# metal-organic compounds

# A pseudo-trigonal bipyramidally coordinated Pt atom in dicarbonyl-bis(octacarbonyl-μ-dicyclohexylphosphidodirhenio)platinum(II)

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In the title compound, $[PtRe_4(C_{12}H_{22}P)_2(CO)_{18}]$ or $[(\mu\text{-}PCy_2)(CO)_8Re_2]_2Pt(CO)_2$ (Cy is cyclohexyl), two phosphido-bridged dirhenium groups are linked by a $Pt(CO)_2$ unit and show different bonding patterns for stereochemical reasons. The Re—Re distances are 3.2620 (15) and 3.0739 (15) Å, and the Pt—Re distances are 2.9165 (12), 2.9025 (15) and 2.8548 (13) Å.

## Comment

As a continuation of our investigations into triangular cluster complexes $M_2Rh(\mu\text{-}PR_2)(\mu\text{-}CO)_2(CO)_8$ ($M$ = Mn, Re; $R$ is an organic residue) as hydroformylation catalysts (Beckers *et al.*, 1995; Haupt *et al.*, 2001), we wished for selectivity reasons to exchange the $Rh^I$ atom for a more nucleophilic $Pt^{II}$ atom as the reaction centre. Platinum(II) carbonyl cluster complexes of this type are very rare (Braunstein *et al.*, 1999).

The molecule $[(\mu\text{-}PCy_2)(CO)_8Re_2]_2Pt(CO)_2$, (I) (Fig. 1), consists of two phosphido-bridged dirhenium carbonyl moieties linked *via* the central Pt atom. The $Pt(CO)_2$ constituent extends the original $(\mu\text{-}P1)Re_2$ core to a four-membered nearly planar $\mu\text{-}PRe_2Pt$ ring. The maximum deviation of an atom from this best plane is 0.082 (6) Å for P1; the $PRe_2/Re_2Pt$ dihedral angle is 8.1°. Both Re atoms have a slightly distorted octahedral coordination from four terminal CO groups, the bridging P and the Pt atom. The CO ligands at both Re atoms show an ecliptic arrangement, with C—Re1—Re2—C torsion angles (here and in the following text as absolute values) ranging from 0.4 to 3.7°. The CO

groups attached to Pt are also in ecliptic positions relative to those at Re1 and Re2, with torsion angles ranging from 0.5 to 6.1°. The Re1—Re2 bond is 3.2620 (15) Å and the $\mu\text{-}P1$ bridge is symmetric with respect to the equivalent P—Re bond lengths of 2.454 (6) and 2.459 (6) Å. The two Pt—Re bonds differ slightly in length [2.9165 (12) and 2.9025 (15) Å for Re1 and Re2, respectively], but they are longer than other unsupported Pt—Re bonds reported in the literature, which range from 2.706 (1) to 2.899 (1) Å (Casey *et al.*, 1987, 1992; Urbancic *et al.*, 1984; Beringhelli *et al.*, 1990, 1993; Mague & Lin, 1994). A $\mu\text{-}H$ bridged Pt—Re edge has been reported with a length of 2.906 (1) Å (Beringhelli *et al.*, 1990).



(I)
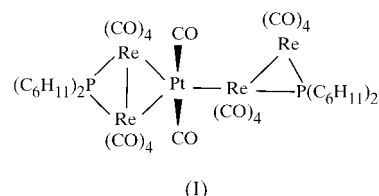
A third but shorter Pt—Re3 bond of 2.8548 (13) Å connects the second $(\mu\text{-}P2)Re_2(CO)_8$ unit to platinum. Again, the Re3—Re4 bond of 3.0739 (15) Å is bridged by a $PCy_2$ ligand and both Re atoms are attached to four terminal CO groups. These groups also show an ecliptical arrangement along the Re—Re vector, with torsion angles in the range 3.7–7.7°. Neglecting the Re—Re bond, Re4 is coordinated by five non-metal atoms, thus realising a distorted square-pyramidal coordination, whereas Re3 reaches a strongly distorted octahedral coordination with the additional Re—Pt interaction. The CO ligands at Re3 and those attached to Pt show a staggered conformation along the Re3—Pt vector, with torsion angles of 58.8 (10) (C9—Pt—Re3—C13) and 57.2 (10)° (C10—Pt—Re3—C12), realising a sterically favourable arrangement. In contrast with the symmetric $\mu\text{-}P1$ bridge, the $\mu\text{-}P2$ atom shows two different P—Re bond lengths of 2.429 (6) (Re3) and 2.396 (6) Å (Re4), the longer one being *trans* to the Re3—Pt bond. With respect to the different Re—Pt—Re angles in the basal $Re_3Pt$ plane of 68.19 (4), 135.80 (4) and 155.33 (4)° for Re1/2, Re1/3 and
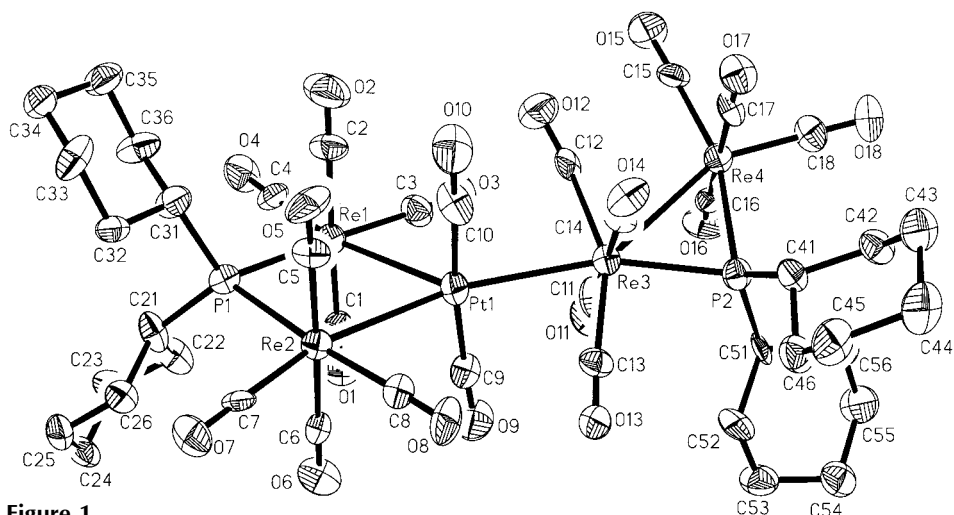


**Figure 1**
The molecular structure of (I) showing 50% probability ellipsoids. H atoms have been omitted for clarity.

Re2/3, respectively, the fivefold coordination geometry around Pt can be described as pseudo-trigonal bipyramidal with CO groups 9 and 10 at the apices. The Re3Pt plane is almost planar, with a maximum deviation from the best plane of 0.082 (2) Å for Pt. A similar Y-shaped planar coordination pattern for the central metal atom with Y-angles of 64, 138 and 158° is known from the coordination of, for example, Ir or Rh in $(\mu\text{-}PR_2)(CO)_8Re_2[\mu\text{-}M(CO)_2PPh_3]$ ($M$ = Ir, Rh) (Haupt *et al.*, 1994). The uncommon coordination geometry observed here for platinum, with the different bonding patterns of one bridging and one end-on linked $(\mu\text{-}PCy_2)(CO)_8Re_2$ unit, must be due to stereochemical reasons. Neither an alternative planar quadratic nor spiro-cyclic Re4Pt arrangement, both then with two bridging Re2 units, would be possible because of the steric repulsion of CO groups 3, 8 and 12, 15, or 9, 10 and 12, 15.

## Experimental

The salts $Pt(COD)(CF_3SO_3)_2$ (COD is cyclooctadiene) and $NEt_4[Re_2(\mu\text{-}PCy_2)(CO)_8]$ were reacted in dichloromethane solution in the presence of gaseous CO (removal of the COD ligand) at 258 K. The only separable product (thin-layer chromatography; eluant: dichloromethane/*n*-hexane, 1/5) was the title compound. Crystals were grown from chloroform/*n*-pentane, although very few were of acceptable quality and scattering power.

### Crystal data

| | |
|---|---|
| $[PtRe_4(C_{12}H_{22}P)_2(CO)_{18}]$ | $D_x = 2.445$ Mg m$^{-3}$ |
| $M_r = 1838.60$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 21 |
| $a = 17.561$ (2) Å |   reflections |
| $b = 16.728$ (3) Å | $\theta = 7.5$–$13.2°$ |
| $c = 17.408$ (6) Å | $\mu = 12.58$ mm$^{-1}$ |
| $\beta = 102.42$ (2)° | $T = 203$ (2) K |
| $V = 4994$ (2) Å$^3$ | Needle, red |
| $Z = 4$ | $0.40 \times 0.05 \times 0.04$ mm |

### Data collection

| | |
|---|---|
| Bruker $P4$ diffractometer | $R_{int} = 0.059$ |
| $\omega$ scans | $\theta_{max} = 26.5°$ |
| Absorption correction: $\psi$ scan | $h = -22 \rightarrow 21$ |
|   (North *et al.*, 1968) | $k = 0 \rightarrow 21$ |
|   $T_{min} = 0.264$, $T_{max} = 0.532$ | $l = 0 \rightarrow 21$ |
| 10719 measured reflections | 3 standard reflections |
| 10342 independent reflections |   every 397 reflections |
| 4254 reflections with $I > 2\sigma(I)$ |   intensity decay: 1% |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.059$ | $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$ |
| $wR(F^2) = 0.170$ |   where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.97$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 10342 reflections | $\Delta\rho_{max} = 1.33$ e Å$^{-3}$ |
| 605 parameters | $\Delta\rho_{min} = -1.09$ e Å$^{-3}$ |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Pt1—Re3 | 2.8548 (13) | Re2—P1 | 2.459 (6) |
| Pt1—Re2 | 2.9025 (15) | Re3—P2 | 2.429 (6) |
| Pt1—Re1 | 2.9165 (12) | Re3—Re4 | 3.0739 (15) |
| Re1—Re2 | 3.2620 (15) | Re4—P2 | 2.396 (6) |
| Re1—P1 | 2.454 (6) | | |
| C9—Pt1—C10 | 172.9 (10) | Pt1—Re2—Re1 | 56.11 (3) |
| Re3—Pt1—Re2 | 155.33 (4) | P1—Re2—Pt1 | 104.08 (15) |
| Re3—Pt1—Re1 | 135.80 (4) | P2—Re3—Pt1 | 163.66 (16) |
| Re2—Pt1—Re1 | 68.19 (4) | C12—Re3—Re4 | 65.8 (7) |
| C3—Re1—Re2 | 126.4 (7) | P2—Re3—Re4 | 49.95 (15) |
| P1—Re1—Re2 | 48.47 (13) | Pt1—Re3—Re4 | 145.35 (4) |
| Pt1—Re1—Re2 | 55.70 (3) | C15—Re4—Re3 | 111.5 (7) |
| P1—Re1—Pt1 | 103.81 (14) | P2—Re4—Re3 | 50.89 (14) |
| C8—Re2—Re1 | 129.2 (7) | Re1—P1—Re2 | 83.19 (18) |
| P1—Re2—Re1 | 48.34 (14) | Re4—P2—Re3 | 79.15 (18) |

The $U$ values of the C atoms were restrained such that anisotropic components along common bonds were approximately equal. The largest peak of residual electron density is 0.9 Å from Re3.

Data collection: *XSCANS* (Siemens, 1995); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1995); 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*.

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