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Chloro(1,5-cyclooctadiene)(triphenylphosphine)-rhodium(I)

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Key indicators
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.011 Å
R factor = 0.036
wR factor = 0.046
Data-to-parameter ratio = 10.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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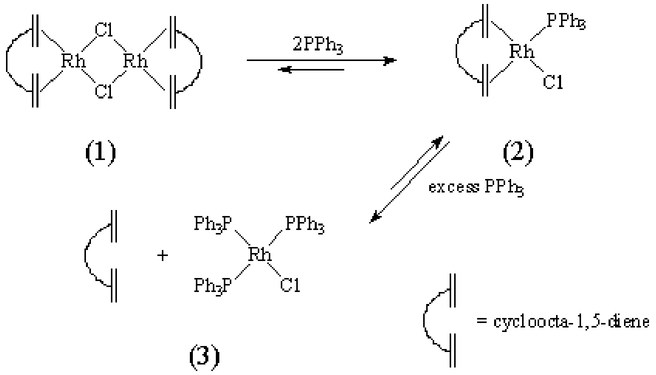
The crystal and molecular structure of the title compound, [RhCl(C_8H_{12}){P(C_6H_5)$_3$}], has been determined by means of X-ray diffraction. Compounds of this nature are important because of their ability to act as homogenous hydrogenation catalysts and to serve as precursors for more elaborate compounds.

Comment

The reaction of the rhodium(I) dimer [(cod)$_2$Rh$_2$Cl$_2$] (cod = cycloocta-1,5-diene), (1), with excess triphenylphosphine quickly gives RhCl(cod)PPh$_3$, (2), and then, in a much slower reaction, gives RhCl(PPh$_3$)$_3$, (3), Wilkinson's catalyst (Osborn *et al.*, 1966), which was one of the first homogenous hydrogenation catalysts. This is illustrated in the scheme below. In our studies of the reaction of triphenylphosphine and bulkier phosphines with (cod)$_2$Rh$_2$Cl$_2$, we have isolated crystals of RhCl(cod)PPh$_3$, suitable for X-ray crystal structure analysis. A similar rhodium(I) bis-alkene–phosphine complex has been studied by X-ray crystal structure analysis and reported in the literature (Iglesias *et al.*, 1987). These compounds are important because of their ability to act as homogenous hydrogenation catalysts and as precursors to more elaborate compounds.



The Rh atom of this molecule is coordinated to one Cl atom, one P atom, and the two double bonds of cyclooctadiene. The Rh–double-bond distances of 2.005 (7) and 2.118 (7) Å are of normal length for this type of rhodium compound. Rh–cod distances and angles for the title compound and some related structures are listed in Table 1. It can be seen that the smaller Cl—Rh—*D* angles correspond to the longer Rh—*D* distances and that the larger Cl—Rh—*D* angles correspond to the shorter Rh—*D* distances (*D* is the midpoint of a cod double bond). This same trend holds true for the title compound.

Experimental

Crystal data

$[RhCl(C_8H_{12})(C_{18}H_{15}P)]$
$M_r = 508.84$
Orthorhombic, $P2_12_12_1$
$a = 16.246$ (3) Å
$b = 8.145$ (2) Å
$c = 16.992$ (4) Å
$V = 2248$ (1) Å^3
$Z = 4$
$D_x = 1.50$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 17 reflections
$\theta = 10.0$–$20.5°$
$\mu = 0.96$ mm^{-1}
$T = 296$ K
Irregular, brown
0.29 × 0.28 × 0.28 mm

Data collection

Picker four-circle diffractometer
ω–2θ scans
Absorption correction: Gaussian (*MolEN*; Enraf–Nonius, 1990)
$T_{min} = 0.776$, $T_{max} = 0.799$
3170 measured reflections
3170 independent reflections
2839 reflections with $I > 2\sigma(I)$

$\theta_{max} = 28.3°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.036$
$wR = 0.046$
$S = 2.18$
2839 reflections
262 parameters

H-atom parameters constrained
$w = 4F^2/[\sigma^2(F^2) + (0.03F^2)^2]$
$(\Delta/\sigma)_{max} = 0.28$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}

Table 1
Rh-to-cod ligand distances and angles (Å, °) in the title compound and in some related structures.

Comp	Rh—*D*1	Rh—*D*2	Cl—Rh—*D*1	Cl—Rh—*D*2	*D*1—Rh—*D*2
A	1.986 (6)	2.013 (6)	178.1 (2)	90.8 (2)	87.7 (3)
B	1.989 (5)	2.026 (5)	177.9 (2)	91.9 (2)	88.2 (2)
C	1.978 (5)	2.001 (5)	175.9 (2)	91.9 (1)	88.0 (2)
D	1.987 (8)	2.118 (6)	177.5 (5)	90.9 (3)	86.8 (4)
(2)	2.005 (7)	2.118 (7)	174.6 (2)	88.8 (2)	86.5 (4)
E	1.988 (6)	2.099 (7)	176.5 (4)	90.4 (3)	86.3 (4)
F	1.996 (9)	2.089 (7)	175.7 (3)	90.2 (2)	85.9 (4)
G	1.994 (4)	2.092 (4)	176.1 (1)	90.1 (1)	84.0 (2)

Notes: *D*1 and *D*2 are the midpoints of the two double bonds in cod; *A* = Rh(cod)Cl[Et_3P=N(C_6H_4)CH_3] (Imhoff *et al.*, 1990); *B* = RhCl(C_8H_{12})($C_9H_{16}N_2$) (Flörke *et al.*, 1992); *C* = RhCl(C_8H_{12})($C_7H_{12}N_2$)·0.5$C_4H_8O_2$ (Flörke *et al.*, 1992); *D* = RhCl(cod)P(*p*-C_6H_4F)$_3$ (Iglesias *et al.*, 1987); (2) = title compound RhCl(cod)P(C_6H_5)$_3$; *E* = RhCl(cod)[P(C_6H_5)$_2$(*o*-tol)] (Hubbard, 1988); *F* = RhCl(cod)[P(C_6H_5)(*o*-tol)$_2$] at 294 K (Hubbard, 1988); *G* = RhCl(cod)[P(C_6H_5)(*o*-tol)$_2$] at 123 K (Pinkerton, 1988).

The structure was refined using a mainframe computer. Because cycles of refinement on the mainframe were so time-consuming, refinement was stopped when the largest ratio of parameter shift to standard uncertainty was equal to 0.28. The large goodness of fit value, 2.18, probably indicates a less than ideal weighting scheme. Unfortunately, the *MolEN* program that was originally used to solve and refine the structure is no longer available to us. Otherwise further refinement could have been undertaken.

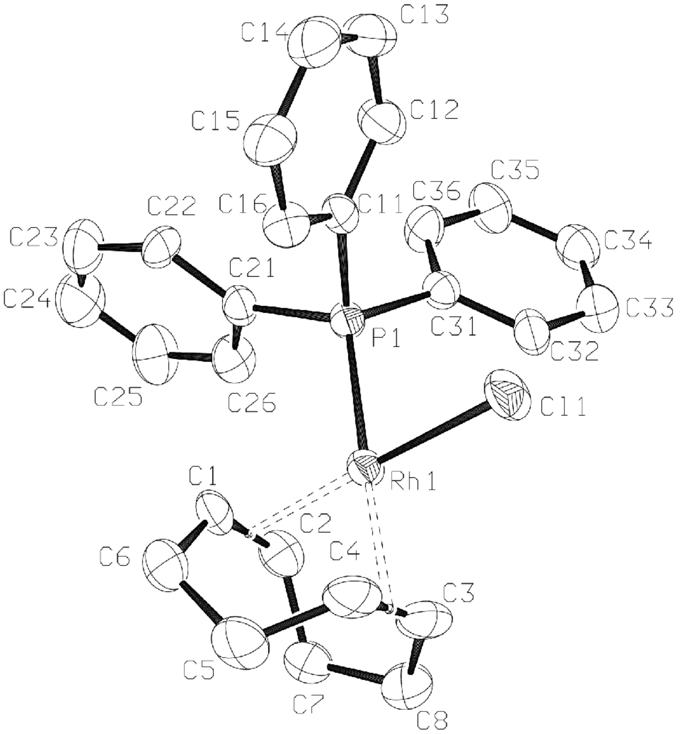


Figure 1
View of RhCl(cod)PPh_3. This diagram illustrates the coordination of the Rh atom to the centers of the double bonds of cod. Displacement ellipsoids are shown at the 50% probability level.

Data collection: *KRISEL CONTROL Software* (KRISEL CONTROL, 1982); cell refinement: *KRISEL CONTROL Software*; data reduction: *MolEN*; program(s) used to solve structure: *MolEN*; program(s) used to refine structure: *MolEN*; molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *Word Pad*, IUCR CIF Template.

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