Organometallic and Coordination Chemistry on Phosphazenes Part I. Zn(II), Pd(II) and Pt(II) Complexes on Schiff Base-containing Cyclophosphazenes

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Abstract

In this paper we report the synthesis of a new class of cyclophosphazene ligands containing six Schiff bases in the side branches, able to bind transition metals. We describe also the complexation reaction on these substrates of Zn(II), Pd(II) and Pt(II) ions.

Elemental analyses together with spectroscopic (IR, UV, ^{1}H and ^{31}P NMR) and mass spectrometric (FAB) characterizations reveal that all the above mentioned cyclophosphazenes are able to coordinate six metal ions.

Introduction

The use of phosphazene compounds as substrates for exploiting organometallic or coordination chemistry has attracted considerable attention [1]. Phosphazene materials, in fact, both cyclic (trimers and tetramers) and polymeric, proved to be suitable matrices for bonding square planar platinum complexes [2, 3], various types of metallocenes [4–11], carborane [12–14], etc., or for coordinating transition metals [15–22], owing to the high versatility of their synthesis [23, 24] and to the remarkable ease of their functionalization [25]. Several applications have been foreseen for these products, for instance as catalysts for hydroformylation [26] or isomerization [17] reactions, anticancer agents [2, 3], electroactive materials [27–30], etc.

Our interest in the coordination chemistry of cyclo- and polyphosphazenes dates back to 1980 [31], when we synthesized a cyclophosphazene containing multiple chelating sites by coupling hexakis(4-formylphenoxy)cyclophosphazene $[NP(-O-C_6H_4-CHO)_2]_3$ with *o*-hydroxyaniline to obtain $\{NP[-O-C_6H_4-CH=N-C_6H_3(2\text{-}OH)]_2\}_3$ **(I)**, a cyclophosphazene which bears six Schiff base units in the side branches, able to bind transition metal ions. However, whereas coordination of the above mentioned metal cations to compound **I** occurs quite readily, the resulting complexes were found to be either insoluble materials, probably due to cross-complexation between coordination sites belonging to different phosphonitrilic trimers, and compounds of rather uncertain stoichiometry, owing to partial hydrolysis of the imino C=N bond. Thus these compounds appear to be useless products for practical applications.

In the light of this previous experience, we reconsidered recently our approach to the coordination chemistry of phosphazene materials by examining the possibility of constructing chelating sites on hexakis(4-amino-3-methyl-phenoxy)cyclophosphazene $\{NP[-O-C_6H_3(3\text{-}CH_3)(4\text{-}NH_2)]_2\}_3$, **(III)**. In this compound the six amino functions can react with aldehydes to produce Schiff bases suitable for metal coordination chemistry.

In this paper (i) we report the preparation of Schiff base-containing cyclophosphazenes by reaction of **III** with several different aromatic aldehydes; (ii) discuss the spectroscopic characterization of these cyclophosphazenes containing side branches suitable for metal coordination; and (iii) describe the synthesis and the characterization of Zn(II), Pd(II) and Pt(II) derivatives of these substrates.

According to Allcock's early studies [32], this work on cyclophosphazene-supported transition metal complexes has to be considered only as a preliminary study for a forthcoming extension of already disclosed procedures to the corresponding phosphazene high polymers.

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Results and Discussion

General Considerations

Primary and secondary amines are versatile organic functionalities which can undergo a variety of important chemical reactions [33]. The introduction of these groups in polymeric substrates is considered a valuable tool in polymer chemistry, very often used to prepare new, highly interesting macromolecules [34].

As for phosphazene materials, their functionalization with $-NH_2$ groups has always been achieved by catalytic reduction of 4-nitrophenoxy-containing phosphazene compounds with molecular hydrogen; $-NO_2$-containing derivatives, in turn, are obtained by reacting 4-nitrophenoxy sodium salt with suitable chlorophosphazenes [35–40]. The resulting $-NH_2$-substituted products are interesting intermediate materials for the preparation of thermally stable, fire resistant resins [36–38], azo dyes [39], chemotherapeutic drugs [40], etc.

However, the preparation of amino- or nitro-substituted phosphazenes is not straightforward.

Several discrepancies, in fact, have been reported in the literature concerning both procedures used by different authors for the synthesis of nitrophenoxy-containing cyclophosphazenes and the melting behavior of these trimers [38]; other problems, moreover, strictly inherent to the insolubility of the nitrophenoxy-substituted phosphazene homopolymer [39], prevented authors from using highly loaded, $-NO_2$-containing, macromolecules in the process for preparing aminophenoxy derivatives.

In the light of these considerations, for our investigations on cyclophosphazene-based transition metal complexes, we discarded 4-nitrophenol as the vehicle for the introduction of amino functions into phosphazene materials, and started to consider as a more suitable candidate 4-nitro-3-methyl-phenol.

The importance of the methyl group in the *meta* position of the aromatic ring in this compound is twofold. First of all, it increases the basicity of the nitrophenoxyde anion used in the reaction with the chlorophosphazene due to inductive +I effect. Secondly, it improves considerably the solubility of the final trimer in organic solvents. On the other hand, no drawbacks have been observed during preparation of cyclophosphazene ligands and complexes due to the steric hindrance of this group (*vide infra*).

Thus, we found that hexakis(4-nitro-3-methyl-phenoxy)-cyclophosphazene can be prepared under relatively mild experimental conditions, using refluxing THF instead of toluene, and also that the reduction of the $-NO_2$ groups can be carried out in a common solvent, like THF, instead of aniline, as previously reported [37–40].

Synthesis and Characterization of NO_2- (II), NH_2- (III) and Imine-containing Cyclophosphazenes Ligands (1–5)

The reaction between hexachlorocyclophosphazene $(NPCl_2)_3$ and 4-nitro-3-methyl-phenol in refluxing THF and in the presence of $KHCO_3$ leads to hexakis(4-nitro-3-methyl-phenoxy)cyclophosphazene (II), according to the following equation

$$N_3P_3Cl_6 + 6HO{-}C_6H_3(4\text{-}NO_2)(3\text{-}CH_3) + 6KHCO_3 \longrightarrow \underset{\mathbf{II}}{N_3P_3[O{-}C_6H_3(4\text{-}NO_2)(3\text{-}CH_3)]_6} + 6KCl + 6CO_2 + 6H_2O$$

The ^{31}P NMR spectrum of II shows a singlet at +6.91 ppm, which is indicative of the successful substitution of the chlorines in $N_3P_3Cl_6$ with six 4-nitro-3-methyl-phenoxy groups to produce equivalent phosphorus atoms in the trimer. The reaction, in fact, occurs smoothly phosphonitrilic ring modification and degradation, and no partially substituted cyclophosphazenes were isolated. Thus, the IR spectrum of II shows no evidence for the formation of P=O or N–H bonds [41] due to the cleavage of the phosphonitrilic ring, and only absorptions in the range of 1257–1150 and 973 cm^{-1} are present [42], attributed to the P=N and P–O–ϕ vibration respectively. Elemental analysis, IR, ^1H and ^{31}P NMR data for this material are reported in the Tables 1 and 2.

The presence of $-NO_2$ groups in the cyclophosphazene II can be deduced by the presence of the band at 1514 cm^{-1} due to the asymmetric $-NO_2$ vibration shifted to lower frequencies by –OR substituent in the *para* position and slightly enhanced by the $-CH_3$ group in the *ortho* position [43], and by the symmetric vibration at 1342 cm^{-1}.

The reduction of the nitro groups in II to yield the corresponding amino moieties in the cyclophosphazene III is carried out in an autoclave at 70 °C and 60 atm. of H_2, in the presence of Pd on carbon as catalyst, according to the following reaction

$$\underset{\mathbf{II}}{N_3P_3[O{-}C_6H_3(4\text{-}NO_2)(3\text{-}CH_3)]_6} \xrightarrow[Pd]{H_2} \underset{\mathbf{III}}{N_3P_3[O{-}C_6H_3(4\text{-}NH_2)(3\text{-}CH_3)]_6}$$

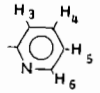
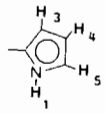
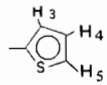
Also for this compound, the sharp singlet in the ^{31}P NMR spectrum at 9.86 ppm indicates the complete reaction of nitro groups to yield six $-NH_2$ functions, whose presence is further supported by IR spectroscopy (bands in the range of 3450–3300 cm^{-1}) and by ^1H NMR in $CDCl_3$. The N–H resonance appears as a broad signal at 4.87 ppm

TABLE 1. Analytical data and characteristic IR bands for the compounds **II**, **III**, **1–13**

Compound	Colour	Analysis (%)[a]				IR (cm^{-1})[b]		
		C	H	N	Cl	ν(C=N)	ν(M–Cl)	Other bands
II	whitish	47.96 (48.14)	3.43 (3.46)	11.96 (12.03)				1257s[c], 1229s[c], 1203s[c], 1150s[c], 973s[c], 1514m[d], 1342m[d]
III	white	59.18 (59.36)	3.46 (3.56)	14.83 (14.84)				1249m[c], 1201m[c], 1144m[c], 970s[c], 1624m[e], 1279s[f], 3338m[g] 3447m[h], 3357s[h], 3247m[h]
1	yellow	66.02 (66.79)	4.80 (4.74)	14.84 (14.98)		1626m		1209s[c], 1144s[c], 969m[c]
2	light yellow	64.85 (65.03)	5.14 (5.00)	15.83 (15.80)		1611s		1253m[c], 1209m[c], 1144s[c], 969m[c], 3335s[h], 3480s[h]
3	yellow	66.98 (67.76)	4.78 (4.86)	8.10 (8.45)		1610s		1258s[c], 1229s[c], 1208s[c], 1148s[c], 970s[c], 3505s[i], 1277s[l]
4	orange–yellow	61.05 (60.37)	4.30 (4.22)	8.70 (8.80)		1609s		1254m[c], 1227s[c], 1208s[c], 1145s[c], 970s[c]
5	white	37.81 (36.97)	4.54 (4.57)	6.90 (6.81)		1600s		1254m[c], 1206s[c], 1145s[c], 965s[c], 1245m[m], 1030m[m]
1·6$ZnCl_2$ **(6)**	deep yellow	39.05 (39.85)	2.85 (2.83)	8.61 (8.94)	17.98 (18.09)	1569m	334m, 313m	1235s[c], 1212s[c], 1150s[c], 973s[c]
1·6$PtCl_2$·6CH_2Cl_2 **(7)**	dark orange	27.78 (28.76)	2.11 (2.24)	5.82 (5.99)	24.43 (24.25)	1584s	340m, 333m	1240m[c], 1219m[c], 1151s[c], 973s[c]
2·6$Znac_2$·12H_2O **(8)**	deep yellow	44.43 (44.11)	4.39 (4.49)	8.18 (7.84)		mk[n]		1257s[c], 1206s[c], 1148s[c], 968s[c], 1546s[o], 1413s[o]
2·6$Pdac_2$ **(9)**	brown	44.76 (43.71)	3.41 (3.71)	10.10 (10.59)		mk[n]		1230m[c], 1200m[c], 1146s[c], 972s[c], 1570s[o], 1420s[o]
3·6$Znac_2$·6H_2O **(10)**	deep yellow	50.30 (49.30)	4.35 (4.13)	5.43 (5.38)		mk[n]		1253m[c], 1209s[c], 1147s[c], 969s[c], 1555s[o,p]
3·6$Pdac_2$ **(11)**	orange	47.93 (46.51)	3.43 (3.42)	5.40 (5.09)		mk[n]		1266m[c], 1204s[c], 1145s[c], 968s[c], 1527s[o,p]
4·6$ZnCl_2$ **(12)**	deep yellow	37.95 (38.68)	2.00 (2.03)	5.51 (5.64)	18.90 (19.03)	1574s	327m, 310m	1250m[c], 1211s[c], 1148s[c], 972s[c]
4·6$PtCl_2$·6CH_2Cl_2 **(13)**	brown	26.96 (28.00)	1.31 (1.27)	3.82 (3.77)	24.99 (25.43)	1558s	332m, 340m	1250m[c], 1214s[c], 1151s[c], 972s[c]

[a]Calculated values in parentheses. [b]Nujol mulls; s = strong, m = medium. [c]Cyclophosphazene ring, P–N and P–O–ϕ, stretchings. [d]ν(N⁻⁻O). [e]N–H bend. [f]ν(C–N). [g]ν(N–H). [h]In THF solution, ν(N–H). [i]In THF solution ν(–O–H--N). [l]Phenolic C–O stretching. [m]ν(C–O–C). [n]Masked by ν(COO). [o]ν_{as}(COO) and ν_s(COO). [p]The ν_s(COO) is masked by nujol absorption.

TABLE 2. ^{1}H and $^{31}P\{^{1}H\}$ NMR data for the compounds **II**, **III**, **1–8**, **10**, **12**, **13**[a]

Compound	Solvent	δ(^{31}P)	^{1}H			Other
			δCH	δMe	δ Ar protons	
II	$CDCl_3$	6.91s		2.51s		7.97–7.85m[b], 7.05–6.96m[b]
III	$CDCl_3$	9.86s		2.01s		6.77–6.46m[b], 4.87br[c]
1	$CDCl_3$	9.29s 9.05s 8.75s	8.448s 8.434s	2.270s 2.261s	$H_6$8.607(J_{6-5}4.4; J_{6-4}1.0)dd $H_{6'}$8.635($J_{6'-5'}$4.4; $J_{6'-4'}$ < 1)dd $H_5$7.313(J_{5-3}0.9)ddd $H_{5'}$7.517($J_{5'-3'}$0.9)ddd $H_4$7.698(J_{5-4}6.3; J_{4-3}1.0)ddd $H_{4'}$7.750($J_{5'-4'}$6.2; $J_{4'-3'}$1.0)ddd $H_3$8.185(J_{3-4}7.8)dd $H_{3'}$8.180($J_{3'-4'}$7.9)dd	
2	CD_2Cl_2	9.48s 9.36s 9.24s 9.11s	8.074s 8.081s 8.099s 8.090s	2.170s 2.184s 2.193s 2.207s	$H_5$6.545(J_{5-4}4.0; J_{5-1}3.0; J_{3-5}1.0)ddd $H_{5'}$6.602($J_{5'-4'}$4.0; $J_{5'-1'}$2.8; $J_{3'-5'}$1.5)ddd $H_4$6.210(J_{4-3}3.0)dd $H_{4'}$6.232($J_{4'-3'}$3.1)dd H_3, $H_{3'}$[d]	 H, H 9.85br[c]
3	$CDCl_3$	9.11s	8.441s	2.290s		7.39–6.69m[b]; 13.2br[e]
4	CD_2Cl_2	9.17s 9.02s	8.381s 8.390s	2.251s 2.211s	$H_5$7.380(J_{3-5}1.5)dd $H_4$7.051(J_{4-5}5.0; J_{4-3}5.0)dd $H_3$7.322 dd	
5	$CDCl_3$	9.43s	8.165s	2.258s		 6.67–7.71m[b]; 3.830[f]
6	DMSO	8.81s	8.592s	2.230s	$H_6$8.625(J_{6-5}4.16; J_{6-4}2.0)dd $H_5$7.470(J_{4-5}7.0; J_{5-3}1.0)ddd $H_4$7.828(J_{4-3}7.0)ddd $H_3$7.026 dd	
7	DMSO	7.77s 7.52s	8.615d $^{3}J_{PtH}$96 $^{4}J_{H-H_6}$2.5	2.316s	$H_6$8.400(J_{6-5}4.5; J_{6-4}2.3)dd $^{3}J_{Pt-H}$40.5 $H_5$7.301(J_{4-5}7.7; J_{5-3} < 1)ddd $H_4$7.936(J_{4-3}7.9)ddd $H_3$7.239ddd	
8	CD_2Cl_2	9.39s 9.28s	8.050s	2.191s	$H_4$6.300(J_{5-4}2.5; J_{4-3}1.2)dd H_3, H_5[d]	2.042s[g]
10	CD_2Cl_2	9.03s	8.480s	2.291s		7.72–6.75m[b]; 2.070s[g]
12	DMSO	8.96s	8.546s	2.145s	$H_4$7.149(J_{4-3}3.9; J_{4-5}7.6)dd $H_3$7.515dd $H_5$7.743(J_{3-5}1.1)dd	
13	DMSO	8.31s 8.21s	8.610 $^{3}J_{PtH}$13.8	2.250s	$H_4$8.100(J_{5-4}7.0; J_{4-3}4.9)dd H_3, H_5[d]	

[a]δ in ppm; J in Hz; ^{1}H and $^{31}P\{^{1}H\}$ NMR chemical shifts were referenced to internal $SiMe_4$ and H_3PO_4 (85%), respectively; s = singlet, m = multiplet, d = doublet, br = broad. [b]Phenyl protons. [c]δ(NH). [d]Masked by phenyl protons. [e]δ(OH). [f]δ(OMe). [g]δCH_3 of the acetate group.

which undergoes H/D exchange in D_2O. Moreover, the presence in the IR spectrum of **III** of characteristic bands at 1249–1144 (ν(P=N)) and 970 cm^{-1} (ν(P–O–ϕ)), very similar to those of **II**, testifies the stability of the cyclophosphazene ring during the reduction reaction. Analytical and spectroscopic data of **III** are reported in Tables 1 and 2.

Compound **III** has been used as starting material for the preparation of cyclophosphazene-containing Schiff bases, bearing multiple dentate sites apt to coordinate transition metals.

According to the literature [33, 44], the classic method for the preparation of Schiff bases and the introduction of carbon–nitrogen double bonds into molecules involves the condensation reaction of amines with a variety of aldehydes (or ketones).

We considered in this paper the reaction of hexakis(4-amino-3-methyl-phenoxy)cyclophosphazene (**III**) with aromatic aldehydes to give the corresponding Schiff bases, as reported in Scheme 1.

Reactions of **III** with aldehydes a–e were carried out in THF for 20 h under nitrogen, at room temperature, by using an excess of aldehyde. The solid products **1**–**5** were obtained in good yield (80–90%); they are air stable, soluble in THF and chlorinated solvents; they gave also satisfactory C, H, N elemental analyses and were characterized by their IR, ^1H and ^{31}P NMR spectra (see Tables 1 and 2).

The IR spectra of **1**–**5** show ν(C=N) in the range of 1600–1626 cm^{-1}, as observed for compounds of the type Ar–CH=N–Ar′ [45].

Owing to the relative rigidity of the carbon–nitrogen double bond and the non-linearity of the structure containing it, N-substituted Schiff bases are potentially capable of existing in two geometrically isomeric forms, represented by structures **A** and **B**.

Each form presents two possible positions of the methyl group relative to the substituent 'Ar'. In compounds **1**–**4**, moreover, four additional isomers are possible, depending on the relative position of the heteroatom present in the 'Ar' substituents.

In the case of N-substituted aldimines, the structures **A** (*anti* isomers) are thermodynamically more stable than **B** [46], so **A** and **A′** forms, instead of **B** and **B′** configurations, are expected for compounds **1**–**5**.

These observations are confirmed by ^1H and ^{31}P NMR data (Table 2). The ^1H NMR spectrum of compound **1** at 400 MHz (see Fig. 1) shows two sets of signals for each proton of the pyridyl groups, as reported in Table 2, indicating the presence of two possible orientations of the heterocyclic moiety. The pattern is in agreement with that reported for organic [47] and organometallic [48] pyridyl systems. Moreover, the –N=C–H proton of compound **1** displays two signals at 8.434 and 8.448 ppm in about 3:2 ratio, but we could not assign them to each isomer. It is noteworthy that for the $-CH_3$ protons, two signals are present at 2.27 and 2.26

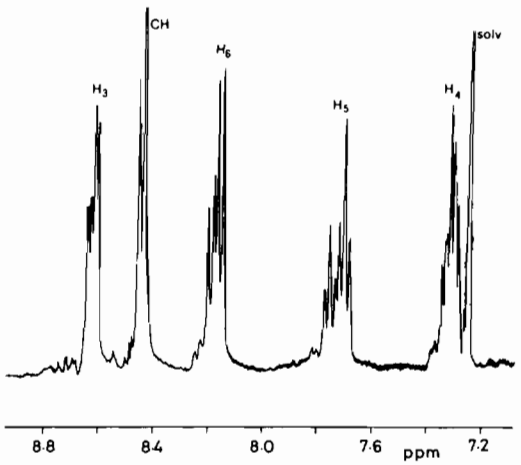
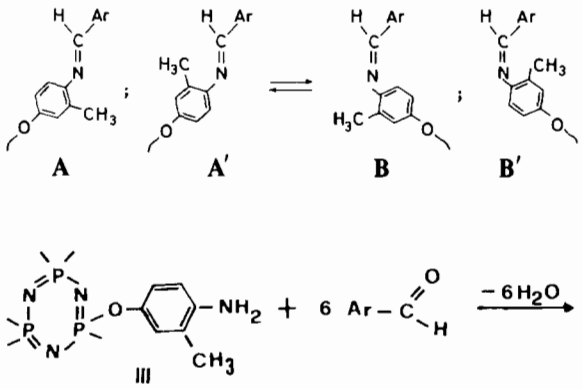
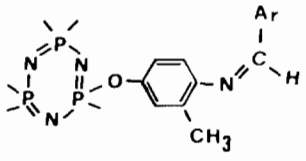


Fig. 1. ^1H NMR spectrum at 400 MHz in $CDCl_3$ of compound **1** in the range 7.2–8.6 ppm.





Ar :		
2-Pyridyl	a	1
2-Pyrrolyl	b	2
2-Salicyl	c	3
2-Thienyl	d	4
p-CH_3O-C_6H_4	e	5

Scheme 1.

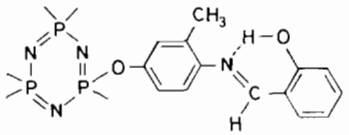
ppm, thus confirming the presence of two diastereoisomeric forms.

In the ^{1}H NMR spectrum of compound **2** (Table 2), however, four signals for N=C(H) and CH_3 protons are observed attributable to different steric orientations of the methyl substituent and the N–H group in the pyrrole.

The random distribution of isomers on the phosphazene phosphorus atoms gives rise to ^{31}P NMR spectra which show a set of signals, i.e. three singlets in the range 9.29–8.75 ppm for compound **1**, and four singlets in the range 9.48–9.11 ppm for compound **2**. This behavior agrees with what we observed previously on chalcone-containing cyclophosphazenes [49].

Similar IR, ^{1}H and ^{31}P NMR patterns are found also for compounds **2** and **4** (see Tables 1 and 2).

In contrast to that observed for compounds **1**, **2** and **4**, the cyclophosphazene **3** exists only in one isomeric form, probably of type A [50], according to the structure



which is less hindered, owing to the intramolecular hydrogen bond formation [45]. In fact, the ^{31}P NMR spectrum of this compound consists of a sharp singlet at +9.11 ppm, and the ^{1}H NMR spectrum shows only one signal for –N=C–H and methyl protons at 8.441 and 2.290 ppm, respectively.

For compound **5**, a singlet has been found in the ^{31}P NMR spectrum at 9.43 ppm. Moreover, in the ^{1}H NMR spectrum, a singlet at 8.165 ppm for –N=C–H proton and a singlet at 2.258 ppm for CH_3 protons are observed. These facts may be due to the great similarity of the two isomers in this case, which are undistinguishable and rapidly interconverting at room temperature.

Synthesis and Characterization of Cyclophosphazene-based Complexes of Zn(II), Pd(II) and Pt(II) (6–13)

The aldimino (2-aryl) (2-aryl = 2-pyridyl (**1**), 2-pyrrolyl (**2**), 2-salicyl (**3**) and 2-thienyl (**4**)) phosphazene derivatives react with six equivalents of Pd(II), Pt(II) or Zn(II) salts according to Scheme 2.

The formulation of hexanuclear adducts **6**–**13** is based on elemental analyses, IR (Table 1), ^{1}H and ^{31}P NMR spectra (Table 2), and, in some cases, on molecular weight determinations by FAB mass measurements.

Upon coordination to metal ions through both N and N, O or S atoms (**1**–**4** respectively), a decrease of the C=N frequency in the ligand [46] of roughly 50 cm^{-1} is always found for compounds **6**, **7**, **12** and **13**. The presence of the $ZnCl_2$ group in **6** and in **12** is confirmed by the ν(Zn–Cl) bands located at 334, 313 and 327, 310 cm^{-1} respectively; moreover, ν(Pt–Cl) in compounds **7** and **13** are observed at 340, 333 and 340, 332 cm^{-1} respectively.

The ^{1}H NMR spectra of compounds **6**–**8**, **10**, **12** and **13** suggest that in solution the α-imino unit –N=C–C=C (X = N, COH, S) assumes only one of the possible configurations which can arise from a *cis* or *trans* arrangement of the conjugate –C=N–C=X double bond system, from the different position of the heteroatom in the substituent 'Ar', and from the different position of the methyl group.

In fact, for compounds **6** and **7**, only one set of signals is observed for the –N=C–H proton, for the methyl group and for the pyridyl system, as reported in Table 2. For compound **7** the coordination is further supported by the observation of the ^{195}Pt satellites with a value of ^3J(PtH) of 96 Hz for the –N=C–H proton. The value is in good agreement with that of coordinated pyridyl systems previously reported [48, 51].

It is noteworthy that the –N=C–H imino proton is a doublet due to a long range ^4J(HH) coupling (2.5 Hz) as already reported for complexes of the type $[PtCl_2(\eta^2$-olefin)(6-R′-pyridine-2-carbaldehyde imine)] [52].

Compound **8** shows in the ^{1}H NMR spectrum one signal for C(H) at 8.050 ppm, one signal for the methyl arylic group at 2.191 ppm and for methylacetate protons at 2.042 ppm and one pyrrolic system, so indicating also for **8** the presence of only one configuration due to coordination to the Zn center.

Analogously, ^{1}H NMR spectra of compounds **10**, **12** and **13** (see Fig. 2) show singlets for C(H) and methyl protons as reported in Table 2.

For compound **13** the coordination is further supported by ^3J(PtH) 13.8 Hz of the C(H) proton signal.

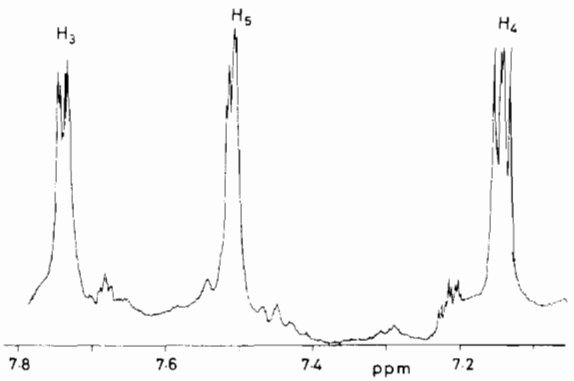
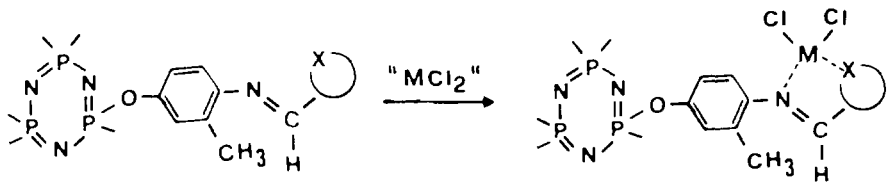
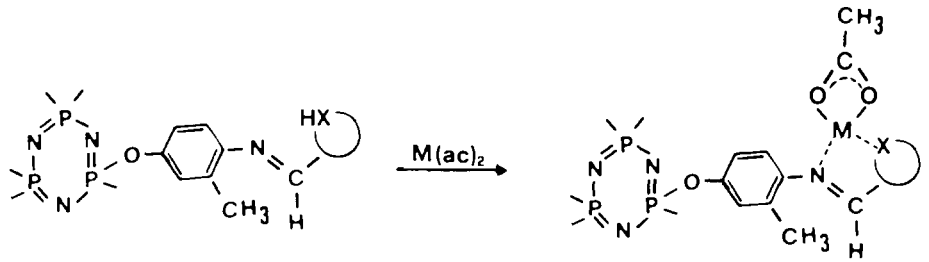


Fig. 2. ^{1}H NMR spectrum at 400 MHz in DMSO-d_6 of compound **13** in the range 7.1–7.8 ppm.



X	"MCl_2"	
2-Pyridyl	$ZnCl_2$	6
2-Pyridyl	$K[PtCl_3(CH_2{=}CH_2)]$	7
2-Thienyl	$ZnCl_2$	12
2-Thienyl	$K[PtCl_3(CH_2{=}CH_2)]$	13



XH	$M(ac)_2$	
2-Pyrrolyl	$Zn(ac)_2$	8
2-Pyrrolyl	$Pd(ac)_2$	9
2-Salicyl	$Zn(ac)_2$	10
2-Salicyl	$Pd(ac)_2$	11

Scheme 2.

The ^{31}P NMR spectra of compounds **6**, **10** and **12** show a singlet at 8.81, 9.03 and 8.96 ppm, respectively, whereas the ^{31}P NMR spectra of compounds **7**, **8** and **13** show two singlets probably due to the more hindered $PtCl_2$ and Zn(acetate) coordinated imino group located differently around the P–N ring. The ^{31}P NMR data are in agreement with those previously reported for other Schiff base phosphazene derivatives [40].

For compounds **9** and **11** no conclusive NMR spectroscopic data are obtained owing to their low solubility in DMSO or in other common organic solvents. However FAB mass spectra of these compounds confirm the proposed formulation.

In FAB mass spectra of compounds **9** and **11**, peaks at *m/z* 2302 (relative absorbance 2.0) and 2473 (relative absorbance 1.5) respectively are present, which correspond to molecular ions. Sequential losses of Pd(ac), acH and $Pd(ac)_2$ are observed in both cases, giving rise to ions at *m/z* 2162, 2082, 1922, and 2309, 2245, 2085 respectively.

The coordination of metal ions to cyclophosphazene-based ligands is further supported by UV spectra of both ligands **1–4** and complexes **8–10**. In fact, the electronic spectra of compounds **1–4** display bands due to strong π–π^* transitions, covering π–π^* transitions, in the range 250–400 nm, attributable to the conjugated chromophore C=N [45], as reported in Table 3. In the electronic spectra of compounds **8** and **10** in THF, new intense bands, typical of the metallocycle chromophore, are observed which can be described as metal-to-ligand charge transfer bands [53].

TABLE 3. UV spectral data for compounds **1**–**4**, **8**, **10**, in THF at room temperature[a]

Compound	$\lambda_{max}(\epsilon_{max})$
1	278(41400), 247(40000), 238[b](38000)
2	326(89700), 295(88600)
3	343(79700), 265(65300), 330[b](75200)
4	340(117200), 295(130000), 267(113400)
8	365(64400), 295(45400)
10	395(41300), 350(40000), 320(44600), 310(46600), 274(66500)

[a]λ are in nm and ϵ in $cm^2\ mol^{-1}$. [b]Shoulder.

Experimental

All solvents were C.Erba analytical grade and were purified according to standard procedures [54]. When necessary they were dried by refluxing over sodium/benzophenone.

Hexachlorocyclophosphazene $(NPCl_2)_3$ was purchased by Shinn Nisso Kako and purified several times by vacuum sublimation.

4-nitro-3-methyl-phenol (Aldrich) was purified prior to use by dissolution in benzene, distillation of water as H_2O/benzene azeotrope, and dried for several days under vacuum.

$ZnCl_2 \cdot 2H_2O$, $Zn(acetate)_2 \cdot 2H_2O$ and $Pd(acetate)_2$ were Aldrich products and used as received. $K[PtCl_3(CH_2CH_2)] \cdot H_2O$ was prepared as reported [55].

All aldehydes used in this work were Aldrich products and were used without further purification.

The Pd on carbon used as catalyst in the reduction process of **II** to **III** was prepared according to the literature (see ref. 54, p. 955, synthesis B).

All compounds of this work were prepared under dry nitrogen atmosphere.

UV and IR spectra were carried out with Shimadzu Bausch & Lomb Model 210 and Perkin-Elmer Model 983 spectrophotometers.

^{31}P and ^{1}H NMR spectra were performed with a Varian FT 80 and with a Bruker AM 400 MHz spectrometer, respectively.

The analysis of acetic acid freed during the synthesis of the compounds **8** and **11** was carried out with a Hewlett Packard 5730 A gas chromatograph, using a WAW packing column SP 1000/1% H_3PO_4 on 100/200 chromosorb at 150 °C, a flow rate of 120 ml/s He and a T.C. detector.

Fast atom bombardment (FAB) mass measurements were performed with a VG ZAB 2F instrument [56] by bombarding glycerol solutions of the sample with 8 KeV Xenon atoms.

Synthesis of Hexakis(4-nitro-3-methyl-phenoxy)-cyclophosphazene (II)

In a three-necked, round-bottomed flask, equipped with a mechanical stirrer and an efficient condenser, 2.00 g (57.47 mmol) of hexachlorocyclophosphazene, 5.51 g (36.00 mmol) of 4-nitro-3-methyl phenol, and 3.60 g (36.00 mmol) of $KHCO_3$ were suspended in 200 ml of anhydrous tetrahydrofuran (THF) and refluxed with stirring for 72 h. The final reaction mixture was centrifuged and the surfactant liquid concentrated with a rotovap to obtain a brown paste. The addition of an excess of methanol leads to a yellow solid, which has been subsequently purified by several recrystallizations from THF/methanol.

Yield 4.5 g (75%). Melting point (m.p.) = 188–189 °C.

Elemental analysis, NMR and IR data are reported in Tables 1 and 2.

Synthesis of Hexakis(4-amino-3-methyl-phenoxy)-cyclophosphazene (III)

The reduction of the nitro group in **II** was obtained with a custom made autoclave at 70 °C and 60 atm. of hydrogen, according to the following procedure. A total of 3.00 g (2.86 mmol) of **II** was dissolved in *c.* 150 ml of anhydrous THF. To this solution 200 mg of palladium on carbon [54], were added. The reaction mixture was transferred to the autoclave, charged with molecular hydrogen until the final pressure of 60 atm. was reached, and allowed to react at 70 °C for 48 h. After the reaction was completed, the solution was filtered and the recovered catalyst used in a successive reduction. The obtained solution was concentrated to *c.* 5 ml and treated with 50 ml of Et_2O to obtain a light brown precipitate. This product was purified by column chromatography on fluorosil (2 × 30 cm) using THF as eluant. The final pale yellow eluate was concentrated under reduced pressure and precipitated by addition of Et_2O to give **III** as a white product. Yield 2.50 g (92%); m.p. 109 °C, dec.

Synthesis of Imine-containing Cyclophosphazene Ligands (1–5)

The following preparation of compound **1** by reaction of **III** with 2-pyridinecarboxyaldehyde is typical for all the compounds of this series.

A total of 849.8 mg (1.0 mmol) of **III** was dissolved in *c.* 150 ml of THF, and an excess of 2-pyridine-carboxyaldehyde (5.70 ml, 60.0 mmol) was added under nitrogen. After 20 h, the solution was concentrated to *c.* 5 ml and precipitated by addition of n-hexane. A light yellow solid was obtained, which was filtered and washed with n-hexane (3 × 20 ml). Yield 1.23 g, 88%; m.p. 102–104 °C. **2**: yield 1.12 g, 85%; m.p. 116–118 °C. **3**: yield 1.18 g, 79%; m.p. 142–143 °C. **4**: yield 1.23 g, 86%; m.p. 127–129 °C. **5**: yield 1.65 g, 89%; m.p. 105–106 °C.

Synthesis of Zn(II), Pd(II) and Pt(II) Complexes on Cyclophosphazenes (6–13)

A typical preparation is reported below for **6**. For products **8** and **10**, moreover, the loss of acetic acid was confirmed by gas chromatography, while for compounds **9** and **11** only CH_2Cl_2 was used as solvent.

In a 100 ml round-bottomed flask, 300 mg (0.21 mmol) of **1** were dissolved in 40 ml of CH_2Cl_2 and added to a solution of $ZnCl_2 \cdot 2H_2O$ (281.6 mg, 1.38 mmol) in 10 ml of MeOH. The obtained yellow solution was stirred for 30 min, treated with active charcoal, filtered, concentrated to 5 ml, and precipitated by adding Et_2O. The obtained yellow product was filtered off and washed with Et_2O to give 0.443 g of **6**, yield 88%, m.p. 246–247 °C.

FAB mass spectrum: *m/z* (relative intensity [probable assignment]): 2344 (2.0, $[M]^+$); 2076 (4.0, $[M - 2ZnCl_2]^+$); 2006 (2.0, $[M - 2ZnCl_2 - Cl_2]^+$); 1936 (2.0, $[M - 2ZnCl_2 - 2Cl_2]^+$); 1866 (8.0, $[M - 2ZnCl_2 - 3Cl_2]^+$). 7: 0.298 g, 85%; m.p. >300 °C. 8: 0.211 g, 90%; m.p. 222–224 °C, dec.

FAB mass spectrum: *m/z* (relative intensity [probable assignment]): 2287 (1.0, $[M \cdot 12H_2O]^+$); 2269 (0.5, $[M \cdot 11H_2O]^+$); 2071 (0.5, $[M]^+$); 1948 (0.25, $[M - Zn(ac)]^+$); 1825 (1.0, $[M - 2Zn(ac)]^+$); 1702 (0.5, $[M - 3Zn(ac)]^+$); **9**: 0.222 g, 96%; m.p. 256–257 °C, dec. **10**: 0.206 g, 88%; m.p. 224–225 °C. **11**: 0.235 g, 95%; m.p. >300 °C. **12**: 0.301 g, 90%; m.p. >300 °C. **13**: 0.197 g, 88%; m.p. 214–216 °C.

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