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Pentacarbonyl-1κ^4C,2κC-[2(η^5)-cyclopentadienyl]-μ-dicyclohexylphosphido-1:2κ^2P-manganeserhodium(*Mn*—*Rh*)

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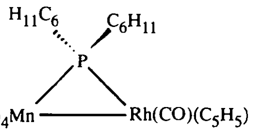
Abstract

The title compound, [MnRh(C_5H_5){μ-P(C_6H_{11})$_2$}(CO)$_5$], is a valence-electron-saturated dinuclear manganese–rhodium cluster compound with an Mn—Rh bond length of 2.763 (1) Å.

Comment

In the literature, there are few structure reports on dinuclear manganese–rhodium cluster complexes (Aldridge *et al.*, 1982; Antonelli & Cowie, 1990; Antonova *et al.*, 1989; Arif *et al.*, 1987; Werner *et al.*, 1985). The title compound, (I), is the first crystallographically characterized example of a fully valence-electron-saturated Mn–Rh compound bearing a bridging phosphido group. The related diphenylphosphido complex has been reported (Blickensdorfer & Kaesz, 1975), but no geometric parameters are available.



(I)

The structure of (I) is shown in Fig. 1. Through the metal–metal bond, the four terminal carbonyl ligands and the bridging phosphido group, the Mn atom attains a slightly distorted octahedral coordination. The Rh atom is coordinated by the μ-P atom, a carbonyl ligand in an axial position and a cyclopentadiene (Cp) group. The resulting arrangement around the Rh atom is a type of piano stool if the center of the Cp ring is looked on as the locus of the Rh—Cp coordination. The axial carbonyl ligands at both metal atoms show an ecliptic arrangement, with a C2—Mn—Rh—C5 torsion angle of 2.3 (2)°. Carbonyl group 3 at the Mn atom and the C32 atom of the Cp ligand subtend a C3—Mn—Rh—C32 torsion angle of −28.1 (2)°, and the torsion angle C3—Mn—Rh—*X* (*X* is the center of the Cp ring) is −25.7 (2)°. The Rh—*X* distance is 1.911 (4) Å. The Mn—Rh bond length of 2.763 (1) Å is clearly elongated compared with that of 2.708 (2) Å in the only other known phosphido-bridged Mn–Rh cluster, (MeCp)Mn(CO)$_2$(μ-^{t}Bu$_2$P)Rh(cod), (II) (Arif *et al.*, 1987; cod is cyclooctadiene). This is in accordance with the degree of electronic saturation of these two cluster complexes. Formally, compound (II) counts 18 electrons at Rh and 16 at Mn, and is thus classified as electronically unsaturated. Hence, saturated compound (I) fulfills the noble gas rule with 18 electrons for both metals. The other above-mentioned dinuclear compounds with a bridged Mn—Rh bond exhibit very different bridging patterns and their metal–metal bond lengths vary from 2.648 (1) to 2.843 (1) Å. Due to the different metal atoms, the μ-P bridge in (I) is unsymmetric, with Mn—P and Rh—P bond lengths of 2.249 (2) and 2.294 (1) Å, respectively, and an enclosed angle Mn—P—Rh of 74.93 (4)°. In contrast, the Mn—P distance in (II) [2.293 (1) Å] is longer than the Rh—P distance [2.262 (2) Å]. In (I), there are no intermolecular contacts shorter than van der Waals distances.

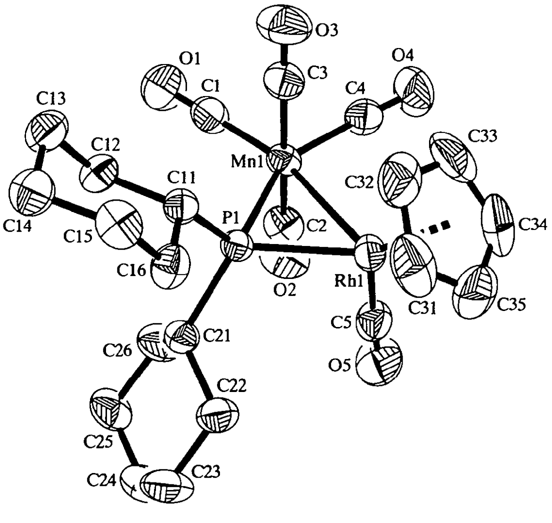


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was prepared by the reaction of Mn$_2$Rh{μ-P(C_6H_{11})$_2$}(μ-CO)$_2$(CO)$_8$ (70 mg, 0.1 mmol) with NaCp in tetrahydrofuran solution (10 ml) at 210 K. It was recrystallized from CH_2Cl_2 solution (Wittbecker, 1997).

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Crystal data

$[MnRh(C_5H_5)(C_{12}H_{22}P)(CO)_5]$
$M_r = 560.26$
Monoclinic
$P2_1/n$
$a = 16.185\ (7)$ Å
$b = 9.110\ (3)$ Å
$c = 17.535\ (8)$ Å
$\beta = 116.85\ (2)°$
$V = 2306.7\ (16)$ Å^3
$Z = 4$
$D_x = 1.613$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 8–18°$
$\mu = 1.362$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.46 \times 0.33 \times 0.15$ mm
Red

Data collection

Siemens $R3$ diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.686$, $T_{max} = 0.815$
5491 measured reflections
5321 independent reflections
3397 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 27.56°$
$h = -21 \rightarrow 18$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 22$
3 standard reflections every 400 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.083$
$S = 1.072$
5321 reflections
264 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.9739P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.439$ e Å^{-3}
$\Delta\rho_{min} = -0.403$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Rh1—P1	2.2937 (14)	Mn1—P1	2.2487 (15)
Rh1—Mn1	2.7632 (10)		
P1—Rh1—Mn1	51.80 (4)	Mn1—P1—Rh1	74.93 (4)
P1—Mn1—Rh1	53.28 (4)		

Data collection: *XSCANS* (Siemens, 1995*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995*b*). 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: JZ1346). Services for accessing these data are described at the back of the journal.

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[2,6-Bis(*N*-*tert*-butyliminomethyl)pyridine-κ^3N](phenolato-κO)rhodium(I)

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Abstract

The title compound, $[Rh(C_6H_5O)(C_{15}H_{23}N_3)]$, is the first Rh^I–phenoxide compound with a tridentate nitrogen ligand to be crystallographically characterized. The Rh^I atom shows an essentially undistorted square-planar conformation, unlike the corresponding chlorine compound, which displays significant non-planarity. The flexibility observed by NMR in solution is partly supported by the conformation found in the crystalline state.

Comment

Recently, a number of studies involving rhodium compounds with various tridentate nitrogen ligands (TNL) have reported the synthesis, properties and oxidation chemistry involving four-, five- and six-coordinate Rh compounds of the types (TNL)RhCl, (TNL)Rh(R)Cl$_2$

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