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Novel rhodium(I) complexes with (2-hydroxyphenyl)diphenylphosphine ligand: catalytic properties and X-ray structures of $Rh(OC_6H_4PPh_2)(CO)(PPh_3)$ and $Rh(OC_6H_4PPh_2)\{P(OPh)_3\}_2 \cdot 0.5C_6H_6$

Anna M. Trzeciak [a], Józef J. Ziółkowski [a,*], Tadeusz Lis [a], Robert Choukroun [b]

[a] *Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie Str., 50-383 Wrocław, Poland*
[b] *Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France*

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Abstract

The novel rhodium complexes with the bidentate PO ligand ($PO = OC_6H_4PPh_2^-$) of the form Rh(PO)(CO)L (L^a = POH = $HOC_6H_4PPh_2$ (**1**), PPh_3 (**2**), $P(NC_4H_4)_3$ (**4**), $PPh_2(NC_4H_4)$ (**6**)) and $Rh(PO)L_2$ ($L^b = P(OPh)_3$ (**3**), $P(NC_4H_4)_3$ (**5**)) were obtained by ligand exchange in Rh(β-diketone)$(CO)_2$, Rh(β-diketone)(CO)L and Rh(β-diketone)L_2 complexes. All complexes of the $Rh(PO)(CO)L^a$ type exist in solution as isomers with both phosphorus atoms in the *trans* position as was shown by $^{31}P\{^1H\}$-NMR. The *trans* influence of the phosphorus atom of a bidentate PO ligand is stronger than that of oxygen atom, which is manifested by the differences of Rh–P bonds in (**2**) (2.283(1) and 2.327(1) Å) and of Rh–P (phosphite) bonds in (**3**) (2.233(2) and 2.139(2) Å). The complexes (**1**) and (**2**) used alone or with an excess of free phosphine (POH, PPh_3, $P(NC_4H_4)_3$) are not active in hexen-1-e hydroformylation at 1 MPa $CO/H_2 = 1$ and at 353 K. The lack of catalytic activity is explained by the extremely high stability of the chelate (PO) ring which does not allow the formation of the active form of the catalyst. In contrast, the complex (**3**) used alone as the catalyst precursor produces 54 and 72.9% of aldehydes when used with a six-fold excess of $P(OPh)_3$. Complex (**1**) modified with $P(OPh)_3$ catalyses hexen-1-e hydroformylation with a 73.6–84.6% yield of aldehydes. Under hydroformylation reaction conditions, the PO ligand is removed from the coordination sphere of (**1**) and complexes of the form $HRh(CO)\{P(OPh)_3\}_3$ and $HRh\{P(OPh)_3\}_4$ are formed.

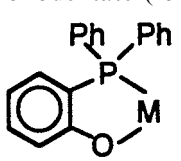
Keywords: Rhodium complexes; Phosphines; Catalysis; X-ray structure

1. Introduction

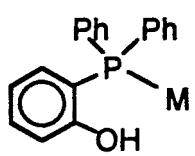
The oxo-phosphorus ligands, which belongs to the group of hemilabile ligands, have recently been applied frequently in such metal complex catalysed processes as hydrogenation, carbonylation, hydroformylation or dehydrogenation [1–5]. The presence of two coordination sites in a P–O ligand, a labile and an inert one in respect to the substitution reaction, make these ligands very attractive.

In catalytic reaction conditions the labile site of the P–O ligand can be substituted easily by the substrate molecule, which facilitates its activation. Therefore, metal complexes with hemilabile ligands are usually activating small molecules, such as CO, CO_2, H_2 [6–8].

Hydroxyphenyl phosphines, which contain hard oxygen and soft phosphorus belong to bifunctional ligands which may coordinate to the metal as bidentate (form A) or monodentate (form B).



form A



form B

* Corresponding author. Tel.: +48-71-3286325; fax: +48-71-3282348.

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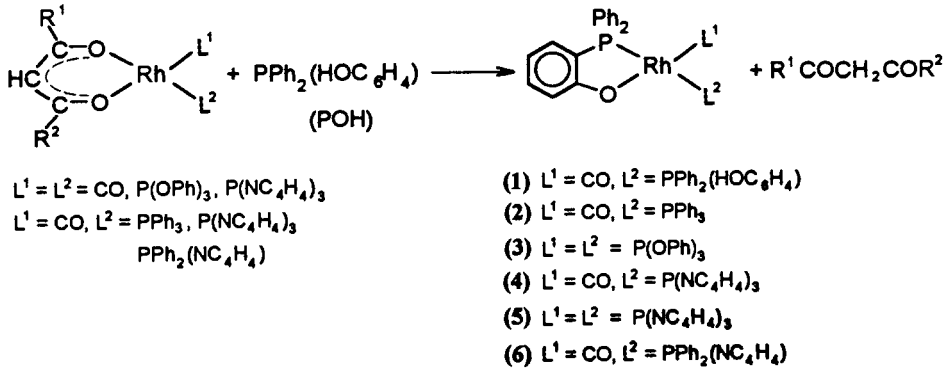


Scheme 1.

The examples of both modes of coordination have been found for ruthenium [9], nickel, palladium, platinum, cobalt [10] and rhenium [11] coordination compounds but till now not for rhodium(I). Some polynuclear rhodium(II) complexes with tris(2,4,6-trimethoxyphenyl)phosphine in which demethylated phosphine coordinates as PO ligand bridging two rhodium(II) ions have been obtained [12].

In this paper we present results of structural as well as reactivity studies of rhodium(I) complexes with (2-hydroxyphenyl)diphenylphosphine (POH).

The main goal of our studies was to investigate the properties of POH phosphine as a modifying ligand in respect of its application in catalytic systems used for olefin hydroformylation. It is well known that the proper selection of ligands coordinated to the metal in homogeneous catalysts is a main factor determining their catalytic activity demonstrated by the high yield and selectivity of the given reaction.

Although triphenylphosphine is a classical example of such effective modifying ligand, we found interesting to study how the presence of OH group in the *ortho* position of the phenyl ring of POH will change its modifying properties. It was expected that structural investigations of the new Rh(I) complexes as well as detailed studies of its preparation may provide some new information about the coordination properties and specificity of both the potential donor atoms in the POH ligand.

Such properties determine the pathway and the mechanism of the ligand substitution reaction in rhodium(I) complexes as catalyst precursors and therefore are important for preparation of the new, catalytically active species.

2. Results and discussion

On the basis of our earlier papers we concluded that with $Rh(acac)(CO)_2$ as a hexen-1-e hydroformylation catalyst precursor only 20% of aldehydes and ca. 80% of hexen-2-e (hexen-1-e isomerization reaction product) are obtained [13]. However, the introduction of PPh_3 to the system increases the yield of aldehydes to 80–90% [13,14].

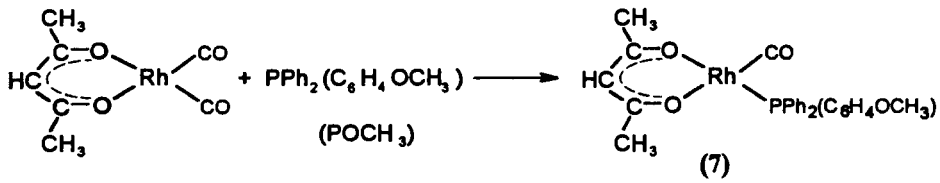
Initial studies of hexen-1-e hydroformylation with the catalytic system containing $Rh(acac)(CO)_2$ and POH (at 1 MPa H_2/CO and 353 K) pointed to a quite different effect of POH ligand on the reaction. Even at a small concentration of POH a significant decrease of the yield of both products, aldehyde and hexen-2-e, was observed as compared with the respective yield in a reaction catalyzed by an $Rh(acac)(CO)_2 + PPh_3$ system. When [POH]:[Rh] = 0.5 only 79.2% of hexen-2-e was found after 2 h and when [POH]:[Rh] = 2 or 3 no reaction products were found.

From these simple experiments one may conclude that the POH ligand not only does not create a catalytically active form of rhodium(I) complex, but even deactivates $Rh(acac)(CO)_2$ as a catalyst precursor. To explain the rather inhibiting effect of the POH ligand on the hydroformylation reaction, the properties of specially prepared complexes with PO have been studied.

2.1. Synthesis of $Rh(PO)(CO)L^a$ and $Rh(PO)L^b_2$ complexes

In syntheses of metal complexes with POH described up to now, chloride complexes were usually used as the substrates: K_2PtCl_4 [10], $\{Ru(\eta\text{-}C_5Me_5)Cl\}_4$ [9], $[ReOCl_4]^-$, $[ReOCl_3(PPh_3)_2]$ [11]. Chlorides were removed as HCl or NaCl (when sodium acetate was added) usually under reflux condition.

We have found, that β-diketonate ligands are substituted easily by PO according to the Scheme 1. In the following Rh(I) complexes: $Rh(acac)(CO)_2$, $Rh(acac)(CO)(PPh_3)$, $Rh(acac)(CO)(P(NC_4H_4)_3)$, $Rh(acac)(CO)(PPh_2(NC_4H_4))$, $Rh(acac)\{P(OPh)_3\}_2$, $Rh(bta)\{P(OPh)_3\}_2$ and $Rh(acac)\{P(NC_4H_4)_3\}_2$ (acac = acetyloacetonate, bta = benzoyloacetonate) total substi-



Scheme 2.

tution of β-diketonate ligand by POH undergoes at room temperature within a few minutes.

Different rhodium(I) complexes with β-diketonates can be used as starting complexes for syntheses and in some cases the same products may be obtained, i.e. reaction of $Rh(bta)\{P(OPh)_3\}_2$ and $Rh(acac)\{P(OPh)_3\}_2$ with POH produce the same complex (**3**) of the form $Rh(PO)\{P(OPh)_3\}_2$. From the observation of the reaction of rhodium(I) β-diketonates with POH phosphine one may conclude that POH always acts first as proton donor and cannot be regarded as normal phosphine with only nucleophilic properties. A good illustration of the properties of POH ligand is provided by its reaction with $Rh(acac)(CO)_2$, which is not typical as compared with other phosphines. Generally, phosphines depending on their σ-donor and/or π-acceptor properties substitute one or two CO ligands in $Rh(acac)(CO)_2$. Therefore, stronger σ-donor phosphines L ($L = PPh_3$, $PPh_2(NC_4H_4)$) produce Rh(acac)(CO)L complexes as the substitution reaction products whereas stronger π-acceptor phosphorus ligands, L, ($L = P(OPh)_3$, $P(NC_4H_4)_3$) give $Rh(acac)L_2$ complexes [15,16]. Regardless of the kind of phosphorus ligands used, an acetylacetonato ligand always remains in the coordination sphere. However, when POH phosphine reacts with $Rh(acac)(CO)_2$, complex (**1**) is formed as a product of the substitution of one CO group by a neutral POH ligand and the simultaneous substitution of acac by an anionic chelating form of phosphine, PO.

Complex (**1**) (Rh(PO)(CO)(POH)) is the only identified product of the reaction of $Rh(acac)(CO)_2$ with POH, regardless of the concentration of phosphine used.

At the ratio [POH]:[Rh] = 1:1, the substitution of CO in $Rh(acac)(CO)_2$ was not complete, which was proved by IR (ν_{CO} observed at 2020 and 2070 cm^{-1}), confirming the presence of unreacted $Rh(acac)(CO)_2$. When POH phosphine was applied in excess, unreacted POH remained in the reaction mixture. The highest yield of complex (**1**) (87%) was obtained at the ratio of [POH]:[Rh] = 2:1.

Apart from the reaction of $Rh(acac)(CO)_2$ with POH (in which acac and CO are substituted by PO and POH, respectively), in all other reactions under studies mainly acac is substituted by PO. In the reaction of POH with $Rh(acac)L_2$ ($L = P(OPh)_3$, $P(NC_4H_4)_3$), only one product of the general formula $Rh(PO)L_2$ was found.

2.1.1. Reaction of $Rh(acac)(CO)_2$ with (2-methoxyphenyl)diphenylphosphine ($POCH_3$)

The replacement of a proton in POH by the methyl group changes tremendously the reactivity of the ligand ($POCH_3$) towards $Rh(acac)(CO)_2$. Regardless of the ratio of [$POCH_3$]:[Rh] only a complex of the form $Rh(acac)(CO)(POCH_3)$, (**7**), is formed (Scheme 2), just as in the reaction with PPh_3. Its spectroscopic parameters (^{1}H-, $^{31}P\{^1H\}$-NMR) are very close to those of $Rh(acac)(CO)(PPh_3)$.

2.2. Spectroscopic characterization of $Rh(PO)(CO)(L^a)$ and $Rh(PO)L_2^b$ complexes

2.2.1. $^{31}P\{^1H\}$-NMR spectra

The $^{31}P\{^1H\}$-NMR spectrum of complex (**1**) was recorded for a reaction mixture containing $Rh(acac)(CO)_2$ + 1.5 POH in a C_6D_6 solution as well as for an isolated compound (**1**) dissolved in $CDCl_3$. Both spectra are identical and characteristic for a structure in which phosphorus atoms are located in the *trans* position. This is manifested by the relatively high value of the coupling constant $^2J(P-P) = 304$ Hz. Similar results were obtained for *trans*-$RhCl(CO)[cp_2ZrCl(PCH_2Ph_2)_2]$ (363.2 Hz) [17] and *trans*-[Rh{$Ph_2PCH\cdots C(\cdots O)$-Ph}$(CO)(PPh_3)$] (301 Hz) [5] complexes. The $^2J(P-P)$ value equal to 307 Hz for complex (**2**) points to the *trans* position of P-atoms in that complex in solution.

$^{31}P\{^1H\}$-NMR measurements made it possible to distinguish different coordination modes of hydroxyphosphine POH. When POH forms a chelate ring the phosphorus signal switches down-field up to δ = ca. 45 ppm, whereas in the case of the coordination of a neutral POH molecule, the $^{31}P\{^1H\}$-NMR signal is observed at about 25 ppm. The assignment of the $^{31}P\{^1H\}$-NMR band at ca. 45 ppm to chelating coordination of PO was clear after comparison with $^{31}P\{^1H\}$-NMR spectra of complexes (**1**), (**2**), (**3**) (Fig. 1) and (**5**) (Table 1).

Complexes with pyrrolyl phosphines ((**4**) and (**6**)) show dynamic properties in solution at room temperature, which is demonstrated by the lack of P–P as well as Rh–P (pyrrolylphosphine) couplings (Fig. 2).

In the $^{31}P\{^1H\}$-NMR spectra of (**4**) and (**6**) measured at 293 K the doublets from the PO ligand at 46.9 and 47.0 ppm, respectively, are observed as well as singlets from N-pyrrolylphosphines at 91.0 and 69.7 ppm. The

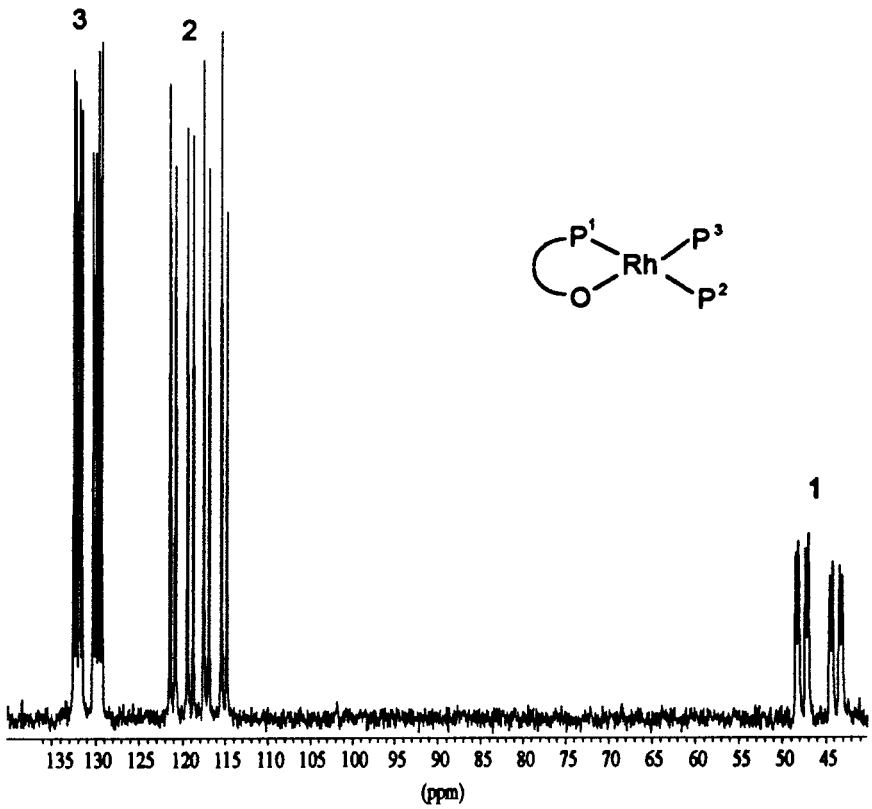


Fig. 1. ^{31}P-NMR spectrum of $Rh(OC_6H_4PPh_2)\{P(OPh)_3\}_2$ (**3**).

lack of a coupling between rhodium and N-pyrrolylphosphine phosphorus indicates the dissociation of coordinated N-pyrrolylphosphine and a dynamic equilibrium of 16 and 14 electron complexes (Scheme 3).

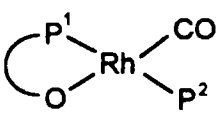
The lowering of temperature to 223 K allowed us to get a well resolved spectrum of complex (**4**) composed of two double doublets, which undoubtedly confirms that both phosphorus ligands PO and $PPh_2(NC_4H_4)$ are located in the *trans* position (Fig. 2). Similar temperature changes of the spectrum of the $[Rh\{Ph_2PCH\cdots C(\cdots O)Ph\}(CO)(PPh_3)]$ complex in which triphenylphosphine dissociates have been observed by other authors [5].

In the case of complex (**6**) the decrease of temperature to 223 K is not sufficient to obtain conditions of slow exchange. The lines assigned to complex (**6**) are broadened and resolved badly, which allowed us only to estimate the parameters of the spectra (Table 1).

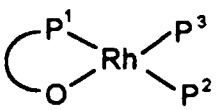
Table 1
^{31}P-NMR data of Rh(PO) complexes (**1**)–(**6**) in C_6D_6

Complex	(**1**)	(**2**)	(**4**)[a]	(**6**)[a]	(**3**)	(**5**)
δ_1	47.4	46.3	44	43.9	45.8	42.3
$J(Rh–P_1)$	132	134	129	132	137.8	141.3
δ_2	25.5	26.3	89	68	118.1	96.7
$J(Rh–P_2)$	136	138	203	153	248	210
δ_3					130.9	106.5
$J(Rh–P_3)$					274	238
$J(P_1–P_2)$	304	308	407	332	480	407
$J(P_1–P_3)$					38	39
$J(P_2–P_3)$					79	64

[a] $CDCl_3$, 223 K.



for: (1), (2), (4), (6)



for: (3), (5)

2.2.2. The exchange of phosphines in complexes of the Rh(PO)(CO)L[a] type

It was expected that phosphines with π-acceptor properties stronger than POH would be able to substitute the POH ligand in (**1**) or the PPh_3 ligand in (**2**). However, the analysis of $^{31}P\{^1H\}$-NMR spectra of a solution containing complex (**1**) and a two-fold excess of $P(NC_4H_4)_3$ showed after 3 h as well as after 12 h unchanged substrates, which excludes the substitution of CO or POH by $P(NC_4H_4)_3$.

On the other hand, both complexes (**1**) and (**2**) react with $P(OPh)_3$ producing complex (**3**), which was proved by $^{31}P\{^1H\}$-NMR spectra measured in situ as well as for the isolated reaction product (Scheme 4).

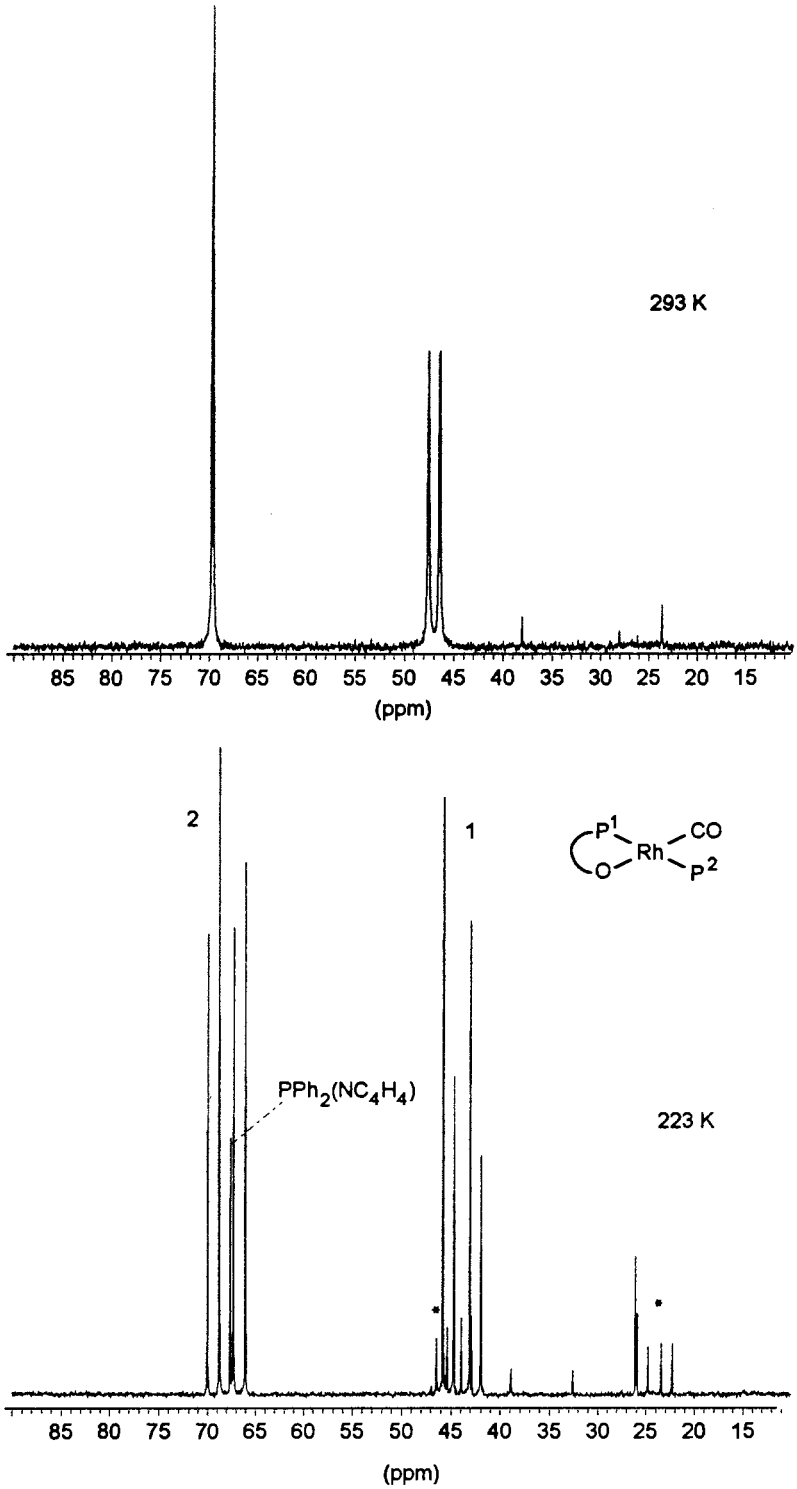
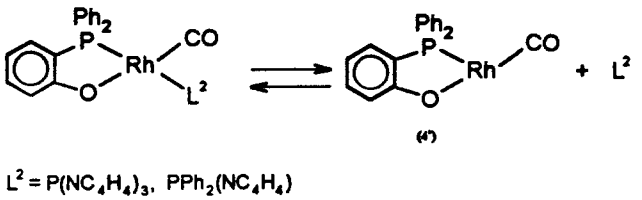


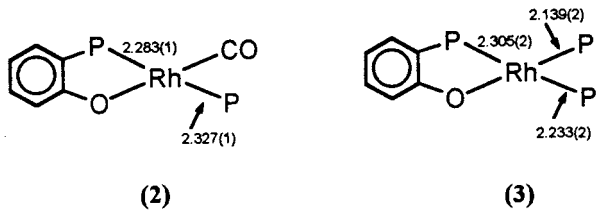
Fig. 2. ^{31}P-NMR spectra of Rh($OC_6H_4PPh_2$)(CO)[$PPh_2(NC_4H_4)$] (**4**) at 293 and 223 K. *Rh(PO)(CO)(POH).

2.2.3. Trans influence in Rh(PO)(CO)(L[a]) complexes

All synthesized complexes of the form Rh(PO)(CO)(L[a]), (**1**), (**2**), (**4**) and (**6**), exist in solution as only one isomer with both phosphorus atoms in the *trans* position. The phosphorus atom of the bidentate POH phosphine results in a stronger *trans* influence than the oxygen atom, which is manifested in different bond lengths proved by X-ray analysis for complexes (**2**) and (**3**). In complex (**2**), the Rh–P bond length of chelating PO and terminal PPh_3 phosphines are different (Scheme 5). The length of the Rh–P(phosphite) bond in complex (**3**) in the *trans* position to the phos-



Scheme 3.

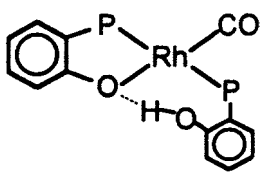


Scheme 5.

phorus atom of the chelating PO ligand is longer than that of the Rh–P bond in the *trans* position to oxygen of the PO ligand (Scheme 5) (Tables 2 and 3).

2.2.4. ^{1}H-NMR spectra

^{1}H-NMR spectra of complexes (**1**)–(**6**) demonstrate multiplets in the region of 6–8 ppm, typical for phenyl protons (see Section 4). In complex (**1**) the signal of the OH group proton is shifted down-field to 12.9 ppm. A similar position of OH resonance was observed in the ^{1}H-NMR spectrum of a ruthenium complex in which the hydrogen bond between the OH group of a monodentate POH ligand and the oxygen atom of a chelating PO ligand was found by X-ray [9]. It is reasonable to propose the presence of a hydrogen bond also in complex (**1**).



2.2.5. IR spectra

The coordination of POH phosphine to rhodium(I) as a PO chelating ligand causes significant changes in the IR spectrum—a shift of frequencies in the region of 850 and 1250 cm^{-1} as well as band splitting at ca. 1460 and 1580 cm^{-1} (Table 4). In rhenium complexes with POH major changes in IR caused by coordination were observed only in the region of 580–900 cm^{-1} [11].

2.3. Molecular structure of (2) and (3) complexes

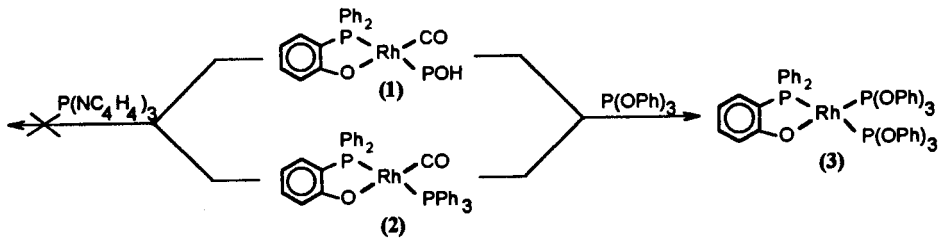
Selected bond distances and angles in complexes (**2**) and (**3**) are given in Table 2 and Table 3, respectively.

Both complexes, (**2**) and (**3**), have a square planar structure (Figs. 3 and 4) with a small deviation (0.024(2) Å) of rhodium atom out of the plane formed by the four atoms coordinated to rhodium in complex (**2**). A five-membered chelate ring formed by the PO ligand coordinating to rhodium is similar in both complexes (**2**) and (**3**) with the Rh–O bonding equal to 2.042(3) and 2.058(3) Å and the Rh–P bonds equal to 2.283(1) and 2.305(2) Å, respectively. The P(1)–Rh–O(6) angle is 83.2(1)° in (**2**) and 83.1(1)° in (**3**). The corresponding angle in the ruthenium complex Ru(η-C_5Me_5)(PO)(POH) is 80.49(7)°, whereas in rhenium(V) complexes it is between 76.1(2) and 80.9(3)° [11].

The Rh–C(7) distance in complex (**2**) equal to 1.795(5) Å is comparable with Rh–C distances in other rhodium–carbonyl complexes [18–20].

The Rh–P(2) bond in complex (**2**), 2.327(1) Å, is elongated in comparison with the Rh–P bonds in Rh(β-diketone)(CO)(PPh_3) type complexes [18–20]. Such a bond elongation could be explained by a stronger *trans* influence of the phosphorus of a PO ligand than that of the oxygen of a β-diketone. In complex (**3**), where the Rh–P(2) bond is 2.139(2) Å, *trans* influence is more distinct, whereas the Rh–P(3) bond is much longer and equals 2.233(2) Å. In the Rh(acac){$P(OPh)_3$}$_2$ complex Rh–P bonds are 2.147(2) and 2.156(2) Å, very close to the Rh–P(2) bond distance in complex (**3**) [21].

The chelate coordination of the PO ligand causes the shift of electron density in the oxophenyl ring, slightly different in complexes (**2**) and (**3**). In both complexes, (**2**) and (**3**), the delocalization of electron density in fragment C(1)–C(6)–C(5) and the elongation of C(1)–C(6) and C(5)–C(6) bonds are observed. The other C–C bond distances in the oxophenyl ring of (**3**) are similar to those in the remaining phenyl rings of phos-



Scheme 4.

Table 2
Selected bond lengths (Å) and angles (°) in $Rh(OC_6H_4PPh_2)(CO)(PPh_3)$ (**2**)

Bond lengths (Å)			
Rh–P(1)	2.283(1)	C(7)–O(7)	1.160(5)
Rh–P(2)	2.327(1)	P(1)–C(1)	1.803(5)
Rh–O(6)	2.042(3)	O(6)–C(6)	1.321(5)
Rh–C(7)	1.795(5)	C(1)–C(6)	1.400(6)
P(1)–C(11)	1.816(5)	P(1)–C(21)	1.818(4)
C(1)–C(2)	1.409(6)	C(2)–C(3)	1.361(6)
C(3)–C(4)	1.406(7)	C(4)–C(5)	1.364(6)
C(5)–C(6)	1.413(6)		
Bond angles (°)			
P(1)–Rh–P(2)	168.4(1)	P(2)–Rh–O(6)	85.8(1)
C(7)–Rh–O(6)	178.0(2)	P(1)–Rh–O(6)	83.2(1)
C(7)–Rh–P(1)	95.3(2)	Rh–P(1)–C(1)	100.2(2)
C(7)–Rh–P(2)	95.9(2)	Rh–O(6)–C(6)	120.3(3)

phine. In the oxophenyl ring of complex (**2**), C(2)–C(3) and C(4)–C(5) bonds of 1.36 Å are in agreement with the double-bond character and the other bonds are longer. The different distribution of electrons in the oxophenyl rings of (**2**) and (**3**) can be explained by the influence of the remaining ligands coordinated to rhodium. In complex (**3**) two π-acceptor $P(OPh)_3$ ligands interact equally on the chelate ring. In complex (**2**) the π-acceptor character of CO and the σ-donor character of PPh_3 cause the unsymmetrical distribution of electrons in the chelating fragment.

2.4. Catalytic activity

The catalytic activity of rhodium(I) complexes with a POH ligand were tested in the hydroformylation reaction of hexen-1-e, under 1 MPa of $CO/H_2 = 1$ at 353 K.

When complexes (**1**) or (**2**) were used alone, after 2 h only ca. 1.5% of hexen-2-e was obtained whereas in a similar reaction catalyzed by $Rh(acac)(CO)_2$ 66.5% of hexen-2-e and 14.2% of aldehydes were produced. Since usually the addition of free phosphorus ligands significantly increases the yield of aldehydes [27], in further experiments an excess of different phosphines, like POH, PPh_3 or $P(NC_4H_4)_3$ was applied; however in all experiments only trace amounts (1.5%) of hexen-2-e or hexen-3-e, the isomerization products of hexen-1-e, were found. The IR spectra of post-reaction mixtures showed unchanged complexes (**1**) or (**2**). It seems to be clear that the high stability of the PO chelate ring in both complexes makes difficult their transformation to the active form of the catalysts. Similarly POH phosphine added to $Rh(acac)(CO)_2$ as a catalyst precursor completely blocks catalytic activity. Contrary to the above mentioned phosphine modifying ligands, phosphite $P(OPh)_3$ is able to transform complex (**1**) to the active form. A three-fold excess of $P(OPh)_3$ per rhodium is already enough to obtain 73.6% of aldehydes (Table 5).

Table 3
Selected bond lengths (Å) and angles (°) in $Rh(OC_6H_4PPh_2)\{P(OPh)_3\}_2 \cdot 0.5C_6H_6$ (**3**)

Bond lengths (Å)			
Rh–P(1)	2.305(2)	P(1)–C(1)	1.804(4)
Rh–P(2)	2.139(2)	C(1)–C(6)	1.413(6)
Rh–P(3)	2.233(2)	O(6)–C(6)	1.311(4)
Rh–O(6)	2.058(3)	P(1)–C(11)	1.823(4)
P(1)–C(21)	1.821(4)	C(1)–C(2)	1.393(5)
C(2)–C(3)	1.390(5)	C(3)–C(4)	1.380(6)
C(4)–C(5)	1.384(6)	C(5)–C(6)	1.412(5)
Bond angles (°)			
P(1)–Rh–P(2)	95.2(1)	P(2)–Rh–P(3)	93.4(1)
P(1)–Rh–P(3)	171.5(1)	P(3)–Rh–O(6)	88.4(1)
P(1)–Rh–O(6)	83.1(1)	Rh–P(1)–C(1)	100.2(2)
P(2)–Rh–O(6)	178.2(1)	Rh–O(6)–C(6)	120.3(3)

To identify the catalytically active form of the catalyst in the reaction under consideration, the solution of complex (**1**) with an excess of $P(OPh)_3$ heated (353 K) under 1 MPa of CO/H_2 during 1 h was analysed by $^{31}P\{^1H\}$-NMR technique. The spectrum showed the origin of the doublets of hydrido phosphito complexes of the form $HRh\{P(OPh)_3\}_4$ (δ 130 ppm, J(Rh–P) 233 Hz) and $HRh(CO)\{P(OPh)_3\}_3$ (δ 140.5 ppm, J(Rh–P) 240 Hz) [22]. It means that under hydroformylation reaction conditions, conducted at the excess of free $P(OPh)_3$, (2-hydroxyphenyl)-diphenylphosphine (POH) was removed from the rhodium coordination sphere and the catalytic system became like $Rh(acac)(CO)_2 + P(OPh)_3$, which had been studied previously [23].

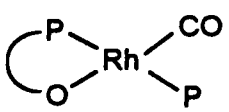
It is worth noting that complex (**3**) alone used as a catalyst for hexen-1-e hydroformylation produces ca. 54% of aldehydes and ca. 43% of hexen-2-e. Spectroscopic analysis based on IR, ^{1}H-NMR and ^{31}P-NMR measurements showed that in the presence of a H_2/CO mixture, complex (**3**) undergoes total transformation into $HRh(CO)\{P(OPh)_3\}_3$ and $Rh_6(CO)_{16}$ within 1 h (Scheme 6). The observed catalytic activity is the joint effect of the parallel action of $HRh(CO)\{P(OPh)_3\}_3$ responsible for hydroformylation and the $Rh_6(CO)_{16}$ cluster, which catalyses the isomerization of olefin. The yield of aldehydes is increased up to 72.9% after the introduction of free $P(OPh)_3$ to the reaction medium. The opposite effect is brought about by POH phosphine, which strongly inhibits the catalytic activity of complex (**3**) and/or retards its action as a homogeneous catalyst (Table 5).

3. Summary

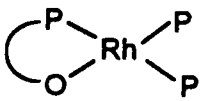
(a) The investigations of the catalytic activity of the complexes under consideration warrant the conclusion that the stability of the chelate ring formed by PO coordinating to rhodium is extremely high, even under

Table 4
IR data (in KBr) of POH ligand and Rh(PO) complexes (cm^{-1})

POH/complex	(1)	(2)	(4)	(6)	(5)
696	697	697	697	697	692
753	750	750	750	750	761
807					
880	861	850	840	850	854
1240	1238		1235	1238	
	1261	1265	1260	1260	1266
1285	1280				
1290		1311	1310	1301	1313
1431	1431	1439	1430	1430	1442
1462	1458	1450	1450	1451	1455
	1480	1480	1470	1480	1482
1579	1550	1550	1540	1530	1551
	1582	1582	1570	1575	1582
ν_{CO}	1966	1963	1986	1966	



for: (1), (2), (4), (6)



for: (5)

conditions of the hydroformylation reaction (353 K and 1 MPa of $H_2/CO = 1$). That fact practically excludes the application of systems containing rhodium complexes and POH for hydroformylation. It is worth noting that almost all other rhodium complexes, irrespective of their structure, are activated under H_2/CO pressure and can be used as catalyst precursors.

(b) In the investigated group of complexes with PO ligands only the phosphito complex (**3**) exhibits catalytic properties, even in the absence of a phosphorus ligand excess.

(c) Only $P(OPh)_3$ is able to convert inactive complexes (**1**) or (**2**) into catalytically active rhodium hydride species. Such properties were not found for N-pyrrolylphosphine, $P(NC_4H_4)_3$, of similar electronic and steric properties.

(d) In contrast to POH, the use of $POCH_3$ phosphine for the modification of a $Rh(acac)(CO)_2$ catalyst precursor showed a similar effect to that of PPh_3. At a five-fold excess of $POCH_3$ the yield of aldehydes increased to 82.3% and that of hexen-2-e 16.5%. The relatively low value of the *n*/*iso* ratio (ca. 1.7) may be caused by the higher steric hindrance of $POCH_3$ phosphine as compared with PPh_3 (Table 6).

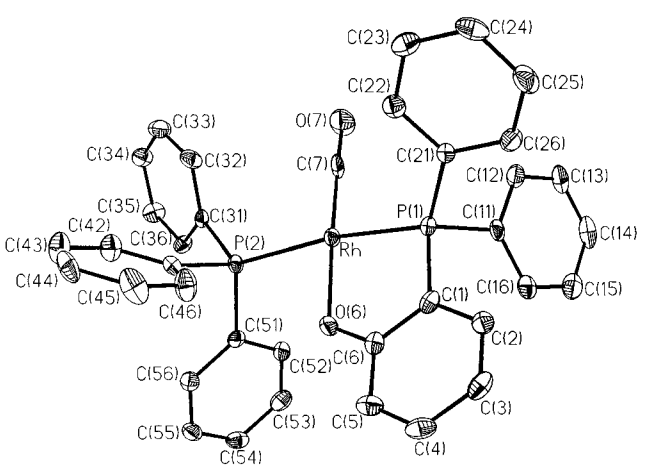


Fig. 3. Molecular structure of $Rh(OC_6H_4PPh_2)(CO)(PPh_3)$ (**2**).

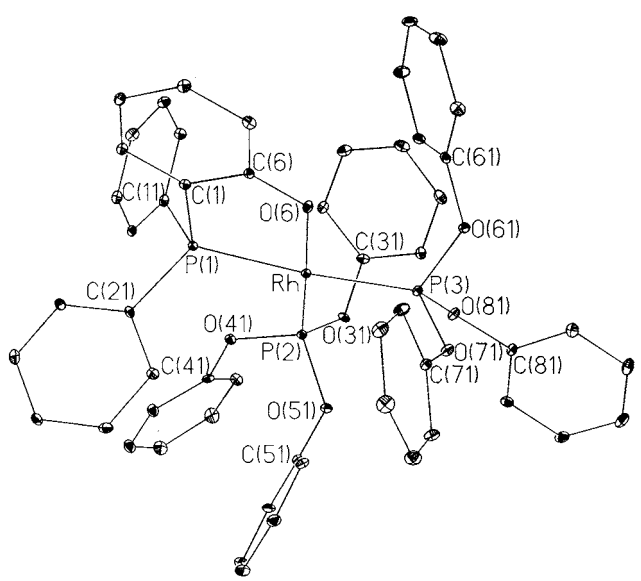


Fig. 4. Molecular structure of $Rh(OC_6H_4PPh_2)\{P(OPh)_3\}_2$ (**3**).

Table 5
Products of hexen-1-e hydroformylation with the complex (**3**) only and with the catalytic systems (**3**)/$P(OPh)_3$, (**3**)/POH and (**1**)/$P(OPh)_3$ at 1 MPa CO/H_2 (1:1), 353 K, after 2 h[a]

Catalytic system	[P]:[Rh]	Hexen-1-e	Hexen-2-e	Aldehydes	*n*/*iso*
(**3**) only	–	2	44	54	2.7
(**3**)/$P(OPh)_3$	6	–	22.3	72.9	7.5
(**3**)/POH	3	100	–	–	–
(**1**)/$P(OPh)_3$	3	0.4	25.9	73.6	3.6
(**1**)/$P(OPh)_3$	6	0.6	14.8	84.6	4.8
(**1**)/$P(OPh)_3$	9	0.4	18.2	80.3	4.6

[a] $[(3)] = 8 \times 10^{-6}$ mol, $[(1)] = 9 \times 10^{-6}$ mol, [hexen-1-e] = 6.5×10^{-3} mol (0.8 cm^3), toluene 1.5 cm^3.

4. Experimental

Rhodium complexes $Rh(acac)(CO)_2$ [24], Rh(acac)(CO)(PPh_3) [25], Rh(acac)(CO)($P(NC_4H_4)_3$) [16], Rh(acac)(CO)($PPh_2(NC_4H_4)$) [16], Rh(acac)$\{P(OPh)_3\}_2$ [26], Rh(bta)$\{P(OPh)_3\}_2$ [17], Rh(acac)$\{P(NC_4H_4)_3\}_2$ [16], $HRh\{P(OPh)_3\}_4$ [28], $HRh(CO)(PPh_3)_3$ [29] and POH [30] were prepared according to the literature.

$PPh_2(CH_3OC_6H_4)$ was purchased from Aldrich Chemical. The solvents were purified using typical procedures. Syntheses were carried out under N_2 atmosphere by using Schlenk technique.

4.1. Rh(PO)(CO)(POH) (*1*)

To the solution of $Rh(acac)(CO)_2$ (0.052 g, 2×10^{-4} mol) in 3 cm^3 of benzene 0.11 g (4×10^{-4} mol) of POH was added and stirred for ca. 1 h, then vacuum evaporated to ca. 50% of the initial volume. Addition of heptane (ca. 2 cm^3) accelerates precipitation. The product was filtrated and washed with heptane. Yield: 0.12 g (87%). Anal. Calc. for $C_{37}H_{29}O_3P_2Rh$: C, 64.74; H, 4.26; Found: C, 64.25; H, 4.19. ^{1}H-NMR(C_6D_6)/δ: 6.69 m (PO), 7.1 m (PO), 7.27 m, 7.88 m, 12.9 (OH).

4.2. Rh(PO)(CO)(PPh_3) (*2*)

This compound was prepared like (**1**) using 0.11 g (2.2×10^{-4} mol) of Rh(acac)(CO)(PPh_3) and 0.065 g (2.3×10^{-4} mol) POH. Yield: 0.125 g (85%). Anal. Calc. for $C_{37}H_{29}O_2P_2Rh$: C, 66.28; H, 4.36; Found: C, 66.00; H, 4.21. ^{1}H-NMR(C_6D_6)/δ: 6.6 m (PO), 7.22 m (PO), 7.42 m, 7.79 m.

Complexes (**4**) and (**6**) were obtained in a similar procedure using as substrates Rh(acac)(CO)($P(NC_4H_4)_3$) and Rh(acac)(CO)($PPh_2(NC_4H_4)$) complexes, respectively.

(**4**): Yield: 81%. Anal. Calc. for $C_{31}H_{26}N_3O_2P_2Rh$: C, 58.39; H, 4.11; N, 6.59; Found: C, 58.76; H, 4.60; N, 6.10. ^{1}H-NMR(C_6D_6)/δ: 6.31 s, 6.7 m, 7.07 m, 7.23 m, 7.84 s.

(**6**): Yield: 82%. Anal. Calc. for $C_{35}H_{28}NO_2P_2Rh$: C, 63.75; H, 4.28; N, 2.12; Found: C, 63.80; H, 4.43; N, 1.98. ^{1}H-NMR(C_6D_6)/δ: 6.47 t, 6.67 t, 7.1 s, 7.3 m, 7.53 m, 7.76 m, 7.92 m.

4.3. Rh(PO)$\{P(OPh)_3\}_2$ (*3*)

To 0.26 g (3.2×10^{-4} mol) of Rh(acac)$\{P(OPh)_3\}_2$ in 3 cm^3 of benzene 0.1 g (3.6×10^{-4} mol) POH was added. The solution was stirred for 1 h and then evaporated under vacuum, washed with heptane and dried. Yield: 0.26 g (81%). Anal. Calc. for $C_{54}H_{44}O_7P_3Rh$: C, 64.79; H, 4.43; Found: C, 64.20; H, 4.15. ^{1}H-NMR(C_6D_6)/δ: 6.5 m, 6.9 m, 7.1 m, 7.2 d, 7.5 d, 7.8 m. The crystals for X-ray analysis have been obtained from a benzene–heptane solution. Recrystallization from a benzene–ethanol solution gave the compound with ethanol in the crystal.

Complex (**5**) was obtained in a similar procedure, using Rh(acac)$\{P(NC_4H_4)_3\}_3$ as a substrate.

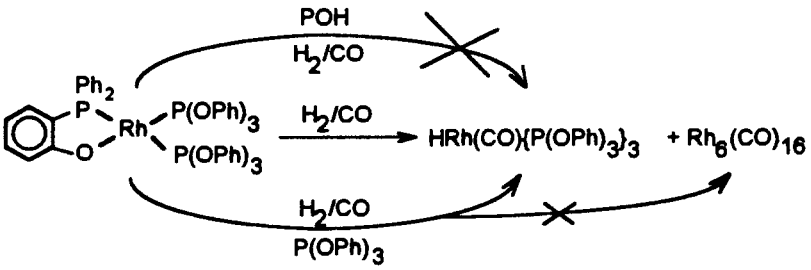
(**5**): Yield: 80%. Anal. Calc. for $C_{42}H_{38}N_6OP_3Rh$: C, 60.13; H, 4.57; N, 10.02; Found: C, 60.00; H, 4.31, N, 9.82. ^{1}H-NMR(C_6D_6)/δ: 5.99, 6.23, 6.35 t, 6.78, 7.03 m, 7.09 s, 7.59 m.

4.4. Rh(acac)(CO)($POCH_3$) (*7*)

^{1}H-NMR (C_6D_6)/δ: 1.41 (CH_3 acac), 1.85 (CH_3 acac), 3.06 (CH_3), 5.21 (CH acac), 6.35 m, 6.55 t, 6.97 m, 7.1 m, 7.88 m. ^{31}P$\{^1$H$\}$-NMR (C_6D_6)/δ: 39.6, *J*(Rh–P) 180 Hz.

5. Hydroformylation experiments

Hydroformylation reactions were performed in a steel autoclave (40 cm^3) under 1 MPa of H_2/CO (1: 1) starting pressure. The catalyst precursor (e.g. $Rh(acac)(CO)_2$ or (**2**) or (**3**), 8×10^{-6}–1×10^{-5} mol) and an appropriate amount of phosphine were weighted in small teflon vessels and introduced to the autoclave under a dinitrogen atmosphere. Toluene (1.5 cm^3) and hexen-1-e (0.8 cm^3, 6.5×10^{-3} mol) were



Scheme 6.

added. The autoclave was closed, purged with dihydrogen and filled with 5 atm. of H_2 and 5 atm. of CO. The autoclave was heated to 353 K and reaction mixture was stirred magnetically. After 2 h the autoclave was cooled and opened. The products were separated from the catalyst by the vacuum distillation and analysed by GC (or GC–MS).

6. Instruments

The following instruments were used: IR spectra: FT-IR Nicolet Impact 400; GC–MS: Hewlett-Packard 5890II; NMR: Bruker 300 MHz (121.5 MHz for $^{31}P\{^1H\}$-NMR). TMS was used as an internal standard in ^1H measurements and 85% H_3PO_4 as an external standard in $^{31}P\{^1H\}$ measurements.

7. Crystallography

7.1. Crystal data for complex 2

Yellow crystals, $C_{37}H_{29}O_2P_2Rh$, $M = 670.45$, monoclinic, space group, $P2_1/n$, $a = 9.871(3)$, $b = 14.688(4)$, $c = 20.768(7)$ Å, $\beta = 95.61(3)°$, $U = 2996.6(16)$ Å^3, $Z = 4$, $D_{calc.} = 1.486$ g cm^{-3}, $F(000) = 1368$, $T = 120(2)$ K, $\mu(Mo–K_\alpha) = 0.71$ mm^{-1}, $\lambda(Mo–K_\alpha) = 0.71073$ Å.

7.2. Crystal data for complex 3

Yellowish needles, $C_{54}H_{44}O_7P_3Rh \cdot 0.5C_6H_6$, $M = 1039.77$, triclinic, space group, $P\bar{1}$, $a = 10.097(4)$, $b = 13.506(6)$, $c = 18.850(8)$ Å, $\alpha = 80.10(4)$, $\beta = 79.04(4)$, $\gamma = 76.06(4)°$, $U = 2427.8(18)$ Å^3, $Z = 2$, $D_{calc.} = 1.422$ g cm^{-3}, $F(000) = 1070$, $T = 120(2)$ K, $\mu(Mo–K_\alpha) = 0.505$ mm^{-1}, $\lambda(Mo–K_\alpha) = 0.71073$ Å.

Table 6
Products of hexen-1-e hydroformylation with the catalytic system $Rh(acac)(CO)_2/POCH_3$ at 1 MPa CO/H_2 (1:1), 353 K, after 2 h[a]

$[POCH_3]$:[Rh]	Hexen-1-e	Hexen-2-e	Aldehydes	*n*/*iso*
0.5	19.2	80.8	–	
2.0	39.4	48.3	12.1	<1
3.0	10.7	63.2	25.9	1.2
5.0	0.8	16.5	82.3	1.7

[a] [Rh] = 1 x 10^{-5} mol, [hexen-1-e] = 6.5 x 10^{-3} mol (0.8 cm^3), toluene 1.5 cm^3.

7.3. Data collection and processing

For both crystals the intensities were collected with a KUMA KM4 four-circle diffractometer in the $\omega - 2\theta$ mode (with crystals of dimensions $0.25 \times 0.2 \times 0.14$ mm for **2** and $0.6 \times 0.05 \times 0.15$ mm for (**3**) and $Mo–K_\alpha$ radiation; 5221 ($2 < \theta < 25°$) of which 4549 unique ($R_{int} = 0.043$) and 8991 ($2 < \theta < 26°$) of which 8217 unique ($R_{int} = 0.068$) reflections were measured, respectively. For both crystals analytical absorption corrections were applied; $T_{min} = 0.842$ and $T_{max} = 0.907$ and $T_{min} = 0.768$ and $T_{max} = 0.956$ for **2** and **3**, respectively. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELXL93 [31]. Atomic scattering factors and anomalous dispersion terms used in the refinement were taken from Ref. [32]. The carbon-bonded hydrogen atoms were included in geometrically calculated positions with d(C–H) = 0.95 Å and with $U_{iso}(H) = 1.2 U_{eq}(C)$. Final $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma |F_o| = 0.0322$ [for $I > 2\sigma(I)$], $wR(F^2) = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2} = 0.0867$, $S = 1.054$ (for all data) for **2** and $R_1 = \Sigma (||F_o| - |F_c||)/\Sigma |F_o| = 0.0334$ [for $I > 2\sigma(I)$], $wR(F^2) = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2} = 0.0886$, $S = 1.021$ (for all data) for **3**.

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