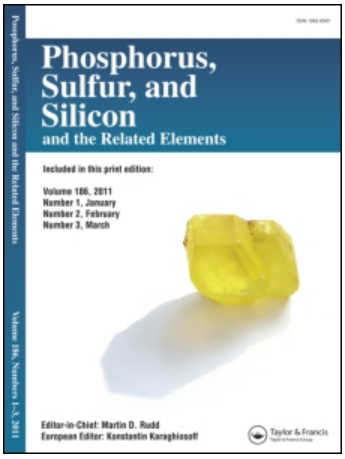

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REACTION OF COMPOUNDS WITH A H-P BOND WITH SCHIFF-BASES

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REACTION OF COMPOUNDS WITH A H-P BOND WITH SCHIFF-BASES

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Addition of compounds with a P-H bond to Schiff bases of both simple and macrocyclic compounds proceeds smoothly as a non catalysed thermally initialised reaction in an inert solvent. For macrocyclic systems and bulky phosphorus substituents a stereoselective formation of the trans isomer was confirmed by X ray analysis. The addition is reversible, and the reverse reaction is catalysed by Lewis acids. The trans orientation of phosphorus substituents on the macrocycle ring, the stereochemical rigidity of molecules and reversibility of the addition limit the use of the compounds formed in such manner as ligands.

Keywords: Schiff bases; macrocycles; addition reaction; X ray structure

INTRODUCTION

Polyazamacrocycles bearing the N-methylenephosphinic or N methylenephosphonic pendant group are of considerable interest as potential medical therapeutical reagents and diagnostic agents.[1–3] Since these applications generally involve complexation with the metal ions, their complexing abilities have been studied both in solution[2–4] and in the solid state.[3,5] We recently reported results dealing with the transition-metal complexes of 1,4,7-triaza-cyclononane-1,4,7-triyl-trimethylene-tris(phosphinic) and 1,4,7,10-tetraazacyclo-dodecane-1,4,7,10-tetrayl-tetramethylene-tetrakis(phosphinic) acids in solution.[6] A comparison of our solution results[6] with the literature[2–4] has shown that complexing properties of the macrocycles are completely changed by the pendant arms, and according to our experiences, a chelatation of $>NCH_2P(R)O_2H$ part plays a predominant role in the complexing proper-

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ties of the macrocyclic ligand in contrast to the original macrocycle. Therefore, we designed a new phosphorylated azacycle with the phosphorus atom directly bonded to a carbon of the cycle (*i.e.* to the rim) for the reasons of lower deformability and consequently expected better selectivity than belongs to the macrocycles with pendant arms mentioned above.

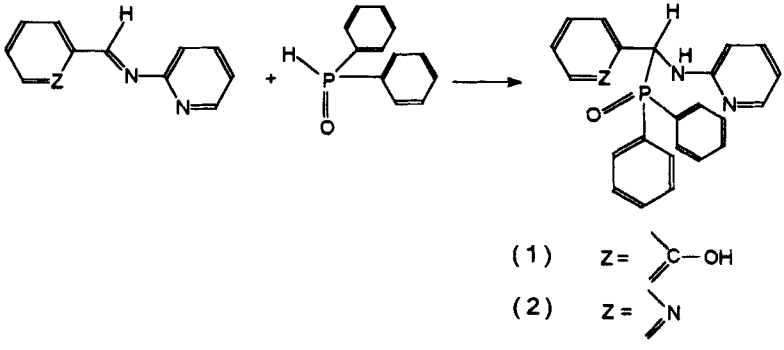
The new type of the macrocycles with a phosphorus group bonded to a carbon atom in the rim could be synthetized by several ways. An addition of the H – P bond to the double bond >C = C< or -N = C< of hydrocarbon derivatives has been well-known for many years and it is a step of Mannich synthesis with hydrogen-phosphorus compounds. Therefore, we expect that the addition could be used for the synthesis of the macrocyclic derivatives starting from easily accessible Schiff bases.

The aim of this paper is to test the mentioned synthetic route for several compounds containting a H-P bond and several compounds containing the -CH=N- system from the simple Schiff-bases to the macrocycles.

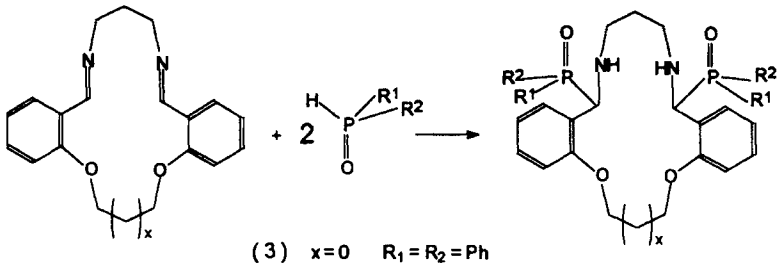
RESULTS AND DISCUSSION

Synthesis, decomposition of products, MS

The synthesis was studied using diphenylphosphine oxide or phenylphosphinic acid ethylester or diethylphosphite and Schiff-bases as is shown in the reaction scheme 1 and 2. The starting compounds were synthesized according to the procedures known from literature[7,8,9].



SCHEME 1



(3) x=0 $R_1 = R_2 = Ph$
(4) x=1 $R_1 = R_2 = Ph$
(5) x=0 $R_1 = Ph, R_2 = OEt$
(6) x=0 $R_1 = OEt, R_2 = OEt$
(7) x=0 $R_1 = Ph, R_2 = OH$
(8) x=0 $R_1 = OH, R_2 = OH$

SCHEME 2

Products were obtained in reasonable yields and were characterized by common spectroscopic methods. Crystals of **1**, **2** and **3** were convenient for the single crystal X-ray analysis and therefore, structures of these compounds were determined (Tables I, II–IV, Figs 1–3).

TABLE I Exprimental data for the X-ray difraction studies of **1**, **2**, **3**

	1	*2*	*3*
Formula	$C_{24}H_{21}N_2O_2P$	$C_{23}H_{20}N_3OP.H_2O$	$C_{43}H_{42}N_2O_4P_2.H_2O.CH_3OH$
M	400.40	385.39	762.78
T /K	293(2)	293(2)	293(2)
Crystal dimension/mm	0.3 × 0.4 × 0.5	0.13 × 0.3 × 0.3	0.35 × 0.58 × 0.7
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1 (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a /Å	9.510(2)	8.910(1)	9.407(1)
b /Å	10.768(2)	13.683(1)	23.247(2)
c /Å	11.178(2)	16.670(1)	18.785(2)

	1	*2*	*3*
α/°	113.35(2)	90	90
β/°	102.81(2)	98.714(9)	102.748(8)
γ/°	93.29(2)	90	90
U / Å^{-3}	1011.1(4)	2008.9(4)	4006.4(8)
Z	2	4	4
D_c/gcm^{-3}	1.315	1.274	1.265
λ/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	0.16	0.15	0.16
F(000)	420	808	1616
Scan mode	θ-2θ	θ-2θ	θ-2θ
θ range of data collection/	2.06–25.97	1.93–24.97	1.42–25.94
Index ranges	0–11;-13–13; -13–13	0–10; 0–15;-19-19	0–11; 0–28; –23 - 22
Number of reflections measured	3991	3756	8358
R_σ	0.0443	0.0354	0.0414
Number of reflections observed [I>2σ(I)]	2823	2468	5149
Number of independent reflections	3953	3444	7670
R_{int}	0.0792	0.0160	0.0645
Coeffitiens in weighting scheme [a]	0.1273; 0.0000	0.0412; 0.4070	0.1245; 9.5775
Data, restrains, parameters	3953; 0; 346	3444; 0; 330	7670; 0; 665
Goodness-of-fit on F^2	1.022	1.048	1.047
Final R, R′ indices [I≥2σ(I)][b]	0.0675; 0.1884	0.0359; 0.0936	0.0959; 0.2829
Maximum shift/e.s.d.	0.000	0.001	0.035
Largest difference peak and hole /eÅ^{-3}	0.60; –0.56	0.21; –0.17	1.06; –1.34

[a] $w = 1/[\sigma^2(F_o^2)+(A\,^*P)^2+B^*P]$ where $P = (F_o^2+2F_c^2)/3$ (SHELXL97, ref. 13).

[b] $R = \Sigma|F_o-F_c|/\Sigma|F_c|$ $R' = [\Sigma w(F_o^2- F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (SHELXL97, ref. 13).

TABLE II Selected bonds (Å) and angles (°) in **1**

Geometry on phosphorus atom					
P-O1	1.480(2)	O1-P-C1	112.5(1)	C1-P-C19	107.2(1)
P-C1	1.837(3)	O1-P-C13	112.0(1)	C13-P-C19	106.3(1)
P-C13	1.800(3)	O1-P-C19	113.9(1)		
P.-C19	1.801(3)	C1-P-C13	104.3(1)		
other parts of molecule					
C1-P	1.837(3)	P-C1-N1	106.0(2)	O1-P-C1-N1	-54.3(2)
C1-C7	1.521(4)	P-C1-C7	114.8(2)	O1-P-C1-C7	74.8(2)
C1-N1	1.449(4)	C7-C1-N1	115.8(2)	P-C1-C7-C8	137.0(3)
C1-H1	0.930(30)			C1-N1-C2-N2	-9.0(4)
N1-C2	1.367(4)	C1-N1-C2	122.2(3)	P-C1-N1-C2	142.9(2)
N1-H1N	0.833(27)			C7-C1-N1-C2	-88.6(4)
C8-O2	1.370(4)	C7-C8-O2	122.4(3)	C1-C7-C8-O2	2.5(4)
O2-H2O	1.043(42)	C9-C8-O2	117.0(3)	C10-C9-C8-O2	-179.7(3)

TABLE III Selected bonds (Å) and angles (°) in **2**

geometry on phosphorus atom				
P-O	1.483(1)	O-P-C1	111.32(9)	C1-P-C18 108.08(9)
P-C1	1.837(2)	O-P-C12	111.84(9)	C12-P-C18 108.87(9)
P-C12	1.803(2)	O-P-C18	110.95(8)	
P-C18	1.805(2)	C1-P-C12	105.58(9)	
other parts of molecule				
C1-P	1.837(2)	P-C1-C7	109.9(1)	O-P-C1-C7 66.4(1)
C1-N1	1.444(2)	P-C1-N1	104.9(1)	O-P-C1-N1 –59.1(1)
C1-C7	1.512(3)	C7-C1-N1	116.2(2)	P-C1-C7-N3 94.8(2)
C1-H1	0.983(18)	C1-N1-C2	123.2(2)	C1-N1-C2-N2 –1.0(3)
N1-C2	1.371(2)			P-C1-N1-C2 139.2(2)
N1-H1N	0.826(20)			C7-C1-N1 -C2 –99.4(2)
C7-N3	1.334(2)			

TABLE IV Selected bonds (Å) and angles (°) **3**

The geometry on phosphorus atoms					
P1–O3	1.504(4)	O3-P1-C9	113.1(2)	C9-P1-C31	105.1(2)
P1-C9	1.854(5)	O3-P1-C21	112.5(3)	C21-P1-C31	109.8(2)
P1-C21	1.801(5)	O3-P1-C31	110.9(3)		
P1-C31	1.809(5)	C9-P1-C21	104.9(2)		
P2–O4	1.493(4)	O4-P2-C13	112.7(2)	C13-P2-C51	104.2(3)
P2-C13	1.870(5)	O4-P2-C41	110.6(3)	C41-P2-C51	111.7(3)
P2-C41	1.809(6)	O4-P2-C51	110.7(3)		
P2-C51	1.794(7)	C13-P2-C41	106.8(3)		
The geometry on C9 and C13 atoms					
C9-P1	1.854(5)	P1-C9-N1	104.8(4)	N1-C9-H9	108(3)
C9-N1	1.453(6)	P1-C9-C8	112.4(3)	C8-C9-H9	102(3)
C9-C8	1.530(6)	P1-C9-H9	111(3)		
C9-H9	0.88(5)	N1-C9-C8	119.2(4)		
C13-P2	1.870(5)	P2-C13-N2	110.7(4)	N2-C13-H13	109(3)
C13-N2	1.455(7)	P2-C13-C14	105.7(3)	C14-C13-H13	108(3)
C13-C14	1.514(7)	P2-C13-H13	103(3)		
C13-H13	0.93(5)	N2-C13-C14	118.6(5)		
The geometry of macrocyclic ring					
O1-C 1	1.430(7)	C19-O1-C1	118.7(5)	C19-O1-C1-C2	160.3(6)
C1-C2	1.505(10)	O1-C1-C2	106.5(6)	O1-C1-C2-O2	-64.9(8)
C2–02	1.413(8)	C1-C2-O2	104.5(6)	C1-C2-O2-C3	-179.6(5)
02-C3	1.371(6)	C2–O2-C3	119.4(5)	C2–O2-C3-C8	-169.2(5)
C3-C8	1.396(7)	O2-C3-C8	115.5(4)	O2-C3-C8-C9	1.8(7)
C8-C9	1.382(8)	C3-C8-C9	119.4(5)	C3-C8-C9-N1	135.4(5)
C9-N 1	1.453(6)	C8-C9-N 1	119.2(4)	C8-C9-N1-C10	-56.5(6)
C10-C10	1.472(7)	C9-N1-C10	115.0(5)	C9-N1-C10-C 1 1	-56.9(6)
C10-C1 1	1.531(8)	N1-C10-C1 1	114.3(5)	N1-C10-C11-C12	-58.3(6)
C11-C12	1.513(7)	C10-C11-C12	114.2(5)	C10-C11-C12-N2	-161.8(4)

The geometry of macrocyclic ring					
C12-N2	1.482(7)	C11-C12-N2	110.7(5)	C11-C12-N2-C13	-73.1(1)
N2-C13	1.455(7)	C12-N2-C13	116.0(4)	C12-N2-C13-C14	-71.1(6)
C13-C14	1.514(7)	N2-C13-C14	118.6(5)	N2-C13-C14-C19	125.2(5)
C14-C19	1.402(7)	C13-C14-C19	122.2(5)	C13-C14-C19-O1	-3.2(7)
C19-O 1	1.377(7)	C14-C19-O 1	114.0(5)	C14-C19-O1-C 1	-177.4(6)

The acids **7** and **8** were prepared by hydrolysis of **5** and **6**. We also tested the reaction of the macrocyclic Schiff base with phenylphosphinic acid in dry toluene to obtain **7** directly by addition of the P-H bond of the acid on the double bond of the cycle. This reaction between phosphinic acid and Schiff bases is known.[10] A formation of **7** was observed in the reaction mixture, and in addition a formation of by-products and also decomposition of **7** was also observed. Therefore, both acids **7** and **8** were synthetized via their esters.

Similar decomposition was observed during prolonged heating of **7** or **8** to 110°C in aqueous solutions, for example, during hydrolysis of **5** or **6** in refluxing hydrochloric acid. The yields of **7** and **8** were decreased using this way and the purity of the products obtained was poor. Compound **7** was found to decompose upon formation to the starting Schiff base and phenylphosphinic acid, and consequently, the Schiff base underwent decomposition to appropriate amine and aldehyde.

The addition of the H-P group to the C=N in Schiff-bases was found to be a remarkably reversible reaction for **3** and **4** as well. This decomposition was studied by ^{31}P NMR spectroscopy in $CDCl_3$, and it was also observed in CD_3OD solutions. According to data given in Table IV compound **3** exists in chloroform solutions at 55°C in an equilibrium with its educts. Although the equilibrium is shifted toward **3**, the presence of a small amount of the educts in the equilibrium points to the difficulities in using **3** as a ligand.

The decomposition of **3** and **4** in solutions was found to be accelerated by cooper(II) cations, especially in the acidic solutions. The copper cation can act as a Lewis acid that during its coordination to the aminophosphinoxide moiety probably activates the C-P bond and makes elimination of the diphenylphosphinoxide unit easier than in the free substrate. This

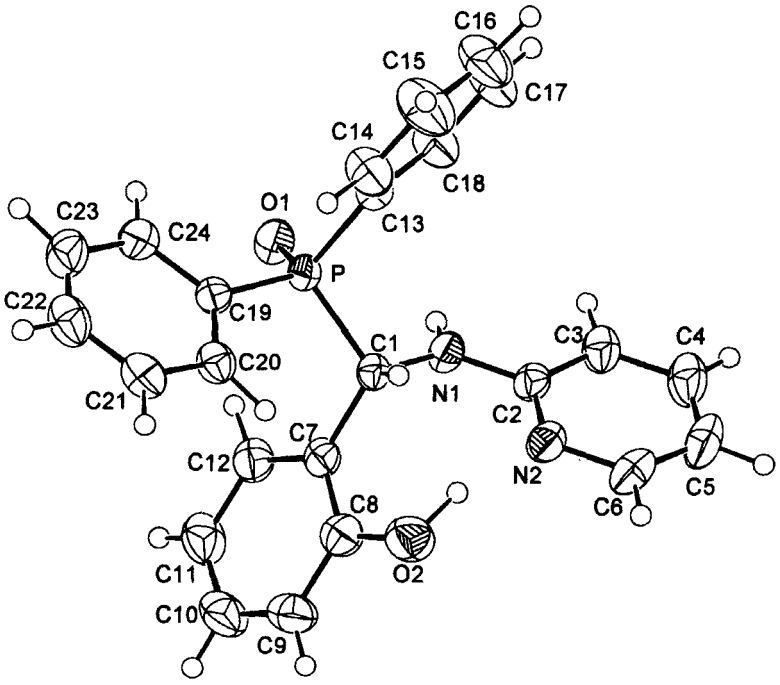


FIGURE 1 Perspective view of molecule of **1** in the X-ray structure with atom labels

decomposition leads to the starting Schiff base, which is destructed in acidic medium, with the formation of the protonised diamine as a terminal product. The presence of this terminal product was easily confirmed by X ray analysis of the $[NH_3CH_2CH_2CH_2NH_3][CuCl_4]$ isolated from the reaction mixture of **4** and $CuCl_2$ in methanol. A similar process is known from the literature[11], where zinc or lanthanide cations were used.

The reversibility of the addition of the H-P moiety to the C=N group manifests itself in the MS spectra. The typical feature of MS spectra of the compound studied was fragmentation according to the scheme:

$M^{\pm}$ → M minus P function(s) → starting Schiff base (→ next fragmentation).

For this reason, all the mass spectra were measured using direct exposure of the sample (not in GC MS mode). We observed a quite intensive molecular ion peak for the compounds of lower molecular weight (**1**, **2**),

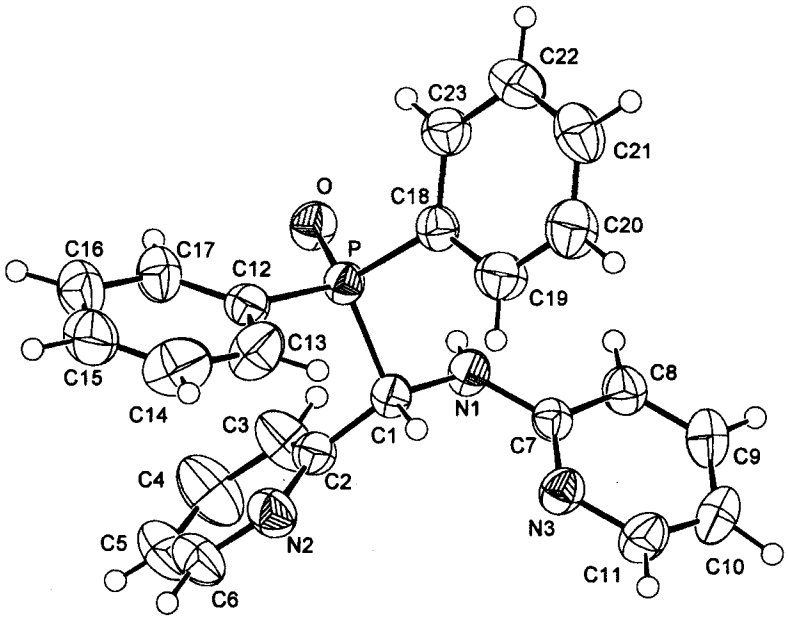


FIGURE 2 Perspective view of molecule of **2** in the X-ray structure with atom labels

while for compounds with higher molecular weight this peak was low (**6**) or absent (**3**, **4**). Apparently, the macrocyclic compounds studied are not stable upon conditions of evaporation and ionisation.

NMR spectra

NMR data of the compounds obtained are collected in the Table V. $^{31}P\{^1H\}$ NMR spectra consist of one singlet in the region expected for the discussed compounds. $^{13}C\{^1H\}$ NMR spectra are complicated by $^{13}C - ^{31}P$ coupling, especially in the aromatic parts. For this reason the NH-^{13}CH-P part only is given. ^1H NMR spectra are in accordance with formulae of **1** – **8**. H,H COSY technique was also used to aid assignment of 1D spectra. The signal of NH-CH-P is hidden in the aromatic region of the ^1H spectra for **1** and **2** and was identified using H,C HMQC technique. ^1H NMR spectra of **3** and **4** are remarkably solvent and concentration dependent. The most suitable solvent for measurement was found to be

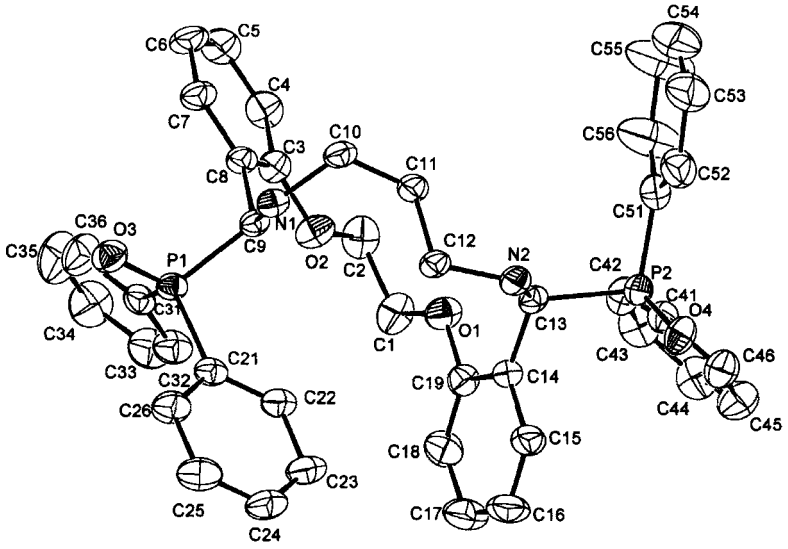


FIGURE 3 Perspective view of molecule of **3** in the X-ray structure of **3**. H_2O. MeOH with atom labels

$CDCl_3$, in which the signal of NH-C<u>H</u>-P is observed as a doublet. In other solvents only broad signals were observed. The ^1H spin systems of $NHCH_2CH_2CH_2NH$ and $O(CH_2)_xO$ parts of **3** and **4** are complicated multiplets, due to interactions of the axial and equatorial hydrogens of the macrocyclic ring.

X-ray analysis

According X-ray analysis the most characteristic feature of the structures **1**, **2** and **3** are the same bond geometry of the fragment

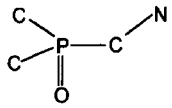


TABLE V NMR data of compounds prepared

nucleus	*assignment*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
$^{13}C\{^1H\}$	NCHP	49.79	56.07	65.32	50.00	/	/	66.81	67.47
	$^1J_{PC}$	83.4	77.4	89.5	81.6	/	/	91.9	105.0
$^{31}P\{^1H\}$		34.87	30.85	31.2	30.31	37.71	23.05	22.3	10.34
^1H	NCHP	5.98*	6.39*	5.15	5.21	4.75	4.79	4.88	5.08
		(1 H)	(1 H)	d(2H)	d(2H)	bd(2H)	bd(2H)	d(2H)	d(2H)
	$^2J_{PH}$	10.0	15.2	11.3	8.8	/	/	13.2	17.3
	$NHCH_2CH_2$ / /			1.45b	1.55q	2.45m	1.58m	2.13bq	2.21b
				q	(2H)	(2H)	(2H)	(2H)	q
				(2H)					(2H)
	$NHCH_2CH_2$	/	/	2.5m	2.5m	3.75m	2.5m	3.0m	3.2m
				(4H)	(4H)	(4H)	(4H)	(4H)	(4H)
	OCH_2	/	/	3.7bs	3.6m	4.4m	4.5m	3.9m	4.6m
	bridge			(4H)	(4H)	(4H)	(4H)	(4H)	(4H)
	OCH_2CH_2	/	/	/	1.93q	/	/	/	/
					(2H)				
	OCH_2CH_3	/	/	/	/	4.2m	4.0m	/	/
						(4H)	(8H)		
	OCH_2CH_3	/	/	/	/	1.2m	1.2m	/	/
						(6H)	(12H)		
	aromatic	7.3m	7.2m	7.2m	7.2m	7.7m	7.3m	7.1m	7.4m
	rings H	(18H)	(18H)	(28H)	(28H)	(18H)	(8H)	(18H)	(8H)

*Hidden among aromatic H signals, see discussion.

It leads to the conclusion that, in contrast to our expectation, this part of the molecule is too rigid for coordination requirements of a metal during complex formation. The part in which molecules **1**, **2** and **3** are different with respect to each other are the phenyl and pyridyl rings.

In **1** we found a presence of hydrogen bonds between the phenolic hydroxyl group and the nitrogen atom of the pyridyl ring, which pro-

foundly changes the orientation of phenolic ring. In the structure 2 this hydrogen bond is not present and the orientation of the pyridyl rings is governed probably by repulsion of the electron pair of the nitrogen atoms.

In the structure of **3** the solvate molecules (H_2O and MeOH) form only one hydrogen bond connecting MeOH with one phosphoryl group (O81 --03 2.738(6) Å: O81--H81 -- 03 142(2)°) of different molecules of **3.** The donor atoms of the macrocyclic ring in **3** form almost a plane (mean deviation 0.21 Å), hovewer, the whole macrocyclic ring is bent (Fig 3). The benzene rings of the macrocycle are oriented to each other with an angle of 60.5° This shape of the molecule **3** seems to be forced by the extremely bulky diphenylphosphine oxide groups and it is disadvantageous for complex formation with metal ions.

The macrocyclic compounds **3 – 8** can exist in the form of *cis* or *trans* isomer, with respect to orientation of diphenylphosphinic pendant groups. The compound **3** contains its pendant groups in *trans* orientation to each other according to X ray difraction analysis (Fig 3). This fact can be explained by high steric requriements of Ph_2PO- group, which directs the stereochemistry of addition reaction to the formation of the *trans* isomer. The *trans* isomer is expected to be a product of thermodynamic control of the addition reaction, with respect to its reversibility observed.

In the case of **4 - 8** the stereoisomer formed remains uncertain. It was not possible to distinguish between *cis/trans* isomer on the base of NMR experiments and we did not obtained **4 – 8** in the form of single crystals suitable for X-ray measurements. Despite of it we suppose that **4** was obtained in the form of the *trans* isomer for the same reasons as **3.**

EXPERIMENTAL

The chemicals used were reagent grade purity, obtained from Fluka. Diphenylphosphine oxide was prepared by established literature procedure.[7] The Schiff bases derived from α -pyridylamine were obtained and purified according ref.[8] The macrocyclic Schiff base 3,4: 9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane was synthetized according to the method of Armstrong and Lindoy.[9] Toluene was dried by refluxing commercial solvent with sodium. Melting points are uncorrected and were measured using Boethius apparatus. X-ray data were col-

lected on Eraf Nonius four cycle diffractometer CAD. NMR spectra were taken on Varian Inova 400, operating at 399.952 MHz ^{1}H, 100.577 ^{13}C and 161.906 MHz ^{31}P resonance frequency. Mass spectra were taken on Incos 50 (Finnigan MAT) spectrometer, ionizing electron energy 70eV, ion source temperature 100°C. Samples were evaporated from a direct exposure probe (heating rate 10 mA/sec). Elemental analysis are given in the form found(theory)%.

Synthesis

N-(2-pyridyl)-1-(2-hydroxyphenyl)-diphenyl(aminomethyl)phosphine oxide **1**: The Schiff base (0.5g, 2.5 mmol) and diphenylphospine oxide (0.5 g, 2.5 mmol) were dissolved in 4 mL of dry toluene and heated to 110°C for 30 min. During this time a white precipitate **1** was formed. The crystallisation of **1** was completed by standing of the reaction mixture in the refrigerator overnight. The product **1** was isolated by suction, washed two times with 95 % EtOH and once with acetone. Yield 82% of white powder, m.p. 225°C (dec.), $C_{24}H_{21}N_2O_2P$: C 71.93 (71.99), H 5.49(5.29), N 6.89(7.00). MS: m/z (relative intensity): 400 (3.5) $M^{\pm}$, 202 (5), 199 (88), 105 (17), 78 (100), 47 (21).

N-(2-pyridyl)-1-(2-pyridyl)-diphenyl(aminomethyl)phosphine oxide **2**: It was prepared in 74% yield according the same procedure as **1** using appropriate Schiff base. White powder without sharp melting point (dec.), $C_{23}H_{20}N_3OP.\ H_2O$: C 68.72(68.48), H 5.35(5.50), N 10.15(10.41). MS: m/z (relative intensity): 385 (5) $M^{\pm}$, 201 (4), 184 (100) 78(34), 51 (45).

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane-2,11-bis (diphenylphosphine oxide) **3**: The macrocyclic Schiff base (x=0) (0.25 g, 0.8 mmol) was disolved in 5 mL of dry toluene and diphenylphosphine oxide (0.51 g, 2.5 mmol) was added in one portion upon stirring. The mixture was refluxed for 2 hours. During this period a precipitate of the desired product usually formed. Then, the mixture was concentrated to half volume and allowed to stand overnight. The product was filtred off, washed with a small amount of cold toluene. Yield 61%, white powder, mp. 201–203°C (dec.), elem. anal.: $C_{43}H_{42}N_2O_4P_2C$ 72.91 (72.46), H 6.07 (6.08), N 3.70 (3.93). MS m/z (relative intensity): 510 (0.5), 456 (0.2), 387 (0.2), 335 (0.7), 309 (50), 201 (100), 124 (44), 77 (78).

This product was recrystallized from a methanol-water mixture to obtain single crystals for X ray structure determination. Compound **3** was obtained in this manner in the stoichiometry **3** . MeOH . H_2O.

3,4:10,11-dibenzo-1,13-diaza-5,9-dioxacyclohexadecane-2,12-bis (diphenylphosphine oxide) **4**:

It was prepared in 67% yield according the same procedure as **3** using macrocyclic Schiff base with x=1. White powder, m.p. 177°C (dec.), elem. anal. $C_{44}H_{44}N_2O_4P_2$ C 71.63(72.71), H 6.09(6.10), N 3.76 (3.85). MS: m/z (relative intensity): 321 (4), 293 (3), 217 (1), 201 (100), 183 (15), 124 (42), 78 (58), 51 (79).

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane-2,11-bis(phenylphosphinic) acid diethylester **5**:

The appropriate macrocyclic Schiff base (x=0) (0.25g, 0.8 mmol) was disolved in 5 mL of dry toluene and HPO(Ph)(OEt) (0.41g, 2.4 mmol) was added. The reaction mixture was refluxed for 3 hours, cooled, evaporated to dryness. The pure **5** was isolated by column chromatography (silica, $CHCl_3$/EtOH = 9: 1) in the form of an oil and with a yield of 76%. For synthesis of **7** compound **5** was used without purification.

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane-2,11-bis (phosphonic) acid tetraethylester **6**:

It was synthetized according to the same procedure as **5**. Diethylphosphite $HPO(OEt)_2$ (0.34 g, 2.5 mmol) was used instead of HPO(Ph)(OEt). MS: m/z (relative intensity): 584 (1) $M^{\pm}$, 529 (0.5), 447 (0.5), 404 (0.5), 309 (100), 155 (33), 111(35), 83(47).

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane-2,11-bis(phenylphosphinic) acid **7**:

Hydrolysis of **5**. The crude product **5** was mixed with 15 mL of HCl (1: 1) and gently refluxed for 3 hours. White crystals of product are formed during this period in yellowish solution. They were filtered off, washed with cold HCl (1: 1), cold MeOH and dried. Recrystallisation form MeOH/H_2O solution yielded 73% of **7** . 5 H_2O in the form of a white powder, mp 230–232°C (dec.), elem. anal. $C_{31}H_{34}N_2O_6P_2$. $5H_2O$ C 54.75 (54.54), H 5.55(6.49), N 3.93 (4.10).

3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane-2,11-bis (phosphonic) acid **8**:

Hydrolysis of **6.** The crude ester **6** was over layered with HCl solution (1: 1) and the mixture was refluxed about 3 hours. The hydrolysis was checked by TLC. When no ester was found in the reaction mixture the

solution was cooled, charcoal was added and boiled for 10 minutes. Then, the solution was filtered and evaporated to dryness. The oil obtained was disolved in methanol. After addition of propylene oxide a white product of **8** formed. The product was filtered off and after standing in a refrigerator for 48 hours, washed with acetone and recrystallized from methanol-water mixture. Yield 44%, decomposes during heating, elem anal. $C_{19}H_{26}N_2O_8P_2$. 6 H_2O C 39.58 (39.31), H 6.12 (6.60), N 4.69 (4.83).

Crystallography

Crystals of **1**, **2** and **3** suitable for X-ray diffraction were obtained from MeOH / acetone / H_2O (2/2/1), acetonitrile and MeOH / H_2O (1/1) (V/V) respectively, by slow evaporation at room temperature. The crystals of all compounds were mounted on the glass fibres using an epoxy glue at random orientations for unit-cell and space-group determinations and for data collections. An Enraf-Nonius CAD4 diffractometer was used for measurements at 293(2) K with Mo-K_α radiation ($\lambda = 0.71073$ Å). Unit-cell dimensions were determinated from angular setting of every 25 high-order (θ from 15 to 16° for **3** and from 14 to 15° for both remaining compounds) reflections using the CAD4 centring routines. Selected crystallographic and other relevant data for both compounds are listed in Table I – IV.

Intensities were collected using variable scan speed to assure constant statistical precision. Three standard reflections measured every hour were used to check the stability of the crystals and of the experimental conditions. The orientation of the crystals were checked by measuring five standards every 100 reflections. The data were corrected for Lorenz-polarisation, but not for absorption. The extinction correction was aplied only in the case of **3** using the procedure included in SHELXL97 (ref.[13]) The structure was solved by a combination of Patterson and Fourier methods (SHELXS86, SHELXL97) (ref.[12,13]) and refined by full-matrix least-squares techniques (SHELXL97) (ref.[13]). Scattering factors for neutral atoms used were included in the program SHELXL97. The hydrogen atoms were found in all structures (with exception of one hydrogen atom on the phenyl ring (on C55) and three hydrogen atoms of the methyl goup in solvate MeOH molecule in the structure of **3**) on the difference maps and refined isotropically.

Atomic coordinates, thermal parameters and full lists of bond lenghts and angles of both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

DECOMPOSITION STUDY OF 3

Compound **3** was found to be unstable to termal decomposition in solutions in indifferent solvents ($CDCl_3$, CD_3OD). Compound **3** slowly decomposes at 55°C during a few hours (for example during NMR experiments at 55°C taking 3 h). In a typical experiment, this reaction was followed by $^{31}P\{^1H\}$ NMR spectroscopy, using solution of 25 mg of **3** in 0.6 ml $CDCl_3$. The approximate composition of solution as a function of time is given in Table VI. The phosphorus containing product of decomposition was found to be starting diphenyl phosphine oxide (according to H-P coupling in the ^{31}P NMR).

TABLE VI The approximate composition of solution **3** as a function of time. solvent: $CDCl_3$

time, hours	*% 3*	*% $Ph_2P(O)H$*
0	100	0
1	96	4
2	95	5
4	93	7
8	91	9

DECOMPOSITION OF 4 BY THE ACTION OF $CuCl_2$

A sample of **4** (36 mg, 0.05 mmol) was dissolved in 5 mL of MeOH containing 1 % of water and slowly warmed to 50°C. This solutions was added to a stirred solution of $CuCl_2 . 2H_2O$ (17 mg, 0.1 mmol) in 3 mL of the same solvent with 2 drops of 30 % aq. HCl. Then, the resulting green-yellow solution was warmed to 50 – 60°C for 15 minutes.

The yellow -brown leaf-like crystals appeared after standing in a refrigerator (0 - 5°C) for three weeks. The crystals were isolated from the yellow-green mother liquid without washing and dried in air at room temperature. About 10 mg of the yellow -brown product were obtained. The single-crystal X-ray diffraction measurement showed the following lattice parameters: a = 7.200(2) Å, b = 18.232(4) Å, c = 7.510(1) Å,

$\alpha = \beta = \gamma = 90°$, corresponding to compound $[NH_3CH_2CH_2CH_2NH_3][CuCl_4]$ (ref.[14]; a = 7.200(2) Å. b = 18.246(6) Å, 7.451(2) Å, $\alpha = \beta = \gamma = 90°$). The identity of the obtained crystals $[NH_3CH_2CH_2CH_2NH_3][CuCl_4]$ was further confirmed by a structure solution and refinement. It led to a final R index of 0.0511 for 2089 observed reflections. The results were identical with previous structure derminations (ref. [14]).

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