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Orthometallation reactions of tris(p-methoxyphenyl)phosphine with dirhodium(II) tetraacetate

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Abstract

Reactions of dirhodium(II)tetraacetate $[Rh_2(OAc)_4]$ with tris(p-methoxyphenyl)phosphine (PMP) at 1:1 and 1:2 molar ratios yield, first appropriate adducts: $[Rh_2(OAc)_4P(p\text{-}CH_3OC_6H_4)_3]$ (**1a**) and $[Rh_2(OAc)_4\{P(p\text{-}CH_3OC_6H_4)_3\}_2]$ (**2a**), and then orthometallated $[Rh_2(OAc)_3\{\mu\text{-}(p\text{-}CH_3OC_6H_3)P(p\text{-}CH_3OC_6H_4)_2\}(HOAc)_2]$ (**1**) and $[Rh_2(OAc)_2\{\mu\text{-}(p\text{-}CH_3OC_6H_3)P(p\text{-}CH_3OC_6H_4)_2\}_2(HOAc)_2]$ (**2**) complexes, respectively. They have been characterized by spectroscopic methods. The molecular structure of **1** has been determined by the X-ray methods. Crystal data: space group $P\bar{1}$, $a = 11.085(5)$, $b = 11.387(5)$, $c = 13.900(6)$ Å, $\alpha = 97.29(3)$, $\beta = 105.23(3)$, $\gamma = 91.93(3)°$. In this compound The Rh–Rh distance is 2.421(1), Rh–P bond length 2.196(2) and Rh–C 1.965(5) Å. Lengths of bonds between rhodium atoms and oxygen atoms of acetato bridges are between 2.021(3) and 2.203(3) Å. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dirhodium(II) tetraacetate; Tris(paramethoxyphenyl)phosphine; Orthometallation

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1. Introduction

The reaction product of dirhodium(II) tetraacetate with triphenylphosphine, first reported by Cotton [1] was one of the first examples of bimetallic orthometallated compounds. Since that time a close attention has been paid to different orthometallated dirhodium(II) compounds with triaryl and alkyl–aryl phosphines because of the growing interest in the problem of activation of the C–H bond [2–17].

Phosphines containing chemilabile methoxy groups are not so intensively studied, except highly basic tris(2,4,6-trimethoxyphenyl)phosphine having very unusual properties [18–27], although they are potentially capable of interacting with rhodium via the oxygen atom of OCH_3 or split off $^{\oplus}CH_3$ cation and form an Rh–O bond. To our best knowledge only reactions of $[Rh_2(OAc)_4(MeOH)_2]$ with $P(o\text{-}CH_3OC_6H_4)Ph_2$ leading to mono- and bis-adduct have been published up to now [28].

We are interested in investigating the reactions of functionalized phosphines with dirhodium(II) carboxylates, the influence of functional groups in the phosphine ligands on their reactivity and structure of their complexes.

Complexes of PMP with transition metals were not extensively investigated. Only a few complexes of this ligand with other metals (Au, Hg, W, Ir, Fe, Pt, Cu, Ru) have been synthesized and crystallographically characterized up to now [29–38].

In this paper we report on the reactions of PMP with $[Rh_2(OAc)_4]$, properties and reactivity of two dirhodium(II) orthometallated complexes: $[Rh_2(OAc)_3\{\mu\text{-}(p\text{-}CH_3OC_6H_3)P(p\text{-}CH_3OC_6H_4)_2\}(HOAc)_2]$ (**1**) and $[Rh_2(OAc)_2\{\mu\text{-}(p\text{-}CH_3OC_6H_3)P(p\text{-}CH_3OC_6H_4)_2\}_2(HOAc)_2]$ (**2**).

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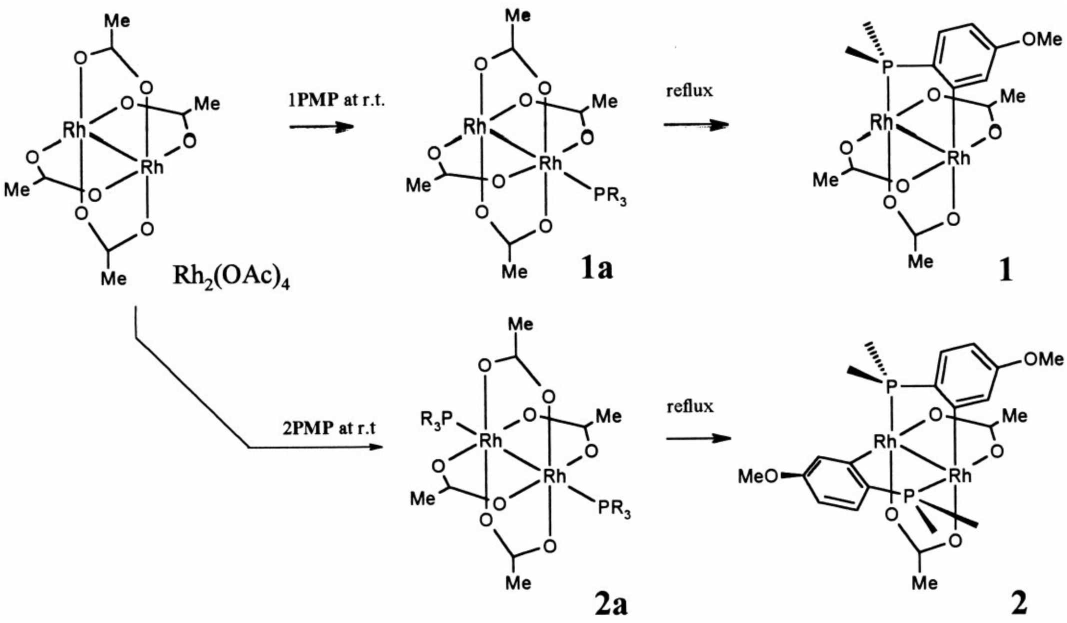

Scheme 1.

2. Results and discussion

The reactions of [Rh$_2$(OAc)$_4$] with PMP at molar ratio P/Rh$_2$ of 1/1 and 2/1 under reflux in HOAc and EtOH yield complexes **1** and **2**, respectively (Scheme 1). They are soluble in CHCl$_3$, DMSO and alcohols and insoluble in H$_2$O and CCl$_4$. The compounds have been characterized by combination of IR, UV–VIS, ^{1}H- and ^{31}P-NMR spectroscopies, as well as elemental analyses.

2.1. Crystal structure of *1*

An OTREP [39] drawing of the molecular structure of **1** is represented in Fig. 1. Details of X-ray data collection are summarized in Table 1. Atomic positional parameters and isotropic thermal parameters for **1** are listed in Table 2, and Table 3 contains selected bond lengths and angles. The structure consists of a binuclear rhodium core bridged by three acetate groups and one PMP ligand in which orthometallation has occurred at one of the phenyl rings. The axial sites are occupied by molecules of acetic acid.

The molecular structure shows slightly distorted octahedral coordination around the central atoms. The complex has almost eclipsed conformation, torsion angles O–Rh–Rh–O are below 10°: O(15)–Rh(1)–Rh(2)–O(25) = 4.7(2), O(16)–Rh(1)–Rh(2)–O(26) = 7.5(2), O(14)–Rh(1)–Rh(2)–O(24) = 6.8(2)°. Slightly larger is the torsion angle of the bridging orthometallated ligand P–Rh(1)–Rh(2)–C(21) = 11.1(2)°. The Rh–Rh distance is 2.421(1) Å, indicating rather strong single bond between two metal atoms. The Rh–P bond length is 2.196(2) and Rh–C is 1.965(5) Å. Lengths of Rh–O$^{\text{equatorial}}$ bonds change in the range 2.021(3) and 2.203(3) Å; the distances between rhodium and oxygen atoms of the bridging OAc$^-$ in *trans* position to the phosphine ligand are much longer than those for *cis* bridging acetates. Weakening of these bonds can be caused by stronger *trans*-effect of phosphorus and carbon ligating atoms in comparison with that of oxygen atoms. The bond length between the phosphorus atom and carbon atom of the metallated ring is shorter by 0.03 Å than those between phosphorus and carbon atoms of nonmetallated rings. All these lengths (1.779(5), 1.813(5) and 1.806(5) Å) are shorter than adequate lengths in free PMP (average 1.827 Å) [40]. The orthometallation does not lead to changes in methoxy substituents, which have almost the same bond lengths and bond angles in complex **1** and in free ligand. They lie approximately in the planes of phenyl rings in **1** and free ligand.

It is interesting that the lengths of rhodium-axial ligand bonds considerably differ: the Rh(2)–O(18) and Rh(1)–O(17) distances are 2.257(4) and 2.341(4) Å, respectively. Both HOAc molecules are coordinating via oxygen atom of carbonyl group, –OH groups are involved in formation of strong hydrogen bonds with oxygen atoms of bridging acetato ligand *trans* to the orthometallated phosphine ligand. The hydrogen bond with oxygen atom *trans* to the carbon of the metallated phenyl ring is stronger than the hydrogen bond with oxygen atom *trans* to the P atom.

Very interesting is the formation of two relatively strong intramolecular C–H...O hydrogen bonds: C(31)–H(31)...O(18) ($d_{\text{C–O}} = 2.940(6)$ Å) between the

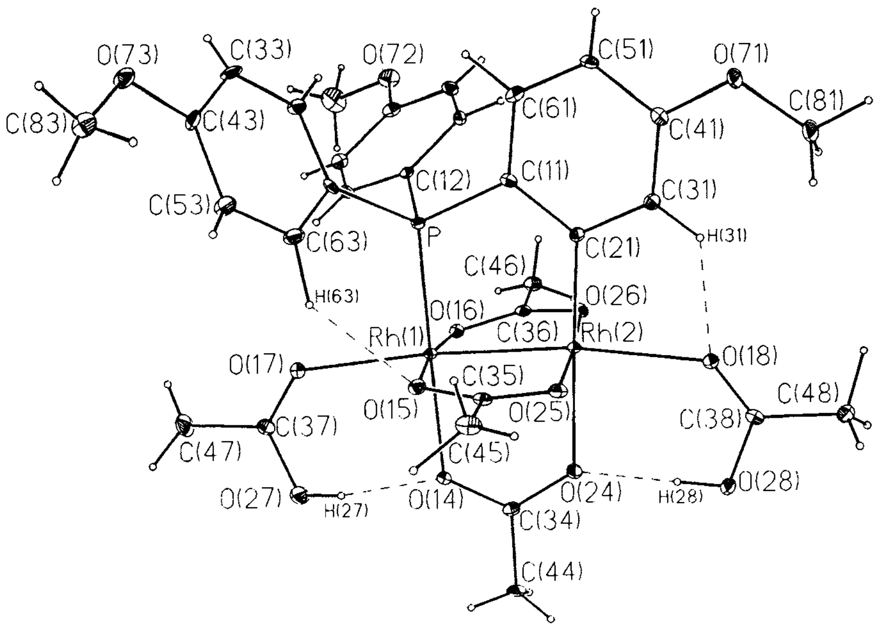

Fig. 1. X-ray crystal structure of **1** with the atomic numbering scheme.

orthometallated phenyl ring and the axial oxygen atom as well as C(63)–H(63)...O(15) ($d_{C-O} = 3.077(6)$ Å) between one of the nonmetallated phenyl rings and oxygen atom of bridging acetato ligand *cis* to the P atom. Two rather weak intermolecular hydrogen bonds are also formed: C(81)–H(811)...O(16(1 + x, y, z)) ($d_{C-O} =$ 3.289(6) Å) and C(48)–H(483)...O(26(1 − x, 1 − y, 1 − z)) ($d_{C-O} = 3.289(6)$ Å).

Table 1
Crystallographic data for 1

Empirical formula	$C_{31}H_{37}O_{13}PRh_2$
Formula weight	854.4
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.085(5)
b (Å)	11.387(5)
c (Å)	13.900(6)
α (°)	97.29(3)
β (°)	105.23(3)
γ (°)	91.93(3)
V (Å^3)	1675.1(13)
Z	2
Temperature (K)	120(1)
$D_{calc.}$ (g cm^3)	1.694
Abs. coeff.: μ (cm^{-1})	1.097
Size (mm)	0.2 × 0.3 × 0.2
Color and habit of the crystals	Deep violet
Wavelength of X-ray	0.71073
Monochromator used	Graphite
Absorption correction	None
Diffractometer	KUMA KM4
Diffraction geometry	κ
2θ range (°)	4–50
Scan type	2θ-ω
Octants collected	Half Evald sphere
Reflections collected	5416
Independent reflections	5416
Observed reflections	3420

2.2. NMR spectra of *1*, *2* and related compounds

$^{31}P\{^1H\}$ and ^1H-NMR spectra and assignments (supported by analysis of $^1H\{^{31}P\}$-NMR spectra) are given in Table 4.

The changes of $^{31}P\{^1H\}$ chemical shift of PMP in adducts **1a** and **2a** caused by coordination are similar to changes in dirhodium(II) complexes with other phosphines [5–7,15,41–43] and are ca. − 30 and − 10 ppm, respectively. Broad signals of ^{31}P and $H^{2,6}$ indicate that both adducts show dynamic properties.

Phosphorus NMR of both metallated complexes **1** and **2** show a doublet of doublets with a typical chemical shift of phosphorus atoms [5–7,15].

Proton NMR spectrum of complex **1** at room temperature consists of five singlets in aliphatic range of the spectrum: three signals of methyl groups of acetato ligands and two of methoxy groups. Differences between chemical shifts of bridging OAc^- ligands in *cis* and *trans* positions to the phosphine bridge and axial molecule of acetic acid indicates that acetato bridge *trans* is rather weakly bound to the Rh–Rh core. This spectrum also shows dynamic properties of axial HOAc ligands as evidenced by the presence of a very broad signal of –OH groups at 12.33 ppm. However, in the spectrum in $CDCl_3$ at 213 K two –OH signals at 14.03 and 11.54 ppm were observed. This indicates that in low temperatures structures of this complex are the same as in the solid state, in which one of the HOAc

Table 2
Final atomic coordinates for nonhydrogen atoms and equivalent temperature factors in **1**

Atom	x	y	z	$U_{(eq)}$
Rh1	0.16760(3)	0.22546(3)	0.64235(3)	0.01172(11)
Rh2	0.32144(3)	0.28541(3)	0.55932(3)	0.01219(11)
P	0.28738(11)	0.30598(10)	0.78994(8)	0.0122(3)
C11	0.4415(4)	0.3405(4)	0.7811(3)	0.0149(10)
C21	0.4571(4)	0.3331(4)	0.6830(3)	0.0135(10)
C31	0.5771(4)	0.3601(4)	0.6748(3)	0.0163(10)
C41	0.6765(5)	0.3947(4)	0.7590(4)	0.0183(11)
C51	0.6593(5)	0.4016(4)	0.8545(4)	0.0181(11)
C61	0.5436(5)	0.3749(4)	0.8663(3)	0.0162(10)
O71	0.7951(3)	0.4209(3)	0.7545(3)	0.0233(8)
C81	0.8152(5)	0.4239(5)	0.6579(4)	0.0257(12)
C12	0.2314(4)	0.4439(4)	0.8363(3)	0.0140(10)
C22	0.1136(5)	0.4442(4)	0.8512(4)	0.0191(11)
C32	0.0630(5)	0.5466(4)	0.8812(4)	0.0187(10)
C42	0.1344(5)	0.6538(4)	0.8976(3)	0.0188(11)
C52	0.2515(5)	0.6547(4)	0.8833(4)	0.0202(11)
C62	0.3000(5)	0.5524(4)	0.8537(3)	0.0159(10)
O72	0.0942(3)	0.7605(3)	0.9272(3)	0.0286(9)
C82	−0.0286(6)	0.7626(6)	0.9399(6)	0.043(2)
C13	0.3017(4)	0.2201(4)	0.8926(3)	0.0141(9)
C23	0.3292(5)	0.2724(4)	0.9920(4)	0.0192(11)
C33	0.3503(5)	0.2065(5)	1.0691(4)	0.0231(12)
C43	0.3447(5)	0.0844(4)	1.0511(3)	0.0206(11)
C53	0.3111(6)	0.0299(5)	0.9516(4)	0.0274(13)
C63	0.2902(5)	0.0971(4)	0.8742(4)	0.0245(11)
O73	0.3711(3)	0.0264(3)	1.1325(2)	0.0254(8)
C83	0.3775(6)	−0.0985(5)	1.1155(5)	0.0280(13)
O14	0.0475(3)	0.1554(3)	0.4967(2)	0.0165(8)
O24	0.1744(3)	0.2288(3)	0.4181(2)	0.0189(8)
C34	0.0736(5)	0.1754(4)	0.4171(3)	0.0158(10)
C44	−0.0198(5)	0.1338(5)	0.3182(4)	0.0214(12)
O15	0.2496(3)	0.0665(3)	0.6445(2)	0.0171(7)
O25	0.3804(3)	0.1193(3)	0.5567(2)	0.0179(7)
C35	0.3355(4)	0.0486(4)	0.6021(3)	0.0162(10)
C45	0.3915(6)	−0.0690(5)	0.6087(5)	0.0251(12)
O16	0.0939(3)	0.3847(3)	0.6225(2)	0.0146(7)
O26	0.2510(3)	0.4482(3)	0.5639(2)	0.0152(7)
C36	0.1544(4)	0.4630(4)	0.5936(3)	0.0149(10)
C46	0.1098(6)	0.5852(5)	0.5982(4)	0.0205(11)
O17	0.0032(3)	0.1688(3)	0.7071(2)	0.0191(8)
O27	−0.1423(4)	0.1003(4)	0.5653(3)	0.0310(10)
C37	−0.1021(5)	0.1289(4)	0.6630(4)	0.0203(11)
C47	−0.1998(6)	0.1062(6)	0.7153(6)	0.0326(14)
O18	0.4420(3)	0.3324(3)	0.4599(2)	0.0202(8)
O28	0.3145(4)	0.2831(4)	0.3060(3)	0.0328(10)
C38	0.4219(4)	0.3236(4)	0.3698(4)	0.0183(11)
C48	0.5194(5)	0.3556(5)	0.3203(4)	0.0237(12)

molecules is coordinated more strongly than the other (Fig. 1). This spectrum does not allow detection of the C(63)–H(63)...O(15) hydrogen bond observed in the solid state. This suggests that even at 213 K in solution energies of vibrations and rotations of nonmetallated rings are higher than energy of hydrogen bond. Chemical and magnetic equivalency of two pairs of protons (H^2–H^6 and H^3–H^5) in nonmetallated rings is very likely caused by unrestricted rotation of phenyl rings and methoxy groups in the $CDCl_3$ solution at high and low temperatures. In the orthometallated ring, due to splitting of H^2, three signals are observed. They are shifted to higher fields, except the signal of $H^{3,m}$, which is significantly shifted to lower fields. This can be connected with relatively strong hydrogen bond $C^{3,m}$–$H^{3,m}$–$O^{axial\ HOAc}$ observed in solid state.

In compound **2** there is only one signal of bridging acetates, which indicates the equivalency of two metallated molecules of PMP [3,5–7]. This conclusion is confirmed by $^{31}P\{^1H\}$-NMR spectrum.

2.3. IR and UV–vis spectra

The IR spectra in KBr pellet and UV–vis spectra in $CHCl_3$ solution of investigated complexes **1** and **2** are summarized in Table 5.

The IR spectra indicate that acetato bridges are symmetrical, because the differences between symmetri-

Table 3
Selected bond angles and distances for **1**

Bond distances (Å)	
Rh(1)–Rh(2)	2.421(1)
Rh(1)–P	2.196(2)
Rh(2)–C(21)	1.965(5)
Rh(1)–O(14)	2.147(3)
Rh(1)–O(15)	2.053(3)
Rh(1)–O(16)	2.035(3)
Rh(2)–O(24)	2.203(3)
Rh(2)–O(25)	2.021(3)
Rh(2)–O(26)	2.035(3)
Rh(1)–O(17)	2.341(4)
Rh(2)–O(18)	2.257(4)
P–C(11)	1.779(5)
P–C(12)	1.813(5)
P–C(13)	1.806(5)
O(27)...O(14)	2.616(6)
O(28)...O(24)	2.582(5)
C(31)...O(18)	2.940(6)
C(63)...O(15)	3.077(6)
Bond angles (°)	
Rh(2)–Rh(1)–P	91.30(5)
Rh(1)–Rh(2)–C(21)	96.0(2)
Rh(2)–Rh(1)–O(14)	88.3(1)
Rh(2)–Rh(1)–O(15)	85.9(1)
Rh(2)–Rh(1)–O(16)	87.2(1)
Rh(1)–Rh(2)–O(24)	85.5(1)
Rh(1)–Rh(2)–O(25)	88.8(1)
Rh(1)–Rh(2)–O(26)	87.4(1)
P–Rh(1)–O(15)	94.7(1)
C(21)–Rh(2)–O(25)	88.4(2)
Rh(1)–Rh(2)–O(18)	171.3(1)
Rh(2)–Rh(1)–O(17)	174.1(1)
C(31)–H(31)...O(18)	124(4)
C(63)–H(63)...O(15)	139(5)
O(27)–H(27)...O(14)	169(6)
O(28)–H(28)...O(24)	179(6)
C(11)–P–C(12)	106.6(3)
C(11)–P–C(13)	107.3(3)

Table 4
^1H-,$^{31}P\{^1H\}$-NMR spectra of PPM and related compounds (in $CDCl_3$, $T = 295$ K)

Compound	Spectrum	Chemical shifts (ppm) and coupling constants (Hz)
PPM	$^{31}P\{^1H\}$-NMR	-10.1 (s)
	^1H-NMR	3.77 (s. H^{OMe}), 7.22 (dd, $6H^{2,6}$) $^3J(H^{2,6}-P) = 8.72$, $^3J(H^{2,6}-H^{3,5}) = 7.40$, 6.85 (dd, $6H^{3,5}$) $^4J(H^{3,5}-P) = 0.90$
1a	$^{31}P\{^1H\}$-NMR	-40.2 (d*) $^1J(P-Rh) = 86.2$
	^1H-NMR	3.80 (s, $9H^{OMe}$), 1.71 (s*, $9H^{Oac}$), 6.88 (d, $6H^{3,5}$) $^3J(H^{3,5}-H^{2,6}) = 8.73$, 7.57(d*, $6H^{2,6}$)
2a	$^{31}P\{^1H\}$-NMR	-22.5 (s*)
	^1H-NMR	3.79 (s, $18H^{OMe}$), 1.64 (s, $12H^{OAc}$), 7.58(s*, $12H^{2,6}$), 6.88 (d, $12H^{3,5}$) $^3J(H^{3,5}-H^{2,6}) = 9.15$
1	$^{31}P\{^1H\}$-NMR	15.2 (dd,) $^1J(P-Rh) = 147.4$, $^2J(P-Rh) = 6.1$
	^1H-NMR	1.31 (s, $6H^{OAc-\textit{cis}}$), 2.31 (s, $3H^{OAc-\textit{trans}}$), 2.19 (s, $6H^{HOAc-axial}$), 3.89 (s, $6H^{Ome}$), 3.92 (s, $3H^{OMe-met.}$), 7.36 (dd, $4H^{2,6}$) $^3J(H^{2,6}-P) = 10.8$, $^3J(H^{2,6}-H^{3,5}) = 8.6$, 6.79 (dd, $4H^{3,5}$) $^4J(H^{3,5}-P) = 2.2$, 6.79 (t, $1H^{3,m.}$) $^4J(H^{3,m}-H^{5,m}) \approx {}^4J(H^{3,m.}-P) = 2.9$, 6.52 (dt, $1H^{5,m}$) $^4J(H^{5,m}-P) \approx {}^4J(H^{5,m.}-H^{3,m}) = 2.2$, 6.74 (dd, $1H^{6,m.}$) $^3J(H^{5,m}-H^{6,m.}) = 7.9$ $^3J(H^{6,m}-P) = 9.3$
2	$^{31}P\{^1H\}$-NMR	17.4 (dd) $^1J(P-Rh) = 168.9$, $^2J(P-Rh) = 7.9$
	^1H-NMR	1.27 (s, $6H^{OAc-bridges}$), 2.13 (s, $6H^{OAc-axial}$), 3.27 (s, $6H^{Ome,m.}$), 3.73 (s, $6H^{OMe}$), 3.77 (s, $6H^{OMe}$), 7.6 –6.2–aromatic protons

* Significantly broadened signal.

cal and asymmetrical stretching vibrations of CO_2 are relatively small. The stretching vibrations ν(Rh–O) for complex **1** are observed almost at the same frequencies as for rhodium acetate.

In the visible region of the electronic spectrum of investigated complex **1** two bands are observed. They appear at 651 and 588 nm and are red-shifted for about 63 and 112 nm, respectively in comparison with rhodium acetate. On the basis of well documented theoretical and experimental analyses of the spectra of binuclear rhodium(II) complexes [44–46] the first band should be assigned to the transition $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$, while the second one to the transition $\pi^*(Rh_2) \rightarrow \delta^*(Rh-L_{equatorial})$. The electronic spectrum of complex **2** shows only one band in the visible region at 584 nm. The energy of the second transition in this compound is most likely higher than in $Rh_2(OAc)_4$ and is hidden beneath the intense CT transitions at wavelengths shorter than 420 nm. The strong changes in energy of the bands in the visible range for both complexes prove that the introduction of orthometallated ligands strongly changes the energy of Rh_2 core orbitals.

3. Experimental

3.1. Procedures and materials

The complex $[Rh_2(OOCH_3)_4]$ [47], was prepared by literature method.

Tris(*p*-Methoxyphenyl)phosphine (PMP) was obtained from Strem and used without further purification. All solvents were deoxidized prior to use.

All operations were performed in dinitrogen atmosphere using standard Schlenk technique. IR spectrum (KBr pellet) were measured on a Bruker IFS 113v and UV–VIS spectra in $CHCl_3$ on a Beckman DU 7500 spectrometer. ^1H-NMR and $^{31}P\{^1H\}$-NMR spectra were measured in $CDCl_3$ on a Bruker AMX 300 spectrometer with traces of $CHCl_3$ as an internal reference for ^1H ($\delta = 7.23$ ppm) and 85% H_3PO_4 in H_2O as an external standard for ^{31}P.

3.2. Synthesis of 1

A suspension of $[Rh_2(OAc)_4]$ (0.177 g, 0.4 mmol) and PMP (0.144 g, 0.4 mmol) in a mixture of 10 cm^3 of ethanol and 10 cm^3 of acetic acid was refluxed with stirring for 5 h. The initial orange color of the reaction mixture was replaced by brown–gray and then the solution became deep violet. The sample was collected during several days by slow evaporation of the solvents in air; in this way crystals also suitable for X–ray analysis were obtained. Yield 0.236 g, 69%. Anal. Calc. for $C_{31}H_{37}O_{13}PRh_2$: C, 43.58%; H, 4.36%. Found: C, 43.42%; H, 4.30%.

3.3. Synthesis of 2

A mixture of $[Rh_2(OAc)_4]$ (0.177 g, 0.4 mmol) and PMP (0.302 g, 0.8 mmol) was suspended in a mixture of 10 cm^3 of ethanol and 10 cm^3 of acetic acid and refluxed with stirring for 8 h. The initial orange suspension turned to brown–gray and then was replaced by a brown–violet solution. Initial volume was reduced to

Table 5
IR spectra (KBr pellet) and UV–VIS spectra (CH_3Cl solution) of complexes **1** and **2**

Compound		$Rh_2(OAc)_4$	**1**	**2**
IR spectrum[a]	$\nu_{as}(CO_2)$	1580 (vs)	1563 (vs)	1567 (vs)
	$\nu_s(CO_2)$	1443 (vs)	1456 (vs)	1457 (s)
	$\nu_{as}(CO_2H)$	—	1686 (vs)	1678 (vs)
	$\nu_s(CO_2H)$	—	1289 (vs)	1286 (vs)
	$\nu_{as}(RhO)$	380 (m)	376 (w)	Not observed
	$\nu_s(RhO)$	354 (m)	320 (w)	Not observed
UV–VIS spectrum[b]	$\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$	588 (230)	651 (165)	584 (450)
	$\pi^*(Rh_2) \rightarrow \delta^*(Rh-L_{eq.})$	446 (95)	558 (235)	Hidden
	$\sigma(Rh-L_{ax.}) \rightarrow \sigma^*(Rh_2)$	220 (10 000)[c]	287 (18 600)	299 (20 400)

[a] ν (cm^{-1}), [b] λ_{max} (nm), [e] ([$dm^3mol^{-1}cm^{-1}$]), [c] $L = H_2O_{ax.}$, [d] $L = HOAc_{axial}$).

1/6 by evaporation of the solvent under vacuum. The precipitate was filtered off and washed with acetic acid. Yield 0.266 g, 58%. Anal. Calc. for $C_{50}H_{54}O_{14}P_2Rh_2$: C, 52.37%; H, 4.75%. Found: C, 52.25%; H, 4.68%.

3.4. X-ray crystallographic measurements

All measurements were made at 120(1) K on Kuma KM4 diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The crystallographic data together with data collection and structure refinement details are given in Table 1. The numbering scheme employed is shown in Fig. 1 drawn with the ORTEP program [39]. The intensities were corrected for Lorentz and polarization effects but absorption and extinction were not applied. The structure was solved by the Patterson method and refined by full matrix least-squares method on F^2. The H atoms were found from difference maps and refined isotropically. The refinement on 572 parameters coverage with $R = 0.0273$ and $wR(F^2) = 0.0683$. The maximum and minimum excursions in the final difference map were 0.82 and -0.71 e Å^{-3}. The refinement was performed using SHELXL program [48]. Selected bond lengths and angles are listed in Table 3.

4. Supplementary material

Tables of X-ray crystallographic data, including atomic coordinates and anisotropic thermal parameters, interatomic distances and angles, and listings of calculated and observed structure factors have been deposited at the Cambridge Crystallographic Data Centre as supplementary material.

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