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Synthesis and properties of pentacoordinated phospha derivatives of *iso*-leucinol A rare example of using of hydrophosphoranes as ligands in asymmetric catalysis

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Abstract

New bicyclic (**1**) and tricyclic (**2a**) hydrophosphoranes have been synthesized from *iso*-leucinol. Complexation of bicyclic hydrophosphorane **1** with $[PdCl_2(COD)]$, $[PdCl_2(RCN)_2]$ and $[Pd(allyl)Cl]_2$ has been found to give chelate products $[PdCl_2(L)]$ and $[Pd(allyl)(L)]^+Cl^-$ containing an "open" form of the phosphorane. Tricyclic hydrophosphorane **2a**, as well as its homologue **2b**, forms metal complexes with P-monodentate binding of a hydrophosphorane, phosphoranide or "open" form of the ligand. Up to 74% ee has been achieved in the Pd-catalyzed alkylation of 1,3-diphenylallyl acetate with dimethyl malonate using **1** and **2a** and **2b** as chiral ligands.

Keywords: Hydrophosphoranes; Palladium complexes; Allylic alkylation

1. Introduction

Hydrophosphoranes (HPs) represent a well-known and extensively developed class of organophosphorus compounds [1], readily available starting from common precursors. They possess interesting stereochemical properties and show unique coordination behavior. At first sight, HPs have no potential donor centers, as the phosphorus atom does not possess any lone electron pair and the lone electron pairs of nitrogens and oxygens are involved in p_π–d_π conjugation with the d-orbitals of the phosphorus atom. However, HPs are able to form various coordinated polyhedra (see [2] and references cited therein). During the last decade, complexation of bicyclic [2–5] and tricyclic HPs [5–11] have been actively investigated. It is noteworthy that tricyclic HPs are the youngest group of hydrophosphorane compounds consisting of not more than 15 members [6,9,12].

Generally, HPs seem to be the most variable organophosphorus ligands, since they are able to act as P-, N-, P,N-, P,O- and N,N-ligands. But, surprisingly, catalytic abilities of this interesting class of phosphorus(V) compounds still have not been investigated. To the best of our knowledge, only one example of using of HPs in asymmetric catalysis

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is known thus far. Namely, a chiral bicyclic aminophosphorane provided 18% ee in the Rh-catalyzed hydrogenation of (*Z*)-α-acetamidocinamic acid [13].

In the present paper, we describe the synthesis of new bi- and tricyclic HPs derived from *iso*-leucinol, their coordination behavior and application in the enantioselective Pd-catalyzed allylic alkylation. Noteworthy, this is the first example of a successful application of HPs in asymmetric metal complex catalysis.

2. Experimental

2.1. General methods

All reactions were performed under argon in dehydrated solvents. IR spectra were recorded on a Specord M80 or Nicolet 750 instruments. ^{31}P, ^{13}C, ^{11}B, ^{1}H NMR spectra were recorded on a Bruker AMX-400 instrument at 162.0, 100.6, 128.4 and 400.13 MHz, respectively. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H and ^{13}C NMR), 85% H_3PO_4 (^{31}P NMR), $BF_3 \times Et_2O$ (^{11}B NMR). ^{19}F NMR spectra were recorded on a Bruker WP-200-SY spectrometer at 188.3 MHz using CF_3COOH as an external reference. ^{15}N NMR spectra were recorded on a Bruker AC-200 spectrometer at 20.3 MHz using NH_4NO_3 as an external reference (with $\delta([NO_3]^-) = 0$). The complete assignment of all the resonances in ^{1}H and ^{13}C NMR spectra was achieved by use of homonuclear decoupling and DEPT techniques, respectively. The X-ray photoelectron spectrum (XPS) was 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 C 1s = 284.6 eV. Electron impact (EI) mass spectra were recorded on a Varian MAT 311 instrument with direct injection of a sample. Plasma desorption (PD) mass spectrometry was implemented on MSVKh TOF spectrometer with Cf-252 fission fragments as ionizing particles. Electrospray ionization (ES) mass spectra were measured on a Micromass BioQ II-ZS mass spectrometer. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

2.2. Synthesis

2.2.1. Synthesis of aminoalcohols

2.2.1.1. (2S,3S)-2-Amino-3-methyl-pentan-1-ol (iso-leucinol). To a cold suspension of $LiAlH_4$ (4.1 g, 0.108 mol) in THF (180 ml), 10 g (0.076 mol) of L-*iso*-leucine was added portionwise. The mixture was allowed to warm up to room temperature, refluxed for 16 h and hydrolyzed with 17 ml of 8% aqueous KOH solution at 0 °C. The reaction mixture was then shortly heated up to boiling point, cooled down to room temperature and filtered. The filter cake was washed with THF (50 ml) and CH_2Cl_2 (2 × 30 ml) and the combined filtrates were concentrated in vacuum. The residue was distilled at 97–98 °C (14 mmHg) to obtain 5.81 g (65% yield) of a colorless oil. $[\alpha]_D^{21} = 3.4$ (*c* 1.1, EtOH). ^{1}H NMR ($CDCl_3$), δ_H (*J*, Hz): 3.60 (1H, dd, $^{2}J = 10.5$, $^{3}J = 3.5$), 3.26 (1H, t, $^{3}J = 9.6$), 2.61 (1H, m), 2.24 OH + NH_2 (3H, s, br), 1.46 (1H, m), 1.32 (1H, m), 1.13 (1H, m), 0.86 (3H, t, $^{3}J = 7.3$), 0.83 (3H, d, $^{3}J = 6.7$). ^{13}C NMR ($CDCl_3$), δ_C: CH_2O 63.79, CHN 56.68, CH 37.68, CH_2 24.98, CH_3 14.80, CH_3 (Et) 10.99.

2.2.1.2. (3S,4S,9S,10S)-3,10-Dimethyl-5,8-diaza-6,7-dioxa-4,9-bis(hydroxymethyl) dodecane. A mixture of *iso*-leucinol (5.76 g, 0.049 mol) and diethyloxalate (3.33 ml, 0.021 mol) was stirred till complete solidifying. The solid product was washed with acetone and dried in vacuum (1 mmHg) for 1 h. White solid, 5.39 g (71% yield). mp 190–191 °C. ^{1}H NMR (D_6-DMSO), δ_H (*J*, Hz): 8.20 (s, 2H, NH), 3.60 (m, 2H, CH_2O), 3.50 (m, 2H, CH_2O), 2.51 (m, 2H, CHN), 1.63 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 1.03 (m, 2H, CH), 0.85 (t, 6H, CH_3, $^{3}J = 6.8$), 0.81 (d, 6H, CH_3, $^{3}J = 7.2$). ^{13}C NMR (D_6-DMSO), δ_C: 159.07 (C=O), 60.99 (CH_2O), 55.79 (CHN), 35.12 (CH), 25.22 (CH_2), 15.58 and 11.26 (CH_3). Anal. Calc. for $C_{14}H_{28}N_2O_2$ (%): C 58.31, H 9.79, N 9.71. Found: C 58.66, H 10.17, N 9.43.

2.2.1.3. (3S,4S,9S,10S)-3,10-Dimethyl-5,8-diaza-4,9-bis(hydroxymethyl)dodecane. The procedure described above for *iso*-leucinol was followed using a suspension of $LiAlH_4$ (3.16 g, 0.083 mol) in THF (120ml), (3*S*,4*S*,9*S*,10*S*)-3,10-dimethyl-5,8-diaza-6,7-dioxa-4,9-bis(hydroxymethyl)dodecane (5.35 g, 0.019

mol) and 13 ml of 8% aqueous NaOH. The residue was azeotropicaly dried with benzene and distilled. Colorless oil, 4.44 g (92% yield). bp 220–223 °C (0.8 mmHg, Kugelrohr). n_D^{20} = 1.4823. ^{1}H NMR ($CDCl_3$), δ_H, (*J*, Hz): 3.40 (m, CH_2O), 3.20 (m, 2H, CH_2O), 2.60 (m, 2H, CH_2N), 2.47 (m, 2H, CH_2N), 2.29 (m, 2H, CHN), 1.36 (m, 2H, CH_2), 1.27 (m, 2H, CH_2), 1.00 (m, 2H, CH), 0.74 (t, 6H, CH_3, ^3J = 9.6), 0.66 (d, 6H, CH_3, ^3J = 6.4). ^{13}C NMR (C_6D_6), δ_C: 63.59 (CHN), 61.28 (CH_2O), 47.62 (CH_2N), 36.00 (CH), 26.65 (CH_2), 14.73 and 12.14 (CH_3). Anal. Calc. for $C_{14}H_{32}N_2O_2$ (%): C 64.57, H 12.39, N 10.76. Found: C 64.22, H 12.05, N 11.03.

2.2.1.4. Synthesis of the deuterium analogue of (3S,4S,9S,10S)-3,10-dimethyl-5,8-diaza-4,9-bis(hydroxymethyl)dodecane. The deuteration reaction was carried out according to the procedure described above for *iso*-leucinol using 17 ml of 8% aqueous NaOD in D_2O.

2.2.2. Synthesis of hydrophosphoranes

2.2.2.1. General procedure 1. A mixture of *iso*-leucinol (3.21 g, 0.028 mol) or (3*S*,4*S*,9*S*,10*S*)-3,10-dimethyl-5,8-diaza-4,9-bis(hydroxymethyl)dodecane (3.55 g, 0.014 mol) and $P(NEt_2)_3$ (3.75 ml, 0.014 mol) was stirred at 120 °C for 40 min. Then the mixture was stirred in vacuum (10 mmHg, 100 °C) for 30 min in order to remove $HNEt_2$ and distilled.

*2.2.2.2. (3S,8S,1′S)-3,8-Di(1′-methyl-propyl)-1,6-dioxa-4,9-diaza-5λ^5-phosphaspiro[4.4] nonane (**1**).* White solid, 2.33 g (65% yield). bp 98–100 °C (0.8 mmHg). mp 46–48 °C. ^{31}P NMR ($CDCl_3$): see Table 1. ^{13}C NMR ($CDCl_3$), δ_C ($J_{C,P}$, Hz): major epimer 62.69 (CH_2O), 54.15 (CHN, ^2J = 10.5), 39.22 (CH, ^3J = 6.6), 25.39 (CH_2), 13.88 and 10.88 (CH_3); minor epimer 62.50 (CH_2O), 54.22 (CHN, ^2J = 10.8), 38.91 (CH, ^3J = 4.0), 25.43 (CH_2), 14.28 and 10.92 (CH_3). MS (EI, 70 eV), *m/z* (*I*, %): 262 (5, $[M]^+$), 205 (59, $[M - Bu]^+$), 146 (100, $[M - C_8H_{20}]^+$). Anal. Calc. for $C_{12}H_{27}N_2O_2P$ (%): C 54.94, H 10.37, N 10.68. Found: C 55.11, H 9.98, N 10.33.

*2.2.2.3. (4S,9S,1′S)-4,9-Di(1′-methyl-propyl)-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (**2a**).* Colorless oil, 2.81 g (72% yield). bp 118–120 °C (0.8 mmHg), n_D^{20} = 1.4941. ^{31}P NMR ($CDCl_3$): see Table 1. ^{13}C NMR ($CDCl_3$): see Table 2. ^{1}H NMR (C_6D_6), δ_H (*J*, Hz): 7.16 (d, 1H, PH, $^1J_{H,P}$ = 705.7), 3.85 (ddd, 1H, CH_2O, $^3J_{H,P}$ = 16.0, ^2J = 8.9, ^3J = 7.0), 3.76 (ddd, 1H, CH_2O, $^3J_{H,P}$ = 13.0, ^2J = 8.9, ^3J = 7.1), 3.67 (ddd, 1H, CH_2O, $^3J_{H,P}$ = 12.8, ^2J = 8.9, ^3J = 6.1), 3.60 (ddd, 1H, CH_2O, $^3J_{H,P}$ = 11.3, ^2J = 8.9, ^3J = 6.9), 3.05 (m, 1H, CH_2N), 2.91 (m, 1H, CHN), 2.80 (m, 1H, CHN), 2.79 (m, 1H, CH_2N), 2.66 (m, 2H, CH_2N), 1.55 (m, 2H, CH), 1.35 (m, 2H, CH_2), 1.05 (m, 2H, CH_2), 0.92 (t, 3H, CH_3, ^3J = 7.1), 0.91 (t, 3H, CH_3, ^3J = 7.1), 0.88 (d, 3H, CH_3, ^3J = 6.8), 0.86 (t, 3H, CH_3, ^3J = 6.8). IR spectrum (KBr, cm^{-1}): ν(P–H) 2348. MS (EI, 70 eV), *m/z* (*I*, %): 288 (12, $[M]^+$), 258 (7, $[M - 2Me]^+$), 231 (100, $[M - Bu]^+$) Anal. Calc. for $C_{14}H_{29}N_2O_2P$ (%): C 58.31, H 10.14, N 9.71. Found: C 58.56, H 9.87, N 10.03.

*2.2.2.4. Synthesis of 1-[^{2}H]-(4S,9S,1′S)-4,9-di(1′-methyl-propyl)-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (**2aD**).* Deuteriophosphorane **2aD** was prepared following the general procedure 1 for **2a** using a deuterium analogue of the diaminodiol. ^{31}P NMR ($CDCl_3$), δ_P (*J*, Hz): −34.39 (d, $^1J_{P,H}$ = 711.7) (60%); −34.82 (t, $^1J_{P,D}$ = 108.5) (40%); ^{2}H NMR ($CHCl_3$), δ_D (*J*, Hz): 6.71 (d, $^1J_{D,P}$ = 108.1).

Table 1
Spectral data for hydrophosphoranes **1** and **2a**

Compound	NMR (in $CDCl_3$)		IR (in CCl_4) (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	−54.32 (740.9) (59%), −53.79 (735.0) (41%)	−322.98 (28.3), −323.47 (31.1)	2379, 2350	3472
2a	−34.39 (711.7)	−318.74, −319.58 (5.5)	2375	–

Table 2
^{13}C NMR data for compounds **2a**, **4a** and **8a** (in $CDCl_3$)

Compound	δC, ($J_{C,P}$, Hz)					
	OCH_2	NCH	NCH_2	CH	CH_2	CH_3
2a	59.79, 59.20	59.59 ($^2J = 8.8$), 55.27 ($^2J = 14.5$)	43.62, 38.54 ($^2J = 14.0$)	36.65 ($^3J = 5.8$), 34.30 ($^3J = 4.9$)	25.75, 25.12	12.69, 12.46, 11.71, 11.52
4a[a] (major isomer)	66.84 ($^2J = 6.81$), 62.24 ($^2J = 6.2$)	64.03, 59.94 ($^2J = 5.7$)	47.59, 43.45 ($^2J = 12.4$)	37.12, 34.26 ($^3J = 2.1$)	26.17, 26.02	15.06, 12.30, 11.76, 10.84
4a[b] (minor isomer)	65.53, 61.79 ($^2J = 10.3$)	62.76, 55.94	47.38, 44.60 ($^2J = 9.6$)	36.81 ($^3J = 3.6$), 33.34	29.45, 25.68	14.78, 12.18, 12.00, 11.00
8a (major isomer)	65.84 ($^2J = 11.4$), 61.51	59.97 ($^2J = 12.9$), 56.64	39.95, 38.20	34.63 ($^3J = 2.5$), 34.08	26.25, 25.37	13.67, 11.99, 11.74 11.16

[a] Major isomer of the **4a**: allyl fragment CH 116.84, CH_2 *trans*-P 79.11 ($^2J = 53.3$), CH_2 *trans*-N 51.54.
[b] Minor isomer of the **4a**: allyl fragment CH 116.49, CH_2 *trans*-P 78.04 ($^2J = 48.7$), CH_2 *trans*-N 52.12.

*2.2.2.5. Synthesis of (4S,9S)-4,9-diethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (**2b**).* The known compound **2b** was synthesized as published [6].

*2.2.3. Synthesis of the lithium derivative of HP **2b***

A total of 0.188 ml of a 1.6 M solution of *n*-BuLi in hexane (3 mmol) was added to a solution of HP **2b** (72 mg, 2.5 mmol) in THF (3 ml) at −78 °C. After stirring for 30 min at −78 °C, the reaction mixture was allowed to reach room temperature and was additionally stirred for 30 min. Then, 1 ml of the resulted solution was transferred into a NMR tube with 0.1 ml of $CDCl_3$ or into an IR cuvette and spectral experiments were carried out.

*2.2.4. Synthesis of 2,11-dioxa-5,8-diaza-1-thiophosphabicyclo[6.3.0] undecane (**5**)*

Sulfur (40 mg, 1.25 mmol) was added to a solution of **2a** (288 mg, 1 mmol) in benzene (5 ml) at room temperature, and the mixture was stirred overnight. The solution was filtered, and the excess solvent removed in vacuum (40 mmHg). The product was precipitated by adding 10 ml of hexane, separated by centrifugation, washed with hexane (5 ml) and dried in vacuum (1 mmHg). White solid, 298 mg (93% yield). mp 97–99 °C. ^{31}P NMR (D_8-toluene), δ_P: 56.40. ^{13}C NMR ($CDCl_3$): see Table 4. IR ($CHCl_3$, cm^{-1}): ν(NH) 3300. Anal. Calc. for $C_{10}H_{21}N_2O_3P$ (%): C 48.38, H 8.53, N 11.28. Found: C 48.62, H 8.84, N 11.01.

2.2.5. Synthesis of palladium complexes

2.2.5.1. General procedure 2. A solution of the corresponding ligand (1 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred solution of [$PdCl_2$(COD)], [$PdCl_2(CH_3CN)_2$], [$PdCl_2(C_6H_5CN)_2$] or [Pd(allyl)-Cl]$_2$ (molar ratio P/Pd = 1/1) in the same solvent (20 ml) at 20 0°C. The reaction mixture was stirred at 20 °C 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 obtained precipitate was separated by centrifugation, washed up with ether (2 × 10 ml) and dried in vacuum (2 mmHg).

*2.2.5.2. [Pd(allyl)(L)Cl] (**4a**).* Yellow solid, 97% yield. mp (dec.) 121–123°C. ^{31}P NMR ($CDCl_3$): see Section 3. ^{13}C NMR ($CDCl_3$): see Table 2. MS (ES): see Section 3. Anal. Calc. for $C_{17}H_{34}N_2O_2PPdCl$ (%): C 43.32, H 7.27, N 5.94. Found: C 43.01, H 7.00, N 6.29.

*2.2.5.3. [Pd(allyl)(L)Cl] (**4b**).* Yellow solid, 96% yield. mp (dec.) 130–131 °C. ^{31}P NMR (C_6D_6), δ_P: 90.62 (80%), 71.66 (20%). ^{13}C NMR ($CDCl_3$): see Table 4. IR (nujol, cm^{-1}): ν(Pd–Cl) 272. MS (PD), *m*/*z* (*I*, %): 374 (19, [*M* − allyl]$^+$), 232 (100, [L]$^+$). Anal. Calc. for $C_{13}H_{26}N_2O_2PPdCl$ (%): C 37.61, H 6.31, N 6.75, P 7.46. Found: C 37.96, H 6.05, N 6.44, P 7.13.

*2.2.5.4. [Pd(L)Cl$_2$] (**7**).* Yellow solid, 93% yield. mp (dec.) 104–106 °C. ^{31}P NMR ($CDCl_3$): see Section 3. ^{13}C NMR ($CDCl_3$), δ_C, ($J_{C,P}$, Hz): 74.38 (^2J = 4.8) 71.91 (^2J = 5.6), 67.16, 66.45 (CH_2O), 60.2, 57.95, 54.52, 52.57 (CHN), 38.76 (^3J = 4.4), 37.64, 37.10 (^3J = 7.4), 35.65 (CH), 26.34, 25.60, 25.45, 24.91 (CH_2), 14.10, 14.04, 13.94, 13.83 ($CH\underline{C}H_3$), 10.96, 10.65, 10.38, 10.19 ($CH_2\underline{C}H_3$), IR (nujol, cm^{-1}): ν(NH) 3294, ν(NH_2) 3210, 3108, ν(Pd–Cl) 334, 280. Anal. Calc. for $C_{12}H_{27}N_2O_2PPdCl_2$ (%): C 32.78, H 6.19, N 6.37. Found: C 33.11, H 5.89, N 6.65.

*2.2.5.5. [Pd(L)Cl(μ-Cl)]$_2$ (**8a**).* Yellow-red solid, 95% yield. mp (dec.) 150–152 °C. ^{31}P NMR (D_6-DMF), δ_P: −18.39 (86%), −23.55 (14%). ^{13}C NMR ($CDCl_3$): see Table 2. IR (nujol, cm^{-1}): ν(Pd–Cl) 334(10), 280(5), 231(9). Anal. Calc. for $C_{28}H_{58}N_4O_4P_2PdCl_4$ (%): C 36.11, H 6.28, N 6.02. Found: C 36.32, H 6.43, N 5.77.

*2.2.6. Synthesis of [Pd(allyl)Cl(L)(BF_3)]x$CHCl_3$ (**6**)*

A solution of $BF_3 \times Et_2O$ (0.503 ml, 4 mmol) in $CHCl_3$ (3 ml) was added dropwise to a solution of palladium complex **4b** (165 mg, 4 mmol) in $CHCl_3$ (3 ml). The reaction mixture was stirred for 30 min. The solvent was then removed in vacuum (40 mmHg) and ether (10 ml) was added to the residue. The obtained precipitate was separated by centrifugation, washed with ether (2 × 5 ml), and dried in vacuum (1 mmHg) to afford **6** as a yellow solid, 233 mg (97% yield). mp (dec.) 128–130 °C. ^{31}P NMR ($CDCl_3$): see Section 3. ^{13}C NMR ($CDCl_3$): see Table 4. ^{19}F NMR ($CDCl_3$), δ_F: −71.44. ^{11}B NMR ($CDCl_3$), δ_B: −1.26. IR (nujol,

cm^{-1}): ν(Pd–Cl) 282. MS (PD): see Section 3. XPS: see Section 3. Anal. Calc. for $C_{14}H_{26}N_2O_2PBF_3PdCl_4$ (%): C 27.96, H 4.36, N 4.66, P 5.15, F 9.48. Found: C 28.31, H 4.03, N 4.29, P 4.87, F 9.16.

2.2.7. Synthesis of palladium complexes *3* and *9a* and *9b*

Compounds **3** and **9a** and **9b** were synthesized for the NMR and IR experiments as follows: a solution of L* (3×10^{-4} mol) in $CHCl_3$ (1.5 ml) was added dropwise to a stirred solution of $[PdCl_2(COD)]$, $[PdCl_2(CH_3CN)_2]$, $[PdCl_2(C_6H_5CN)_2]$ (3×10^{-4} mol) or $[Pd(allyl)Cl]_2$ (1.5×10^{-4} mol) in the same solvent (1.5 ml). Then, a 1 ml sample of the resulted solution was transferred into a NMR tube or IR cuvette and spectral experiments were carried out.

A general procedure for the catalytic experiments has been reported previously [14].

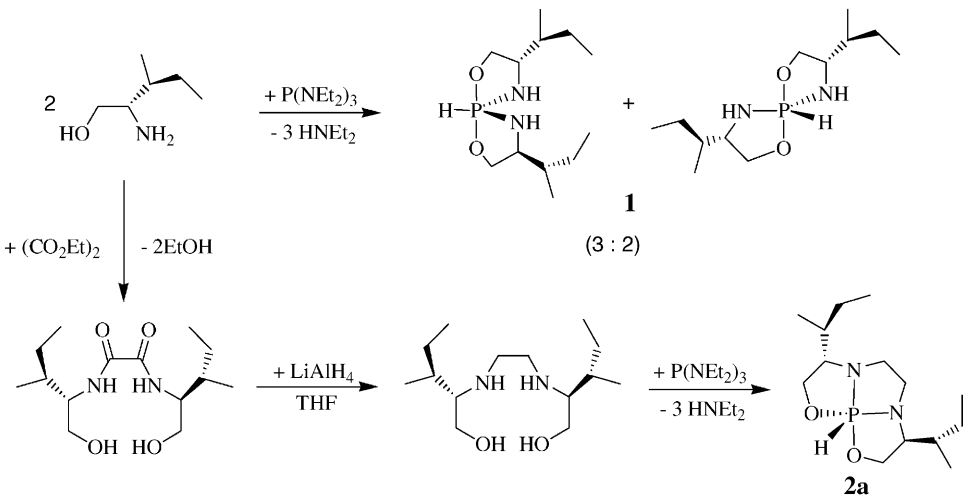
2.3. X-ray structure determination

Single crystals suitable for X-ray analysis were obtained by sublimation in vacuum. Crystallographic data for $C_{12}H_{27}N_2O_2P$ (**1**): at 110 K crystals are orthorhombic, space group $P2_12_12_1$, a = 10.883(2) Å, b = 14.185(2) Å, c = 20.165(3) Å, V = 3113.0(9) $Å^3$, Z = 8, M = 657.78, d_{calc} = 1.119 g cm^{-3}, μ(Mo Kα) = 11.19 cm^{-1}, $F(0\,0\,0)$ = 1152. Intensities of 15,688 reflections were measured with a Smart 1000 CCD diffractometer at 110 K λ(Mo Kα) = 0.71073 Å, ω-scans with 0.3° step in ω and 20 s per frame exposure, $2\theta < 52°$), and 6074 independent reflections (R(int) = 0.0880) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms linked to the nitrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation while the positions of the rest hydrogen atoms were calculated geometrically and refined in the riding model approximation. The refinement of the absolute structure have led to the Flack parameter value of 0.03(2) in the case of *S,S* configuration of all chiral carbon centers. The refinement converged to wR_2 = 0.1319 and GOF = 0.843 for all independent reflections (R_1 = 0.0531 was calculated against F for 2680 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL 5.1.

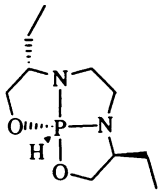
3. Results and discussion

3.1. Synthesis and properties of HPs

Compounds **1** and **2a** were obtained according to the following (Scheme 1). Besides, the previously synthesized in our group HP **2b** was used.



Scheme 1.



2b

Spectral parameters of HPs **1** and **2a** are summarized in Tables 1 and 2 and in Section 2. Buono et al. [9] as well as we did not detect possible "open" P(III)-tautomers of HPs **1** and **2a** and **2b**. HP **1** represents a 3:2 mixture of two epimers on phosphorus stereocenter—TBP (R_P) and TBP (S_P) (Table 1). The ^{31}P NMR spectrum of HP **2a** shows only one signal at δ_P −34.4. The signal did not change until −80 °C in CH_2Cl_2. It could be due to the presence of only one stereomer of the tricyclic phosphorane [12] or due to the fast TBP(R_P) − TBP(S_P) epimerization following the low-energy Berry pseudorotation process [9]. By this way, the conformation of the phosphorus center for **2a** and **2b** is assigned arbitrarily on all schemes in this paper.

The X-ray investigation has revealed that compound **1** crystallizes as single diastereomer with two independent molecules per unit cell. The geometry of two independent molecules is nearly the same. The only difference that has been found is the variation of the five-membered ring conformation. The principal bond lengths and angles are characterized by the expected values for the TBP phosphoranes with oxygens in apical positions [15,16]. The degree of distortion from the idealized TBP geometry calculated according to [17] is only 6.1%.

The unusual feature of the crystal structure of 1 is the distortion of the C_2 symmetry appeared in the unequivalence of the P–O apical and P–N equatorial bond lengths (Fig. 1). The observed elongation of the P(1)–O(2) and shortening of the P(1)–N(2) bonds probably arise from the difference in strengths of the H bonds formed by these atoms.

The analysis of the crystal structure has revealed that molecules are assembled into the infinite chains directed along crystallographic axis *c* by means of N–H···O hydrogen bonds. The N···O distances characterizing the strengths of the N(1)–H(1N)···O(1′) and N(1′)–H(1′N)···O(1) (ca. 2.944(3) Å)

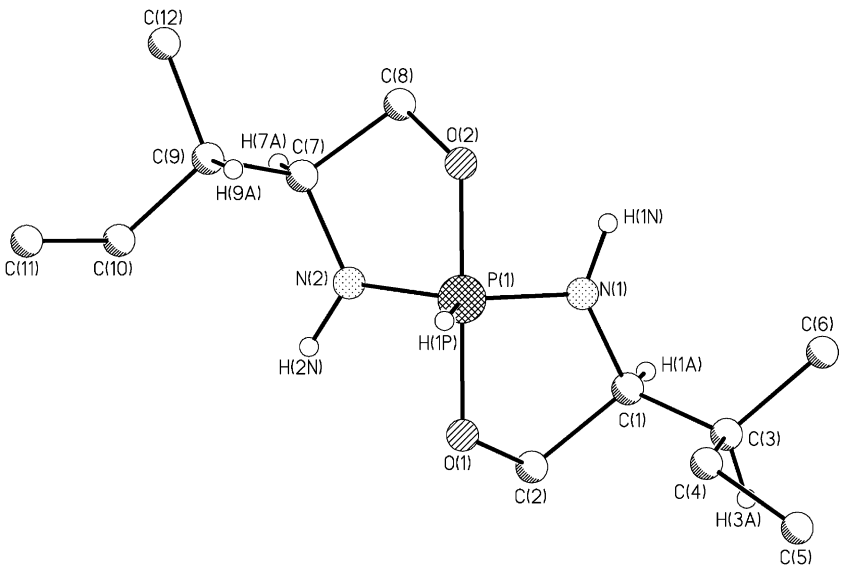


Fig. 1. The general view of one of the independent molecules in **1**. The averaged values of the selected bond lengths (Å) for two independent molecules: P(1)–N(1) 1.647(3), P(1)–N(2) 1.660(3), P(1)–O(1) 1.717(3), P(1)–O(2) 1.729(3), O(1)–C(2) 1.415(5), O(2)–C(8) 1.432(5), N(1)–C(1) 1.459(5), N(2)–C(7) 1.454(5), N(1)–P(1)–N(2) 124.3(2); the averaged values of the selected bond angles (°): N(1)–P(1)–O(1) 88.76(2), N(2)–P(1)–O(1) 92.9(2), N(1)–P(1)–O(2) 92.4(2), N(2)–P(1)–O(2) 88.2(2), O(1)–P(1)–O(2) 177.6(2), C(2)–O(1)–P(1) 112.7(3), C(8)–O(2)–P(1) 112.6(3), C(1)–N(1)–P(1) 119.9(3), C(7)–N(2)–P(1) 118.8(3).

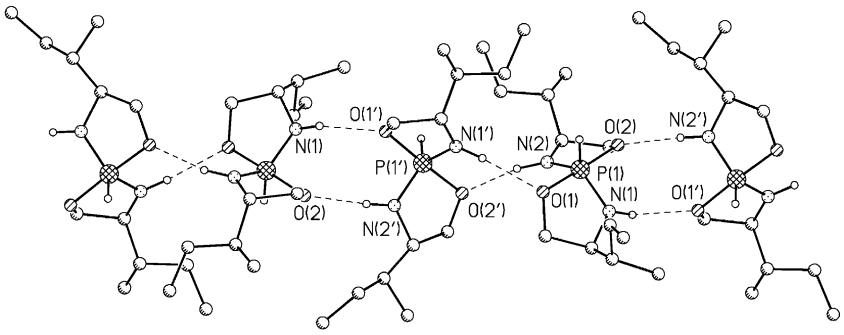


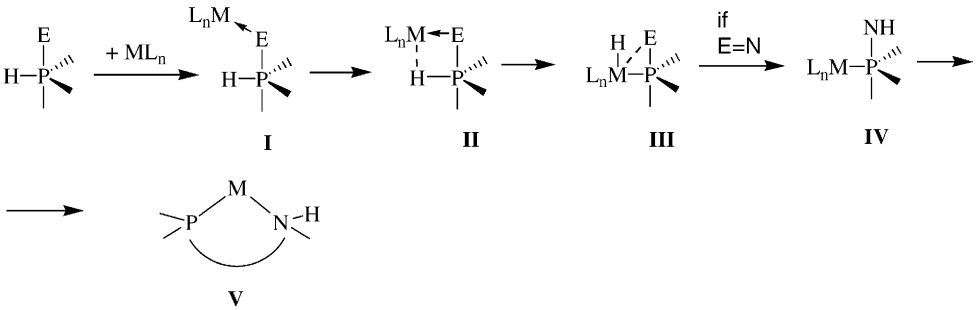
Fig. 2. The scheme illustrating the formation of the H bonded chains in **1**.

bonds are slightly longer than those for N(2)–H(2N) $\cdots$ O(2) and N(2′)–H(2′N) $\cdots$ O(2) (ca. 3.128(3) Å) bonds, what consequently can alter the degree of the oxygen electron lone pair donation to the corresponding equatorial P–N antibonding orbitals (Fig. 2).

The absence of the $^{1}J_{N,P}$ coupling for one of the signals in the ^{15}N NMR spectrum of HP **2a** (Table 1) is noteworthy. Analogous situation was observed for compound **2b** [6]. Probably due to the larger length of the apical P–N bond the $^{1}J_{N,P}$ coupling value is too small.

Previously [5] we suggested a mechanism for HPs complexation without a participation of their P(III)-tautomers According to the proposed mechanism, the first step is formation of complex (**I**), which contains a hydrophosphorane coordinated with an apical donor atom. This adduct is followed by formation of agostic (**II**) [18,19] and metal-hydride (**III**) intermediates. Then reductive elimination leads to a metallated phosphorane (**IV**), which is able to reorganize finally into a chelate metallacycle (**V**) (Scheme 2).

Due to the formation of complex **I** as a key step of complexation, the Lewis basicity of HPs is an important criterion for their coordination activity. That is why we applied the Koppel and Payu method for the estimation of the HPs' **1** and **2a** Lewis basicity (see [5] and references cited therein). The method is based on the B_{PhOH} parameter, which is the shift of the ν(OH) absorption band in the IR spectrum of PhOH in CCl_4, induced by the formation of a hydrogen bond with the acceptor (B): $B_{PhOH}(cm^{-1}) = \nu_{PhOH}(CCl_4) - \nu_{PhOH\cdots B}(CCl_4)$ (see [5] and references cited therein). Thus, HP **1** with $B_{PhOH} = 332\,cm^{-1}$ is a strong oxygen-containing Lewis base. For comparison, B_{PhOH} for THF is $287\,cm^{-1}$ and for *t*-Bu_2O is $321\,cm^{-1}$. There was no clear maximum in the IR spectrum of the **2a**/PhOH system, but B_{PhOH} for **2a** is not less than $430\,cm^{-1}$. The more precise result was obtained using another criterion, namely a shift of the ν(C–D) band in the IR spectrum of $CDCl_3$ [5]. The obtained value of $\Delta\nu$(C–D) for **2a** ($49\,cm^{-1}$) revealed that HP **2a** is a stronger nitrogen-containing



Scheme 2.

Table 3
Enantioselective Pd-catalyzed allylic substitution of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate using ligands **1** and **2a** and **2b**

Entry	Ligand	Base[a]	Solvent	Precatalyst	L/Pd	Isolated yield (%)	ee (%) (conf.)[b]
1	**1**	**A**	CH_2Cl_2	$[Pd(allyl)Cl]_2$	2.5	3	1 (*S*)
2	**1**	**A**	THF	$[Pd(allyl)Cl]_2$	2.5	10	34 (*S*)
3	**2a**	**A**	CH_2Cl_2	$[Pd(allyl)Cl]_2$	2.5	7	61 (*R*)
4	**2a**	**A**	Toluene	$[Pd(allyl)Cl]_2$	2.5	10	61 (*R*)
5	**2a**	**A**	THF	$[Pd(allyl)Cl]_2$	2.5	16	74 (*R*)
6	**2a**	**A**	THF	$[Pd(allyl)Cl]_2$	5	9	42 (*S*)
7	**2a**	**A**	THF	$[PdCl_2(CH_3CN)_2]$	2.5	17	60 (*R*)
8	**2a**	**A**	THF	$[PdCl_2(C_6H_5CN)_2]$	2.5	12	53 (*R*)
9	**2a**	**B**	CH_2Cl_2	$[Pd(allyl)Cl]_2$	1	98	52 (*S*)
10	**2a**	**B**	CH_2Cl_2	$[Pd(allyl)Cl]_2$	2.5	77	41 (*S*)
11	**2a**	**B**	THF	$[PdCl_2(C_6H_5CN)_2]$	2.5	9	55 (*S*)
12	**2b**	**A**	CH_2Cl_2	$[Pd(allyl)Cl]_2$	2.5	4	27 (*R*)
13	**2b**	**A**	THF	$[Pd(allyl)Cl]_2$	2.5	9	22 (*R*)
14	**2b**	**B**	CH_2Cl_2	$[Pd(allyl)Cl]_2$	1	96	27 (*R*)

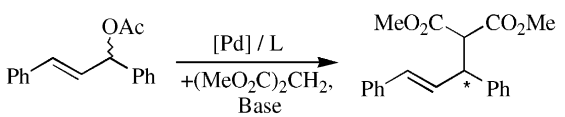
[a] **A**: NaH; **B**: BSA, KOAc.
[b] ee measured by HPLC (Chiracel OD).

donor than pyridine (27 cm^{-1}) and ethylenediamine (41 cm^{-1}), and is only slightly weaker than Et_3N (70 cm^{-1}). Similar results have been previously obtained for compound **2b** [5]. In contrast, due to absence of apical nitrogen atoms in the structure of hydrospirophosphorane **1**, this compound is not a nitrogen-containing Lewis base and its $\Delta\nu$(C–D) parameter is close to 0. So, a higher coordination activity of HPs **2a** and **2b** in comparison with HP **1** should be expected.

3.2. Catalytic application of hydrophosphoranes

Ligands **1** and **2a** and **2b** were tested in the Pd-catalyzed enantioselective allylic substitution reaction (Table 3) (Scheme 3).

Hydrospirophosphorane **1** showed low results (up to 34% ee). The most probable reason for such a low enantioselectivity seems to be the existence of the palladium complexes of **1** as an almost equal mixture of P*-epimers. From this point of view, tricyclic phosphoranes are preferable, because their metal complexes are normally obtained as an only one predominating stereoisomer.

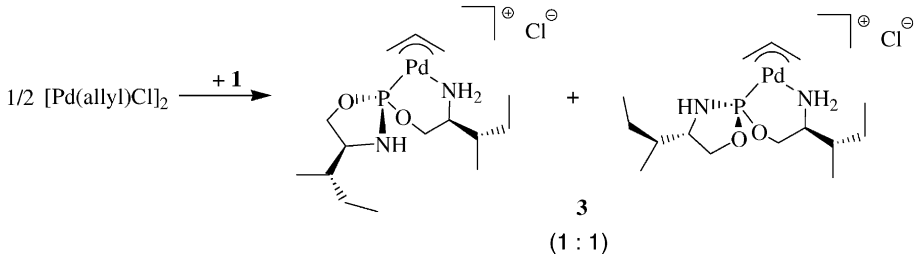


Scheme 3.

While the results achieved with HP **2b** were low (up to 27% ee), application of ligand **2a** allowed to reach a significantly higher stereoselectivity (up to 74% ee). Obviously, the reason for the difference is the more sterically demanding *sec*-Bu substituent in the molecule of **2a**. It is possible, however, that additional chiral centers in the molecule of HP **2a** help to improve the enantioselectivity.

Generally, the enantioselectivity of the catalytic process involving **2a** depends on several factors, such as base, L/Pd ratio, solvent and metal precursor. Using of NaH provides better optical yield. A decreasing of Pd/L ratio improves both optical and chemical yields (Table 3, entries 5 and 6; 9 and 10). THF is a solvent of choice in most cases. The most effective from metal precursors is $[Pd(allyl)Cl]_2$ (Table 3, entry 5) Notably, variation of the factors mentioned above could be accompanied by change of the configuration of the predominating enantiomer of the product (Table 3).

So, tricyclic HPs represent a versatile instrument for asymmetric catalytic processes. Their "open" forms are stereoindividual bicyclic aminophosphites with P* and C* stereocenters. It should be noted that the synthesis of such P(III)-compounds with reasonable chemical and optical purity is rather complicated [11]. But tricyclic HPs contain the P(III)-fragments in a "hidden" form and, what is very important, they



Scheme 4.

are readily synthetically available. So, their prospects in asymmetric catalysis look very attractive.

3.3. Synthesis of the palladium derivatives of HPs

The success in the using of HPs as chiral ligands for transition metal-catalyzed enantioselective reactions inspired us to investigate thoroughly the complexation of the ligands with various palladium precursors.

3.3.1. Complexation with [Pd(allyl)Cl]$_2$

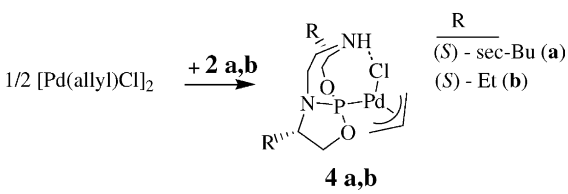
The reaction of HP **1** with [Pd(allyl)Cl$_2$] resulted in the formation of cationic complex **3** (Scheme 4).

The ^{31}P NMR spectrum of the reaction mixture showed two significantly broaden signals at δ_P 135.01 and 139.18 (1:1). These chemical shifts are characteristic for such type of complexes with aminoamidophosphites [20]. The IR spectrum of the solution contained an absorption band ν(N–H) 3320 cm^{-1} of the amino group of a phospholane cycle and ν(NH$_2$) 3200 and 3124 cm^{-1} bands related to the distant amino group bonded with a metal atom. But no absorption band ν(Pd–Cl) was detected, what confirms a moving of a chloro ligand away from the coordination sphere of palladium. The mass spectrum (PD method) showed peaks of a solvated cation **3** [Pd(allyl)(L) × 2CHCl$_3$]$^+$ (*m*/*z*, %): 648 (24) and [Pd(L)]$^+$ 368 (100).

It is noteworthy that the formation of complex **3** proceeds rather slowly. After 10 h, the ^{31}P NMR spectrum of the 0.5[Pd(allyl)Cl$_2$]/**1** system still contained a peak of the initial HP (23%) and a resonance at δ_P −7.01 ($^1J_{P,H}$ 675.4 Hz) (7%), which corresponds to the agostic intermediate **II** (Scheme 2). While coordination of the metal atom with an apical donor atom of HP leads to a growing of $^1J_{P,H}$ (see above), an agostic binding P–H···M, in contrast, leads to its decrease due to elongation of the P–H bond [18,19]. Complete disappearing of all the intermediates required more than 24 h reaction time. However, during this time some products of decomposition (δ_P 48.26, 26.40, 24.16, 4.82) appeared in the reaction mixture. An attempt to speed up the reaction by refluxing resulted in the reorganization of the products into a set of unidentified products with δ_P 82.39–56.70. Due to these reasons we could not isolate complex **3** in analytically pure form.

Unless HP **1**, compounds **2a** and **2b** formed neutral palladium(II) complexes with P-monodentate binding of their "open" forms (Scheme 5).

Investigation of the complexation of **2b** in a CHCl$_3$/CH$_2$Cl$_2$ mixture using dynamic ^{31}P NMR spectroscopy showed that the reaction starts at as low temperature as −80 °C. At this temperature, the reaction mixture consisted of traces of the initial **2b** (δ_P −37.00, $^1J_{P,H}$ 713 Hz), intermediate **I** (Scheme 2) (δ_P −23.80, $^1J_{P,H}$ 767.3 Hz) and a few complexes of the "open" form of the hydrophosphorane (δ_P 90.59, 89.66, 71.93, 70.62, 65.53, 65.08). Therefore, HP **2b** possessing higher Lewis basicity demonstrated a striking difference in reactivity in comparison to HP **1**, which reacted very slowly even at room temperature. The signal of intermediate **I** (Scheme 2)



Scheme 5.

Table 4
^{13}C NMR data for compounds **4b**, **5** and **6** (in $CHCl_3$)

Compound	δ_C ($J_{C,P}$, Hz)				
	OCH_2	NCH	NCH_2	CH_2	CH_3
4b[a]	68.34, 66.86 ($^2J = 7.8$),	60.26, 57.89 ($^2J = 5.5$)	45.64, 43.28	24.80, 24.10 ($^3J = 4.9$)	10.68, 8.84
5	68.08 ($^2J = 6.4$), 64.89	60.86, 57.43 ($^2J = 13.7$)	46.18, 43.75 ($^2J = 4.6$)	24.93, 24.83 ($^3J = 5.7$)	10.00, 8.18
6[b]	63.38 ($^2J = 12.1$), 62.46	62.26, 60.71	45.63, 40.71 ($^2J = 11.4$)	24.54, 21.68	10.22, 8.94

[a] Allyl fragment: CH 116.79 ($^2J = 11.1$), CH_2 *trans*-P 78.47 ($^2J = 50.7$), CH_2 *trans*-N 51.62.
[b] Allyl fragment: CH 118.52, CH_2 *trans*-P 80.66 ($^2J = 48.0$), CH_2 *trans*-N 55.52.

slowly decreased while the temperature was rising and completely disappeared at −20 °C. After 1 h at 20 °C the ^{31}P NMR spectrum showed the following peaks: δ_P 90.62, 89.59 (1:1, 71%); 72.00, 70.42 (1:1, 13%); 65.73, 65.18 (1:1, 16%). After 1 h of refluxing, the two latter signals had disappeared. In our opinion, these signals correlate with the stereomers of the [Pd(allyl)(η^1-P^N)$_2$]$^+$Cl$^-$ complex, which was involved into conproportionation reaction with initial $[Pd(allyl)Cl]_2$ at high temperature to form **4b**. In the ^{31}P NMR spectrum of the system $[Pd(allyl)Cl]_2$/4L (L = **2b**) in $CDCl_3$ the signals δ_P 65.73 and 65.18 dominated.

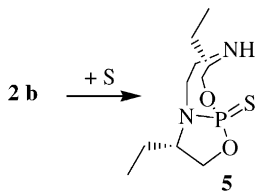
The final ^{31}P NMR spectrum of the formed in situ complex **4b** contained singlets at δ_P 90.62 and 89.59 (1:1, 79%) and minor ones at δ_P 72.00 and 70.42 (1:1, 21%). The minor forms seem to be the P*-epimers of the major ones. Another possible explanation is that they simply have more stronger transannular P···N contacts [2] and can be described as complexes with a "semi-open" phosphorane. The reason for doubling the signals of both the major and minor forms is the existence of endo- and exo-isomers for the complexes [21,22]. Analogously, the ^{31}P NMR spectrum of the resulting solution of $[Pd(allyl)Cl]_2$/2L (L = ***2a***, $CHCl_3$, 1 h of refluxing) contained the following signals of **4a**: δ_P 91.05 (45%), 90.68 (37%), 66.86 (8%), 65.35 (10%).

The ^{13}C NMR data were in a good agreement with the suggested structures (Tables 2 and 4). Particularly, the ^2J(C, P) values (49–53 Hz) are characteristic for the carbon atoms of an allylic fragment *trans*-located to the phosphite center [20,23]. Notably, there is a clear similarity between the ^{13}C NMR spectra of several derivatives of an "open" form of HP **2b**: [Pd(allyl)(η^1-P^N)Cl] **4b** (Table 4), [W(CO)$_5$(η^1-P^N)] [10] and specially synthesized derivative **5** (Table 4) (Scheme 6).

The conformation of **5** shown in Scheme 6 was assumed basing on the results of computer calculations by AM1 method. The conformation has some similarity with a "semi-open" phosphorane structure.

The IR spectra of complexes **4a** and **4b** (in $CHCl_3$) have strong symmetric adsorption bands of terminal chlorides: ν(Pd–Cl) 276 and 278 cm^{-1}, correspondingly. For comparison, ν(Pd–Cl) for initial $[Pd(allyl)Cl]_2$ is 250 cm^{-1} [24,25]. Besides, the IR spectra of **4a** and **4b** contain broad bands ν(N–H) with maximums at 3240 cm^{-1} (**4a**) and 3230 cm^{-1} (**4b**). Generally, so low values are characteristic of coordinated secondary aminogroups [2], but in this case this seems to be a result of superposition of two effects, which decrease the frequencies in IR spectra. Namely, intramolecular hydrogen bond N–H···Cl and transannular attractive contact Pd···N. In a known complex with a similar structure, [Pd(allyl)(η^1-Ph$_2$PCH(Ph)N(Ph)H)Cl], an intramolecular N–H···Cl bond has been found by single crystal X-ray analysis and ν(N–H) was equal to 3300 cm^{-1} [22].

In the ^2H NMR spectrum of compound **4a** synthesized from the deuterium derivative of HP **2a** were found two broaden singlets corresponding to the



Scheme 6.

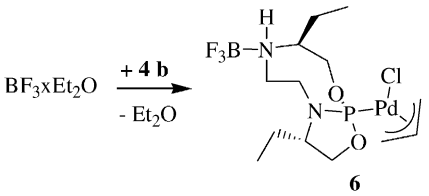
deuterons of the aminogroups of the major (δ_D 3.35) and minor (δ_D 3.75) forms.

The electrospray mass spectrum of complex **4a** contains the following peaks, *m/z* (*I*, %): [Pd(allyl)-(L)Cl × THF + H]$^+$ 544 (10) of the solvate of **4a**, [Pd(allyl)(L)]$^+$ 436 (100), [L]$^+$ 288 (12).

Obviously, formation of cationic chelates [Pd(allyl)-(η^2-P^N))]$^+$Cl$^-$ from complexes **4a** and **4b** requires a chloro ligand leaving away from the coordination sphere of palladium. But all the attempts to exchange chloride anions with non-nucleophilic $AgBF_4$ were unsuccessful. In the case of **4b**, the desired product [Pd(allyl)(η^2-P^N)]$^+BF_4^-$ was obtained in a very low yield (10%). The ^{31}P NMR spectrum of the product contained some amount of broaden singlets δ_P 131.55 and 130.75, but the most intensive peaks in the spectrum were singlets at δ_P 64.53 and 64.08, which correspond, probably, to [Pd(allyl)(η^1-P^N)$_2$]$^+BF_4^-$. The reason for the fact is likely to be a low activity of the "open" forms of HPs **2a** and **2b** as chelate forming ligands. The chelate forming fragment in their structures is a perhydrophosphocine cycle. But it has been revealed before that such types of P(III)-ligands, e.g. perhydro-6-methyl-2-phenyl-1,3,6,2-dioxazaphosphocine, act as P-monodentate ligands when coordinated to palladium. And the structure of [Pd(2-Me-allyl)(η^1-PhP(OC$_2$H$_4$)$_2$ NMe)Cl] was even proved by single crystal X-ray analysis [26].

A presence of a non-coordinated amino group in complexes **4a** and **4b** was confirmed by their ability to react with Lewis acids, e.g. boron trifluoride. On the base of **4b**, complex **6** was synthesized in almost quantitative yield. In this case, the "open" form of the HP serves as a bridge between the boron and palladium atoms (Scheme 7).

The structure of the product **6** was proved by ^{31}P NMR (δ_P 128.20, $CDCl_3$), ^{13}C NMR (Table 4) and IR data (ν(N–H) 3140 cm^{-1}, ν(Pd–Cl) 284 cm^{-1}, $CHCl_3$). The XPS spectrum of the system had following lines E_b (eV): Pd 3d5/2 338.2, P 2p 133.6, Cl 2p 198.9, F 1s 686.3, B 1s 194.1, N 1s 400.0 and 402.9. The E_b values for boron and fluoride are typical for boron trifluoride complexes with amines [27]. The energy of Cl 2p is significantly higher than 198.5 eV, what means the chloro atom is coordinated [28]. Noteworthy, there are different values of E_b N 1s. The major one corresponds to nitrogen bonded with the boron atom [27]. Finally, the plasma desorption mass spectrum of **6** showed the following peaks of a solvate of the complex and its fragments, *m/z* (*I*, %): [Pd(allyl)(L)(BF_3)Cl × $CHCl_3$]$^+$ 602 (23), [Pd(allyl)(L)(BF_3) × $CHCl_3$]$^+$ 567 (17), [Pd(allyl)(L)]$^+$ 380 (34), [Pd(L)]$^+$ 339 (20), [L]$^+$ 232 (100).

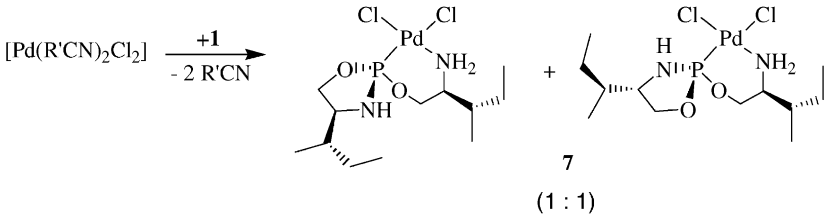


Scheme 7.

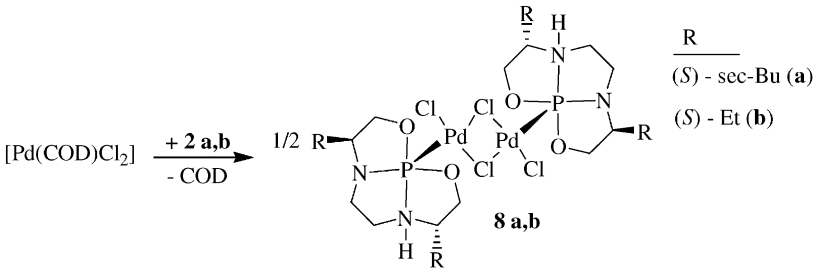
3.3.2. *Complexation with [PdCl$_2$(COD)]*

The reaction with HP **1** led to the formation of chelate palladium(II) complexes with *cis*-coordination of chloro ligands (Scheme 8).

It was proved by the characteristic [3,4] spectral parameters of compound **7**. Thus, the ^{31}P NMR spectrum (in $CDCl_3$) contained the signals of the both P*-stereomers of the complex at δ_P 96.57 and 95.72 in almost equal quantities. The IR spectrum of **7** (in $CDCl_3$) showed ν(N–H) bands at 3297 cm^{-1} of endo-cyclic secondary amino group, ν(NH_2) bands at 3195 and 3109 cm^{-1} of the primary amino group



Scheme 8.



Scheme 9.

coordinated to palladium and ν(Pd–Cl) bands at 330 and 282 cm^{-1} of the terminal chloro ligands. The ^{13}C NMR data (Section 2) are also in a good agreement with the suggested structure.

In contrast, reaction of the tricyclic HPs resulted in the formation of a phosphoranide derivatives of palladium(II) (Scheme 9).

The spectral parameters of the new complex **8a** are very close to the parameters of the recently synthesized in our group complex **8b** [6]. In the ^{31}P NMR spectrum of **8a** ($CDCl_3$) two broaden singlets δ_P −26.44 (33%) and −20.43 (67%) were observed. These signals again could be attributed to the *cis*- and *trans*-isomers of **8a** [6] or to the epimers on P*-stereocenter. In the IR spectrum of **8a** ($CHCl_3$) was found a broad ν(N–H) band at 3110 and three ν(Pd–Cl) bands at 342, 284 and 230 cm^{-1} of terminal and bridged chloro ligands with 10:5:8 ratio. Unusually strong *trans*-effect of the phosphoranide ligand is noteworthy. It leads to abnormally low ν(Pd–Cl) frequency (230 cm^{-1}) for the chloro ligand *trans*-located to the bridged one.

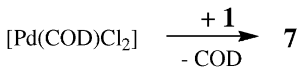
The ^{13}C NMR data for **2a** and **8a** are very similar, as expected (Table 2). Significant upfield shifts of the resonances of the NCH_2 carbon atoms, caused by protonation of the apical nitrogen atoms [6], are worthy of note. Complexes **8a** and **8b** are quite stable and do not reorganize into chelates even at refluxing in toluene. This striking difference in coordination behavior between HPs **1** and **2a** and **2b** can be explained in terms of macrocyclic stabilization [2], which favors tricyclic systems. Interestingly, deprotonation of HP **2b** with *n*-BuLi did not lead to a creation of a phosphoranide salt. The ^{31}P NMR spectrum of the reaction mixture contained signals only of lithium derivatives of "open" forms: δ_P 172.5, 163.8, 97.2, 96.0. But the reaction of HPs **2a** and **2b** with [$PdCl_2$(COD)] formed metallated phosphoranes **8a** and **8b** in almost quantitative yields. This provides an additional proof for active participation of the transition metal atom in the process of proton migration from the phosphorus atom (Scheme 2).

3.3.3. Complexation with [$PdCl_2(R'CN)_2$] ($R' = CH_3$, C_6H_5)

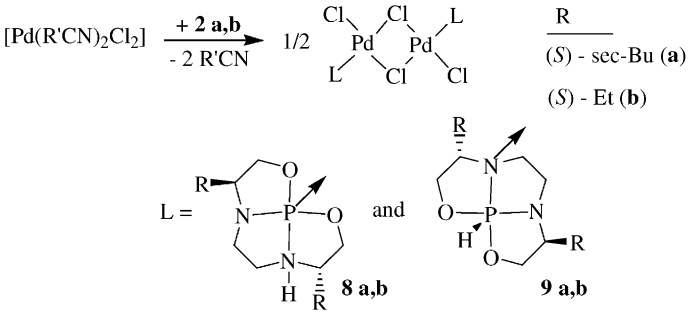
Reaction of HP **1** with the mentioned precursors resulted in complexes **7** as the 1:1 mixture of diastereomers, which were investigated by ^{31}P, IR spectroscopy and elemental analysis (Scheme 10).

At the same time, reactions with **2a** and **2b** gave mixtures of products, all of them being P(V) derivatives (Scheme 11).

Thus, in the ^{31}P NMR spectra of the products were observed two singlet resonances of compounds **8a** and **8b** together with the two doublet peaks of adducts **9a** and **9b**, which remained hydrophosphorane structure: δ_P −29.10 ($^1J_{P,H}$ = 829.1 Hz), δ_P −33.10 ($^1J_{P,H}$ = 827.7 Hz), **9a**, and −33.00 ($^1J_{P,H}$ = 823.4 Hz), −36.10 ($^1J_{P,H}$ = 818.5 Hz), **9b**. The complexes of the both types were detected in equal amounts and they are structural isomers. As well as in the case of **8a** and **8b**, the double set of corresponding signals of **9a** and **9b** can be explained by the presence of *cis*- and *trans*-isomers or P*-epimers. The IR spectra of **8a** and **8b** (in situ in $CHCl_3$) showed broaden bands ν(N–H) 3110 and 3100 cm^{-1}, correspondingly. For **9a** and **9b** ν(P–H) bands at 2436 and 2431 cm^{-1} were observed. No bands of the nitrile ligands were found. It should be noted that decreasing of the $^1J_{P,H}$ and



Scheme 10.



Scheme 11.

ν(P–H) values in the ^{31}P NMR and IR spectra of **9a** and **9b** comparing to **2a** and **2b** is a reasonable evidence for coordination of the apical nitrogen atoms of the HPs with the palladium atom ([2,8] and references cited therein).

Compounds **9a** and **9b** are the first known existing at room temperature adducts of tricyclic HPs, in which their apical donor centers are coordinated to d_8 transition metals ions. Such products have been previously detected only at low temperatures [5]. Unfortunately, it was impossible to separate the mixtures of **8** and **9** due to instability of **9a** and **9b**. And it is not a surprise, since complexes **9a** and **9b** represent intermediates of the complexation process (intermediate **I** at Scheme 2).

4. Conclusions

New pentacoordinated phospha derivatives of *iso*-leucinol, namely bicyclic hydrospirophosphorane **1** and tricyclic hydrophosphorane **2a**, have been synthesized and characterized. Bicyclic HP **1** forms chelate complexes with all the palladium precursors. Tricyclic HP **2a**, as well as the previously synthesized **2b**, acts as a monodentate ligand. Tricyclic HPs have been found to be stronger Lewis bases and, in complete accordance with the proposed complexation mechanism, they demonstrated higher coordination activity than bicyclic hydrospirophosphoranes. For the first time hydrophosphoranes were successfully used as chiral ligands for asymmetric catalysis, affording up to 74% ee in the Pd-catalyzed allylic alkylation reaction.

5. Supplementary materials

Crystallographic data for the structural analysis of HP **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC (12 Union Road, Cambridge CB2 1EZ, UK. Direct line: +44-1223-762910; Tel.: +44-1223-336408; fax: +44-1223-336033) No. 187702.

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