

Synthesis and X-ray Structure of the Heterotrinnuclear Complex $[\text{Pd}\{(\mu\text{-Cl})(\eta^2\text{-}\mu\text{-P}(\text{O})(\text{OMe})_2)\text{Rh}(\text{cod})\}_2]$. An Unusual Bridging Coordination Mode Involving Phosphonate Ligands

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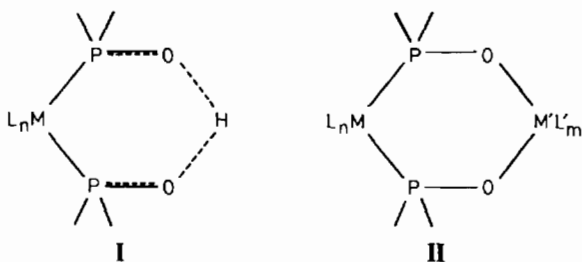
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Recent studies [1–3] have shown that the hydrogen-bonded proton of phosphonate complexes of type **I**, can be easily removed to give a variety of bimetallic derivatives of type **II**, in which the anion derived from **I** may be regarded as an analogue of β -diketonates [1, 2]. We wish to report the synthesis and the crystal and molecular structure of an unexpected heterotrinnuclear complex that shows a novel heterometallic mixed phosphonate–chlorine bridge.

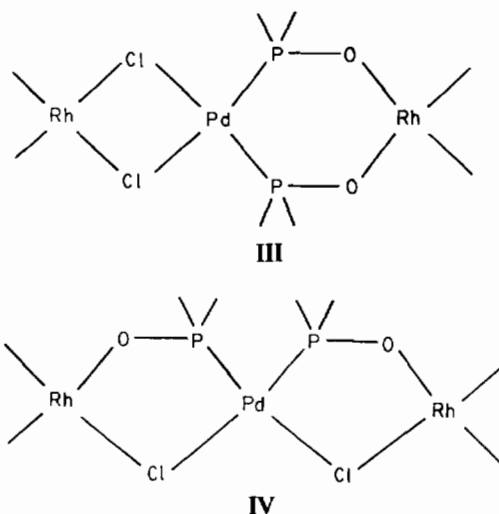


A dichloromethane solution (10 ml) of the complex $[\text{CIPd}\{P(\text{O})(\text{OMe})_2\}_2\text{H}]_2$ (0.2 mmol) [4] was treated under purified nitrogen with $[\text{Rh}(\text{acac})(\text{cod})]$ (0.4 mmol) [5]. After stirring for 5 h, the solution was evaporated to dryness. The extraction of the solid residue with dichloromethane or chloroform led to the separation of an insoluble white solid of the polymer $[\text{Pd}\{P(\text{O})(\text{OMe})_2\}_2]_n$ [4] and a yellow solution. The trinnuclear complex $[\text{Pd}\{(\mu\text{-Cl})(\mu\text{-P}(\text{O})(\text{OMe})_2)\text{Rh}(\text{cod})\}_2]$ (**1**) was obtained, after partial evaporation of this solution and addition of methanol, as a yellow microcrystalline solid. Similar results with a better yield were obtained when the reaction was performed in methanol (92%). Analytical and IR data support the trinnuclear formulation. *Anal. Calc.* for **1**: C, 29.4; H, 4.4. *Found*: C, 29.3; H, 4.7%.

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The ^1H NMR spectrum of this complex shows the characteristic virtual triplet signal assigned to the methyls of the phosphonate ligands [6] (δ 3.67 ppm (vt, 12H, OMe), $J(\text{P-H})$ 12.7 Hz) and broad resonances of the coordinated cyclooctadiene (δ 4.20 ppm (m, 8H, CH=CH); δ 2.42 ppm (s, br, 8H, CH₂); δ 1.70 ppm (m, 8H, CH₂)). A clear single signal is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (δ 95.9 ppm) in a similar region to that reported in the related complexes $[\text{PdCl}_2\{P(\text{OEt})_2\text{Cl}\}_2]$ (δ 112.1 ppm) and $[\text{Pd}_2(\mu\text{-Cl})_2\{(P(\text{OEt})_2\text{O})_2\text{H}\}_2]$ (δ 73.4 ppm) [7].

Assuming that no reorganization on the palladium coordination sphere has taken place during the reaction, there are only two possible structures for **1**: (i) an 'asymmetric' arrangement **III** exhibiting two different types of bridges (see below), or (ii) a 'symmetric' structure **IV** with two identical chloride/phosphonate bridges between the metals.



The removal of the bridging proton in complexes with structure **I** normally gives rise to binuclear or polynuclear complexes with phosphonate, or related phosphite ligands, bridging the metals through a double P–O bridge as shown in structure **III**, where the anion derived from the *cis*-phosphonate complex shows a similar coordination behaviour to that reported for β -diketonates [2, 8]. In our case, none of the spectroscopic data reported above excluded any of the proposed structures, neither **III**, nor **IV**, and hence we decided to carry out an X-ray molecular structure determination.

Crystal data: $\text{C}_{20}\text{H}_{36}\text{Cl}_2\text{O}_6\text{P}_2\text{PdRh}_2$, $M = 817.56$, monoclinic, space group $P2_1/c$, $a = 15.685(1)$, $b = 7.3863(4)$, $c = 24.670(2)$ Å, $\beta = 105.46(1)^\circ$, $V = 2754.7(4)$ Å³, $Z = 4$, $D_c = 1.971$ g cm⁻³, $F(000) = 1616$, $\mu(\text{Mo K}\alpha) = 21.47$ cm⁻¹. Data were collected to $2\theta_{\text{max}} = 45^\circ$ on a Siemens AED2 diffractometer

and corrected semiempirically for absorption. The structure was solved by heavy atom and Fourier methods and refined by full-matrix least-squares, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogens were partially located in a difference Fourier map and included in the last cycle of refinement riding on their carbon atoms. For 3229 unique reflections with $I \geq 3\sigma(I)$, final agreement factors are $R = 0.021$ and $R_w = 0.025$. The final atomic coordinates are given in Table I.

The structure of $[\text{Pd}\{\mu\text{-Cl}\}(\mu\text{-P}(\text{O})(\text{OMe})_2)\text{Rh}(\text{cod})_2]_2$ (**1**) is represented in Fig. 1. The most relevant bond parameters of the complex are collected in Table II. Interestingly, the molecular structure of **1** is trinuclear with two 'Rh(cod)' units bridged by a pair of identical Cl/P–O groups to both sides of a square-planar palladium atom. The phosphonate ligands maintain their relative *cis*-disposition as in the parent compound, and are linked to the

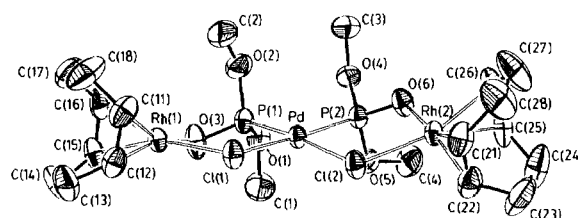


Fig. 1. Molecular structure and atom labelling scheme for the complex $[\text{Pd}\{\mu\text{-Cl}\}(\mu\text{-P}(\text{O})(\text{OMe})_2)\text{Rh}(\text{cod})_2]_2$ (**1**).

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) for the Non-hydrogen Atoms of the Complex $[\text{Pd}\{\mu\text{-Cl}\}(\mu\text{-P}(\text{O})(\text{OMe})_2)\text{Rh}(\text{cod})_2]_2$ (**1**)^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Pd	2434(1)	4772(1)	2740(1)
Rh(1)	818(1)	6173(1)	3614(1)
Rh(2)	3179(1)	4154(1)	1354(1)
Cl(1)	1139(1)	6574(2)	2729(1)
Cl(2)	2381(1)	6033(2)	1825(1)
P(1)	2579(1)	3901(2)	3626(1)
P(2)	3552(1)	3017(2)	2670(1)
O(1)	3559(2)	3710(5)	4007(1)
O(2)	2296(3)	1878(5)	3688(2)
O(3)	2090(2)	5156(6)	3919(1)
O(4)	3704(2)	1184(4)	3013(1)
O(5)	4437(2)	4053(5)	2957(1)
O(6)	3507(2)	2526(5)	2070(1)
C(1)	4069(4)	5332(9)	4163(3)
C(2)	1404(4)	1357(10)	3434(3)
C(3)	3108(4)	–320(8)	2832(3)
C(4)	5278(3)	3371(9)	2899(3)
C(11)	–555(3)	6265(8)	3260(2)
C(12)	–247(3)	8003(8)	3431(2)
C(13)	–375(5)	8890(9)	3955(3)
C(14)	250(4)	8349(9)	4483(3)
C(15)	782(4)	6681(8)	4440(2)
C(16)	418(4)	4973(8)	4281(2)
C(17)	–556(5)	4579(10)	4140(3)
C(18)	–1047(5)	5106(13)	3577(3)
C(21)	2479(4)	5059(8)	551(2)
C(22)	3211(4)	6143(9)	757(3)
C(23)	4050(6)	6043(11)	554(4)
C(24)	4586(5)	4382(11)	727(3)
C(25)	4230(4)	3055(10)	1077(2)
C(26)	3490(4)	1995(9)	887(2)
C(27)	2914(6)	1999(13)	290(3)
C(28)	2398(6)	3614(11)	113(3)

^ae.s.d.s given in parentheses.

TABLE II. Selected Bond Distances (Å) and Angles (°) for the Complex $[\text{Pd}\{\mu\text{-Cl}\}(\mu\text{-P}(\text{O})(\text{OMe})_2)\text{Rh}(\text{cod})_2]_2$ (**1**)^a

Pd–P(1)	2.231(3)	P(1)–Pd–P(2)	91.80(9)
Pd–P(2)	2.224(2)	P(1)–Pd–Cl(1)	92.04(8)
Pd–Cl(1)	2.423(2)	P(1)–Pd–Cl(2)	173.13(7)
Pd–Cl(2)	2.423(3)	P(2)–Pd–Cl(1)	174.52(11)
		P(2)–Pd–Cl(2)	89.06(8)
		Cl(1)–Pd–Cl(2)	87.59(8)
Rh(1)–Cl(1)	2.386(3)	Cl(1)–Rh(1)–O(3)	87.7(1)
Rh(1)–O(3)	2.076(3)	Cl(1)–Rh(1)–C(112) ^b	93.9(1)
Rh(1)–C(11)	2.098(5)	Cl(1)–Rh(1)–C(156) ^b	177.9(1)
Rh(1)–C(12)	2.102(5)	O(3)–Rh(1)–C(112) ^b	178.4(2)
Rh(1)–C(15)	2.088(6)	O(3)–Rh(1)–C(156) ^b	90.2(1)
Rh(1)–C(16)	2.107(6)	C(112)–Rh(1)–C(156) ^b	88.2(1)
Rh(2)–Cl(2)	2.370(3)	Cl(2)–Rh(2)–O(6)	88.0(1)
Rh(2)–O(6)	2.085(3)	Cl(2)–Rh(2)–C(212) ^b	93.4(1)
Rh(2)–C(21)	2.102(5)	Cl(2)–Rh(2)–C(256) ^b	178.1(1)
Rh(2)–C(22)	2.090(7)	O(6)–Rh(2)–C(212) ^b	177.4(2)
Rh(2)–C(25)	2.108(7)	O(6)–Rh(2)–C(256) ^b	90.0(2)
Rh(2)–C(26)	2.100(7)	C(212)–Rh(2)–C(256) ^b	88.5(2)
P(1)–O(3)	1.505(4)	Pd–P(1)–O(3)	111.2(2)
P(2)–O(6)	1.507(4)	P(1)–O(3)–Rh(1)	127.8(2)
C(11)–C(12)	1.397(8)	Pd–P(2)–O(6)	112.6(2)
C(15)–C(16)	1.397(8)	P(2)–O(6)–Rh(2)	129.0(2)
C(21)–C(22)	1.381(8)		
C(25)–C(26)	1.375(9)		

^ae.s.d.s given in parentheses. ^bC(112), C(156), C(212) and C(256) represent the midpoints of the olefinic bonds C(11)–C(12), C(15)–C(16), C(21)–C(22) and C(25)–C(26), respectively.

palladium through the P atoms and to the rhodium atoms through the oxygens. All the metals present distorted square-planar coordination, but the distortion at Pd is considerably larger with a maximum perpendicular deviation from the least-squares plane of 0.120(2) Å for the P(1) atom. The coordination planes of both Rh(1) and Rh(2) atoms are not coplanar with the central plane of palladium, being set at respective dihedral angles of 18.7(1) and –17.3(1)°.

The bond lengths involving the Pd atom are all closely similar to those previously observed in $[\text{Pd}_2\text{-}(\mu\text{-Cl})_2\{(\text{P}(\text{OEt})_2\text{O})_2\text{H}\}_2]$ [7]. As in this case, the relative short Pd–P distances (average 2.228(3) Å)

are not completely unexpected in view of the low *trans*-influence of the chloride ligand and the high electronegativity of the methoxy substituents. The Pd–Cl length, 2.423(2) Å, is slightly longer than those found in $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{P}(\text{OEt})_2\text{O}\}_2\text{H}\}_2$ (2.393(2) Å), where a double chloride bridge is present.

The phosphoryl P=O bond distances, 1.505(4) and 1.507(4) Å, compare well the values reported in the related pentanuclear compound $\text{U}\{\text{Ni}(\text{P}(\text{O})(\text{OCH}_3)_2)_2(\text{C}_5\text{H}_5)\}_4$ (av. 1.51(1) Å) [9] where the uranium atom is connected to each Ni by a double dimethoxy–phosphonate bridge, or with those observed in $[\text{Pd}_2(\mu\text{-Cl})_2\{\text{P}(\text{OEt})_2\text{O}\}_2\text{H}\}_2$ (av. 1.502(6) Å) where the phosphoryl oxygens are linked by a hydrogen bond. These values are on the long end of the bond distance range usually associated with metal-coordinated phosphoryl groups, and are clearly indicative of a remaining partial double bond character [10]. The P–OEt bond distances, average 1.579(4) Å, are in the normal range for these distances [10].

Regarding the two Rh centres, the most interesting feature concerns the coordination of the 1,5-cyclooctadiene. Normally, as described for typical transition metal–olefin bonds involving $d_{\pi}-\pi^*$ metal \rightarrow olefin back-donation, the shorter metal–olefin distance is associated with the longer C–C bonds, and vice versa. However, in our case, both Rh–C (av. 2.099(6) Å) and olefinic C–C (av. 1.388(8) Å) distances are in the lower part of the ranges reported for these types of bonds [11]. This fact probably reflects the high electronegativity of the atoms coordinated on the opposite side of the metal (oxygen and chloride), which make the rhodium atom electronically poor, and force a cyclooctadiene coordination through strong σ - and weak π -components.

In this context it should be pointed out that Rh–Cl and Rh–O bond distances compare well with data reported in similar Rh(I) complexes; for instance, the dimer compound $[\text{Rh}(\mu\text{-Cl})(\text{cod})]_2$ (Rh–Cl 2.38(1) Å) [12] and the trinuclear complex $[\text{Rh}_3(\mu_3\text{-Onapy})(\text{CO})_2(\text{cod})_2]$ (av. Rh–O 2.103(7) Å) [13].

At present we do not have a clear understanding of the reasons for such a novel coordination observed for the *cis*-phosphonate groups. Further work in this area is in progress.

Supplementary Material

Tables of anisotropic thermal parameters, hydrogen atomic coordinates, bond distances, angles and least-squares planes, and observed/calculated structure factors are available from the author (F.J.L.) on request.

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