

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF
(η^5 -PENTAMETHYLCYCLOPENTADIENYL)(METHYLDIPHENYLPHOSPHITE-*P*)DICHLORORHODIUM(III)M. Nieuwenhuyzen¹, G.C. Saunders²¹The School of Chemistry, Queen's University Belfast, David Keir Building, Belfast, BT9 5BA, United Kingdom²Department of Chemistry, The University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand,
e-mail: g.saunders@waikato.ac.nz

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The molecule (η^5 -pentamethylcyclopentadienyl)(methyl-diphenylphosphinite-*P*)dichlororhodium(III), $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2(\text{PPh}_2\text{OMe})]$, crystallizes in the monoclinic crystal system in space group $P2_1/c$ with unit cell parameters $a = 16.056(3) \text{ \AA}$, $b = 9.4331(18) \text{ \AA}$, $c = 15.745(3) \text{ \AA}$, $\beta = 108.330(4)^\circ$, $V = 2263.8(7) \text{ \AA}^3$ and $Z = 4$. There is three-legged piano stool geometry about Rh. The Rh—P distance of $2.278(2) \text{ \AA}$ is shorter than those of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2(\text{PPh}_2\text{OR})]$ where R is an aryl group, and longer than those found in $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\{\text{PPh}(\text{OR})_2\}]$. The structure reveals significant distortion of the pentamethylcyclopentadienyl towards ' η^3, η^2 -enylene' coordination.

Keywords: η^5 -pentamethylcyclopentadienyl, ring slippage, rhodium, X-ray structure.

Since the first report of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})_2] [1]$ many pentamethylcyclopentadienyl rhodium complexes have been synthesized and studied. In particular $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhX}_2(\text{L})]$ ($X = \text{halide}$) complexes containing phosphine or phosphite ligands have provided a rich chemistry. In contrast, complexes bearing the related phosphinite ($\text{PR}_2\text{OR}'$) and phosphonite ligands ($\text{PR}(\text{OR}')_2$) have been little studied. The electronic and steric properties of phosphonites and phosphinites are intermediate between those of the analogous phosphine and phosphite ligands. For example, the cone angles of trimethylphosphite, dimethylphenylphosphonite, methyl-diphenylphosphinite and triphenylphosphine are $107, 115, 132$ and 145° respectively [2], the σ -donor capacity increases in the order $\text{P}(\text{OMe})_3 < \text{PPh}_2(\text{OMe}) < \text{PPh}(\text{OMe})_2 < \text{PPh}_3$ and the π -acidity increases in the order $\text{PPh}_3 < \text{PPh}_2(\text{OMe}) < \text{PPh}(\text{OMe})_2 < \text{P}(\text{OMe})_3$ [3]. Although there is an abundance of structural data concerning the phosphine complexes, $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhX}_2(\text{PR}_3)]$, there is a paucity regarding the analogous phosphinite complexes: The structures of only three complexes of formulation $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhX}_2(\text{PR}_2\text{OR}')] have been described. For two R is phenyl and R' is aryl [4, 5] and for the other R is ethyl and R' is benzyl [6]. Here we report the structure of (η^5 -pentamethylcyclopentadienyl)(methyl-diphenylphosphinite-*P*)dichlororhodium(III), **1**, in which R' is alkyl.$

Experimental. A small number of crystals of compound **1** were obtained as a by-product of the reaction between $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})_2]$ and $\text{Ph}_2\text{POC}_6\text{H}_4\text{CHO}$ -2 in methanol. Diffraction data of a single crystal were collected at $153(2) \text{ K}$ on a Bruker SMART diffractometer using the SAINT-NT [7] software with graphite-monochromated MoK_α radiation. Crystallographic and refinement data are given in Table 1. Lorentz and polarization corrections were applied. Empirical absorption corrections were applied using SADABS [8]. The structure was solved using direct methods and refined with the programme package SHELXTL [9]. The non-hydrogen atoms were refined with anisotropic thermal

Table 1

Crystallographic data and refinement parameters for compound 1

Parameter	Value
Empirical formula	C ₂₃ H ₂₈ Cl ₂ OPRh
Molecular mass	525.23
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg.	16.056(3), 9.4331(18), 15.745(3); 108.330(4)
<i>V</i> , Å ³ , <i>Z</i>	2263.8(7), 4
<i>d</i> _{calc} , g·cm ⁻³	1.541
μ, mm ⁻¹	1.073
<i>F</i> (000)	1072
Crystal size, mm	0.24×0.08×0.08
θ data collection range, deg.	0.99—25.00
Intervals of reflection indices	-19 ≤ <i>h</i> ≤ 12, -11 ≤ <i>k</i> ≤ 11, -14 ≤ <i>l</i> ≤ 18
Measured reflections	8580
Independent reflections	3935 [<i>R</i> (int) = 0.0849]
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	2121
Parameters	259
Goodness of fit on <i>F</i> ² , <i>S</i>	0.940
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0521, <i>wR</i> 2 = 0.1129
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1176, <i>wR</i> 2 = 0.1378
Weighting scheme	$w^{-1} = [\sigma^2(F_o)^2 + (0.546 \times \{\max F_o ^2 + 2 F_c ^2\}/3)^2]$
Residual electron density (max / min), e·Å ⁻³	-0.874 / 0.641

parameters. Hydrogen atom positions were added, and idealized positions and a riding model with fixed thermal parameters (U_{ij}) $1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH₃) were used for subsequent refinements. The function minimized was $\sum[w(|F_o|^2 - |F_c|^2)]$. Selected geometric parameters are given in Tables 2 and 3. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters (CCDC number: 833578).

Table 2

Bond lengths (d, Å) for compound 1

Bond	<i>d</i>
Cp*—Rh	1.840(8)
Rh1—Cl1	2.409(2)
P1—C11	1.799(8)
P1—O31	1.607(6)
Rh1—P1	2.278(2)
Rh1—Cl2	2.409(2)
P1—C21	1.811(8)
O31—C31	1.451(10)

Note: Cp* indicates the centroid of the C₅ ring.

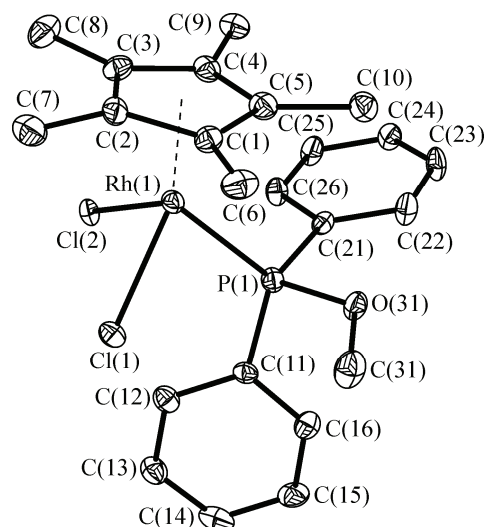
Table 3

Bond angles (ω, deg.) for compound 1

Angle	ω	Angle	ω
Cp*—Rh—P1	129.6(2)	Cp*—Rh—Cl1	121.1(2)
Cp*—Rh—Cl2	122.0(2)	P1—Rh1—Cl1	90.16(8)
P1—Rh1—Cl2	89.64(8)	Cl1—Rh1—Cl2	94.73(7)
Rh1—P1—C11	120.9(3)	Rh1—P1—C21	113.3(3)
Rh1—P1—O31	114.3(2)	C11—P1—C21	104.4(4)
C11—P1—O31	102.6(3)	C21—P1—O31	98.6(3)
P1—O31—C31	119.6(5)		

Note: Cp* indicates the centroid of the C₅ ring.

Fig. 1. Molecular structure of compound **1**. Thermal ellipsoids are at 50 % probability level. Hydrogen atoms are omitted for clarity



Results and discussion. The structure of **1** (Fig. 1) reveals the expected three-legged piano stool geometry about the rhodium atom (Tables 2 and 3). The Rh—P distance of 2.278(2) Å is significantly shorter than those of 2.301(3) and 2.2944(11) Å of respectively $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2(\text{PPh}_2\text{OC}_6\text{H}_3\text{F}_2\text{-2,6})]$ **2** [4] and $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\{\text{PPh}_2\text{O}(\text{C}_5\text{H}_3\text{N-3})\text{-2-NHCH}_2\text{PPh}_2\}\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)]$ **3** [5] in which R' is aryl, but similar to those of 2.282(1) and 2.285(1) Å of the two independent molecules of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\cdot(\text{PEt}_2\text{OCHCF}_3\text{Ph})]$ **4** [6], in which R' is benzyl. The Rh—P distance of **1** is longer than those found for the phosphonite complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\{\text{PPh}(\text{OPh})_2\}]$ of 2.258(3) and 2.254(3) [4] and for the phosphite complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\{\text{P}(\text{OC}_6\text{H}_4(\text{CF}_2)_5\text{CF}_3\text{-4})_3\}]$ of 2.237(3) Å [10], although it is similar to that of 2.268(3) Å of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\{\text{P}(\text{OEt})_3\}]$ [11]. The Rh—Cl distances are identical (2.409(2) Å) and are similar to those of 2.401(3) and 2.406(4) of the complex **2** and the shorter Rh—Cl distance of **3** of 2.4015(10).

There is a significant distortion of the pentamethylcyclopentadienyl ring from C_5 symmetry about the Rh—C₅(centroid) axis. The data suggest slight ring slippage from cyclopentadienyl to ' η^3, η^2 -enylene' coordination [12, 13] with C(5) the centre of the allyl functionality (Table 4). The ene functionality is approximately *trans* to the phosphorus atom of the phosphinite ligand, which exerts a greater *trans* influence than chloride. The ene Rh—C(2) and Rh—C(3) distances of 2.252(8) and 2.248(8) Å respectively are significantly longer than the three enyl Rh—C distances, which lie in the range 2.160(8) to 2.193(9) Å. Consistent with this the C(2)—C(3) distance of 1.379(12) is significantly shorter than the other C—C bond distances. However, the internal ring C—C—C angles are virtually

Table 4
Comparative geometric parameters of the $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}$ fragment for compounds **1**—**4** (*d*, Å, ω, τ, deg.)

Bond, Angle	1	2	3	4	
	<i>d</i>				
Rh1—C1	2.173(8)	2.14(1)	2.167(3)	2.161(4)	2.129(4)
Rh1—C2	2.252(8)	2.22(1)	2.237(3)	2.226(4)	2.238(4)
Rh1—C3	2.248(8)	2.22(1)	2.241(3)	2.225(4)	2.233(4)
Rh1—C4	2.160(8)	2.18(1)	2.171(3)	2.181(4)	2.177(4)
Rh1—C5	2.193(9)	2.19(1)	2.181(3)	2.184(4)	2.195(4)
C1—C2	1.459(11)	1.44(2)	1.444(4)	1.454(6)	1.439(6)
C2—C3	1.379(12)	1.39(2)	1.412(4)	1.403(6)	1.381(7)
C3—C4	1.448(12)	1.41(2)	1.459(4)	1.448(6)	1.481(7)
C4—C5	1.439(12)	1.48(2)	1.428(5)	1.459(6)	1.426(6)
C5—C1	1.423(11)	1.39(2)	1.438(4)	1.431(6)	1.435(6)
	<i>ω</i>				
P1—Rh1—C ₂ [*]	156.6(2)	157.6(4)	153.43(8)	159.4(1)	161.4(1)
	<i>τ</i>				
P1—Rh1—Cp [*] —C ₂ [*]	171.8(8)	−169.6(7)	−164.0(2)	168.1(4)	172.8(4)

Note: Cp* indicates the centroid of the C₅ ring, and C₂^{*} indicate the centre of the 'ene' bond (C₂—C₃).

identical, lying in the range 106.8(8) to 109.3(8)°. Similar distortions are evident in the structures of **2**, **3** and **4**.

The Cp*—Rh—P angle of **1** is 129.6(2), which is consistent with that of 130.85(10) of **2**, which involves the bulkier ligand PPh₂(OC₆H₃F₂-2,6). The Cp*—Rh—Cl angles of **1** are 121.1(2) and 122.0(2)°, which are intermediate between those of 118.5(1) and 124.2(1)° of **2**. The P—Rh—Cl angles of 90.16(8) and 89.64(8)° and the Cl—Rh—Cl angle of 94.73(7)° fall within the range 84.8 to 98.4 found for [(η⁵-C₅Me₅)RhCl₂P] complexes where P is phosphine, phosphinite, phosphonite or phosphite [3, 4, 10, 14—21].

The geometry about phosphorus is distorted tetrahedral and is identical within experimental error to that displayed in the structure of **2** with the exception of the Rh—P distance and the P—O distance (1.607(6) Å), which is shorter than those of 1.669(9) and 1.641(2) Å of **2** and **3** respectively.

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