of (II) with the H atom omitted. Displacement ellipsoids are plotted at the 50% probability level.

O1···O7 separation on the hydrogen side [3.800 (5) Å] is much larger than that for O3···O6 [3.351 (5) Å] on the Mn(CO)<sub>5</sub> side. This is accompanied by the unexpected arrangement of the Mn(CO)<sub>5</sub> group which shows an eclipsic arrangement of its carbonyl ligands with respect to the already mentioned axial carbonyl ligands. This gives rise to somewhat short intramolecular distances which include the axial carbonyl ligands [O6···O12 3.111 (6) and O3···O10 3.135 (5) Å], as well as the equatorial groups 2 and 5 with an average O···O distance of 3.184 (6) Å to the carbonyl groups 9 to 12. This observed eclipsic arrangement of the carbonyl ligands is unusual and all examples of related complexes with a terminal *M*(CO)<sub>5</sub> group attached to a  $\mu_2$ -P atom

documented so far show the Mn(CO)<sub>5</sub> group rotated about the  $\mu$ -P—M bond by about 45° to give a staggered arrangement of the carbonyl ligands (Huttner, Mohr, Friedrich & Schmid, 1978; Ajulu, Hitchcock, Mathey & Nixon, 1993; Flörke & Haupt, 1995).

Intermolecular contacts shorter than the sum of van der Waals radii are valid only for the packing of (I), with C15—H15A...Br 2.89 Å (corrected for C—H = 1.08 Å).

## Experimental

Complex (I) was obtained as a by-product from the reaction of [Mn<sub>2</sub>( $\mu$ -H){ $\mu$ -PH(C<sub>6</sub>H<sub>11</sub>)}] with the non-nucleophilic base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and C<sub>2</sub>H<sub>5</sub>Br in THF solution at 298 K. For complex (II), [Mn<sub>2</sub>( $\mu$ -Br)( $\mu$ -PH<sub>2</sub>)(CO)<sub>8</sub>] (Schäfer, 1978) was reacted with BrMn(CO)<sub>5</sub> in THF solution at 195 K. The solution was then allowed to reach room temperature and after 3 h the solvent was vacuum stripped. Complex (II) was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane solution.

### Compound (I)

#### Crystal data

[Mn<sub>2</sub>Br(C<sub>6</sub>H<sub>12</sub>P)(CO)<sub>8</sub>]

$M_r = 529.0$

Monoclinic

$P2_1/n$

$a = 9.933(2) \text{ \AA}$

$b = 17.111(3) \text{ \AA}$

$c = 12.076(2) \text{ \AA}$

$\beta = 108.21(2)^\circ$

$V = 1949.7(6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.802 \text{ Mg m}^{-3}$

$D_m$  not measured

#### Data collection

Siemens R3 diffractometer

$\omega$ - $2\theta$  scans

Absorption correction:

$\psi$  scans (North, Phillips & Mathews, 1968)

$T_{\min} = 0.461$ ,  $T_{\max} = 0.500$

4650 measured reflections

4450 independent reflections

2319 reflections with

$I > 2\sigma(I)$

#### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.0448$

$wR(F^2) = 0.0994$

$S = 1.032$

4448 reflections

239 parameters

H atoms riding, except H1 coordinates refined

$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 1.4278P]$

where  $P = (F_o^2 + 2F_c^2)/3$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 7.5$ – $17.0^\circ$

$\mu = 3.463 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prism

$0.41 \times 0.22 \times 0.20 \text{ mm}$

Orange

$R_{\text{int}} = 0.036$

$\theta_{\text{max}} = 27.56^\circ$

$h = -12 \rightarrow 12$

$k = 0 \rightarrow 22$

$l = 0 \rightarrow 15$

3 standard reflections

every 400 reflections

intensity decay:

insignificant

$(\Delta/\sigma)_{\text{max}} = -0.001$

$\Delta\rho_{\text{max}} = 0.381 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.363 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL

Extinction coefficient:

0.00026 (14)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I)

Br1—Mn2	2.5459 (12)	Mn1—P1	2.370 (2)
Br1—Mn1	2.5495 (10)	Mn2—C5	1.798 (5)
Mn1—C1	1.798 (6)	Mn2—C6	1.849 (6)
Mn1—C2	1.829 (6)	Mn2—C8	1.861 (6)
Mn1—C4	1.850 (6)	Mn2—C7	1.863 (6)
Mn1—C3	1.853 (6)	Mn2—P1	2.371 (2)
Mn2—Br1—Mn1	93.21 (4)	P1—Mn2—Br1	81.94 (4)
P1—Mn1—Br1	81.89 (5)	Mn1—P1—Mn2	102.68 (6)

### Compound (II)

#### Crystal data

[Mn<sub>3</sub>Br(PH)(CO)<sub>13</sub>]

$M_r = 640.84$

Triclinic

$P\bar{1}$

$a = 8.735(2) \text{ \AA}$

$b = 8.953(1) \text{ \AA}$

$c = 13.837(4) \text{ \AA}$

$\alpha = 81.57(2)^\circ$

$\beta = 84.59(2)^\circ$

$\gamma = 74.68(2)^\circ$

$V = 1030.6(4) \text{ \AA}^3$

$Z = 2$

$D_x = 2.065 \text{ Mg m}^{-3}$

$D_m$  not measured

#### Data collection

Siemens R3m diffractometer

$\omega$ - $2\theta$  scans

Absorption correction:

$\psi$  scans (North, Phillips & Mathews, 1968)

$T_{\min} = 0.486$ ,  $T_{\max} = 0.652$

4984 measured reflections

4760 independent reflections

3612 reflections with

$I > 2\sigma(I)$

#### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.0398$

$wR(F^2) = 0.0951$

$S = 1.018$

4760 reflections

285 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.2887P]$

where  $P = (F_o^2 + 2F_c^2)/3$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7$ – $17^\circ$

$\mu = 3.889 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prism

$0.37 \times 0.20 \times 0.11 \text{ mm}$

Red

$R_{\text{int}} = 0.041$

$\theta_{\text{max}} = 27.56^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = 0 \rightarrow 18$

4 standard reflections

every 400 reflections

intensity decay:

insignificant

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.488 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.696 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL

Extinction coefficient:

0.0037 (6)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II)

Br1—Mn1	2.5439 (9)	Mn2—C5	1.786 (4)
Br1—Mn2	2.5457 (9)	Mn2—C8	1.825 (4)
Mn1—C2	1.792 (4)	Mn2—C6	1.855 (5)
Mn1—C4	1.845 (4)	Mn2—C7	1.855 (4)
Mn1—C3	1.859 (4)	Mn2—P1	2.4113 (12)
Mn1—C1	1.860 (4)	Mn3—P1	2.4505 (12)
Mn1—P1	2.4092 (11)		
Mn1—Br1—Mn2	94.48 (3)	Mn1—P1—Mn2	101.64 (4)
P1—Mn1—Br1	81.62 (3)	Mn1—P1—Mn3	123.66 (4)
P1—Mn2—Br1	81.55 (3)	Mn2—P1—Mn3	124.11 (4)

For both compounds, program(s) used to solve structures: *SHELXTL* (Siemens, 1995); program(s) used to refine structures: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1213). Services for accessing these data are described at the back of the journal.

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## Layered Tetramethylammonium Vanadium Oxide $[N(CH_3)_4]V_3O_7$ by X-ray Rietveld Refinement

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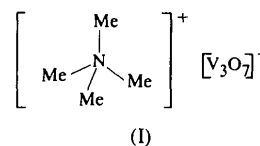
## Abstract

Tetramethylammonium trivanadium heptaoxide crystallizes in the monoclinic space group  $P2_1/n$  when prepared hydrothermally. Its structure was solved from conventional X-ray powder diffraction with final  $R(\text{Bragg}) = 0.052$  and  $R(\text{prof}) = 0.078$ . Vanadium coordination polyhedra are square pyramids and a tetrahedron which

form layers parallel to the  $bc$  plane. The tetramethylammonium cations are incorporated between the layers.

## Comment

Recently, using mild hydrothermal synthesis (Whittingham *et al.*, 1995), we have produced metastable vanadium oxides with the vanadium in a reduced oxidation state:  $[N(CH_3)_4]V_4O_{10}$  (Zavalij, Whittingham, Boylan, Pecharsky & Jacobson, 1996),  $Li_xV_{2-y}O_{4-y} \cdot H_2O$  (Chirayil, Zavalij & Whittingham, 1996a) and  $Li_xV_{2-y}O_{4-y}$  (Chirayil, Zavalij & Whittingham, 1996b) with open frameworks, as well as a cluster compound  $\{[Li(H_2O)_4]_2V_{10}O_{28} \cdot 4H_2O\}^{4-}$  (Zavalij, Chirayil, Whittingham, Pecharsky & Jacobson, 1997) with vanadium in the highest oxidation state. We report here the structure of a new layered vanadium oxide  $[N(CH_3)_4]V_3O_7$ , (I).



Two V atoms have square-pyramidal (SP) coordination with double-bonded O atoms in the vertex, while a third V atom has a tetrahedral coordination. The square pyramids form a  $VO_3$  chain along the  $b$  axis by sharing the two edges of their base (Fig. 1). The middle square pyramid (V1) shares two opposite edges of the base and the corner pyramid (V2) shares two neighbor-

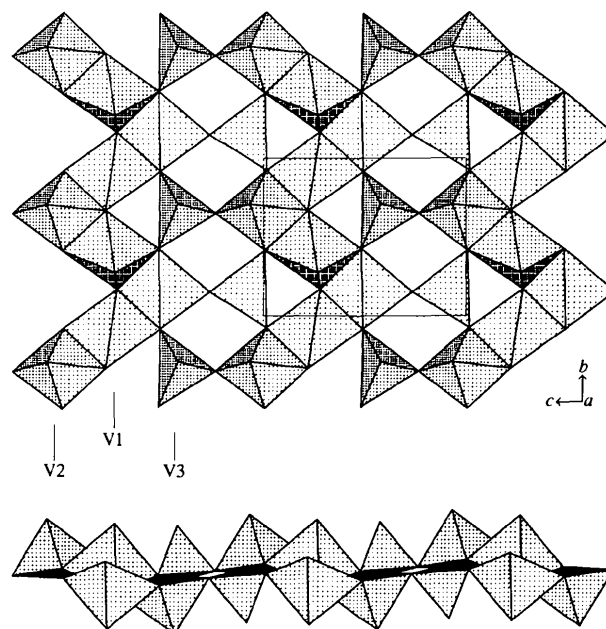


Fig. 1.  $V_3O_7$  layer shown by square pyramids (middle, V1; corner, V2) and tetrahedra (V3).