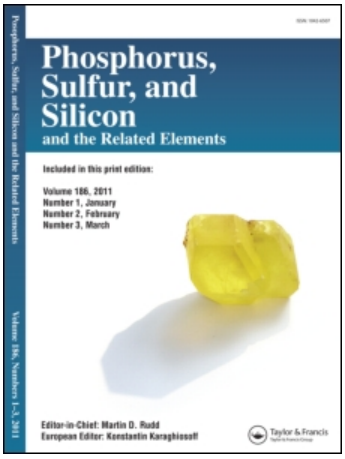

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COORDINATION OF (4S, 9S)-4,9-DIETHYL-2,11-DIOXA-5, 8-DIAZA-1 δ^5-PHOSPHATRICYCLO[6.3.0.0^{1,5}]UNDECANE WITH RETENTION OF HYDROPHOSPHORANE STRUCTURE: OBTAINING AND CHARACTERISTIC FEATURES OF ADDUCTS WITH BF_3 AND $ZnCl_2$

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COORDINATION OF (4S, 9S)-4, 9-DIETHYL-2, 11-DIOXA-5, 8-DIAZA-1 λ^5- PHOSPHA-TRICYCLO[6.3.0.0$^{1.5}$]UNDECANE WITH RETENTION OF HYDROPHOSPHORANE STRUCTURE: OBTAINING AND CHARACTERISTIC FEATURES OF ADDUCTS WITH BF_3 AND $ZnCl_2$

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Reactions of tricyclic hydrophosphorane, (4S, 9S)-4, 9-diethyl-2, 11-dioxa-5, 8-diaza-1 λ^5-phospha-tricyclo[6.3.0.0$^{1.5}$]undecane (**1**), with $BF_3 \times Et_2O$ and with $ZnCl_2$ under mild conditions have been investigated. The phosphorane ligand in the complexes obtained (**2** and **3**, respectively) was found to maintain its tricyclic structure, while the BF_3 and $ZnCl_2$ groups coordinate to the apical nitrogen and oxygen atoms of the trigonal bipyramid of phosphorane. The structure of the complexes has been evaluated by the following set of methods: IR and NMR ^{11}B, ^{13}C, ^{19}F, ^{31}P spectroscopy, mass-spectrometry, X-ray photoelectron spectroscopy, ultracentrifugation and elemental analysis. Spectral peculiarities and dynamic behavior in different solvents of compound **2** have been examined in detail.

Keywords: tricyclic hydrophosphoranes; chirality; BF_3 complexes; $ZnCl_2$ complexes

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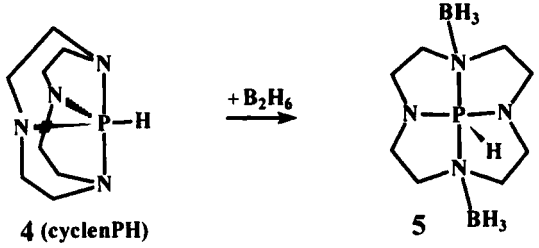
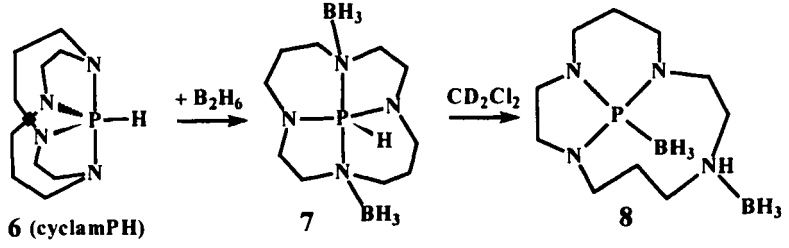
INTRODUCTION

Complexation of hydrophosphoranes (HP) is usually known to be accompanied either by fracturing of the initial phosphorane framework or by the formation of phosphoranide derivatives [1]. Retention of the HP structure is not, however, often observed. Such cases are well-known for tetracyclic HPs. Thus, for example, cyclenPH reacts easily with diborane, producing a stable bis-adduct **5** [2]:



4 (cyclenPH) **5**

No monoborane complex could be found in the reaction mixture even after adding 0.5 mole B_2H_6 to 1 mole of **4**: adduct **5** is formed again, whereas the other half of the initial cyclenPH remains unchanged. The same adduct is formed by cyclamPH:

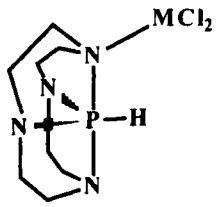


6 (cyclamPH) **7** **8**

though, when dissolved in CD_2Cl_2, it slowly (within a few weeks) isomerizes into **8**. A similar reaction of cyclenPH with $ZnCl_2$ or $CdCl_2$ gives complexes **9a, b** [3].

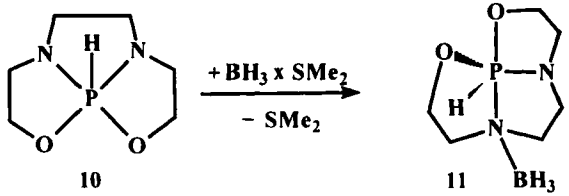
It is worth saying that so far all attempts to isolate adducts with the chemical composition 1:2 by adding excess $ZnCl_2$ or $CdCl_2$ have failed.

The ability of the tetracyclic HPs to enter N-mono and N,N-bidentate coordination with apropriate Lewis acids is provided by both the strong



M=Zn (**9a**), Cd (**9b**)

macrocyclic effect, which protects the HP structure, and by marked basicity of axial nitrogen atoms. Spectrally, the above type of coordination is observed as a downfield shift $\Delta\delta p$ in NMR ^{31}P spectra and an increase of $^{1}J(P,H)$ [1]. Similar rules are also valid for the youngest group of HPs – tricyclic compounds. In 1990 Vannoorenberghe and Buono reported [4] on obtaining the first representatives of this group as well as a stable monoborane complex of one of them:



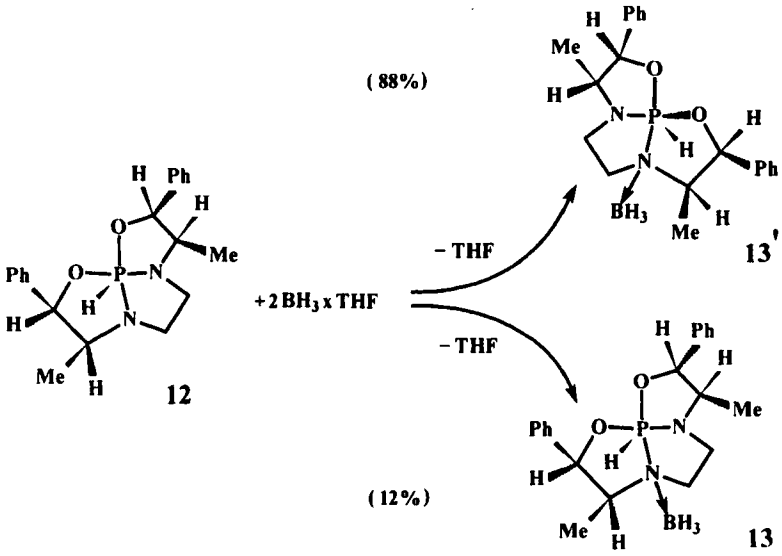
10 **11**

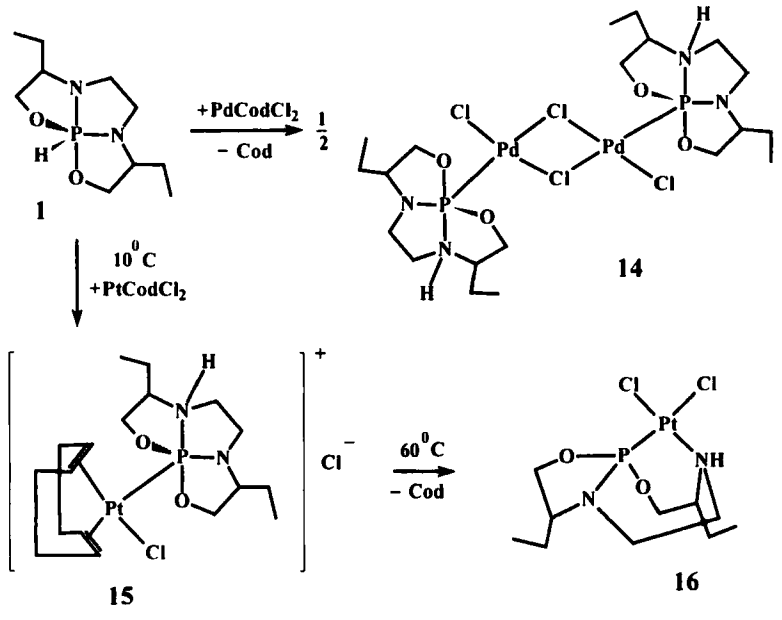
Later some other analogous adducts, including one of the tricyclic HP **12** on the base of norephedrine [5], were also described.

In that case, the minor epimer **13** results from a direct bonding of BH_3 to the apical nitrogen atom of molecule **12**, whereas epimer **13′** is formed as a result of BH_3 attack on the equatorial nitrogen atom, followed by the shift of the N-BH_3 group to the axial position by pseudorotation.

Earlier, we reported the syntheses of palladium [6] and platinum [7] complexes of new tricyclic HP **1**, in which phosphoranide and P,N-bidentate coordination of the HP had been realized.

This article is devoted to investigation of boron and zinc derivatives of **1**. A distinguishing feature of these compounds is the retention of the HP structure.





RESULTS AND DISCUSSION

The trigonal bipyramid (TBP) geometry of the tri- and tetracyclic HPs causes a considerable lengthening of the axial P-N and P-O bonds in comparison with equatorial bonds and an absence of pπ-dπ conjugation of apical atoms with d-orbitales of the phosphorus atom. For compounds **4** and **12**, this is in good agreement with the results of the X-ray analysis [5, 9]. In this case, the apical nitrogen atoms acquire an sp^3 hybrid state (for compound **12**, the valence angles for N_{ax} are in the range between 108° and 114° [5]). That is why the atoms possess some n-donor ability. One can expect the structural peculiarities described above to be valid for the new tricyclic HP **1**, too. Indeed, the calculation of molecular structure of compound **1** by quantum-chemical semiempirical AM1 method with a full geometry optimization [10] predicts the TBP configuration of the compound with the apical positioning of N or O atoms of each N/O pair (see Figure **1**), and the characteristic values of valence angles for the phosphorus atom (see Table **I**). We can also note a distinct lengthening of the axial P-N and P-O bonds in comparison with equatorial ones and smaller values of valence angles at N(5) in comparison with those at N(9), which results from the different hybridization of the nitrogen atoms: sp^3 for N(5), but sp^2 for N(9), the latter standing in a pπ-dπ conjugation with the phosphorus atom. It is necessary to mention that the results of the calculation on the whole are in good agreement with the X-ray data for an analogous phosphorane **12** [5]. Taking into account the structural parameters of **12**, we can suppose even higher sp^3-hybride character of N(5) in the real molecule of compound **1** than that obtained by the calculations. Indeed, this conclusion is confirmed by the chemical properties of **1** as a Lewis base.

It should be noted that parameter B_{PhOH} suggested by Coppel and Payju [11] is a reliable criterium of Lewis basicity. This parameter is based on the shift of ν(OH) absorption band in IR spectrum of phenol (solution in CCl_4):

$$B_{PhOH}\,(cm^{-1}) = \nu_{PhOH}\,(CCl_4) - \nu_{PhOH\cdots B}\,(CCl_4)\,,$$

which is induced by the formation of a hydrogen bond with acceptor B. Indeed, addition of **1** to a CCl_4 solution of PhOH (c=0.01M) in a molar ratio of **1**/PhOH = 2/1 [11] causes an almost complete disappearance of the ν(OH) band at 3612 cm^{-1} of the unbound OH group in the IR spectrum of phenol. Unfortunately, the ν(OH) absorption band of associated OH

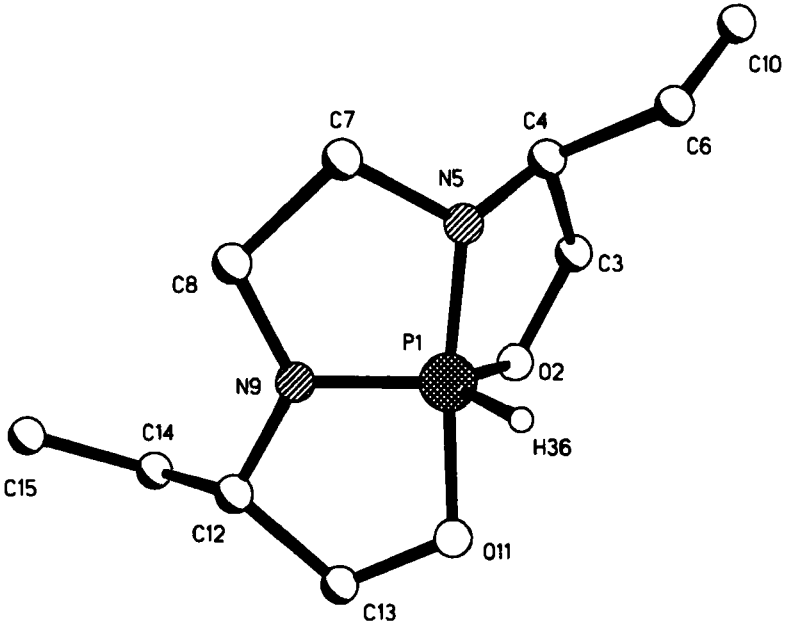


FIGURE 1 The calculated molecular structure of compound **1** (AM1 method)

groups has no distinct maximum. Instead, a lengthy plateau from 3180 cm^{-1} to 3010 cm^{-1} is observed. That is why it is impossible to define the exact B_{PhOH} value of **1**. Still, it obviously exceeds 420 cm^{-1} which should be compared with the following B_{PhOH} (cm^{-1}) values: t-Bu_2O 321; C_5H_5N 472; Et_3N 650 [11]. A peculiar shape of the ν(OH) band of the adduct HP **1** with PhOH is supposed to be explained by the existence of several associates in which hydrogen bonds PhOH···B are formed via either apical nitrogen atom or apical oxygen atom or, possibly, by involving both donor centers according to 2PhOH···B type. In this case each type of associates contributes to the formation of the ν(OH) band observed.

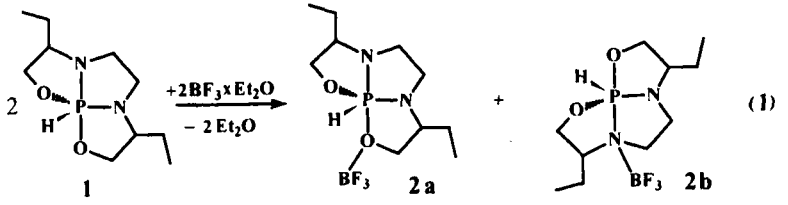
A less ambiguous result has been obtained by examining the shift of the ν(C-D) band in IR spectrum of $CDCl_3$. This shift also can serve as a criterium for the donor ability of amines[12]. The isolated molecule $CDCl_3$ in CCl_4(c= 0.12M) is represented by a narrow band with a maximum at 2255 cm^{-1}. Compound **1** being added to this solution in a molar ratio **1**/$CDCl_3$ = 1/1 brings about a splitting of the ν(C-D) band because of par-

tial formation of the hydrogen bond $Cl_3CD\cdots B$. Herein the maximum of the initial monomer band remains in the same position, and an additional broad band of the associate appears, shifted some 57 cm^{-1} toward lower frequencies (ν(C-D) 2198 cm^{-1}). This shift appreciably exceeds the values of Δν(C-D) shifts of $CDCl_3$ in complexes with pyridine (27 cm^{-1}), ethylenediamine (41 cm^{-1}), and approaches the Δν(C-D) value of the associate with triethylamine (70 cm^{-1}) [12]. Thus, **HP 1** behaves as a n-donor which is stronger than pyridine and ethylenediamine, but slightly weaker than triethylamine.

TABLE I Bond lengths (Å) and angles (°) for compound **1**

		Bond lengths	
P-0(2)	1.661	N(5)-C(7)	1.435
P-O(11)	1.702	N(9)-C(8)	1.427
P-N(5)	1.667	C(3)-C(4)	1.561
P-N(9)	1.612	C(7)-C(8)	1.569
P-H(36)	1.305	C(12)-C(13)	1.565
O(2)-C(3)	1.402	C(4)-C(6)	1.536
N(5)-C(4)	1.436	C(6)-C(10)	1.507
O(11)-C(13)	1.394	C(12)-C(14)	1.534
N(9)-C(12)	1.431	C(14)-C(15)	1.506
		Bond angles	
O(2)-P-O(11)	83.0	C(4)-N(5)-P	114.8
O(2)-P-N(5)	93.0	C(7)-N(5)-P	113.2
N(5)-P-N(9)	95.1	C(4)-N(5)-C(7)	119.7
N(9)-P-O(11)	92.2	C(8)-N(9)-P	116.5
N(5)-P-O(11)	172.8	C(12)-N(9)-P	118.4
O(11)-P-H(36)	85.8	C(8)-N(9)-C(12)	125.1
N(5)-P-H(36)	90.8	O(2)-C(3)-C(4)	108.6
0(2)-P-N(9)	120.2	C(3)-C(4)-N(5)	106.4
N(9)-P-H(36)	120.5	O(11)-C(13)-C(12)	108.4
O(2)-P-H(36)	118.4	N(9)-C(12)-C(13)	105.1
P-O(2)-C(3)	115.2	N(5)-C(7)-C(8)	108.0
P-O(11)-C(13)	114.4	C(7)-C(8)-N(9)	106.5

Taking into account the above findings, it can be supposed that compound **1** coordinates certain Lewis acids without breaking its HP structure. Indeed, under mild conditions **1** reacts with $BF_3 \times Et_2O$ giving adduct **2** which exists as a mixture of two structural isomers:



Being isolated from solution, the mixture of compounds **2a** and **2b** presents a colorless paraffin-like mass, which easily dissolves in various organic solvents. Compounds **2a** and **2b** readily form monohydrates. This follows from the results of both elemental analysis and plasma desorption mass spectrometry, m/z (I, %): 318 $[M+H_2O]^+$ (5), 232 $[M\text{-}BF_3]^+$ (100). The ion peak of the associate with m/z 552 $[M+H_2O+\mathbf{1}+2H]$ (10) can also be observed in the mass spectrum. Evidently this ion exists due to intramolecular hydrogen bonds.

In the IR spectrum of the product of reaction (**1**) one can observe a wide ν(O-H) band with a maximum at 3219 cm^{-1} which is characteristic of crystallized water [13] and a doublet of ν(P-H) bands at 2475 cm^{-1} and 2413 cm^{-1}. This fact is a convincing evidence of the hydrophosphorane nature of the adduct **2**, as well as of binding of BF_3 to its apical donor centers, since a considerable increase in the ν(P-H) value takes place as compared to that of the initial compound **1** (2370cm^{-1} and 2348cm^{-1}[6]). Thus, protonation of the apical nitrogen atom in cyclenPH causes an increase of the ν(P-H) frequency by 90 cm^{-1}, and methylation by 115 cm^{-1}.

The results of the analysis of complex **2** by X-ray photoelectron spectroscopy (XPS) are shown in Table **II**. Taking into account a relative error of 10 to 20 % [15] with respect to actual atomic concentrations, which is characteristic of XPS, we can note a good correlation of XPS quantitative analysis and elemental analysis data (see Experimental Part). The higher value of E_b for N1s, namely, 401.7eV, corresponds to coordinated nitrogen atoms in the isomer **2b**, whereas the smaller value of 400.2eV - to noncoordinated nitrogen atoms of both isomers. According to the quantitative

XPS analysis data, 2.7 % out of total 7.8 % N (See Table **II**) is the share of the coordinated N atoms, and thus the ratio of two isomers in the adduct can be estimated as 30 % of **2a** and 70 % of **2b**. Indeed, converting free amines into their BF_3 complexes appreciably increases their values of E_b N1s (eV), e.g.: $EtNH_2$ 399.1, $EtNH_2{\times}BF_3$ 401.6; and C_5H_5N 399.5, $C_5H_5N{\times}BF_3$ 401.6 [16]. It was also shown in the same article [16] that the lower is the E_b B1s value in BF_3 adducts with nitrogen-containing compounds, the more electron density is donated from N to B atom and the stronger is the B-N bond. For example, E_b B1s (eV) values are the following: $CH_3CN{\times}BF_3$ 195.7, $NH_3{\times}BF_3$ 195.1, $C_2H_5NH_2{\times}BF_3$ 194.8, $(C_2H_5)_3N{\times}BF_3$ 194.5, 2,6-$(CH_3)_2C_5H_3N{\times}BF_3$ 194.3 [16]; $(CH_3)_3N{\times}BF_3$ 193.8 [17]. From this point of view, HP **1** as a nitrogen-containing Lewis base is stronger than pyridine and ethylamine and weaker than Et_3N (E B1s of **2b** 194.1eV, see Table **II**). This conclusion stands in good agreement with the above results of estimating the donor ability of **1** on the base of $\Delta\nu$(C-D).

TABLE II XPS data for compound **2**

Element	*Found, %*	*Calcd., %*	*XPS line*	*E_b, eV*
O	15.1	15.09	O1s	533.3
N	7.8	8.81	N1s	400.2, 401.7
P	10.7	9.75	P2p	134.4
B	3.2	3.40	B1s	194.1
F	14.8	17.92	F1s	686.4

Further information on the structure of the adduct **2** has been obtained by the multinuclear NMR technique. Thus, $^{31}P\{^1H\}$ NMR spectrum of a saturated solution of **2** (c = 1 M, $CDCl_3$) exhibits four resonances, δp (Integral intensities, %): two quartets -26.6 ppm (5), ^3J(P, F) 19.7 Hz and −29.3 ppm (59), ^3J(P,F) 11.0 Hz; as well as two broadened singlets −32.5 and −34.6 ppm. These singlets merge at the baseline, their total integral intensities amounting to 36 %. Recording the ^{31}P NMR spectrum of the same solution without the proton decoupling has allowed us to estimate the ^1J(P, H) value for the main form δp −29.3 ppm as 833.1 Hz. It was not

possible to determine the $^{1}J(P, H)$ values for the other forms precisely because of the broadening of resonances, however, it is clear that they amount to 820–870 Hz. The $^{13}C\{^{1}H\}$ NMR spectrum of the solution investigated exhibits one single set of resonances (see Table **III**) which corresponds to the dominating form with δ_P – 29.3 ppm. ^{11}B NMR spectrum shows a quartet of doublets δ_B 0.35 ppm, $^{1}J(B, F)$ 22.3 Hz, $^{2}J(B, P)$ 2.3 Hz with a similar weak resonance at its base (their total integral intensity makes up 63 %) and a narrow singlet δ_B –1.3 ppm (37%), see Figure **2**. ^{19}F NMR spectrum exhibits quartets of doublets δ_F –68.1 ppm, $^{1}J(F, B)$ 22.4 Hz, $^{3}J(F, P)$ 19.2 Hz (5%); δ_F –72.6 ppm, $^{1}J(F, B)$ 22.1 Hz, $^{3}J(F, P)$ 12.1 Hz (58%) and narrow singlets δ_F –73.3 ppm (7%) and δ_F –73.4 ppm (30%). The 1 to 4 ratio of integral intensities of the two last from the above mentioned resonances indicates that they belong to fluorine atoms bonded immediately to ^{10}B and ^{11}B nuclei, the natural content of which makes up 19.9 and 80.1 %, respectively.

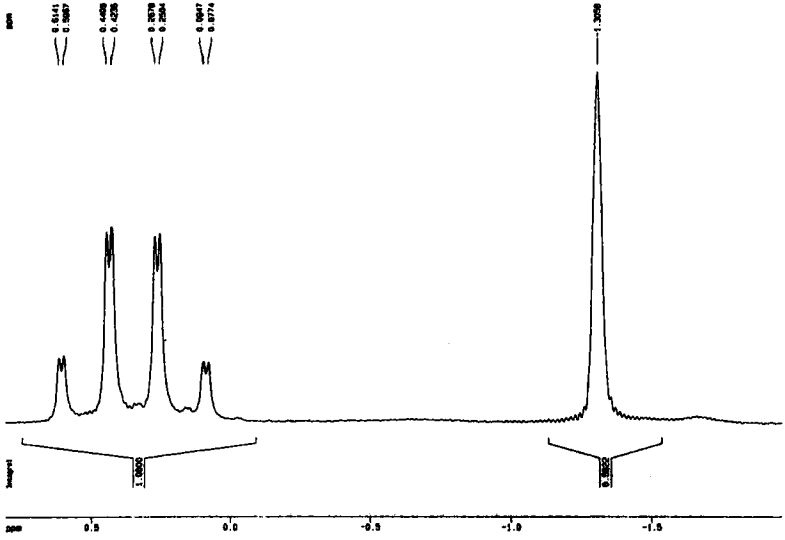


FIGURE 2 ^{11}B NMR spectrum of compound **2** (CDCl3)

^{31}P NMR spectrum of the diluted $CDCl_3$ solution of **2** (c = 0.1 M) shows the same resonances, δ_P (integral intensity, %): –26.6 ppm (7), $^{1}J(P, H)$ 824.0 Hz, $^{3}J(P, F)$ 19.8 Hz; –29.3 ppm (55.4), $^{1}J(P, H)$ 834.6 Hz, $^{3}J(P, F)$

10.9 Hz; −32.1 ppm (23), ^{1}J(P, H) 828.6 Hz; −34.6 ppm (16), ^{1}J(P, H) 861.7 Hz and differs from the mentioned above saturated solution spectrum by the shape of two upfield resonances which are narrow singlets (see Figure **3**). In ^{13}C NMR spectrum also there are narrow resonances. That is why we can observe not only resonances of the major form **2b** but resonances of both epimers **2a** (see Table **III**), which are not observed in the spectrum of the saturated solution. ^{11}B and ^{19}F NMR data are identical to those for a saturated solution.

In general, the NMR spectral data for the $CDCl_3$ solutions of **2** lead us to the following conclusions:

TABLE III ^{13}C NMR data for compounds **1** [6], **2** and **3** (δ_C, ppm; J(C, P), Hz)

Compounds	*Carbon atom*				
	$POCH_2$	*PNCH*	*$PNCH_2$*	*CH_2*	*CH_3*
1 ($CDCl_3$)	64.0	56.6, ^{2}J 7.8	42.5, ^{2}J 6.2	26.2, ^{3}J 8.2	8.9
	62.5	52.8, ^{2}J 15.2	38.1, ^{2}J 15.1	23.7, ^{3}J 4.8	8.7
2 ($CDCl_3$), c=1M	64.6	56.4	40.2, ^{2}J 8.2	24.4	10.2
(base epimer **2b**)	62.8	56.2	38.0	19.6	7.9
2 ($CDCl_3$), c=0.1M:					
major epimer **2b**	64.4	55.9, ^{2}J 6.1	39.6, ^{2}J 8.0	23.9	10.1
	62.5	55.6, ^{2}J 15.4	37.8	19.3	7.7
major epimer **2a**	67.3	54.9, ^{2}J 2.8	39.5	24.1	13.0
	64.6	54.8, ^{2}J 3.7	38.9, ^{2}J 3.7	21.6	9.2
minor epimer **2a**	65.0	54.0	36.9, ^{2}J 8.0	24.0	9.8
	63.7	53.6	35.5	19.2	8.5
2 (D_6-acetone),	68.6	57.2, ^{2}J 15.3	41.4, ^{2}J 6.9	25.5	10.4
c=0.1M	65.9	56.4 ^{2}J 18.0	40.8	25.0	9.7
(major epimers **2a**	65.8	56.0 ^{2}J 4.6	38.6, ^{2}J 8.3	23.0	8.6
and **2b**)	64.8	55.4 ^{2}J 9.7	36.8	20.2	8.4
3 (D_7-DMF)	65.1	54.9, ^{2}J 10.1	39.9, ^{2}J 7.3	23.6	8.4
	64.2	54.2, ^{2}J 14.4	36.6	22.0	8.0

1. All products detected are of HP nature, which can be proven by the presence of direct ^{1}J(P, H). The products contain BF_3 fragments bonded to apical donor centers, and this can be proven by the considerable increase of the ^{1}J(P, H) value (by 110–148 Hz) and by downfield

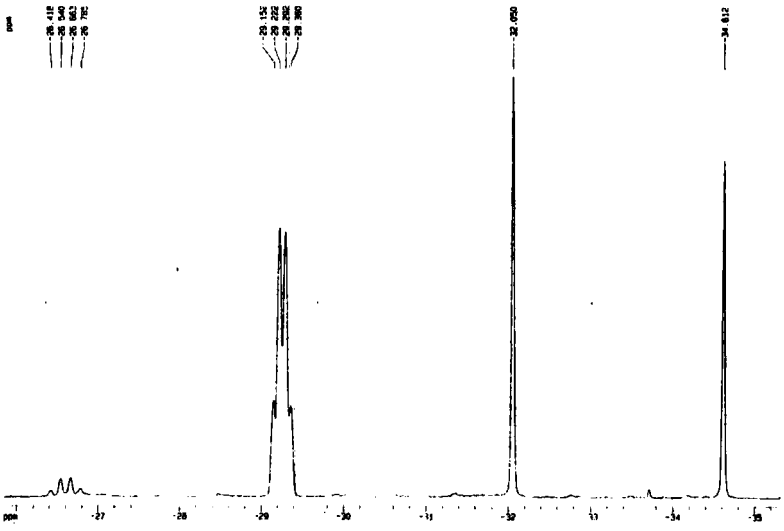


FIGURE 3 ^{31}P NMR spectrum of the diluted solution of compound **2** (CDCl3)

coordination shifts $\Delta\delta_P$ 2–10 ppm in comparison with the initial **1** (δ_P –36.4 ppm, $^1J(P, H)$ 713.8 Hz ($CDCl_3$)[6]). As mentioned above, such spectral peculiarities of HP complexes with the preserved HP structure can be regarded as reliable regularities[1,2,14]. For example, when compound **10** converts into **11**, the downfield shift $\Delta\delta_P$ 12 ppm and the increase in $^1J(P, H)$ by 119 Hz have been observed [4]. The increase in $^1J(P, H)$ and ν(P-H) depends on the P-H bond shortening (for compound **5** in comparison with **4** by 0.2 Å[18], for cyclenPH×2HO_2CCF_3- by 0.24 Å[14]). This shortening was explained by the decrease of the size of phosphorus orbitales resulting from the increase in electronegativity of equatorial atoms in corresponding adducts[18].

2. Quadruplets δ_P –26.6 ppm, –29.3 ppm in the ^{31}P NMR spectrum, like corresponding multipletes δ_P –68.1 ppm, δ_F –76.6 ppm in the ^{19}F NMR spectrum, are referred to two epimers of the complex **2b,** which are analogous to **13** and **13'**[5]. In the ^{11}B NMR spectrum the main epimer is represented by the doublet of quadruplets δ_B 0.35 ppm. ^{13}C NMR spectral data are collected in Table **III**. One can see that spectral characteristics of the bicyclic amidophosphite complex $P(OCHMeCH_2)_2N{\times}BF_3$ (δ_P 144.5 ppm (q) and δ_P 155.4 ppm (q), $^3J(P,$

F) 28.5 Hz; δ_B0.9 ppm (d of q), ^{1}J(P, B) 15.4 Hz, ^{2}J(B, P) 4.5 Hz; δ_F −95.6 ppm (m), ^{1}J(F, B) 15.4 Hz, ^{3}J(F, P) 28.5 Hz [19]) are rather close to those of **2b.** In this case, upfield resonances δ_P −32.1 and −34.6 ppm are referred to two epimers of the complex **2a.** In the NMR ^{11}B spectrum, the epimers display one singlet δ_B −1.3 ppm, and in the ^{19}F NMR spectrum two singlets δ_F −73.3 and −73.4 ppm can be observed. We can add that the diastereomers of $P(OCHMeCH_2)_2N{\times}BF_3$ mentioned above and having different values of δ_P, do not show different resonances in the ^{11}B and ^{19}F NMR spectra[19]. The absence of ^{3}J(P, F), ^{1}J(B, F), ^{2}J(B, P), ^{1}J(F, B), ^{3}J(F, B) in ^{31}P, ^{11}B, and ^{19}F NMR spectra of the complex **2a** should be noted, too. In our opinion, this fact is connected with the fast rate of exchange processes in the system. For example, as a result of fast dissociation of TiF_4complexes with donor solvents: cis-$TiF_4{\times}2B \leftrightarrow TiF_4{\times}B + B$, one single resonance is observed in the ^{19}F NMR spectrum at 0°C instead of two equally intensive triplets which are detected at −30°C[20]. Besides, in ^{19}F NMR spectra of some weak adducts of BF_3[21], ^{1}J(F, B) are not observed due to fast formation and breaking of coordinate bonds. In particular, exchange of the BF_3 fragment between two lone pairs of sulfur atom is characteristic of the $Et_2S{\times}BF_3$ adduct. Unfortunately, cooling the $CDCl_3$ solution of compound **2** down to −55°C has not given rise to profound changes in ^{31}P{^{1}H} and ^{11}B NMR spectra, but only results in some broadening of resonances.

It is necessary to note that when defining the composition of the adduct **2** according to XPS data (30% **2a** and 70% **2b**) and according to multinuclear NMR of $CDCl_3$solution (36% **2a** and 64% **2b**) the results are very similar. It is interesting that in $CDCl_3$ solution (c = 0.1 M) the share of isomer **2a** grows gradually with time, and the share of **2b** decreases After storage of the solution for two weeks in an inert atmosphere, its ^{31}P NMR spectrum exhibits the following resonances, δ_P, ppm (integral intensity, %): −26.7 (2), −29.3 (22), −32.1 (43), −34.6 (33). After boiling a solution of compound **2** in chloroform for 5 hours, its ^{31}P NMR spectrum shows only resonances of epimers **2b:** −32.6 ppm (55%) and −35.2 ppm (45%); this ratio is not affected by further boiling.

The ratio of isomers of the complex **2** depends on the solvent nature. Thus, in a D_6-acetone solution (c = 0.1 M), each isomer is represented by one of epimers: δ_P −26.7 ppm, ^{1}J(P, H) 827.7 Hz (50%) for **2b** and δ_P −29.2 ppm, ^{1}J(P, H) 810.3 Hz (45%) for **2a.** Their ^{13}C NMR spectral data

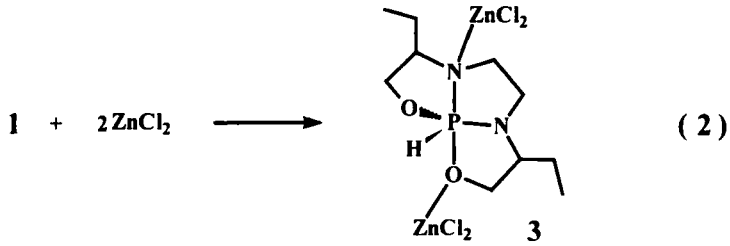
are shown in Table **III**. Minor epimers **2b** (δ_P −24.7 ppm) and **2a** (δ_P −31.4 ppm) in the solution are presented in trace quantities, only: 3% and 2%, respectively. NMR $^{31}P\{^1H\}$ analysis of solution **2b** in D_8-toluene (c = 0.05 M) has shown that **2b** is represented by the single epimer (δ_P −37.2 ppm), while **2a** dominates in the form of both diastereoisomers: δ_P −41.0 ppm (37%) and −43.5 ppm (50%). At the same time, it can be noted that the nature of the solvent heavily affects the values of chemical shifts δ_P of isomers of the complex **2**, as they differ in $CDCl_3$ and D_8-toluene by 8–9 ppm. Apparently, this is connected with the change of specific solvation (chloroform is an amphyproton solvent) into nonspecific one (toluene does not form hydrogen bonds). It should be added, that 2 is much less soluble in toluene than in chloroform. At heating a solution of compound **2** in D_8-toluene up to +95°C, the resonance of **2b** δ_P −37.2 ppm disappears, and two upfield resonances of **2a** merge into one broad singlet δ_P −40.7 ppm, which is probably connected with a fast, in the NMR time scale, interconversion of two epimers in a pseudorotation process.

In order to better understand regularities of HP **1** complexation, the course of reaction (**1**) has been controlled by ^{31}P NMR spectroscopy. The reaction was found to proceed immediately and quantitatively, since the spectrum of the reaction solution in $CDCl_3$ (c = 0.9 M), right after the reagents have been mixed together, exhibits resonances of final products, δ_P, ppm (integral intensity, %): − 26.6, ^1J(P, H) 826.0 Hz (17); −29.3, ^1J(P, H) 835.0 Hz (28) and − 34.3, ^1J(P, H) 784.9 Hz (55); the resonance of the initial **1** is absent. Whereas two downfield resonances, which look like quadruplets (1:3:3:1) in the $^{31}P\{^1H\}$ NMR spectrum, are assigned to epimers **2b,** the singlet δ_P − 34.3 ppm belongs to new form **2a′** with an oxygen-type coordination of HP **1**. The ^1J(P, H) value of **2a′** is by 45–75 Hz smaller than that of the **2a** epimer. It can be supposed that diastereoisomers **2a** and the new form **2a′** differ by the degree of distortion of an ideal TBP geometry in the direction of a square pyramid. This distortion is more significant in **2a′,** because it is characterized by a smaller ^1J(P, H) value[18]. Interestingly, the isomerization of **2b** into **2a′** proceeds faster than into **2a** (see above), and, after a week, the ^{31}P NMR spectra of the reaction mixture displays the following resonances, δ_P, ppm (integral intensity, %): −26.6 (1), −29.3 (11), −34.3 (88). At the same time, the rate of isomerisation of **2b** into **2a′** decreases with the growth of concentration of the reaction solution. If c = 1.5 M, even two months later the solution contains nearly equal quantities of **2b** (δ_P −26.8 ppm, 5% and δ_P −29.4 ppm, 40%) and **2a′** (δ_P −34.4 ppm, 55%), the resonance of the latter being broadened.

We can suppose it is the transfer of the BF_3 fragment from the nitrogen to oxygen donor center, accompanied by pseudorotation without breaking of the HP tricyclic structure, that lies in the base of the isomerisation process of **2b** into **2a** or **2a'**. However, like in the work[22], the data collected are still insufficient for a more detailed description of the reaction mechanism.

No adduct of composition $1{\times}2BF_3$ is formed when the process **(1)** is conducted at a mole ratio of B/P = 2. Only resonances of the isomers **2a** and **2b** (57 and 43 %, respectively) are observed in the ^{31}P NMR spectrum of the reaction solution in $CDCl_3$ (c = 0.1 M), while conversion of mono- to diprotonated cyclen PH leads to increasing of $^1J(P, H)$ by 80 Hz[14]. At the same time, the ^{11}B NMR spectrum exhibits two characteristic resonances of **2a** and **2b** and, in addition to this, a considerable broadening in the δ_B –0.5 ppm region. As 50 % of the total integral intensity are contributed from the latter, it should be assigned to unreacted $BF_3{\times}Et_2O$. It may very well participate in exchange with complex **2**: $1{\times}BF_3 + BF_3{\times}Et_2O \leftrightarrow 1{\times}2BF_3 + Et_2O$. However, we failed to isolate the individual complex $1{\times}2BF_3$, because the standard procedure of product isolation (see Experimental Part) leads to obtaining adduct **2,** only. Obviously, the presence of one strong electron-accepting BF_3 fragment in the adduct **2** deminishes the basity of the second apical donor center, thus preventing formation of a stable complex $1{\times}2BF_3$.

On the contrary, in the process of reaction of HP **1** with $ZnCl_2$, adduct $1{\times}2ZnCl_2$ is formed, which is evident from the results of elemental analysis (see Experimental Part):



(2)

Being very hygroscopic, the zinc complex of HP **1** forms dihydrate easily, due to coordination of H_2O molecules by each of two metal atoms. The IR spectrum of the hydrate shows broadened ν(O-H) absorption band at 3145 cm^{-1} of coordinated H_2O [13] and ν(P-H) band at 2431 cm^{-1}. XPS

data are also in good agreement with the structure suggested for **3**, E_b (eV); P2p 134.3, N1s 400.6, C12p 199.1, Zn2p 1023.1 (for example, for $ZnCl_2(NH_2OH)_2$ E_b Cl2p 199.2, E_b Zn2p 1023.0[15]). To our regret, it was impossible to distinguish signals of different nitrogen and zinc atoms because of the well known superposition effect[23]. It is possible that complex **3** is a polymer with phosphorane molecules as N, O -bidentate bridges between two neighboring polynuclear chains $[ZnCl_2]_n$. The authors of the work[13] also point to the possible polymer nature of **9a, b.**

Compound **3** is insoluble in usual organic solvents with the exception of DMSO and DMF. Its HP nature is also proved by ^{31}P NMR results of solution of **3** in D_7-DMF where a doublet resonance δ_P −34.5 ppm, $^1J(P, H)$ 804.1 Hz can be registered. It should be noted that **9a, b** demonstrate a small downfield coordination shift $\Delta\delta_P$ and a considerable increase of $^1J(P, H)$[3]. The ^{13}C NMR data for **3** (D_7-DMF) are collected in Table **III**. The molecular mass of **3** M = 747 (± 5 %) has been measured by the ultracentrifugation in DMF. This value considerably exceeds the calculated one (504) indicating either an intensive specific solvation of **3** (for $[Zn_2Cl_4(\eta\text{-}L)]\times 3DMF$, M = 723) or disproportionation in the coordination-active solvent: $2[Zn_2Cl_4(\eta\text{-}L)] \rightarrow [Zn_2Cl_2(\eta\text{-}Cl)_2L_2] + 2ZnCl_2$ (the calculated value of M for the binuclear complex is 736).

EXPERIMENTAL PART

Infrared spectra were recorded on a Specord M80 or Nicolet 750 spectrophotometers. ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer at 128.38, 100.61 and 161.98 MHz, respectively. ^{19}F NMR spectra were recorded on a Bruker WP-200-SY spectrometer at a 188.312 MHz using CF_3COOH as an external reference. ^{11}B, ^{13}C and ^{31}P chemical shifts were referenced to external $BF_3\times Et_2O$, internal $CDCl_3$ (δ_C 76.9 ppm) and external 85 % H_3PO_4 standards, respectively. Plasma desorption mass spectra were recorded on a MSVKh time-of-flight spectrometer with ionization by californium-252 fission fragments. Sedimentation analyses were performed on a MOM-3180 analytical ultracentrifuge. 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 per-

formed at C1s 284.6 eV. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

All reactions were carried out in the atmosphere of dry argon. Solvents were purified according to published procedures[8]. $P(NEt_2)_3$ and $BF_3 \times Et_2O$ were distilled before use. (3S,8S)-4,7-diaza-3,8-bis (hydroxymethyl)decane was purified as reported earlier [6]. $ZnCl_2$ was purchased from Aldrich and dried in vacuum (1 mm Hg) at 150 °C for 1 hr in the presence of P_2O_5 immediately before use.

(4S, 9S)-4, 9-diethyl-2, 11-dioxa-5, 8-diaza-1λ^5-phosphatricyclo [6.3.0.0^{1,5} undecane (1)

This compound, described by us earlier[6], has been synthesized by a new method in according to the following technique. A solution of (3S,8S)-4,7-diaza-3,8-bis(hydroxymethyl)decane (4.086 g, 0.02 mol) and $P(NEt_2)_3$ (4.947 g, 0.02 mol) in toluene (50 ml) was stirred at reflux for 1 hour. All volatiles were then removed in vacuum. Distillation of the residue at 98 °C and 0.8 mm Hg gave compound **1** as a colorless liquid (3.763 g, 81 % yield). n_D^{20} 1.4990; $[\alpha]_D^{20}$ +156.8° (5.62 g in 100 ml $CHCl_3$)[6].

Borontrifluoride – (4S, 9S)-4, 9-diethyl-2, 11-dioxa-5, 8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane-water (1/1/1) (2)

A solution of $BF_3 \times Et_2O$ (0.377 ml, 3 mmol) in methylene dichloride (10 ml) was added dropwise to a solution of compound **1** (0.697 g, 3 mmol) in the same solvent (10 ml) at 20°C. The reaction mixture was stirred for 1 hr. The solvent was then removed at 40 mm Hg, and the residue was heated in vacuum (0.8 mm Hg) at 60 °C for 1 hour to give compound **2** as a colorless hygroscopic solid in a quantitative yield. m.p. 39–43°C. Anal. Calcd. for $C_{10}H_{23}N_2BF_3O_3P$: C, 37.74; H, 7.23; N, 8.81; F, 17.92; P, 9.75; H_2O, 5.66. Found: C, 37.80; H, 6.99; N, 9.03; F, 17.87; P, 9.40; H_2O, 5.99.

(4S, 9S)-4, 9-diethyl-2, 11-dioxa-5, 8-diaza-1λ^5-phosphatricyclo [6.3.0.0^{1,5}]undecane - zinc dichloride – water (1/2/2) (3)

A solution of compound **1** (0.232 g, 1 mmol) in diethyl ether (15 ml) was added dropwise to a solution of zinc dichloride (0.341 g, 2.5 mmol) in the

same solvent (50 ml) at 20 °C. The reaction mixture was stirred for 1 hr. The formed precipitate was centrifuged, washed with ether (3×50 ml) and dried in vacuum (1mm Hg) at 50 °C to give compound **3** as a white hygroscopic solid (96 % yield). m.p. 86–87 °C. Anal. Calcd. for $C_{10}H_{25}N_2O_4PCl_4Zn_2$: C, 22.19; H. 4.62; N, 5.18; P, 5.73; Cl. 26.22; H_2O, 6.66. Found: C, 22.32; H, 4.85; N, 5.03; P, 5.53; Cl, 26.31; H,O, 6.54.

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