

## The first example of a silver–manganese–rhenium cluster complex: heptacarbonyl- $1\kappa^3C, 2\kappa^4C$ - $\mu$ -dicyclohexylphosphido- $1:2\kappa^2P$ -bis(triphenylphosphine)- $1\kappa P, 3\kappa P$ -triangulo-manganese–rhenium–silver with disordered solvent<sup>1</sup>

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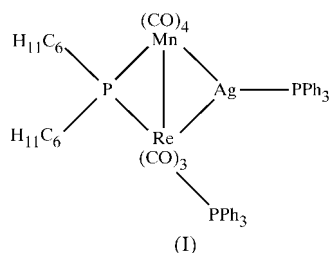
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The title compound,  $[\text{ReMnAg}(\text{C}_{12}\text{H}_{22}\text{P})(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})_7]$ , is the first crystallographically characterized silver–manganese–rhenium cluster. Due to intramolecular steric repulsion, the central  $\text{AgMnRe}(\mu\text{-P})$  ring deviates greatly from planarity. Metal–metal distances are Mn–Re 3.1712 (8), Ag–Mn 2.7367 (8) and Ag–Re 2.8485 (6) Å.

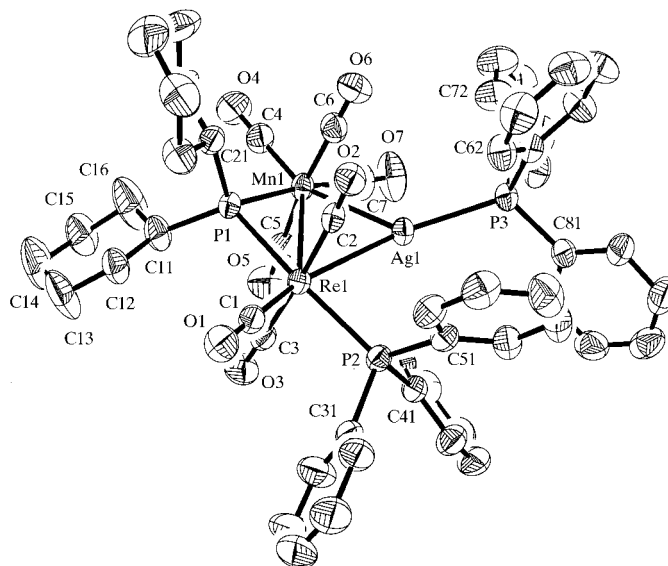
### Comment

Compounds of the type  $M_2(M'PR_3)(\mu\text{-}PR'_2)(\text{CO})_8$  ( $M_2 = \text{Mn}_2, \text{Re}_2, \text{MnRe}$ ;  $R, R' =$  organic residue) serve as precursor complexes for the synthesis of metallatetrahedrane structures (Haupt *et al.*, 1999; Petters, 1999). In this context, the title compound, (I), is the first crystallographically characterized heteronuclear coin metal–manganese–rhenium cluster.



The basic structural element is the  $\text{AgMnRe}$  triangle with a  $\mu\text{-PCy}_2$  group (Cy is cyclohexyl) which bridges the Mn–Re bond to form an  $\text{AgMnReP}$  ring. Similar ring patterns are known for related compounds, *e.g.*  $\text{Re}_2(\text{CuPPh}_3)(\mu\text{-PCy}_2)(\text{CO})_8$  (Flörke & Haupt, 1992),  $\text{Mn}_2(\text{AuPMe}_2\text{Ph})(\mu\text{-PPh}_2)(\text{CO})_8$  (Iggo *et al.*, 1984) or  $\text{Re}_2(\text{AuPPh}_3)(\mu\text{-PPh}_2)(\text{CO})_7(\text{PPh}_2)$  (Haupt *et al.*, 1999). The Mn atom has four terminal

carbonyl groups and the P atom as non-metal ligands. Its distorted octahedral coordination sphere is completed by the Ag atom. The same coordination geometry is valid for the Re atom, but one equatorial CO group is substituted by a  $\text{PPh}_3$  ligand. These ligands at both metal atoms show eclipsed arrangements, with C–Mn–Re–C and C–Mn–Re–P torsion angles ranging from 1.2 (2) to 7.9 (4)° (absolute values). The central  $\text{AgMnReP}$  ring is not planar but folded along the Mn–Re bond, with a  $\text{PMnRe/ReMnAg}$  dihedral angle of 24.4 (1)°. This corresponds to a position of the Ag atom 0.949 (1) Å above the  $\text{MnReP1}$  plane and is in contrast to related but nearly planar ring structures of the type  $M_2(M'PR_3)(\mu\text{-}PR'_2)(\text{CO})_7L$ , where the coin metal deviations are only in the range 0.011 (1) to 0.260 (2) Å from the  $M_2P$  planes [ $M = \text{Re}, M' = \text{Ag}, L = \text{CO}$  (Flörke & Haupt, 1999);  $M' = \text{Cu}$  (Flörke & Haupt, 1992);  $M' = \text{Au}, L = \text{ax-PhPh}_2$  (Haupt *et al.*, 1999);  $M = \text{Mn}, M' = \text{Au}, L = \text{CO}$  (Iggo *et al.*, 1984; Haupt *et al.*, 1992, 1995)]. This strong folding of the  $\text{AgMnReP}$  ring is obviously due to endeavours to minimize intramolecular steric repulsions between the  $\text{PPh}_3$  ligand on the Ag atom and that attached to rhenium, which is in an equatorial position *trans* to the  $\mu\text{-P}$  bridge. The P2 atom of this  $\text{PPh}_3$  ligand lies 0.165 (1) Å below the plane in consideration. Comparison with the related monosubstituted but almost planar compound  $\text{Re}_2(\text{AuPPh}_3)(\mu\text{-PPh}_2)(\text{CO})_7(\text{PPh}_2)$ , with an axially attached  $\text{PPh}_2$  ligand, shows that the Au atom is only 0.011 (1) Å above the  $\text{Re}_2P$  plane. The Mn–Re single bond of (I) measures 3.1712 (8) Å; this is nearly the same as the value of 3.164 (1) Å in  $\text{MnRe}(\text{RhPPh}_3)(\mu\text{-PCy}_2)(\text{CO})_8$  (Beckers *et al.*, 1995), but clearly longer than the value of 3.0397 (7) Å in  $\text{MnRe}(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_8$  (Flörke *et al.*, 1995), both of which represent the only other known  $\mu\text{-P}$ -bridged Mn–Re complexes. The  $M\text{-P1}$  bond lengths of 2.3193 (14) Å (Mn) and 2.4020 (12) Å (Re) reflect the different metal radii; the enclosed Mn–P–Re angle is 84.37 (4)°. The Ag–Mn and


**Figure 1**

The molecular structure of the title compound with the H atoms omitted. Displacement ellipsoids are drawn at the 50% probability level.

<sup>1</sup> Dedicated to Professor Hans-Jürgen Haupt on the occasion of his 65th birthday.

Ag—Re single-bond lengths are 2.7367 (8) and 2.8485 (6) Å, respectively. This is the first characterized unsupported Ag—Mn bond, as the only other known Ag—Mn structure units are bridged by  $\mu$ -CO,  $\mu$ -H or  $\mu_3$ -H ligands and exhibit metal—metal distances ranging from 2.902 to 3.044 Å (Horton *et al.*, 1988; Carreño *et al.*, 1992, 1994). Few Ag—Re interactions have been reported, of which the related  $\text{Re}_2\text{Ag}(\mu\text{-P})$ -type structures show Ag—Re bond lengths of 2.7957 (7) and 2.8235 (7) Å in  $\text{Re}_2(\text{AgPPh}_3)(\mu\text{-PCy}_2)(\text{CO})_8$  (Flörke & Haupt, 1999), and 2.8199 (9) and 2.8476 (6) Å in  $\text{Re}_2(\text{AgPPh}_3)[\mu\text{-S}(2\text{-naphthyl})](\text{CO})_8$  (Egold *et al.*, 1999). The distorted Y-shaped coordination at the Ag atom, with Re—Ag—P3, Mn—Ag—P3 and Re—Ag—Mn angles of 155.10 (3), 131.20 (4) and 69.16 (2)°, respectively, is a common structural pattern known from other  $M_2(M'PR_3)$  units, *e.g.*  $\text{Re}_2[M'(\text{CO})_2\text{PPh}_3](\mu\text{-PR}_2)(\text{CO})_8$  with  $M' = \text{Rh}$  or  $\text{Ir}$  (Haupt *et al.*, 1994), or the above-mentioned coin metal complexes  $M_2(M'PR_3)(\mu\text{-PR}'_2)(\text{CO})_7L$ .

## Experimental

A solution of  $\text{MnRe}(\mu\text{-H})(\mu\text{-PCy}_2)(\text{CO})_8$  (0.189 mmol) in tetrahydrofuran (8 ml) was reacted at 183 K with one equivalent of *n*-BuLi in hexane. After stirring for 15 min, the solution was allowed to warm to room temperature and one equivalent of  $\text{ClAgPPh}_3/\text{PPh}_3$  was added. After removal of the solvent, the products were separated by thin-layer chromatography (eluant  $\text{CH}_2\text{Cl}_2/n$ -hexane, 1:1). The title compound was recrystallized from  $\text{CH}_2\text{Cl}_2/n$ -hexane.

### Crystal data

$[\text{ReMnAg}(\text{C}_{12}\text{H}_{22}\text{P})(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})_7]$	$Z = 2$
$M_r = 1266.89$	$D_x = 1.531 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.583$ (1) Å	Cell parameters from 31 reflections
$b = 12.842$ (2) Å	$\theta = 7.4\text{--}17.5^\circ$
$c = 20.728$ (3) Å	$\mu = 2.91 \text{ mm}^{-1}$
$\alpha = 96.70$ (1)°	$T = 293$ (2) K
$\beta = 98.76$ (1)°	Prism, orange
$\gamma = 113.20$ (1)°	$0.42 \times 0.22 \times 0.08 \text{ mm}$
$V = 2747.4$ (6) Å <sup>3</sup>	

### Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.022$
$\omega$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 15$
$T_{\text{min}} = 0.508$ , $T_{\text{max}} = 0.844$	$k = -16 \rightarrow 15$
14452 measured reflections	$l = -26 \rightarrow 26$
12576 independent reflections	3 standard reflections
8862 reflections with $I > 2\sigma(I)$	every 397 reflections
	intensity decay: <1%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.087$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.89$	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
12576 reflections	$\Delta\rho_{\text{min}} = -0.92 \text{ e \AA}^{-3}$
614 parameters	Extinction correction: <i>SHELXL</i>
H-atom parameters constrained	Extinction coefficient: 0.00034 (7)

H atoms were included in the refinement as riding, with isotropic displacement parameters  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The substantial anisotropic displacement parameters of the cyclohexyl C11—C16

**Table 1**

Selected geometric parameters (Å, °).

Re1—P1	2.4020 (12)	Ag1—P3	2.4688 (12)
Re1—P2	2.4168 (12)	Ag1—Mn1	2.7367 (8)
Re1—Ag1	2.8485 (6)	Mn1—P1	2.3193 (14)
Re1—Mn1	3.1712 (8)		
P1—Re1—P2	169.54 (4)	P3—Ag1—Re1	155.10 (3)
P1—Re1—Ag1	97.42 (3)	Mn1—Ag1—Re1	69.16 (2)
P2—Re1—Ag1	74.86 (3)	P1—Mn1—Ag1	102.66 (4)
P1—Re1—Mn1	46.71 (3)	P1—Mn1—Re1	48.92 (3)
P2—Re1—Mn1	123.50 (3)	Ag1—Mn1—Re1	57.086 (18)
Ag1—Re1—Mn1	53.757 (17)	Mn1—P1—Re1	84.37 (4)
P3—Ag1—Mn1	131.20 (4)		

atoms indicate some degree of (orientational) disorder which was impossible to resolve. Therefore, the geometric parameters for this cyclohexyl group are less reliable. Additionally, it was not possible to resolve diffuse electron-density residuals (enclosed solvent molecules). Treatment with the *SQUEEZE* facility from *PLATON* (Spek, 1990), with a localized void of about 215 Å<sup>3</sup> at (0,  $\frac{1}{2}$ , 0) and 24 recovered electrons, resulted in a smooth refinement. Since a few low-order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for  $D(\text{calc})$ ,  $F(000)$  and the molecular weight are only valid for the ordered part of the structure.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS* (Bruker, 1996); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1486). Services for accessing these data are described at the back of the journal.

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