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Complexation of hydrophosphoranes: possible mechanism and coordination activity

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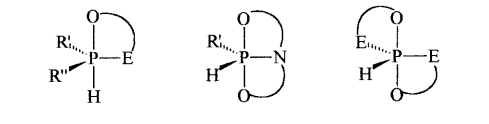
Abstract

Complexation of (4*S*,9*S*)-4,9-diethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (**1**) and 3,3,8,8-tetramethyl-1,6-dioxa-4,9-diaza-5λ^5-phosphaspiro[4,4]nonane (**2**) with $[Rh(CO)_2Cl]_2$; 2,3,7,8-dibenzo-1,6-dioxa-4,9-diaza-5λ^5-phosphaspiro-[4,4]nonane (**3**) with $[Rh(CO)_2Cl]_2$ and $[MCl_2(COD)]$ (M = Pd, Pt); (2S,7S)-2,7-dimethyl-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4,4]nonane (**4**) with $[Rh(CO)_2Cl]_2$ and $[PdCl_2(COD)]$ has been studied. The products have been characterized by ^{1}H-, ^{2}H-, ^{13}C-, ^{31}P-NMR, IR spectroscopy, laser desorption mass spectrometry and X-ray photoelectron spectroscopy. A possible mechanism for hydrophosphoranes complexation is discussed. A correlation between Lewis basicity and coordination activity has been found for ligands **1**–**3**. Phosphorane **4** was shown to coordinate by means of the P(III)-tautomer. © 2000 Elsevier Science B.V. All rights reserved.

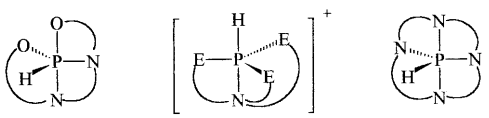
Keywords: Hydrophosphoranes; Rhodium complexes; Palladium complexes; Complexation; X-ray analysis.

1. Introduction

Hydrophosphoranes (HP) form the original class of pentacoordinated phosphorus compounds, represented by monocyclic [1,2], bicyclic (condensed [3,4] and spiro structures [5,6]), tricyclic (neutral [7,8] and cationic [9,10]) and tetracyclic [11,12] systems:



E = NR, C=. E = NR, O.



E = NR, O.

At first sight, there are no donor centers in these molecules, as the phosphorus atom does not possess any lone electron pair, and the lone electron pairs of the nitrogen and oxygen atoms must be involved in pπ–dπ-conjugation with d-orbitals of the phosphorus atom. However, HPs are used in coordination chemistry for more than two decades [13], demonstrating the ability to P-, N-, P,N-, P,O- and N,N-binding. The whole spectrum of HPs coordination behavior can be divided into two branches: complexation with retention and with breaking of the phosphorane fragment. The choice depends on the number of cycles in the HP molecule: the more cycles the phosphorus atom is included in, the higher is the ligand tendency to preserve the phosphorane frame, due to a macrocyclic effect [8,14]. That is why a complexation of bicyclic HPs is normally accompanied by destruction of the phosphorane structure by breaking a P–E bond and forming an 'open-chain' P(III)-derivative that bears a distant amino or hydroxy group, while tri- and tetracyclic systems often coordinate by preserving the pentacoordi-

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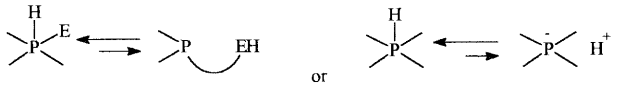
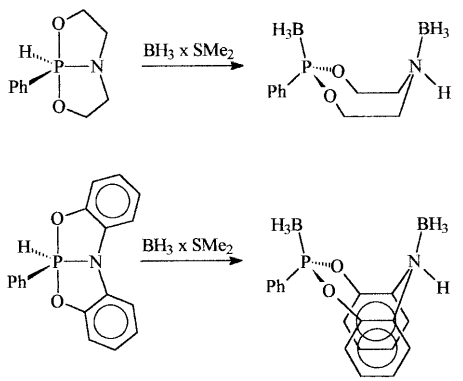
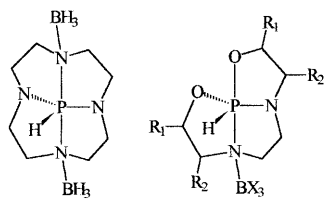
nated phosphorus [7,8,13–15]. In the latter case, either a complete retention of the HP frame (when Lewis acids, e.g. $ZnCl_2$, $CdCl_2$, BH_3, BF_3 bind to the most basic nitrogen apical atom [7,8,13,16,17]), or phosphoranide type binding to metal atom [13,18] can take place. When a destruction of the phosphorane motif or a phosphoranide type coordination takes place, a transfer of proton from the phosphorus atom to the nitrogen or oxygen atom is observed. This proton migration can be realized both through a tautomeric equilibrium [18] or through cooperation with the transition metal atom (in the process of oxidative addition by means of P–H bond breaking).



Thus, two different mechanisms of HPs coordination are possible. The exact contribution of each way is influenced by the nature of HP and Lewis acid, and the reaction conditions. To our mind, a complexation with the P(III)-tautomer is possible only for those HPs in which these tautomers are spectrally detectable [19,20] or/and which form proper adducts with Lewis acids that are unable to oxidative addition as BH_3, BF_3. For instance, bicyclic aminophosphoranes give borane derivatives of the 'open-chain' P(III)-tautomers [21,22]:

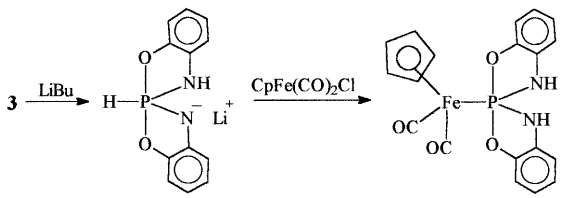


On the contrary, tetracyclic cyclenPH exists as a P(V)-compound in solution, solid state and gas phase [23]. In the case of neutral tricyclic HPs ('triquinphosphoranes'), P(III)-tautomers were not detected either [14,16]. These both types of HPs form adducts with BX_3 with retention of the HP frame, only [7,8,13,16,17,24]:

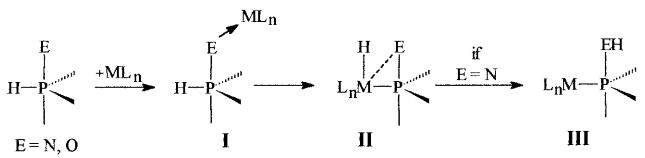


R_1	R_2	X
H	H	H
H	Me	H
H	Et	H
H	iPr	H
H	iBu	H
H	Ph	H
H	Bn	H
Ph	Me	H
H	Et	F

Phosphorane–phosphoranide acid–base equilibrium was not spectrally proved; phosphoranides with BX_3 and MCl_2 (M = Zn, Cd) are not known either [13]. To deprotonate the overwhelming majority of HPs, the assistance of the strong Brønsted base is required, but even under these conditions the phosphoranide salt is not always produced. Thus, polymeric $[Li(THF)cyclenP]_n$ was described [25], while our efforts to obtain an analogous lithium salt of a tricycylic phosphoranide anion using LiBu and HP **1** failed, the ^{31}P-NMR spectrum of the reaction solution in THF showing resonances of products with broken phosphorane frame only (δ_P 131.8, 102.4, 101.6, 60.8). Interestingly, when reacting with LiBu, HP **3** gives not the phosphoranide but an amide salt, which, nevertheless, produces a metal complex of the phosphoranide type [26]:



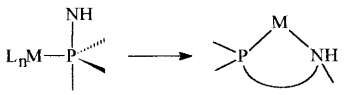
So, a general conclusion can be made that the formation of complexes containing phosphoranide or/and 'open-chain' tautomers for some HPs requires a direct assistance of a transition metal atom in the proton migration. Then, complexation of HPs follows the scheme:



First stage is the formation of adduct **I**, in which the apical nitrogen (oxygen) atom is coordinated. For a number of metals, e.g. Zn(II) and Cd(II), and for boron this stage is also the last one. If an oxidative addition is possible, the reaction goes on, giving metal-hydride intermediate **II**. The existence of such an intermediate was earlier supposed by M. Lattman [27], when analyzing a reaction of cyclenPH with metal carbonyls. He suggested this reaction to be analogous to the oxidative addition of Me_3SiH to $Co_2(CO)_8$. It should be added that metal-hydride intermediates are characteristic of complexation of secondary phosphines, hydrophosphoryle compounds [28,29] and also of Ph_2HPS [30]. The following reductive elimination leads to metallated phosphoranes **III**. For tri- and tetracyclic HPs this process is stimulated by the strong basicity of the apical sp^3-hybride nitrogen atom (these HPs give salts when reacting with CF_3COOH or HI [13,14]). In the case of bicyclic HPs, a preliminary pseudorotation resulting in

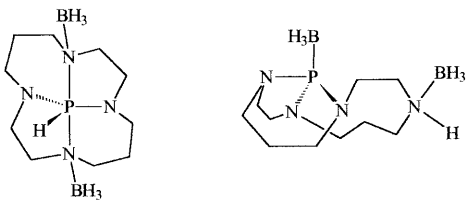
transformation of a P–N bond into an apical one, seems to be followed by the transfer of the proton to the nitrogen atom (perhaps, the both above processes proceed synchronously). It should be noted that the X-ray diffraction analysis of Phoran's molybdenum phosphoranide demonstrated an unusual apical location of the nitrogen atom [31].

Metallated phosphoranes of type **III** either undergo a P–NH bond break, thus losing the phosphorane structure and acquiring a distant amino group [13] or can be isolated (in the case of tricyclic HP [14,15]).

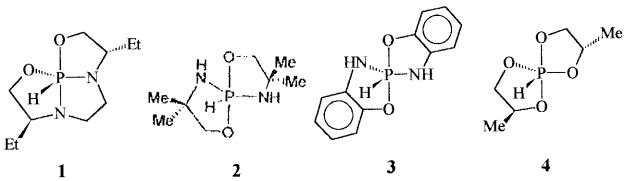


Tetracyclic HPs possessing two apical nitrogen atoms, gave products of disproportion of type-**III** compounds [13].

Summarizing all the facts, we suppose the complexation of tri- and tetracyclic HPs to proceed with the considerable assistance of transition metals. An exception is cyclamPH which shows a tautomeric equilibrium detectable by ^{31}P-NMR spectroscopy. Moreover, the borane derivatives of both the tautomers were obtained [13,24]:



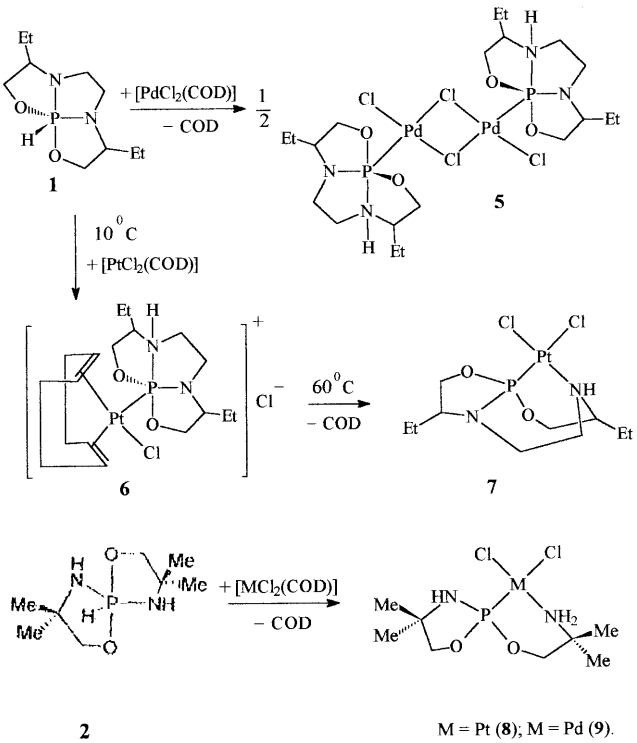
However, taking into account the existence of the borane adduct with the preserved phosphorane frame, the ability of cyclamPH to coordinate under certain conditions by oxidative addition can not be excluded. Perhaps, this is true for those bicyclic nitrogen-containing HPs for which a tautomeric equilibrium has been found [19]. The number of HPs reacting only by coordination of the P(III)-tautomer seems to be rather limited. They are mostly represented by tetraoxa HPs unable to form intermediates of type **III**. The present paper illustrates the concept described above by studying the coordination behavior of several different HPs:



1 2 3 4

2. Results and discussion

Complexation of ligands **1**,**2** with [$PdCl_2$(COD)] and [$PtCl_2$(COD)] has been recently studied [14,15,32]:



M = Pt (**8**); M = Pd (**9**).

Complexation of **3** and **4** is discussed for the first time. The principal spectral parameters of compounds **1**–**4** are summarized in Table 1.

Single crystal X-ray diffraction analysis has been carried out and the structure of hydrospirophosphorane **3** was determined (Fig. 1). Structure of this compound was previously described by Meunier and co-workers [33], however the quality of that data could not be considered sufficient for the interpretation of hydrogen

Table 1
Spectral data for compounds **1**–**4**

Compound	NMR (in $CDCl_3$)		IR (in $CHCl_3$), cm^{-1}		B_{PhOH}, cm^{-1}
	^{31}P-NMR δ_P (^1J(P,H) (Hz))	^{15}N-NMR δ_N (^1J(N,P) (Hz))	ν(P–H)	ν(N–H)	
1	−36.4 (713.8)	−318.4, −319.6 (47.1)	2436		>420
2	−56.7 (737.5)	−30.3 (30.7), ^1J(N,H) 88.3	2376, 2344	3464, 3340	354
3	−47.7 (834.0)	−298.5 (27.6), ^1J(N,H) 91.1	2436	3460	0
4	−27.7 (817.0), −27.5 (815.7), −27.1 (819.8)		2418		254

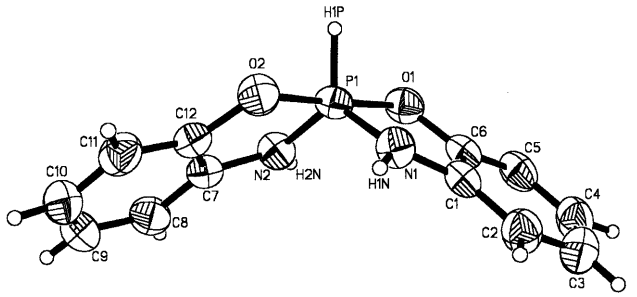


Fig. 1. A general view of compound **3** and the numbering scheme. Thermal ellipsoids are drawn in the 50% probability level. Selected bond lengths (Å): P(1)–N(2) 1.6496(13), P(1)–N(1) 1.6623(15), P(1)–O(2) 1.7203(12), P(1)–O(1) 1.7325(11), P(1)–H(1P) 1.271(17). Selected angles (°): N(2)–P(1)–N(1) 121.77(7), N(2)–P(1)–O(2) 89.85(6), N(1)–P(1)–O(2) 91.39(6), N(2)–P(1)–O(1) 91.92(6), N(1)–P(1)–O(1) 89.04(6), O(2)–P(1)–O(1) 177.62(5), C(6)–O(1)–P(1) 112.38(9), C(12)–O(2)–P(1) 112.64(9), C(1)–N(1)–P(1) 114.8(1).

atoms positions. That is why we reinvestigated the molecular structure of **3** to generate much more precise data.

The phosphorus atom is a slightly distorted trigonal bipyramid with the two oxygen atoms in apical positions and the nitrogen atoms and H-atom in equatorial positions. This conclusion arises from O–P–O and N–P–N bond angles which are 177.62(5) and 121.77(7)°, respectively. Approximate non-crystallographic two-fold axis lies along the P–H bond. Two equal benzophosphorane parts of the molecule differ from each other by the conformation of five-membered rings and nitrogen atoms configuration. The rings have envelope conformations, one being more distorted than the other (atom P1 deviates from the plane of the rest atoms of the cycles by 0.26 and 0.14 Å, respectively). Atom N1 has a trigonal pyramidal configuration (the sum of bond angles around it is 355(3)°), whereas N2 is approximately planar (the sum of bond angles around it is 360(3)°). The flattening of the nitrogen atoms is probably caused by the formation of intermolecular H-bonds N–H···O of different strength: H1N···O1′ $(-x,\ 1.5+y,\ 1.5-z)$ (the H···O distance is 2.27 Å, the N–H···O angle is 159.2°) and H2N···O2′ $(1+x,\ -0.5-y,\ -0.5+z)$ (the H···O distance is 2.42 Å, the N–H···O angle is 157.1°).

The experiment quality allowed the H atoms positions to be refined. But, it should be noted that the P–H distance (1.27(2) Å) was found to be somewhat shorter than that presented in the earlier study [33] (1.47–1.50 Å). This fact can be probably explained by the lower quality of structure refinement in the related investigations.

In the crystal, molecules of **3** form stacks along the crystallographic axis *c*. The molecules within one stack and from different stacks are connected by the H-bonds referred above.

When forming adducts **I**, HPs act as the Lewis bases; so, the dependence of coordination activity of HPs from their basicity must be observed. As a quantitative criterion of basicity, we use the B_{PhOH} parameter suggested by Koppel and Payu [34], the shift of ν(O–H) absorption band in the IR spectrum of PhOH in CCl_4, which is induced by the formation of a hydrogen bond with the acceptor (*B*), lying in the basis of the parameter: B_{PhOH} $(cm^{-1}) = \nu_{PhOH}$ $(CCl_4) - \nu_{PhOH\cdots B}(CCl_4)$. Unfortunately, the absorption band of **1**/PhOH associate has no clear maximum, instead of which we observed a plateau in the 3180–3010 cm^{-1} interval. That is why the exact value of B_{PhOH} for compound **1** is impossible to determine. However, it certainly exceeds 420 cm^{-1} [17] (compare with B_{PhOH} (cm^{-1}): *t*-Bu_2O 321, C_5H_5N 472, Et_3N 650 [29]). The more exact result was obtained by studying the ν(C–D) band shift in the IR spectrum of $CDCl_3$, which is also used as the criterion of the donor ability of amines [35]. The determined value $\Delta\nu(C–D) = 57$ cm^{-1} [17] exceeds the one for pyridine (27 cm^{-1}), ethylenediamine (41 cm^{-1}) and is approaching that for Et_3N (70 cm^{-1}) [35]. In this way, HP **1** is a stronger N-donor than pyridine and ethylenediamine, being inferior to triethylamine only.

Using the described technique, B_{PhOH} values for the rest of the HPs were estimated precisely (Table 1). Compound **2** was found to be a strong oxygen-containing Lewis base, conspicuously leaving behind various simple ethers (compare with B_{PhOH} (cm^{-1}): THF 287, *t*-Bu_2O 321).

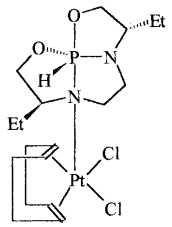
Addition of PhOH in equimolar quantity into a CCl_4 solution of compound **2** does not influence the shape, intensity and location of the ν(N–H) and ν(P–H) bands (Table 1). It supports the idea that in the formation of the associate with PhOH, just the apical oxygen atoms of **2** and not the apical nitrogen atoms after a pseudorotation of TBP take place.

The same is supported by the invariability of the ν(C–D) band, when an equimolar quantity of **2** is added into a CCl_4 solution of $CDCl_3$. It should be noted that $\Delta\nu$(C–D) is a sensitive and very specific criterion for the donor ability of the nitrogen-containing Lewis bases [35]. The invariability of ^{1}H-NMR spectral data for **2** [32], after adding PhOH into its CCl_4 solution, is observed.

The practical absence of the Lewis basicity for **3** (Table 1) is explained by the delocalization of lone electron pairs of the nitrogen and oxygen atoms through interaction with benzene rings. HP **4** demonstrates a basicity which is characteristic of simple ethers (e.g. B_{PhOH} (cm^{-1}): Me_2O 246, EtOAllyl 256, $CMe_2(OMe)_2$ 257, 1,4-dioxane 237 [35]). Importantly, a linear correlation (with correlation coefficient $R = 0.974$ [36]) between the B_{PhOH} scale and the generally accepted [37] Guttman scale of donor numbers DN was established.

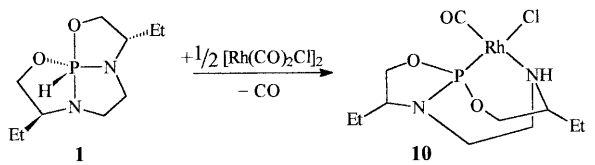
To examine the coordinating activity and mechanisms of HPs **1**–**4** complexation, dynamic ^{31}P-NMR spectroscopy has been used. Tricyclic HP **1** has been found to be the most active, its Lewis basicity being the greatest one, because of the presence of the apical sp^3-nitrogen

atom. Already at −93°C in the reaction of **1** and $[PtCl_2(COD)]$, the formation of the adduct with δ_P −35.7, ^1J(P,H) 742.2 Hz (in CD_2Cl_2) has been observed:



Increasing of ^1J(P,H), compared to the initial HP is a characteristic feature of adducts by apical donor center [8,13,16,17,38]. Heating the reaction solution up to −65°C leads to the appearance of complex **6** (δ_P −12.6, ^1J(P,Pt) 5110 Hz). In the reaction of **1** with $[PdCl_2(COD)]$ (CD_2Cl_2, −93°C) a series of doublet resonances δ_P -3.7 ± 35.8, ^1J(P,H) 781–874 Hz referring to the adducts with coordinated nitrogen and oxygen atoms is observed. At −35°C they are replaced by two other resonances: δ_P −34.4 (^1J(P,H) 835.0 Hz) and δ_P −36.5 (^1J(P,H) 830.1 Hz). Finally, heating the solution up to −10°C results in the formation of complex **5** and disappearance of all the intermediates.

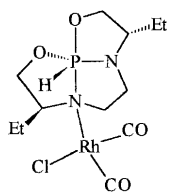
Interaction of HP **1** with $[Rh(CO)_2Cl]_2$ leads to the breaking of the phosphorane structure and the formation of chelate complex **10**:



1 **10**

The conversion is supported by the spectral data for the reaction solution ($CHCl_3$): δ_P 160.5, ^1J(P,Rh) 234.6 Hz (^{31}P-NMR); ν(N–H) 3240, ν(CO) 2000, ν(Rh–Cl) 294 cm^{-1} (IRS); MS (MALDI) m/z (I,%): 399 (10) $[M]^+$, 335 (5) $[M–Cl–CO]^+$, 232 (100) $[L]^+$. ^{2}H-NMR spectrum contains a narrow singlet δ_D 3.44 assigned to the deuterium atom of the N–D group (deuterium-enriched HP **1** [14] has been applied). Such a resonance as well as a narrow ν(N–H) band at 3240 cm^{-1} in the IR spectrum indicates, to our mind, formation of the hydrogen bond Cl···H–N similar to the analogous chlorocarbonyl rhodium complex with the 'open-chain' Phoran [39]. By the way, a similar metal chelate was obtained for the 'open-chain' form of cyclamPH [40], while the attempt to initiate a tautomeric rearrangement of cyclamPH by $[Rh(CO)_2Cl]_2$ addition failed [38]. ^{13}C-NMR data for the resulting solution of **10** in $CDCl_3$ are in good agreement with its supposed structure, as the parameters of the ligand parts of complexes **7** [15] and **10** (Table 2) are quite homologous. The band ν(CO) 2000 cm^{-1} is typical of chlorocarbonyl Rh(I) complexes with aminoamidophosphites [41]; and E_b Cl2p 198.7 eV in the X-ray photoelectron spectrum of **10** (see Section 3) points to the presence of coordinated chlorine ligand [42] in a terminal position (ν(Rh–Cl) 294 cm^{-1}) [41].

Analogous to the reactions with $[MCl_2(COD)]$ (M = Pt, Pd; see above), the ^{31}P-NMR spectrum of system **1**/0.5$[Rh(CO)_2Cl]_2$ (in $CDCl_3$) already at −93°C shows doublet resonances of adducts by apical donor centers: δ_P −21.6, ^1J(P,H) 767.5 Hz; δ_P −25.6, ^1J(P,H) 812.9 Hz; δ_P −27.5, ^1J(P,H) 816.8 Hz; δ_P −35.5, ^1J(P,H) 753.3 Hz, a peak of the free HP **1** being not found. When the temperature increases up to −55°C, the doublet resonance of the final product **10** δ_P 160.5, ^1J(P,Rh) 232.0 Hz appears; at −40°C the series of the upfield resonances (see above) is replaced by two nearly equally intensive doublets δ_P −33.9, ^1J(P,H) 835.0 Hz and δ_P −35.8, ^1J(P,H) 823.0 Hz. They are supposed to refer to the epimers of the adduct retaining the HP frame:



With the increasing of the temperature, these doublets smoothly disappears (completely at 0°C), and the peak of complex **10** grows, becoming the only one after staying at 20°C for 3 h.

Additionally, in the -90 ± 20°C temperature range we observed a series of doublet peaks δ_P 41.0–54.8, ^1J(P,Rh) 133.7–198.8 Hz, which are referred to the intermediates typical of the interaction between $[Rh(CO)_2Cl]_2$ and P(III)-ligands [43–45] ('open-chain' tautomer of **1** in our case).

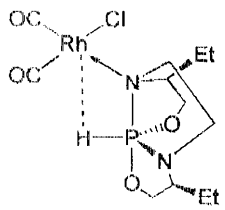
Table 2
^{13}C-NMR data for compounds **7** and **10** (in $CDCl_3$)

Compound	δ_C					
	CO	OCH_2	NCH	NCH_2	CH_2	CH_3
7		74.2, ^2J(C,P), 5.4, 71.0	63.7, 60.2	52.9, 41.7, ^2J(C,P) 7.3	23.9, 23.0	10.1, 9.8
10	187.4, ^1J(C,Rh), 78.1, ^2J(C,P) 15.5	72.5, 68.0	61.7, 59.5	50.2, 42.0	24.1, 22.4	9.8, 9.3

Table 3
^{1}H-NMR data for compound **11** (δ_H, J (Hz)) in $CDCl_3$

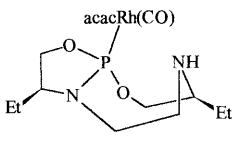
	Hydrogen atom							
	NH_2		N–H	CH_2 of metalacycle		CH_2 of phosphacycle		CH_3
	H_a	H_e		H_a	H_e	$H_{pseudo\ a}$	$H_{pseudo\ e}$	
δ_H	2.98 br d, $^2J(H_a,H_e)$ 12.0	2.89 br d, $^2J(H_e,H_a)$ 12.0	3.73 d, ^2J(H,P) 27.7	3.78 m	3.68 m	4.06 dd, $^2J(H_a,H_e)$ 8.8, ^3J(H,P) 4.1	3.93 m, $^2J(H_e,H_a)$ 8.8, ^3J(H,P) 17.9, ^4J(H,NH) 0.7	1.34 s, 1.26 s, 1.24 s, 1.22 s

Interestingly, a broad multiplet δ_H −2.55 was observed in ^{1}H-NMR spectrum of the reaction mixture in the -60 ± 20°C temperature range. A characteristic chemical shift of the resonance [46] allows us to make a conclusion that an intermediate containing agostic P–H···Rh bond presents in the reaction mixture:

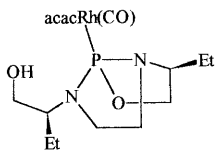


Note, there are a lot of examples of agostic bonds C–H···M, B–H···M and N–H···M, but agostic bond P–H···M was not observed earlier [47]. Metal-hydride intermediates of type **II** are supposed to be very unstable, as their proton resonances was not observed in the ^{1}H-NMR spectrum even at a low temperature.

HP **1** reacts readily not only with $[Rh(CO)_2Cl]_2$, that is able to dissociate to give highly reactive 14-electron $[Rh(CO)_2Cl]$ particles [29], but with 16-electron $acacRh(CO)_2$, as well. The process in system **1**/$acacRh(CO)_2$ (in $CDCl_3$) starts already at −50°C leading to a mixture of products. Among them there are complexes of the 'open-chain' forms of ligand **1**:



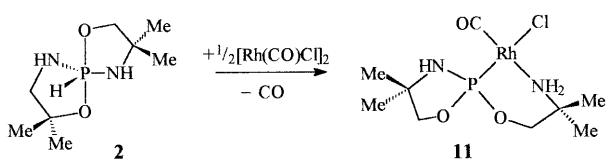
δ_P 159.7, ^{1}J(P,Rh) 231.5 Hz



δ_P 80.4, ^{1}J(P,Rh) 272.2 Hz

The greater ^1J(P,Rh) value is explained by the higher π-acidity of constrained aminophosphane structure of the 'open-chain' form bearing a free hydroxy group [48].

As HP **1**, phosphorane **2** reacts with $[Rh(CO)_2Cl]_2$ to give a chelate derivative of the 'open-chain' form.



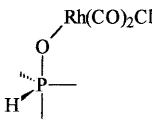
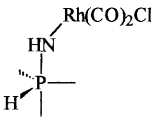
2 **11**

The structure of the product is supported by the spectral data of the reaction solution in CH_2Cl_2: δ_P 135.3, ^1J(P,Rh) 240.5 Hz (90%) and δ_P 130.5, ^1J(P,Rh) 256.4 Hz (10%) (^{31}P-NMR); ν(NH) 3280, 3248 cm^{-1}, $\nu(NH_2)$ 3200, 3128 cm^{-1}, ν(CO) 2008 cm^{-1}, ν(Rh–Cl) 315 and 289 cm^{-1} (IRS). There are ^1J(P,Rh), ν(CO), ^1J(C,Rh) and ^2J(C,P) values characteristic [41] of chelate chlorocarbonyl Rh(I) complexes with aminoamidophosphites (see Section 3). The minor form with greater ^1J(P,Rh) and ν(CO), also observed in the DMF solution (see Section 3), is supposed to be a stereomer. Thus, for the similar compound $[(\eta^2\text{-}O(CH_2)_2OPOCH(CH)_3\text{-}CH_2NMe_2)Rh(CO)Cl]$, the X-ray analysis showed the presence of two independent molecules in the elementary cell of its monocrystal. In one of the molecules, a rhodium atom occupies a pseudo equatorial position in the phospholane cycle, in the other it is located pseudo axially [43]. It should be noted that ^{1}H- (Table 3) and ^{13}C- (see Section 3) NMR data for **11** are analogous to the earlier described chelate complexes **8** and **9**, **8** being characterized by X-ray diffraction [32].

The dynamic ^{31}P-NMR spectral data for system **3**/$0.5[Rh(CO)_2Cl]_2$ (in $CDCl_3$) in the -50 ± 20°C temperature range are shown in Table 4. As it has been already marked, the greater ^1J(P,H) value, in comparison with the starting HP, as well as a downfield shift of δ_P indicate the formation of an adduct by the apical atom [8,13,16,17,38]–by the oxygen atom, in this case (Table 4). The peak δ_P −24.2 with the smaller ^1J(P,H) value equal to 703.4 Hz was rather unexpected. This peak is supposed to refer to the adduct by the apical nitrogen atom of the phosphorane undergone a pseudo rotation.

It should be underlined that HP **2** is much less reactive than HP **1**. This fact is in good agreement with the smaller Lewis basicity of **2** (Table 1). Thus, in the reaction with $[Rh(CO)_2Cl]_2$, the initial **2** exists in the system up to 20°C (Table 4), while the starting **1** was not observed even at −93°C (see above); final product **11** appears only at −35°C, while product **10**-already at −55°C. In addition, the reaction of HP **2** with $[MCl_2(COD)]$ (M = Pd, Pt) gets start only at a temperature above 20°C [32]. Moreover, even after 16 h of refluxing a mixture **2**/$AcacRh(CO)_2$ in CH_2Cl_2, 40% of

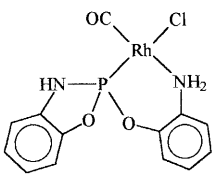
Table 4
Dynamic ^{31}P-NMR data for the reaction solution **2**–0.5$[Rh(CO)_2Cl]_2$ in $CDCl_3$

^{31}P-NMR peak,	The temperature of the solution, °C					Compound
δ_P, I	-50	-35	-20	-5	20	
-56.9,	51*	34	30	27	0	ligand **2**
^1J(P,H) 735.9 Hz						
-49.5,	41	42	28	11	0	
^1J(P,H) 773.6 Hz						
-24.2,	8	20	23	8	0	
^1J(P,H) 703.4 Hz						
132.9,	0	4	19	54	100	complex **11**
^1J(P,Rh) 243.7 Hz						

[a] Integral intensity (%).

the initial phosphorane remains unreacted (monitored by ^{31}P-NMR). Unfortunately, in the reaction, besides the product acacRh(CO)(HNC(Me)$_2$CH$_2$OPOCH$_2$-C(Me)$_2$NH$_2$) (δ_P 135.5, ^1J(P,Rh) 243.0 Hz), nearly equal quantities of the product of ligand decomposition (δ_P 24.8) are formed, preventing isolation of the target complex. Keeping in mind that $[MCl_2(COD)]$ and acacRh(CO)$_2$ react with P(III)-ligands immediately and quantitatively, we can make a conclusion that coordination of ligand **2**, as in the case of **1**, is realized by means of oxidative addition, P(III)-tautomer being detected spectrally neither at room temperature nor at 150°C [19,32].

An analogous mechanism of complexation should be expected for HP **3** as well, because its P(III)-tautomer was not ^{31}P-NMR spectrally detected in the 20–150°C range [19]. Much earlier, HP **3** was shown not to give the indicative for trivalent phosphorus compounds reaction with $HgCl_2$ [49]. A practically full absence of Lewis basicity for HP **3** (according to B_{PhOH} criterion, see Table 1) must considerably impede the formation of adduct **I** and strongly decrease the phosphorane reactivity. Indeed, **3** does not react with $[Rh(CO)_2Cl]_2$ (P/Rh = 1) in boiling chloroform. In 1,4-dioxane, the reaction starts only at 95°C, 30% of the ligand remaining unconverted after 1.5 h of boiling (monitored by ^{31}P-NMR). Unfortunately, side reactions giving fine dispersed metallic rhodium and products of the ligand decomposition (δ_P 16.5 and 0.5 (DMSO)) made the obtaining of the analytically pure complex impossible. ^{31}P-NMR and IR spectral data on the reaction solution in dioxane support the main product to be a derivative of the 'open-chain' form of HP **3**:



δ_P 142.7, ^{1}J(P,Rh) 280.3 Hz;

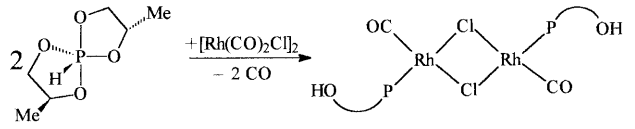
ν(N-H) 3224 cm^{-1} (br.), ν(NH$_2$) 3130 cm^{-1} (br.),

ν(CO) 2025 cm^{-1}, ν(Rh-Cl) 320 cm^{-1}.

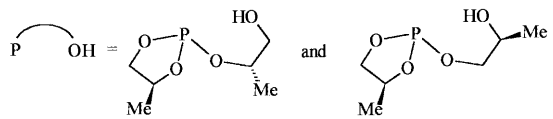
In the same way, **3** reacts with $[MCl_2(COD)]$ (M = Pd,Pt) only under a prolonged (not less than 3 h) refluxing in toluene. Precipitates obtained are mixtures of metal derivatives of the 'open-chain' form of **3**: δ_P 77.4, 63.0, 56.7, 55.6, 43.2 (acetone-d_6) in the case of $[PdCl_2(COD)]$; δ_P 89.3, ^1J(P,Pt) 6288 Hz; δ_P 66.0, ^1J(P,Pt) 5240 Hz; δ_P 57.8, ^1J(P,Pt) 5620 Hz (DMF-d_7) in the case of $[PtCl_2(COD)]$. So, there is a strong correlation between the Lewis basicity of HP **1**–**3** and their activity in complexation.

It is necessary to pay attention to the estimation of molecular masses of hydrophosphorane rhodium complexes. Recently, we described the products of interaction between $[Rh(CO)_2Cl]_2$ and some homologues of HP **2** as tetra- and hexanuclear complexes $[Rh(CO)ClL]_n$, $n = 4$ and 6 [50,51]. This conclusion was based on the data of sedimentation analysis of their DMSO solutions. However, some new data for complex **11**, among them strong spectral analogy with metal-chelates **8** and **9** [32], demands more profound analysis of the situation. It has been concluded that a wrong interpretation of sedimentation analyses data took place in articles [50,51]. Thus, a well known complex $[RhCl(COD)]_2$ [52] has been shown to give analogous overestimated mass results (in C_6H_6). This fact proves a necessity for a very cautious and accurate interpretation of sedimentation analyses data concerning rhodium complexes.

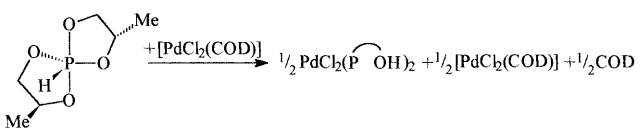
As for the HP **4** complexation, its reaction with $[Rh(CO)_2Cl]_2$ leads to the binuclear product that contains the 'open-chain' form coordinated in the P-monodentate mode:



The spectral data on the reaction solution in $CDCl_3$ are characteristic [50,51] of such structures: δ_P 138.7, ^1J(P,Rh) 277.7 Hz, δ_P 138.3, ^1J(P,Rh) 273.0 Hz, δ_P 136.8, ^1J(P,Rh) 276.1 Hz, δ_P 136.5, ^1J(P,Rh) 274.6 Hz (^{31}P-NMR); ν(OH) 3428 cm^{-1} (br.), ν(CO) 2028 cm^{-1}, ν(Rh–Cl) 286 cm^{-1} (IRS). A presence of four doublet resonances in the ^{31}P-NMR is explained by coordination of two structural isomers of 'open-chain' form, each of them being represented by two epimers at the phosphorus atom:



The ^{31}P-NMR spectrum of reaction mixture **4**/$[PdCl_2(COD)]$ (in $CDCl_3$) shows a complicated set of peaks within the range from 112.9 to 109.8, and the IR spectrum contains absorption bands ν(OH) 3424 cm^{-1} (br) and ν(Pd–Cl) 330, 304 cm^{-1}. The ^{13}C-NMR spectrum contains the equally intensive resonances of unreacted $[PdCl_2(COD)]$ (δ_C 117.5 and 31.3) and of free COD (δ_C 128.8 and 28.2) [52]. These spectral data prove [53,54] a formation of *cis*-$[PdCl_2(P^{\frown}OH)_2]$, represented, as the rhodium complex, by a set of isomers. Indeed, when the reaction is conducted at a molar ratio P/Pd = 2, ^{31}P-NMR and IR spectral data for the resulted solution are identical to those given above. So, complexation of HP **4** follows the scheme:



As the 'open-chain' tautomer of **4** a priori has a small Tolman cone angle [55], the formation of $PdCl_2L_2$ even at a molar ratio of reagents P/Pd = 1 is quite a natural phenomenon [56].

So, HP **4**, as a matter of fact, behaves like a P-monodentate phosphite ligand. Interestingly, reaction in systems **4**/0.5$[Rh(CO)_2Cl]_2$ and **4**/$[PdCl_2(COD)]$ (in $CDCl_3$) gets started already at −50°C and −15°C, respectively, what contradicts the moderate Lewis basicity of the phosphorane (see Table 1). Besides, there are no signals for apical adducts of type **I** in the ^{31}P-NMR spectra of the mentioned reaction mixtures, and a smooth disappearance of the starting ligand peak is accompanied by a simultaneous growth of resonances of the complexes. We suppose these facts to be explained by coordination of HP **4** through its P(III)-tautomer, a considerable amount of which (4–5% depending on the solvent) can be detected in solution (δ_P 143.2, 143.1, 139.4, 139.0). At 127°C in ortho-xylene, its share increases up to 25%, returning to initial 5% when cooling down to 20°C.

Coordination of tetraoxo HP **4** through oxidative addition is prevented by its low basicity, which does not allow an apical adduct **I** and intermediate **III** to be formed. That is why the coordination activity of **4** should have been lower than that of phosphoranes **1** and **2**, coming close to that of **3**. But, **4** readily reacts with the starting metal complexes, owing to the P(III)-tautomer.

So, correlation between Lewis basicity and coordination activity of hydrophosphoranes as well as spectroscopic data for reaction mixtures proves complexation of HPs **1**–**3** through oxidative addition of P(V)-tautomer. HP **4** coordinates through 'open-chain' P(III)-tautomer and behaves like a P-monodentate phosphite ligand.

3. Experimental

3.1. General methods

All reactions were carried out in an atmosphere of dry argon. Solvents were purified according to standard procedures. IR spectra were recorded on a Specord M80 or Nicolet 750 instruments. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX 400 instrument at 400.1 and 100.6 MHz, respectively. ^{31}P-NMR spectra were recorded on a Bruker AMX-400 (at 162.0 MHz) and on a Bruker WP-200-SY (at 81.0 MHz) instruments. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H- and ^{13}C-NMR) and 85% H_3PO_4 (^{31}P-NMR). Plasma-desorption mass spectra were recorded on a time-of-flight MSVKh mass spectrometer with Cf-252 fission fragments as ionizing particles; laser desorption mass spectra were recorded on a time of flight Vision 2000 mass spectrometer with matrix assisted laser desorption ionization (MALDI) using UV laser (337 nm). The X-ray photoelectron (XPS) spectra were measured on a Kratos XSAM 800 spectrometer calibrated against Ag line at 368.3 eV, Cu line at 932.7 eV and Au line at 84.0 eV; correction for the sample charging was performed at C1s 284.6 eV. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

Table 5
Crystallographic data for compound **3**

Compound	**3**
Empirical formula	$C_{12}H_{11}N_2O_2P$
Color, habit	Colorless, parallelepipeds
Formula weight	246.2
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
Temperature (K)	293(2)
Unit cell parameters	
a (Å)	11.376(2)
b (Å)	10.620(2)
c (Å)	9.455(2)
β (°)	92.66(3)
Volume (Å^3)	1141.1(4)
D_{calc} (g cm^{-3})	1.433
μ (mm^{-1})	0.231
$F(000)$	512
Collected reflections	3455
Independent reflections	3311
R_{int}	0.045
Diffractometer	Enraf–Nonius CAD-4
$2\theta_{max}$ (°)	60
Refined reflections	3271
Reflections with $F>4\sigma(F)$	2384
R_1 (observed)	0.039
wR_2 (all data)	0.121
S (all data)	1.009

3.2. Synthesis

Ligands **1** [14] and **2** [32] were synthesized following the described procedures.

3.2.1. Synthesis of 1,6-dioxa-4,9-diaza-2,3,7,8-dibenzo-5λ^5-phosphaspiro[4.4]nonane (3)

Ligand **3**, which was discovered earlier [57], was synthesized according to the following technique: a solution of $P(NEt_2)_3$ (2.47 g, 1×10^{-2} mol) and 2-aminophenol (2.18 g, 2×10^{-2} mol) in toluene (25 ml) was stirred under reflux for 2 h. Then the solvent was evaporated in vacuum (40 mmHg), and the residue was dried in vacuum (10 mmHg) at 80°C for 0.5 h. The product was purified by recrystallization from a 1:1.5 benzene-hexane mixture. White crystals. Yield 1.355 g (55%). M.p. 156°C. Crystals suitable for X-ray analysis were obtained from benzene by slow evaporation.

3.2.2. Synthesis of 2S,7S-dimethyl-1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nonane (4)

Ligand **4**, which was described earlier in a racemic form [58], was synthesized from optically active precursor according to the following technique: a mixture of (*S*)-propane-1,2-diol (2.77 g, 3.6×10^{-2} mol) and $P(NEt_2)_3$ (5 ml, 1.8×10^{-2} mol) was stirred at 130°C for 1 h. Then the mixture was stirred in vacuum (1.5 mmHg, 50°C) for 45 min in order to remove $HNEt_2$ and distilled at 1.5 mmHg to give **4** as a colorless liquid (1.97 g, 60% yield). B.p. 68°C (1.5 mmHg). Found: C, 40.29; H, 7.42; P, 17.01. *Anal.* Calc. for $C_6H_{13}O_4P$: C, 39.99; H, 7.28; P, 17.20%.

3.2.3. Synthesis of {(4S,9S)-4,9-diethyl-2,11-dioxa-5,8-diaza-1-phosphabicyclo[6.3.0]undecane-P,N}-chlorocarbonyl rhodium (I) (10)

A solution of compound **1** (0.093 g, 4×10^{-4} mol) in $CHCl_3$ (10 ml) was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (0.078 g, 2×10^{-4} mol) in the same solvent (20 ml) at 20°C. The reaction mixture was stirred for 30 min. the excess of the solvent was then removed in vacuum (40 mmHg), and 10 ml of diethyl ether was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (10 ml) and dried in vacuum (1 mmHg) to give the product **10** as a brown solid (0.145 g, 91% yield). M.p. (dec.) 206–208°C. XPS spectrum, eV: N 1s 399.7, Rh 3d5/2 309.4, Cl 2p 198.7, P 2p 133.7. Plasma desorption mass spectrum, m/z (I, %): 335 (7) $[M-Cl-CO]^+$, 232 (100) $[L]^+$. IR spectrum (press KBr, cm^{-1}): ν(CO) 1990. Found: C, 33.17; H, 5.32; N, 7.07; P, 7.78. *Anal.* Calc. for $C_{11}H_{21}ClN_2O_3PRh$: C, 33.51; H, 5.66; N, 6.68; P, 7.61%.

3.2.4. Synthesis of {2-(2′-amino-2′-methylpropoxy)-4,4-dimethyl-1,3,2-oxazaphospholidine-P,N}-chlorocarbonyl rhodium (I) (11)

A solution of compound **2** (0.082 g, 4×10^{-4} mol) in dietyl ether (10 ml) was added dropwise to a solution of $[Rh(CO)_2Cl]_2$ (0.078 g, 2×10^{-4} mol) in the same solvent (20 ml) at 20°C. The reaction mixture was stirred for 30 min. The excess of the solvent was then removed in vacuum (40 mmHg), and 10 ml of hexane was added to the residue. The precipitate obtained was separated by centrifugation, washed with hexane (10 ml) and dried in vacuum (1 mmHg) to give the product **11** as a yellow solid (0.124 g, 83% yield). M.p. (dec.) 158–160°C. ^{31}P-NMR, δ_P (^1J(P,Rh) (Hz)): 133.5 (243.6) (DMSO-d_6); 134.1 (245.1) ($CDCl_3$); 134.5 (240.0)–87% and 130.9 (260.8)–13% (DMF-d_7). ^{13}C-NMR, δ_C: CO 188.3 (^1J(C,Rh) 71.0, ^2J(C,P) 22.5 Hz); $POCH_2$ (P-cycle) 76.8 (^2J(C,P) 7.1 Hz); $POCH_2$ (metal-cycle) 72.0; CNH_2 56.3; CNH 48.7 (^2J(C,P) 3.5 Hz); CH_3 28.4 (^3J(C,P) 3.2 Hz), 28.2 (^3J(C,P) 3.0 Hz), 28.5, 25.0. IR spectrum (nujol, CsI, cm^{-1}): ν(NH) 3281, 3238; $\nu(NH_2)$ 3197, 3122; ν(CO) 2000; ν(Rh–Cl) 310, 290. Found: C, 29.03; H, 5.15; N, 7.53; P, 8.33. *Anal.* Calc. for $C_9H_{19}ClN_2O_3PRh$: C, 29.13; H, 5.30; N, 7.42; P, 8.02%.

Rhodium and palladium derivatives of ligand **4** were spectrally investigated in situ without isolation of target products. They were formed by slow adding a solution of compound **4** (0.046 g, 3×10^{-4} mol) in $CDCl_3$ (1 ml)

to a stirred solution of an equimolar quantity of a corresponding initial metal complex in $CDCl_3$ (2 ml).

3.3. X-ray structure determination

Crystallographic data for compound **3** are given in Table 5.

The structure was solved by direct method using SHELXTL-PLUS-5 program package [59]. Positions of hydrogen atoms were located from the difference map of electron density. All H-atoms were refined in isotropic approximation.

4. Supplementary material

Tables of the X-ray structure determination summary (crystal data, data collection, structure solution and refinement), tables of the non-hydrogen atom coordinates with their isotropic equivalent and anisotropic displacement parameters, tables of the hydrogen atom coordinates, full tables of the molecular geometry parameters and tables of X-ray structure factors are available from the authors upon request.

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References

[1] R.A. Kemp, Phosphorus Sulfur Relat. Elem. 87 (1994) 83.
[2] D.A. Predvoditelev, G.A. Urvantseva, E.E. Nifantiev, Zh. Obshch. Khim. 43 (1973) 1801.
[3] D. Houalla, J.F. Brazier, M. Sanchez, R. Wolf, Tetrahedron Lett. (1972) 2969.
[4] C. Pradat, J.G. Riess, D. Bondoux, B.F. Mentzen, I. Tkatchenko, D. Houalla, J. Am. Chem. Soc. 101 (1979) 2234.
[5] M.G. Newton, J.E. Collier, R. Wolf, J. Am. Chem. Soc. 96 (1974) 6888.
[6] P.F. Meunier, J.A. Deiters, R.R. Holmes, Inorg. Chem. 15 (1976) 2572.
[7] M. Tlahuextl, F.J. Martinez-Martinez, M.J. Rosales-Hoz, R. Contreras, Phosphorus Sulfur Relat. Elem. 123 (1997) 5.
[8] C. Marchi, F. Fotiadu, G. Buono, Organometallics 18 (1999) 915.
[9] C. Lensink, S.K. Xi, L.M. Daniels, J.G. Verkade, J. Am. Chem. Soc. 111 (1989) 3478.
[10] M.A.H. Laramay, J.G. Verkade, J. Am. Chem. Soc. 112 (1990) 9421.
[11] J.E. Richman, T.J. Atkins, Tetrahedron Lett. (1978) 4333.
[12] T.J. Atkins, J.E. Richman, Tetrahedron Lett. (1978) 5149.
[13] K.N. Gavrilov, I.S. Mikhel, Uspekhi Khimii 65 (1996) 242.
[14] K.N. Gavrilov, I.S. Mikhel, D.V. Lechkin, A.I. Rebrov, G.V. Tcherkaev, G.I. Timofeeva, M.G. Vinogradov, Zh. Neorg. Khim. 42 (1997) 1676.
[15] I.S. Mikhel, K.N. Gavrilov, D.V. Lechkin, A.I. Rebrov, Izvest. Akad. Nauk (1997) 1416.
[16] Y. Vannoorenberghe, G. Buono, J. Am. Chem. Soc. 112 (1990) 6142.
[17] K.N. Gavrilov, A.V. Korostylev, P.V. Petrovsky, A.Yu. Kovalevsky, V.A. Davankov, Phosphorus Sulfur Relat. Elem. 155 (1999) 15.
[18] K.B. Dillon, Chem. Rev. 94 (1994) 1441.
[19] R. Burgada, C. Laurenco, J. Organomet. Chem. 66 (1974) 255.
[20] K. Gavrilov, A. Teleshev, E. Nifantyev, J. Organomet. Chem. 461 (1993) 233.
[21] R. Contreras, D. Houalla, A. Klaebe, R. Wolf, Tetrahedron Lett. 22 (1981) 3953.
[22] R. Contreras, A. Murillo, G. Uribe, A. Klaebe, Heterocycles 23 (1985) 2187.
[23] D.V. Khasnis, M. Lattman, U. Siriwardane, S.K. Chopra, J. Am. Chem. Soc. 111 (1989) 3103.
[24] J.M. Dupart, S. Pace, J.G. Riess, J. Am. Chem. Soc. 105 (1983) 1051.
[25] M. Lattman, M.M. Olmstead, P.P. Power, D.W.H. Rankin, H.E. Robertson, Inorg. Chem. 27 (1988) 3012.
[26] H. Hakazawa, K. Kubo, K. Migoshi, J. Am. Chem. Soc. 115 (1993) 5863.
[27] M. Lattman, S.K. Chopra, E.G. Burns, Phosphorus Sulfur Relat. Elem. 30 (1987) 185.
[28] R. Schunn, Inorg. Chem. 12 (1973) 1573.
[29] M. Bennett, T. Mitchell, J. Organomet. Chem. 70 (1974) 30.
[30] V. Marsala, F. Faraone, P. Piraino, J. Organomet. Chem. 133 (1977) 301.
[31] F. Jeanneaux, A. Grand, J.G. Riess, J. Am. Chem. Soc. 103 (1981) 4272.
[32] A.V. Korostylev, O.G. Bondarev, K.A. Lyssenko, A.Yu. Kovalevsky, P.V. Petrovskii, G.V. Tcherkaev, I.S. Mikhel, V.A. Davankov, K.N. Gavrilov, Inorg. Chim. Acta 295/2 (1999) 164.
[33] P.F. Meunier, R.O. Day, J.R. Devillers, R.R. Holmes, Inorg. Chem. 17 (1978) 3270.
[34] I.A. Koppel, A.I. Payju, Reactsionnaya sposobnost' organicheskih soedinenii 11 (1974) 121.
[35] Yu.I. Naberukhin, M.N. Buslaeva, K.T. Dudnikova, Zh. Koord. Khim. 8 (1982) 29.
[36] R.G. Makitra, Ya. N. Pirig, Reactsionnaya sposobnost' organicheskih soedinenii 16 (1979) 103.
[37] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH, Weinheim, 1988.
[38] J.-M. Dupart, G. Le Borgne, S. Pace, J.G. Riess, J. Am. Chem. Soc. 107 (1985) 1202.
[39] D. Bondoux, B.F. Mentzen, I. Tkatchenko, Inorg. Chem. 20 (1981) 839.
[40] J.-M. Dupart, A. Grand, J.G. Riess, J. Am. Chem. Soc. 108 (1986) 1167.
[41] K.N. Gavrilov, Zh. Neorg. Khim. 42 (1997) 433.
[42] V.I. Nefedov, Rentgenoelectronnaya Spectroscopiya Khimicheskih Soedinenii, Khimiya, Moscow, 1984.
[43] A.T. Teleshev, K.N. Gavrilov, A.R. Bekker, N.N. Nevsky, E.E. Nifantyev, Zh. Obshch. Khim. 62 (1992) 2470.
[44] K.N. Gavrilov, Zh. Neorg. Khim. 20 (1994) 853.
[45] E. Rotondo, G. Battaglia, G. Criordano, F.P. Cusmano, J. Organomet. Chem. 450 (1993) 245.
[46] M. Brookhart, M.L.H. Green, J. Organomet. Chem. 250 (1983) 395.
[47] A.G. Ginzburg, Russ. Chem. Rev. 57 (1988) 2046.

[48] J. Febvay, D. Grec, J.G. Riess, Inorg. Chem. 20 (1981) 4285.
[49] N.A. Tikhonina, V.A. Gilyarov, M.I. Kabachnik, Izvest. Akad. Nauk SSSR (1973) 1426.
[50] K.N. Gavrilov, I.S. Mikhel, Zh. Neorg. Khim. 39 (1994) 461.
[51] K.N. Gavrilov, Zh. Neorg. Khim. 39 (1994) 1660.
[52] M.F. Rettig, R.M. Wing, G.R. Wiger, J. Am. Chem. Soc. 103 (1981) 2980.
[53] I.S. Mikhel, A.I. Rebrov, K.N. Gavrilov, Zh. Neorg. Khim. 42 (1997) 1687.
[54] I.S. Mikhel, K.N. Gavrilov, A.I. Polosukhin, A.I. Rebrov, Izv. Acad. Nauk (1998) 1627.
[55] C.A. Tolman, Chem. Rev. 77 (1997) 313.
[56] I.M. Al-Najjar, Inorg. Chim. Acta 128 (1987) 93.
[57] M. Sanchez, J.-F. Prazier, D. Houalla, R. Wolf, Bull. Soc. Chim. Fr. (1967) 3930.
[58] H. Germa, M. Sanchez, R. Burgada, R. Wolf, Bull. Soc. Chim. Fr. (1970) 612.
[59] G.M. Sheldrick, SHELXTL-PLUS, PC Version, A System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data, Rev. 5.02, Siemens Analytical X-ray Instruments Inc., Germany, 1994.