Polish J. Chem., **77**, 749–756 (2003)

Rhodium Complexes with $HP(O)R_2$ (R = Ph, OPh) Ligands – Structure and Catalytic Reactions with Phenylacetylene*

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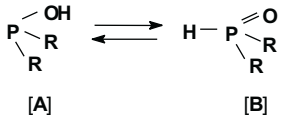
(Received October 30th, 2002)

In the reaction of $Rh(acac)(CO)_2$ with $HP(O)(OPh)_2$ the hydride rhodium(III) complex, $HRh\{[P(OPh)_2O]_2H\}_2$ **(1)**, was obtained. Complex **(1)** at room temperature catalyzes dimerization of phenylacetylene to *trans*-diphenylbutenyne (PhCH=CHC≡CPh). The reaction of $[RhCl(cod)]_2$ with $HP(O)Ph_2$ and PPh_3 led to the following new rhodium complexes: *trans*-$RhCl[P(OH)Ph_2]_2(PPh_3)$ **(2)**, *trans*-$RhCl[P(OH)Ph_2](PPh_3)_2$ **(3)**, $HRh[P(OH)Ph_2]_3$ **(4)** and $RhCl_2\{[PPh_2O]_2H\}_2[P(OH)Ph_2]_2$ **(5)**, characterized by ^1H and ^{31}P NMR spectra. The hydride complex **(4)** catalyzes a coupling of $HP(O)Ph_2$ with PhC≡CH (phosphorylation reaction) to 1-(diphenylphosphinyl)-2-phenylethene ($PhCH=CHP(O)Ph_2$). In the first step of this reaction **(4)** reacts with PhC≡CH forming alkene complex $Rh(CH=CHPh)[P(OH)Ph_2]_3$ **(6)**.

Key words: rhodium complexes, catalysis, phosphorylation reaction

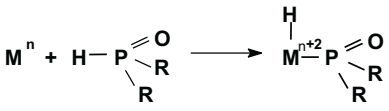
The secondary phosphine oxides ($HP(O)R_2$) and hydrogen phosphonates ($HP(O)(OR)_2$) are existing in two tautomeric forms ([A] and [B]) containing tricoordinated phosphorus and tetracoordinated phosphorus, respectively, usually with excess of form [B] (1):



(1)

where: R = Ph or OPh

Tautomeric form [B] coordinate to transition metals M^n (n = 0, 1+, 2+) usually *via* oxidative addition (2). The reaction products are new metal complexes in M^{n+2} oxidation state containing M-H and M-P bondings [3–6].



(2)

* Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

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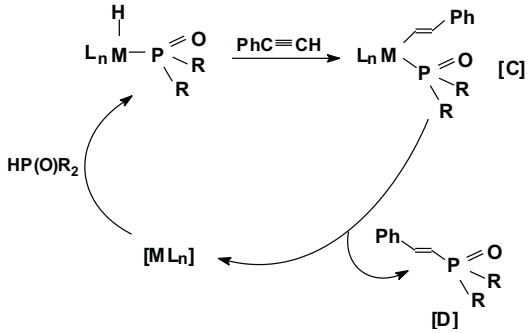
Compounds of formula $P(OH)R_2$, containing tricoordinated phosphorus, [A], coordinate to transition metals *via* phosphorus atom forming M-P bondings [4,7]. There is observed an increasing interest of transition metal complexes with those ligands (both $HP(O)R_2$ and $HP(O)(OR)_2$) because of their catalytic activity, *e.g.* in alkenylphosphine oxides and alkenylphosphonates synthesis (phosphorylation reaction). These compounds, which may be obtained in reaction of phosphine oxides or hydrogen phosphonates with unsaturated compounds like alkenes, dienes, alkynes, allenes are very important substrates for synthesis of many different organophosphorus compounds [3,7–10] (Scheme 1).

Scheme 1



The carbon-carbon double bonds in alkenylphosphine oxides [C] react with nucleophilic reagents like alcohols, tiols, amines and phosphines leading to the formation of very interesting bifunctional compounds (bidentate ligands). Different complexes of Pd [3,7–10,13], Rh [4,11] and Ru [12] were found as active catalysts of phosphorylation reaction. Those complexes are formed „*in situ*" in reaction of metal catalyst precursors and $HP(O)Ph_2$ or cyclic diphosphites. It is worth to note, that according to our knowledge till now, the phosphorylation products with catalysts containing diphenylphosphito ligand ($L_nM(H)[P(O)(OPh)_2]$) were not obtained. According to widely accepted catalytic phosphorylation mechanism [4,9,11] the reaction starts with coordination of $HP(O)R_2$ to the metal and formation of alkenyl complex [C], which next is transformed to the reaction product [D] (Scheme 1).

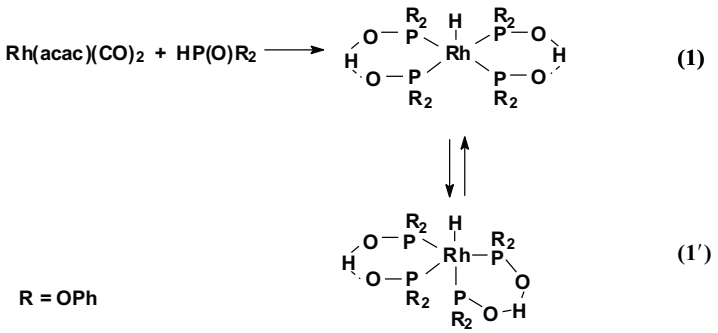
This paper presents structural studies of rhodium complexes with diphenylphosphine oxide ($HP(O)Ph_2$) and diphenylphosphonate ($HP(O)(OPh)_2$) as well as studies on their different reactivity towards phenylacetylene.

RESULTS AND DISCUSSION

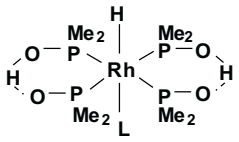
Rhodium(III) complex, $HRh\{[P(OPh)_2O]_2H\}_2$ (1): In reaction of $Rh(acac)(CO)_2$ with excess of $HP(O)(OPh)_2$ the hydride complex of formula $HRh\{[P(OPh)_2O]_2H\}_2$ **(1)** is formed, where $[P(OPh)_2O]_2H$ means chelating diphosphorus – cyclic ligand sta-

bilized with hydrogen bondings (-O-H...O-) (Scheme 2). The formation of cyclic chelates was earlier found for other phosphonato ligands [1,5,6]. The structure of complex **(1)** was proposed on the basis of ^{1}H NMR and ^{31}P NMR studies. ^{1}H NMR spectrum of **(1)** shows typical signal of hydride at δ = –8.1 ppm as doublet of quintets. This univocally indicates the presence of rhodium complex in which hydride ligand is coupled with four equivalent phosphorus (^{31}P) and one rhodium (^{103}Rh) nuclei. The equivalence of phosphorus ligands is proved by ^{31}P NMR spectrum, presenting the doublet at δ = 97.6 ppm (J_{Rh-P} 127.8 Hz). The low value of J_{Rh-P} coupling constant is characteristic for Rh(III) complex. The IR spectrum shows intense ν(Rh-H) frequency (assigned for Rh-H bonding) at 2130 cm^{-1} and the lack of ν(OH) frequency expected *ca.* 3400 cm^{-1}.

Scheme 2



In similar reaction of Rh(acac)$(CO)_2$ with HP(O)$(OMe)_2$ and ligand L the hexacoordinated Rh(III) complexes of formula HRh{[P$(OMe)_2$O]$_2$H}$_2$L (L = CO, PPh_2Me, P^nBu_3, P$(O^iPr)_3$) were obtained [5]. Ligand L coordinates in *trans* position to hydride ligand [5].



The complex **(1)** does not react with CO, P$(OPh)_3$ and PPh_3, with the last two ligands probably because of steric hindrance reasons. Additionally, in solution we observed some amounts of another hydride complex, showing in hydride region of ^{1}H NMR a doublet of double quartets (Fig. 1). Rather high value of coupling constant J_{P-H} (229 Hz) suggests *trans* position of H^- and one of P-atoms. This compound can be considered as an isomer of complex **(1)** of trigonal bipyramidal symmetry **(1′)** (Scheme 2).

Reaction of (1) with phenylacetylene: Reaction of **(1)** with phenylacetylene was ^{1}H NMR monitored. It was found that after addition of phenylacetylene to **(1)** besides the signal at 3.1 ppm (derived from CH proton of phenylacetylene) a new doublet at δ = 5.7 ppm (J_{H-H} 16.7 Hz) appeared. According to literature data [14,15] we propose

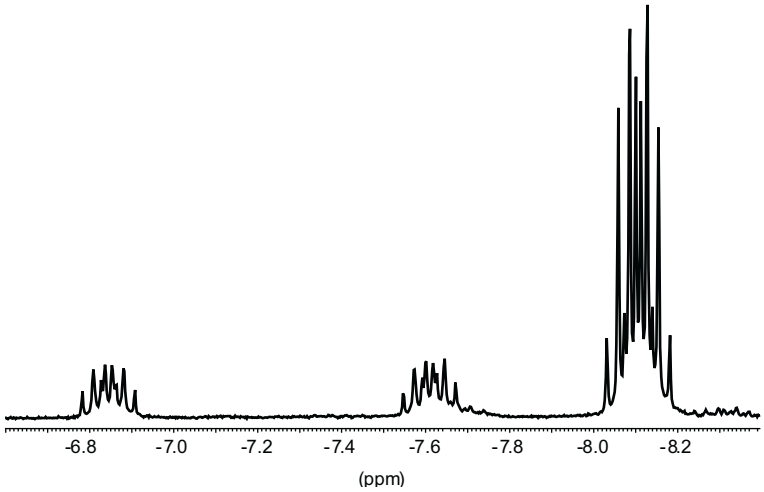
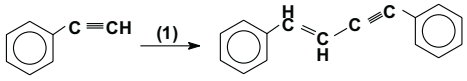


Figure 1. ^{1}H NMR spectrum in hydride region of complexes **(1)** (δ = –8.1 d of q) and **(1′)** (δ = –7.23 d of d q).

formation of *trans*-diphenylbutenyne (PhCH=CHC≡CPh) as a product of phenylacetylene dimerization (3). This reaction product was identified with GC-MS, as characteristic signal recorded at m/e 204.



(3)

The complex **(1)** catalyzes dimerization of phenylacetylene at room temperature both in benzene as well as in dichloromethane. Depending on [PhC≡CH]:[Rh] concentration ratio, the yield of the dimer (PhCH=CH≡CPh) was varying from 12 to 92% (Table 1). In some of experiments we observed formation of low concentration (*ca.* 5%) of acetophenone as a side product. The structure of **(1)** does not change during the reaction course, what was proved by ^{31}P NMR measurements. Catalytic phosphorylation reaction was not successful and we did not observe any product of interaction of $HP(O)(OPh)_2$ with PhC≡CH, both with **(1)** as well as with $Rh(acac)(CO)_2$ *in situ*. This is in agreement with observations of other authors [9].

Table 1. The yield of *trans*-diphenylbutenyne obtained in the reaction of **(1)** with PhC≡CH at room temp.

[PhC≡CH]:[Rh]	Solvent	Time h	Yield %
15:1	CH_2Cl_2	24	92
15:1	C_6H_6	24	83
90:1	CH_2Cl_2	24	12
		48	34

Reactions of $[RhCl(cod)]_2$ with $HP(O)Ph_2$: It was announced earlier that $[RhCl(cod)]_2$ is a good catalyst precursor of phosphorylation with $HP(O)Ph_2$ [11], but very little is known about the catalytically active complexes in that system. The formation of hydride rhodium complex, detected by ^{1}H NMR measurements in reac-

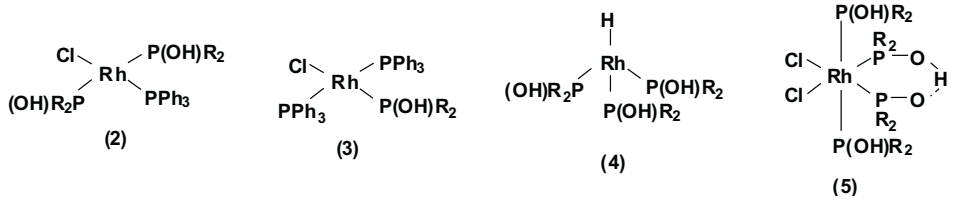
tion of [RhCl(cod)]$_2$ with HP(O)Ph_2, was reported, however, the structure of that complex was not proposed [11].

In our studies the reaction of [RhCl(cod)]$_2$ with HP(O)Ph_2 in solution was monitored with ^{1}H and ^{31}P NMR. In some experiments triphenylphosphine has been added to check its competition with HP(O)Ph_2 in coordination to rhodium. In the reaction of [RhCl(cod)]$_2$ with PPh_3 and HP(O)Ph_2 (ratio [Rh]:[PPh3]:[HP(O)Ph_2] = 1:2:2) three rhodium(I) complexes have been identified with ^{31}P NMR method. Two of them are square planar complexes with PPh_3 and P(OH)Ph_2, of proposed formula: *trans*-RhCl[P(OH)Ph_2]$_2$(PPh_3) **(2)** and *trans*-RhCl[P(OH)Ph_2](PPh_3)$_2$ **(3)**. Both complexes were characterized by ^{31}P NMR spectra of AB_2X type (A,B = ^{31}P, X = ^{103}Rh) (Table 2). Third complex, **(4)**, is a hydride rhodium(I) complex what was proved by the presence of quartet at δ = –16.5 ppm ($J_{P\text{-}H}$ 22.9 Hz) in ^{1}H NMR. The doublet in ^{31}P NMR spectrum of **(4)** indicates on equivalence of three phosphorus ligands and this allows to propose the composition of complex under discussion as HRh[P(OH)Ph_2]$_3$ **(4)**. This complex has probably the tetrahedral structure, similar to that proposed for HRh(PPh_3)$_3$ [16,17].

Table 2. ^{31}P NMR data of rhodium complexes formed in the reaction of [RhCl(cod)]$_2$ with HP(O)Ph_2 and PPh_3.

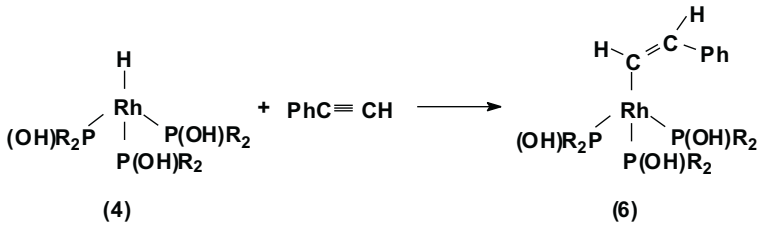
Complex	δ_1 (HP(O)Ph_2), ppm J(Rh-P), Hz	δ_2 (PPh_3), ppm J(Rh-P), Hz	J(P-P), Hz
trans-RhCl[P(OH)Ph_2]$_2$(PPh_3) **(2)**	88.7 dd, 113.8	30.2 dt, 135.2	17.9
trans-RhCl[P(OH)Ph_2](PPh_3)$_2$ **(3)**	78.7 dt, 100.4	17.9 dd, 120.6	17.2
HRh[P(OH)Ph_2]$_3$ **(4)**	95.5 d, 142.3		
$RhCl_2${[PPh_2O]$_2$H}$_2$[P(OH)Ph_2]$_2$ **(5)**	88.2 dt, 112.1 73.3 dt, 107.8		19.7
Rh(CH=CHPh)[P(OH)Ph_2]$_3$ **(6)**	86.3 d, 149.8		

In another experiment the concentration of HP(O)Ph_2 was twice increased, ([Rh]:[PPh_3]:[HP(O)Ph_2] ratio was equal 1:2:4) and the hydride complex **(4)** was found as the main reaction product. In such conditions, the complexes **(2)** and **(3)** are present in traces, whereas a new Rh(III) complex appears. This complex, $RhCl_2${[PPh_2O]$_2$H}[P(OH)Ph_2]$_2$ **(5)**, has a characteristic ^{31}P NMR spectrum of A_2B_2X type (A,B = ^{31}P, X = ^{103}Rh) composed with two doublets of triplets (Table 2).



Similar complex $RhCl_2(R_2POHOPR_2)_2(R_2POH)_2$ (R_2P = $OCH_2CMe_2CH_2OP$) with secondary cyclic phosphite was earlier reported [6].

The ratio of reaction components [Rh]:[PPh_3]:[$HP(O)Ph_2$] equals 1:2:4 was found as optimal for performance of the reaction with phenylacetylene, because of high concentration of hydride complex **(4)**, potential catalyst of phosphorylation reaction. Indeed, the analysis of the mixture containing $[RhCl(cod)]_2$, two phosphorus ligands ($HP(O)Ph_2$, PPh_3) and phenylacetylene, after 15 h of the reaction at [PhC≡CH]:[Rh] (ratio = 4) proved the presence of 1-(diphenylphosphinyl)-2-phenylethene ($PhCH=CHP(O)Ph_2$), the phosphorylation reaction product. This compound was spectroscopically identified by the signals at 25.2 ppm in ^{31}P NMR (very close value to literature data 24.4 ppm [11]) and characteristic doublet of doublets at 6.88 ppm in ^{1}H NMR (literature value 6.83 dd [11]). There was no hydride complex in the reaction mixture, however, a small amount of the new rhodium complex **(6)** appeared, demonstrated by the doublet at 86.3 ppm in ^{31}P NMR spectrum. We claim that complex **(6)** was also formed in the reaction of **(4)** with phenylacetylene. Immediately after addition of PhC≡CH to the solution containing hydride complex **(4)**, the disappearance of doublet at 95.5 ppm and appearance of a new doublet at 86.3 ppm was observed in ^{31}P NMR spectrum. Simultaneously we observed disappearance of the hydride signal in ^{1}H NMR. In accordance to the literature data [4] this results may be interpreted as an evidence of phenylacetylene coordination to rhodium with formation of an alkene complex **(6)** (4). Similar alkene complex was identified in reaction of $HRhCl(PPh_3)_2[P(O)(OCMe_2CMe_2O)_2]$-$[P(OH)(OCMe_2CMe_2O)_2]$ with PhC≡CH [4]. The compound **(6)** was identified by us also in reaction of $[RhCl(cod)]_2$ with $HP(O)Ph_2$ and PhC≡CH, as the main rhodium containing product.



(4) (6) (4)

Moreover, in this reaction at the absence of PPh_3, the product of phosphorylation ($PhCH=CHP(O)Ph_2$) was also obtained, what may point out that the rhodium complex catalyzing this reaction has no other than $HP(O)Ph_2$ phosphorus ligands in coordination sphere.

CONCLUSIONS

The above presented results demonstrate different coordination behaviour of $HP(O)Ph_2$ and $HP(O)(OPh)_2$ ligands in respect to rhodium as well as differences in reactivity of rhodium complexes with these ligands toward PhC≡CH. $HP(O)(OPh)_2$ as a ligand shows stronger than $HP(O)Ph_2$ tendency to form the stable chelating rings.

Hydride complex **(1)** catalyzes dimerization of phenylacetylene but not of phosphorylation. It seems indeed that the reason of such discrepancy is inhered in diffe-

rent stability of chelate bond stability and that phosphorylation reaction requires terminally bonded $P(O)(OPh)_2^-$ ligand.

Rhodium complexes with $HP(O)Ph_2$ ligand are more various and contain ligands coordinated both as bidentate as well as monodentate one. Besides of that in reaction mixture there are coexisting Rh(I), **(2)**, **(3)**, **(4)**, and Rh(III) **(5)** complexes. Phenylacetylene coordinates to rhodium hydride complex **(4)** forming alkene complex **(6)**, whereas dimerization of phenylacetylene is not observed.

EXPERIMENTAL

Rhodium complexes were obtained according to literature methods: $Rh(acac)(CO)_2$ [18] and $[RhCl(cod)]_2$ [19]. $HRh(O)(OPh)_2$ was purchased from Aldrich. $HP(O)Ph_2$ was obtained by hydrolysis of $PClPh_2$. To 10 ml of cold water 1 g $PClPh_2$ was added slowly and the mixture was stirred for 2 h. The HCl formed was removed by stream of N_2. The product was dried under P_4O_{10}. All syntheses were performed under N_2 using standard Schlenk technique.

Synthesis of (1): To 0.1 g of $Rh(acac)(CO)_2$ 0.3 ml of $HP(O)(OPh)_2$ was introduced and the mixture was stirred *ca*. 15 min. Next 3 ml of benzene were added and the stirring was continued 3 h. The volatizes were removed under reduced pressure and next 4 ml of hexane were added to the residue, forming white powder of the final product. Yield: 0.3 g. Anal. Calcd. for $RhC_{48}H_{43}O_{12}P_4$: C, 55.5; H, 4.1. Found: C, 55.3; H, 4.2. ^{1}H NMR, $CDCl_3$, δ (ppm): –8.1, doublet of quintets, $J_{P\text{-}H}$ 8.0, $J_{Rh\text{-}H}$ 12.5 Hz; 7.5 m **(1)**, –7.23, doublet of double quartets, $J_{P\text{-}H}$ 229, $J_{P\text{-}H}$ 7.8, $J_{Rh\text{-}H}$ 16.2 Hz **(1′)**. ^{31}P NMR, $CDCl_3$, δ (ppm): 97.6, $J_{Rh\text{-}P}$ 127.8 Hz.

Reaction of (1) with PhC≡CH in NMR tube: To 0.032 g of **(1)** in $CDCl_3$ 0.02 ml of PhC≡CH was added and after 15 min NMR measurements were performed.

Reaction performance of $[RhCl(cod)]_2$ with $HP(O)Ph_2$ and PPh_3: The solution containing 0.028 g (5.5×10^{-5} mol) of $[RhCl(cod)]_2$ and 0.055 g (2.1×10^{-4} mol) of PPh_3 in 4 ml of benzene was stirred for 5 min and then 0.55 g (2.7×10^{-4} mol) of $HP(O)Ph_2$ was added. The orange solution was stirred overnight, benzene was removed under reduced pressure, the orange residue was dissolved in $CDCl_3$ and analyzed by means of ^{1}H and ^{31}P NMR spectroscopy.

Reaction performance of $[RhCl(cod)]_2$ with $HP(O)Ph_2$, PPh_3 and PhC≡CH: The sample was prepared as described above using 0.022 g of $[RhCl(cod)]_2$, 0.053 g of PPh_3, 0.1 g of $HP(O)Ph_2$ and 0.05 ml of PhC≡CH. In similar way the sample without PPh_3 was prepared using 0.015 g of $[RhCl(cod)]_2$, 0.064 g of $HP(O)Ph_2$ and 0.03 ml of PhC≡CH.

Acknowledgments

Grant no PBZ-KBN 15/09/T09/99/01d is gratefully acknowledged. Authors are indebted to Dr. H. Bartosz-Bechowski for preparation of $P(OH)Ph_2$.

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