Inorg. Chem. **1994**, *33*, 3085-3090

Reactions of Palladium Chloride with Amino Spirocyclic Cyclotriphosphazenes: Isolation and Crystal Structures of Novel Mono- and Bimetallic Complexes Formed by the Hydrolysis of a λ^5-Diazaphospholane Ring[1]

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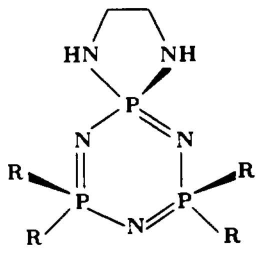
Received June 16, 1993[⊗]

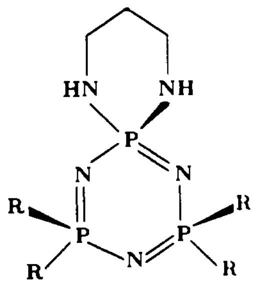
The reaction of the amino spirocyclic cyclotriphosphazene $N_3P_3(NMe_2)_4(NHCH_2CH_2CH_2NH)$ (**2**) with palladium chloride gives the stable chelate complex $[PdCl_2{\cdot}\mathbf{2}]$ (**4**). An X-ray crystallographic study reveals that one of the nitrogen atoms of the diaminoalkane moiety and an adjacent phosphazene ring nitrogen atom are bonded to the metal. An analogous reaction with the phosphazene $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ (**1**) gives initially a similar complex which undergoes facile hydrolysis to give the novel monometallic and bimetallic complexes $[PdCl_2{\cdot}HN_3P_3(O)(NMe_2)_4(NHCH_2CH_2NH_2)]$ (**5**) and $[PdCl\{N_3P_3(NMe_2)_4(NCH_2CH_2NH_2)\}]_2(O)$ (**6**), which have been structurally characterized; in the former, an (oxophosphazadienyl)ethylenediamine is chelated to the metal whereas, in the latter, an oxobridged bis(cyclotriphosphazene) acts as a hexadentate nitrogen donor ligand in its dianionic form. Crystal data for **4**: $a = 14.137(1)$ Å, $b = 8.3332(5)$ Å, $c = 19.205(2)$ Å, $\beta = 96.108(7)°$, $P2_1/c$, $Z = 4$, $R = 0.027$ with 3090 reflections ($F > 5\sigma(F)$). Crystal data for **5**: $a = 8.368(2)$ Å, $b = 16.841(4)$ Å, $c = 16.092(5)$ Å, $\beta = 98.31(2)°$, $P2_1/n$, $Z = 4$, $R = 0.049$ with 3519 reflections ($F > 5\sigma(F)$). Crystal data for **6**: $a = 22.455(6)$ Å, $b = 14.882(3)$ Å, $c = 13.026(5)$ Å, $\beta = 98.55(2)°$, $C2/c$, $Z = 4$, $R = 0.038$ with 3023 reflections ($F > 5\sigma(F)$).

The coordination chemistry of cyclophosphazenes is of great interest[2] because their polymeric analogues can function as supported catalysts. The cyclophosphazenes are poor donors unless electron-releasing substituents such as alkyl or amino groups are attached to the skeleton. In contrast to the numerous well-characterized complexes of amino- and methylcyclotetraphosphazenes and their higher homologues, complexes with strongly basic cyclotriphosphazenes are few in number[3,4] and no well-characterized example is known despite the ready accessibility of such cyclotriphosphazenes. A possible reason for this is the apparent "rigidity" of the small six-membered phosphazene ring and steric hindrance in inducing the ring nitrogen to bind to a metal. However, this difficulty has been overcome in our laboratory by the use of amino spirocyclic substituents, and the ability of spirocyclic cyclotriphosphazene to form complexes readily with nickel(II) and cobalt(II) chlorides has been demonstrated.[4] In this paper, we have extended this approach to synthesize and structurally characterize the palladium chloride complexes of the two spirocyclic cyclotriphosphazenes **1** and **2**. The main objective of the study is to investigate the effect of the spiro ring size on the nature of the resulting complexes.

Experimental Section



R = NMe$_2$ (1)



R = NMe$_2$ (2)

The cyclotriphosphazenes $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ (**1**)[5] and $N_3P_3(NMe_2)_4(NHCH_2CH_2CH_2NH)$ (**2**)[4] were synthesized according to the literature methods. The ^1H and ^{31}P NMR spectra were recorded using a Bruker ACF-200 spectrometer with Me_4Si and 85% H_3PO_4 as internal and external standards, respectively. Positive chemical shifts are downfield from the standard.

Synthesis of 4. A mixture of ligand **2** (1.00 g, 2.61 mmol) and palladium chloride (0.23 g, 1.30 mmol) in acetonitrile (35 mL) was stirred at room temperature (~25 °C) for 48 h. The yellow precipitate that formed was washed with acetonitrile and dried in vacuum. Yield: 0.5 g (69%). It decomposes above 190 °C. Anal. Found (calcd): C, 24.7 (23.6); H, 5.9 (5.7); N, 23.6 (22.5). IR (cm^{-1}): ν_{PN} 1308 (m), 1227 (s), 1188 (s), 1164 (s). ^1H NMR ($CDCl_3$): 3.87 (br, NH), 3.18 (d, 10 Hz), 2.86 (d, 13 Hz), 2.71 (d, 11 Hz), 2.54 (d, 12 Hz), 1.85 (m), 1.66 ppm (m). ^{31}P NMR (CH_2Cl_2): 43.1 (A), 18.3 (M), 15.4 ppm (X); $J_{AM} = J_{MX} = 38$, $J_{AX} = 32$ Hz.

Synthesis of 5 and 6. A mixture of ligand **1** (0.5 g, 1.36 mmol) and palladium chloride (0.25 g, 1.41 mmol) in acetonitrile (25 mL) was stirred at room temperature (~25 °C) for 8 h. The yellow precipitate that formed was washed with acetonitrile and dried in vacuum (yield 40%). The compound was identified as **5**. Anal. Found (calcd): C, 22.2 (21.2); H, 6.0 (5.7); N, 22.2 (22.3). IR (cm^{-1}): ν_{PN} 1308 (s), 1221 (s), 1182 (s); ν_{PO} 1263 (s). ^{31}P NMR ($MeOH/CH_2Cl_2$): 21.0 (A), 19.1 (M), 2.8 ppm (X); $J_{AM} = 36$, $J_{AX} = 22$, $J_{MX} = 40$ Hz. The mother liquor was cooled at -10 °C for 24 h to give small quantities of **6** (<5%). Addition of water to the mother liquor and heating the solution to 80 °C and cooling it to -10 °C led to the precipitation of additional quantities of **5** (overall yield 0.56 g, 75%).

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1994.

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0020-1669/94/1333-3085$04.50/0

Table 1. Crystallographic Data for **4**–**6**

	4	**5**	**6**
mol formula	$C_{11}H_{32}N_9P_3Cl_2Pd$	$C_{10}H_{32}N_9OP_3Cl_2Pd$	$C_{20}H_{60}N_{18}OP_6Cl_2Pd_2$
mol wt	560.6	564.6	1038.4
cryst size, mm	0.10 × 0.10 × 0.35	0.28 × 0.30 × 0.35	0.12 × 0.12 × 0.45
space group	$P2_1/c$	$P2_1/n$	$C2/c$
a, Å	14.137(1)	8.368(2)	22.455(6)
b, Å	8.3332(5)	16.841(4)	14.882(3)
c, Å	19.205(2)	16.092(5)	13.026(5)
β, deg	96.108(7)	98.31(2)	98.55(2)
V, Å^3	2250	2244	4305
Z	4	4	4
d(calc), g·cm^{-3}	1.649	1.671	1.602
μ, cm^{-1}	12.12	10.99	11.56
no. of obsd reflns	3090 ($F > 5\sigma(F)$)	3519 ($F > 5\sigma(F)$)	3023 ($F > 5\sigma(F)$)
final R^a	0.027	0.049	0.038
final $R_w{}^b$	0.031		0.047
k; g^b	1; 0	0; 0	1; 0.012157

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(\|F_o| - |F_c\|)/\sum w^{1/2}|F_o|]$; $w = k/[\sigma^2(F_o) + gF_o{}^2]$.

Table 2. Fractional Atomic Coordinates for **4**

atom	x/a	y/b	z/c	$U_{eq}{}^a$
Pd1	0.93155(2)	0.08168(3)	0.74074(1)	294(1)
Cl1	1.08147(7)	0.0853(1)	0.70729(5)	501(3)
Cl2	0.87023(8)	0.1617(1)	0.63148(5)	535(3)
P1	0.86560(6)	0.0759(1)	0.86786(4)	268(2)
N1	0.8085(2)	0.0849(3)	0.7905(1)	295(8)
P2	0.69510(6)	0.0409(1)	0.77541(4)	272(2)
N2	0.6584(2)	−0.0529(3)	0.8392(1)	343(9)
P3	0.71181(6)	−0.0767(1)	0.91575(4)	290(3)
N3	0.8229(2)	−0.0293(4)	0.9248(1)	336(10)
N11	0.9705(2)	0.0008(3)	0.8435(1)	299(9)
C12	1.0625(2)	0.0495(4)	0.8852(2)	383(11)
C13	1.0666(3)	0.2277(5)	0.9013(2)	420(12)
C14	0.9846(3)	0.2829(5)	0.9385(2)	449(13)
N15	0.8927(2)	0.2592(3)	0.8944(1)	361(9)
N21	0.6712(2)	−0.0685(3)	0.7050(1)	358(9)
C22	0.7051(3)	−0.2330(5)	0.7059(2)	572(15)
C23	0.6446(3)	−0.0046(6)	0.6356(2)	635(17)
N31	0.6386(2)	0.2099(4)	0.7600(2)	453(10)
C32	0.6816(3)	0.3601(5)	0.7430(2)	594(16)
C33	0.5348(3)	0.2147(6)	0.7577(3)	821(22)
N41	0.7057(2)	−0.2619(4)	0.9453(2)	385(8)
C42	0.7816(3)	−0.3783(5)	0.9356(2)	504(15)
C43	0.6108(3)	−0.3350(5)	0.9418(3)	594(16)
N51	0.6491(2)	0.0228(4)	0.9702(2)	411(10)
C52	0.6183(5)	0.1853(6)	0.9505(3)	903(24)
C53	0.6742(4)	0.0053(7)	1.0450(2)	727(20)

[a] $U_{eq} = {}^1/_3(\sum_i\sum_j U_{ij} a^*_i b^*_j \vec{a}_i \cdot \vec{b}_j)$ (×10^4 Å^2).

Table 3. Fractional Atomic Coordinates for **5**

atom	x/a	y/b	z/c	$U_{eq}{}^a$
Pd1	0.19662(7)	−0.01239(3)	0.04010(4)	250(2)
Cl1	0.0934(3)	−0.0736(1)	0.1511(1)	342(6)
Cl2	0.2160(3)	0.1080(1)	0.1072(1)	410(7)
P1	0.3033(2)	−0.1941(1)	−0.0021(1)	257(6)
N1	0.2150(8)	−0.2303(4)	0.0762(4	314(22)
P2	0.1237(2)	−0.3174(1)	0.0814(1)	270(6)
N2	0.0809(8)	−0.3540(4)	−0.0090(5)	347(23)
P3	0.1821(2)	0.3368(1)	−0.0836(1)	283(6)
N3	0.2818(8)	−0.2563(4)	−0.0770(5)	349(26)
N11	0.1773(7)	−0.1127(4)	−0.0374(4)	255(22)
C12	0.2042(11)	−0.0852(5)	−0.1242(5)	357(27)
C13	0.3345(10)	−0.0213(5)	−0.1127(5)	353(29)
N14	0.2841(8)	0.0402(4)	−0.0577(4)	326(23)
O1	0.4635(6)	−0.1602(3)	0.0268(4)	366(20)
N21	−0.0403(8)	−0.3076(5)	0.1244(5)	408(26)
C22	−0.1884(12)	−0.2795(8)	0.0730(8)	643(45)
C23	−0.0331(14)	−0.2878(8)	0.2130(7)	630(44)
N31	0.2439(8)	−0.3703(4)	0.1516(5)	383(24)
C32	0.1838(14)	−0.4492(6)	0.1692(8)	640(42)
C33	0.4148(13)	−0.3676(7)	0.1531(9)	678(46)
N41	0.0481(9)	−0.3450(5)	−0.1705(5)	412(23)
C42	−0.1141(13)	−0.3128(8)	−0.1713(7)	621(44)
C43	0.1057(15)	−0.3417(8)	−0.2508(8)	685(46)
N51	0.3136(9)	−0.4073(5)	−0.0938(5)	454(28)
C52	0.2579(15)	−0.4891(6)	−0.0997(9)	689(46)
C53	0.4763(12)	−0.3941(7)	−0.1101(8)	597(44)

[a] $U_{eq} = {}^1/_3(\sum_i\sum_j U_{ij} a^*_i b^*_j \vec{a}_i \cdot \vec{b}_j)$ (×10^4 Å^2).

X-ray Crystallography. Single crystals suitable for the crystallographic studies were obtained by diffusion of dichloromethane into a solution of **5** in a methanol/dichloromethane mixture or by diffusion of petroleum ether into a solution of **6** or **4** in dichloroethane. The crystals were mounted on an Enraf-Nonius CAD-4 diffractometer that used graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation and was equipped with a PDP-11 microcomputer. The crystal of the dipalladium complex **6** was coated with liquid paraffin to protect it from the atmosphere. Cell dimensions were obtained using 25 randomly selected well-centered reflections. The intensity data were collected at 291 K using an $\omega/2\theta$ scan mode in the θ range 1–25°. Three standard reflections were used to check the orientation changes of the crystal (checked after every 400 reflections). Three standard reflections were used to check the decay (checked after every 3600 s of exposure). No significant decay was observed for any of the compounds. The data were corrected for Lorentz and polarization effects but not for absorption.[6]

The structures were solved by the Patterson heavy-atom method and by subsequent difference Fourier syntheses using SHELX-76. All non-hydrogen atoms were refined anisotropically. The N–H and CH_2 hydrogens and some of the CH_3 hydrogens were located from the difference maps and refined isotropically but not refined in the final cycles; other CH_3 hydrogens which did not appear in the difference maps were not included in the calculations. The crystal data and some details of the refinement are given in Table 1. The fractional atomic coordinates for the non-hydrogen atoms are given in Tables 2–4.

Results and Discussion

Synthesis and Spectral Characterization of 4. The reaction of **2** with palladium chloride in CH_3CN is straightforward, and complex **4** is precipitated in ~70% yield. It is soluble in dichloromethane and chloroform. The IR spectrum of this complex shows splitting of P–N stretching frequencies (1227, 1188, 1164 cm^{-1}) compared to that observed for ligand **2** (1190, 1150 (shoulder) cm^{-1}). The ^1H NMR spectrum shows the nonequivalence of NMe_2 and NCH_2 protons; the NH proton signal is observed as a broad peak at ~3.9 ppm. The two $P(NMe_2)_2$ phosphorus nuclei are nonequivalent as shown by the AMX pattern (δ_P 43.1, 18.3, 15.4 ppm) observed in the ^{31}P NMR spectrum in contrast to the A_2X pattern observed for ligand **2** (δ_P 26.7, 17.8 ppm; $^2J_{PP}$ = 40 Hz). These data show that one of the P_3N_3 ring nitrogen atoms is involved in coordination. The considerable downfield shift (by 25.3 ppm) of the spiro phosphorus in complex **4** is attributed to a four-membered chelate ring (see below). The two $P(NMe_2)_2$ phosphorus nuclei are shielded (by

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(6) Absorption correction was applied for **5** using the program ABSORB.[7] The R factor remained the same, and there were no significant changes in the bond parameters.

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Table 4. Fractional Atomic Coordinates for **6**

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Pd1	–0.00495(1)	–0.11963(2)	0.36356(2)	414(2)
Cl1	–0.0683(1)	0.0075(1)	0.3541(1)	566(4)
P1	0.0655(1)	–0.2741(1)	0.2738(1)	471(4)
N1	0.0726(2)	–0.2156(3)	0.1688(3)	462(11)
N1′	–0.0726(2)	–0.2156(3)	0.3312(3)	462(12)
P2	0.1008(1)	–0.2629(1)	0.0722(1)	572(4)
N2	0.1482(2)	–0.3380(4)	0.1092(4)	857(20)
P3	0.1552(1)	–0.3873(1)	0.2190(1)	752(6)
N3	0.1143(2)	–0.3490(3)	0.2987(4)	639(17)
O1	0.0000	–0.3212(3)	0.2500	503(16)
N11	0.0599(2)	–0.2139(3)	0.3754(3)	495(12)
C12	0.1158(2)	–0.1765(4)	0.4326(4)	585(17)
C13	0.1239(2)	–0.0808(4)	0.3930(4)	643(19)
N14	0.0660(2)	–0.0329(3)	0.3939(3)	541(13)
N21	0.0514(2)	–0.3025(3)	–0.0212(3)	700(17)
C22	0.0264(5)	–0.3910(5)	–0.0078(6)	1084(38)
C23	0.0083(4)	–0.2425(5)	–0.0861(5)	993(31)
N31	0.1312(2)	–0.1796(3)	0.0123(4)	750(18)
C32	0.1771(3)	–0.1275(5)	0.0778(7)	952(32)
C33	0.1510(4)	–0.2025(6)	–0.0876(6)	1173(38)
N41	0.2278(3)	–0.3822(5)	0.2706(5)	1026(26)
C42	0.2557(4)	–0.2845(8)	0.2808(7)	1389(53)
C43	0.2507(6)	–0.4335(10)	0.3569(15)	2613(100)
N51	0.1412(4)	–0.4958(4)	0.2025(6)	1210(34)
C52	0.1176(6)	–0.5474(6)	0.2658(11)	1529(54)
C53	0.1843(8)	–0.5360(11)	0.1324(14)	1257(50)[b]
C53′	0.1412(13)	–0.5559(19)	0.1053(22)	1326(85)[b]

[a] $U_{eq} = {}^1/_3(\sum_i\sum_j U_{ij}a^*_i b^*_j \vec{a}_i \vec{b}_j)$ ($\times 10^4$ Å^2). [b] U_{iso}; s.o.f. C53:C53′ = 0.6: 0.4.

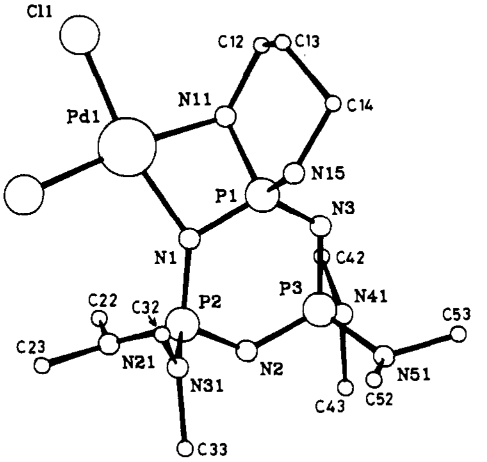

Figure 1. PLUTO diagram of **4** (view along *y* axis).

8.4 and 11.2 ppm) as compared to the ligand; the more shielded phosphorus is assigned to the one closer to the donor phosphazene ring nitrogen atom on the basis of its weaker coupling with the P(spiro) phosphorus nucleus.

Crystal Structure of 4. A single-crystal X-ray diffraction study of **4** confirms that cyclophosphazene **2** acts as a bidentate chelate ligand and forms a strained four-membered chelate ring. One of the nitrogen atoms of the diaminoalkane moiety and an adjacent phosphazene ring nitrogen atom are bonded to the metal. A PLUTO diagram of the molecule is shown in Figure 1; selected bond parameters are given in Table 5. This is the first structurally characterized complex of a highly basic (fully aminated or alkylated) cyclotriphosphazene and also the first example of a palladium chloride complex of an aminocyclophosphazene.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for **4**

Pd1–Cl1	2.279(1)	N1–P2	1.640(3)
Pd1–Cl2	2.283(1)	P2–N2	1.586(3)
Pd1–N2	2.072(3)	P2–N21	1.636(2)
Pd1–N11	2.103(2)	P2–N31	1.631(3)
P1–N1	1.615(3)	N2–P3	1.592(2)
P1–N3	1.571(3)	P3–N3	1.611(3)
P1–N11	1.720(3)	P3–N41	1.650(4)
P1–N15	1.643(3)	P3–N51	1.663(4)
N1–Pd1–N11	73.75(9)	Pd1–N1–P2	140.2(2)
Cl2–Pd1–N11	172.85(8)	N1–P2–N2	111.6(1)
Cl1–Pd–N1	168.88(8)	N21–P2–N31	106.1(2)
Cl1–Pd1–Cl2	90.61(4)	P2–N2–P3	127.8(2)
N11–P1–N15	104.1(1)	N2–P3–N3	115.5(2)
N1–P1–N3	118.3(2)	N41–P3–N51	101.5(2)
Pd1–N1–P1	93.5(1)	P1–N3–P3	120.3(2)
P1–N1–P2	122.4(2)	Pd1–N11–P1	89.51(9)

The phosphazene ring P–N bonds in **4** are nonequivalent and vary over the range 1.571(3)–1.640(3) Å. The two P–N bonds around the coordinating ring nitrogen atom (N1) are longer than the others; between the two, the one forming part of the four-membered chelate ring (P1–N1) is shorter (1.615(3) Å) than the other (P2–N1) bond (1.640(3) Å). Among the P–N bonds exocyclic to the P_3N_3 ring, the donor nitrogen (N11)–phosphorus bond is the longest (1.720(3) Å) in the complex, but is still shorter than the P–N single-bond distance (see the P1–N11 distance of **5**: 1.77 Å). The phosphazene ring nitrogen–metal bond is shorter (2.072(3) Å) than the other metal–nitrogen bond (2.103(2) Å), consistent with the view that, in fully aminated cyclophosphazenes, the ring nitrogen is a better donor than the exocyclic nitrogen atoms. The Pd–N distances are longer than those in $[PdCl_2(en)]$[8] whereas the Pd–Cl distances are shorter. Evidently, the spirocyclic phosphazene is a poorer donor than ethylenediamine.

The phosphazene ring is in the chair form; P1 (spiro phosphorus) and N2 deviate from the mean plane formed by the other four atoms (by –0.24 and 0.14 Å, respectively). The exocyclic diaminoalkane moiety (spiro ring) is also in a distorted chair form. The geometry around the metal is nonplanar. The four-membered chelate ring is also distinctly nonplanar.

Synthesis and Characterization of 5 and 6. The reaction of $N_3P_3(NMe_2)_4(NH(CH_2)_2NH)$ (**1**) with palladium chloride in acetonitrile leads to the precipitation of a novel hydrolyzed product, **5**, in 40% yield. The ^{31}P NMR spectrum of the mother liquor shows the absence of this hydrolyzed complex. Cooling this solution to –10 °C for 24 h leads to the precipitation of a small quantity (<5%) of another product, **6**, which is soluble in dichloromethane and dichloroethane. Addition of water to the filtrate followed by heating for 1 h and cooling the contents to –10 °C results in precipitation of a further quantity of **5**, thereby raising its yield to 75%. Complex **5** is not soluble in any single solvent but dissolves in mixed solvents such as dichloromethane/acetonitrile, dichloromethane/methanol, or chloroform/methanol. Complex **6** is highly sensitive to moisture both in solution and in the solid state. For this reason satisfactory elemental analyses could not be obtained for **6**.

The CHN elemental analyses of **5** shows a 1:1 metal:ligand ratio, but its IR spectrum is quite different from that of **4**; a new band appears at 1263 cm^{-1}. The ^{31}P NMR spectrum of complex **5** displays an AMX pattern with resonances at 21.0, 19.1, and 2.8 ppm; and $^2J_{PP}$ values are J_{AM} = 36, J_{AX} = 22, and J_{MX} = 40 Hz. The two resonances at 21.0 and 19.1 ppm can be assigned to the phosphorus atoms bearing NMe_2 groups. However, the upfield shift of 32.7 ppm for the other phosphorus cannot be explained entirely on the basis of coordination of the cyclophosphazene to the metal. The observed chemical shift 2.8 ppm is in the region of the P=O phosphorus of the oxocyclotriphosphazadienes[10] and clearly shows that hydrolysis has occurred presumably to cleave the five-membered PN_2C_2 ring.

Crystal Structure of 5. A perspective view of the structure of **5** is shown in Figure 2. The P_3N_3 ring is in the oxophosphazadiene

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(8) In $[PdCl_2(en)]$, the Pd–N and Pd–Cl distances are 1.978 and 2.309 Å, respectively.[9]

(9) Iball, J.; MacDougal, M.; Scrimgeour, S. N. *Acta Crystallogr.* **1975**, *31B*, 1672.

(10) The $\delta_{P=O}$ chemical shifts for $HN_3P_3(O)Cl_2(NEt_2)_3$, $HN_3P_3(O)(OMe)_5$, and $HN_3P_3(O)(NHBu^t)_2(OMe)_3$ are 0.1, 2.1, and 3.1 ppm, respectively.[11]

(11) Krishnamurthy, S. S.; Woods, M. *Annu. Rep. NMR Spectrosc.* **1987**, *19*, 175.

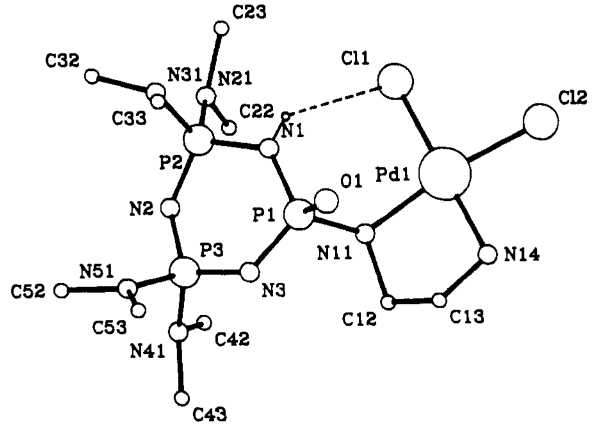

Figure 2. PLUTO diagram of **5** (view along *x* axis; intramolecular H-bond shown with dashed line).

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for **5**

Pd1–Cl1	2.333(2)	N1–P2	1.662(7)
Pd1–Cl2	2.292(2)	P2–N2	1.573(8)
Pd1–N11	2.092(7)	P2–N21	1.632(8)
Pd1–N14	2.032(7)	P2–N31	1.659(7)
P1–N1	1.666(7)	N2–P3	1.593(8)
P1–N3	1.587(8)	P3–N3	1.587(7)
P1–N11	1.772(7)	P3–N41	1.667(8)
P1–O1	1.469(5)	P3–N51	1.643(8)
N1···Cl1 (*x*,*y*,*z*)	3.132(7)	N11···Cl2(–*x*,–*y*,–*z*)	3.321(6)
N14···Cl1(–*x*,–*y*,–*z*)	3.344(7)	N14···O1(1–*x*,–*y*,–*z*)	2.914(8)
N11–Pd1–N14	84.0(3)	N1–P2–N2	110.1(4)
Cl2–Pd1–N11	171.6(2)	N21–P2–N31	103.3(4)
Cl1–Pd1–N14	179.2(2)	P2–N2–P3	123.4(5)
Cl1–Pd1–Cl2	92.2(1)	N2–P3–N3	115.9(4)
N11–P1–O1	105.9(3)	N41–P3–N51	103.6(4)
N1–P1–N3	108.6(4)	P1–N3–P3	128.0(5)
P1–N1–P2	128.2(4)	Pd1–N11–P1	116.3(3)

form with the phosphoryl phosphorus attached to one of the nitrogen atoms of ethylenediamine (en). Both the exocyclic ethylenediamino nitrogen atoms are coordinated to the metal to form a five-membered chelate ring; it can be considered as a palladium chloride complex of a mono-N-substituted derivative of ethylenediamine, $[PdCl_2(RHNCH_2CH_2NH_2)]$ (R = oxophosphazadienyl). Such a monosubstituted ethylenediamine complex has not been characterized structurally hitherto. This complex displays several novel structural features. Selected structural parameters for **5** are given in Table 6.

The phosphazadiene ring is nonplanar; the phosphorus atom P2 and the adjacent nitrogen N2 deviate by –0.13 and 0.23 Å, respectively, from the mean plane formed by P1,N1,P3,N3. The chelate ring is highly puckered. The geometry around the metal is nearly planar. The phosphazadiene ring P–N bonds are not equal. The bonds around the ring nitrogen (N1) bearing the proton are longer (1.666(7) and 1.662(7) Å) than the other P–N bonds (1.573(8)–1.593(8) Å). A similar lengthening in bond lengths is observed in the oxophosphazadiene $HN_3P_3(O)Ph_2(OMe)_3$ (1.663 and 1.672 Å).[12] The exocyclic P1–N11 bond distance (1.772(7) Å) is close to that of a P–N single bond.

The metal–nitrogen bonds are different; the one to the NH_2 nitrogen (2.032(7) Å) is shorter than that (2.092(7) Å) to the NH(PO) nitrogen. The metal–chlorine distance *trans* to the longer M–N bond is shorter and *vice versa*. These data show that the NH_2 nitrogen (N14) is a stronger donor than the nitrogen (N11) attached to the phosphorus.

This complex shows an interesting packing in the crystal lattice through several hydrogen bonds. Hydrogen bonds involving the three NH protons of the ethanediamine moiety and the three proton acceptors (P=O oxygen and two chlorine atoms) result in a linear polymeric network along the *x* axis with alternate sets of two and four hydrogen bonds (Figure 3). There is also a strong intramolecular H-bond between the proton attached to the phosphazadiene ring nitrogen N1 and the chlorine Cl1 (see Figure 2). The AMX type ^{31}P NMR spectrum for the complex suggests that the intramolecular hydrogen bond persists in solution too. The ^{31}P NMR spectra of the oxophosphazadienes are of the A_2X type owing to rapid proton exchange, and the AMX limit can be reached at lower temperatures.[12] Because of intramolecular hydrogen bonding in **5**, the proton is rigidly bonded to one of the ring nitrogen atoms adjacent to the P=O group and an AMX spectrum is observed even at ambient temperature.

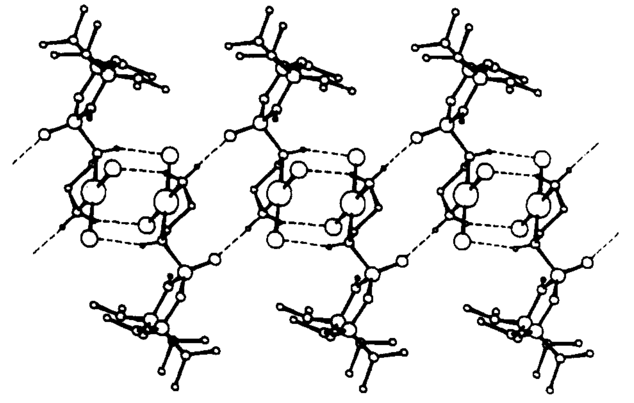

Figure 3. Polymer chain of **5** (view along *z* axis; intermolecular H-bonds shown with dashed lines; intramolecular ones not shown).

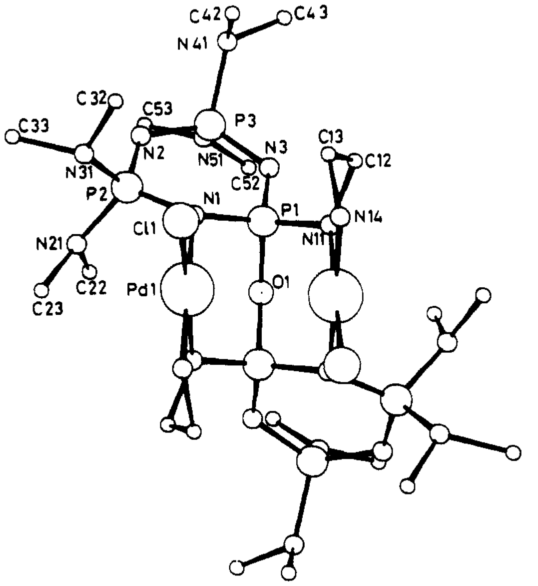

Figure 4. PLUTO diagram of **6** (view along *y* axis).

Crystal Structure of the Dipalladium Complex 6. The structure of the dipalladium complex **6** possesses several novel features. It has a 2-fold axis of symmetry passing through the oxygen atom which bridges the two phosphazene rings. The phosphazene, an oxobis(cyclotriphosphazene) derivative, acts as a hexadentate NNNNNN donor ligand with chelating and bridging modes of coordination. The PLUTO diagram of the molecule is shown in Figure 4. The selected bond parameters are given in Table 7.

The phosphazene ring is in a distorted chair form; nitrogen N1 and phosphorus P3 deviate by –0.39 and 0.07 Å, respectively, from the mean plane formed by P1,P2,N2,N3. The P–N bonds within the phosphazene ring are nonequivalent and are in the range 1.649(4)–1.563(5) Å. The bonds around the coordinating phosphazene ring nitrogen (N1) are longer (1.649(4) and 1.648(5) Å) while those one bond away from N1 are shorter

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(12) Dhathathreyan, K. S.; Krishnamurthy, S. S.; Vasudeva Murthy, A. R.; Cameron, T. S.; Chan, C.; Shaw, R. A.; Woods, M. *J. Chem. Soc., Chem. Commun.* **1980**, 231.

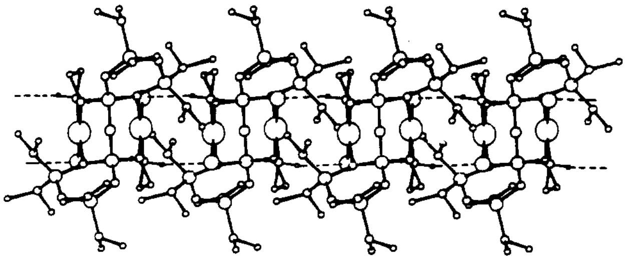


Figure 5. Polymer chain of 6 (view along *y* axis; intermolecular H-bonds shown with dashed lines; intramolecular ones not shown).

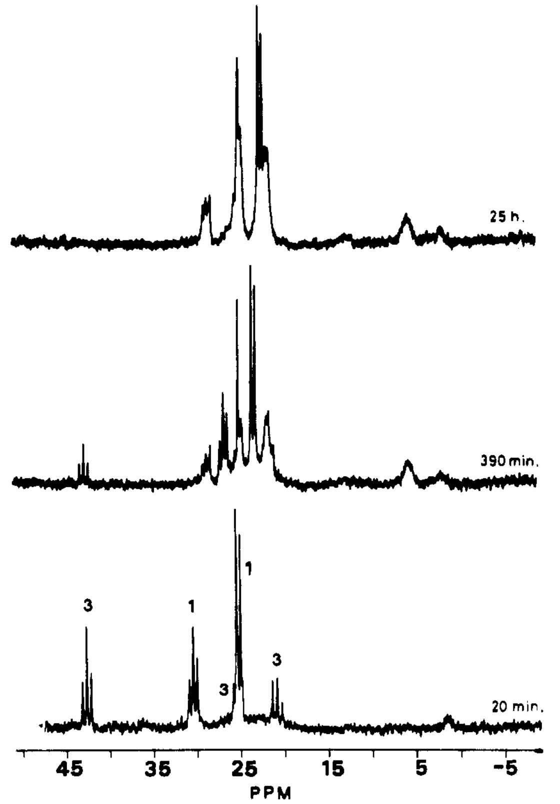


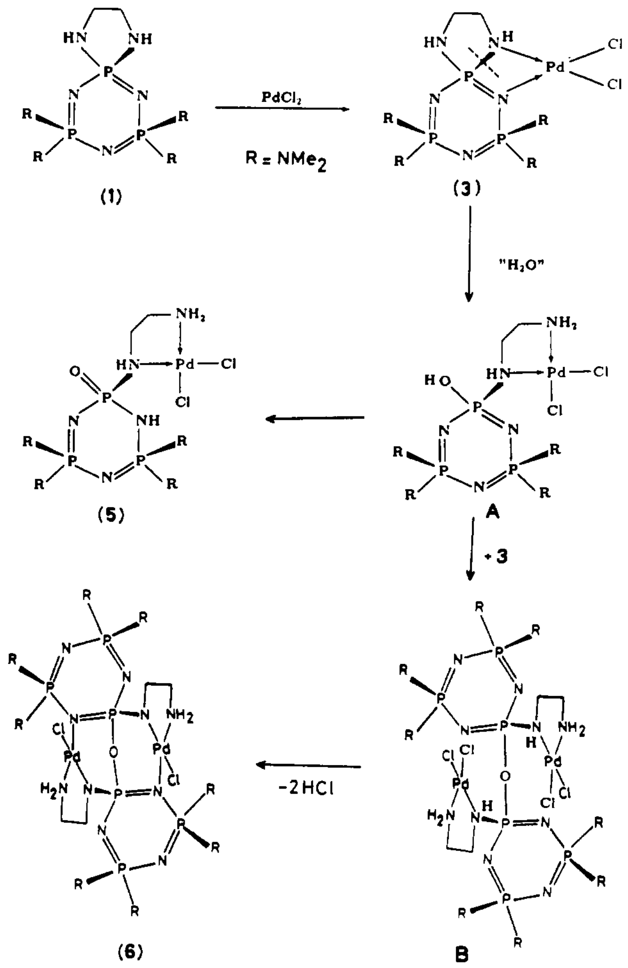
Figure 6. Monitoring of the hydrolysis of **1** in the presence of PdCl$_2$ by ^{31}P NMR spectroscopy (spectra recorded at various time intervals after mixing the reactants).

Table 7. Selected Bond Distances (Å) and Bond Angles (deg) for **6**

Pd1–Cl1	2.358(2)	P2–N21	1.630(4)
Pd1–N1′	2.081(4)	P2–N31	1.664(5)
Pd1–N11	2.012(4)	N2–P3	1.594(5)
Pd1–N14	2.043(4)	P3–N3	1.590(5)
P1–N1	1.649(4)	P3–N41	1.670(7)
P1–N3	1.563(5)	P3–N51	1.653(6)
P1–O1	1.617(3)	N51–C53	1.546(21)
P1–N11	1.618(4)	N51–C53′	1.550(30)
N1–P2	1.648(5)	C53–C53′	1.023(33)
P2–N2	1.569(5)		
N14···Cl1($-x,y,{}^1/_2-z$)	3.294(4)	N14···Cl1($-x,-y,1-z$)	3.297(4)
N11–Pd1–N14	83.7(2)	P1–N1–P2	120.2(3)
N1′–Pd1–N14	175.6(2)	N1–P2–N2	112.9(3)
N1′–Pd1–N11	92.0(2)	N21–P2–N31	101.6(2)
Cl1–Pd1–N14	87.2(1)	P2–N2–P3	125.1(3)
Cl1–Pd1–N11	170.8(1)	N2–P3–N3	115.5(3)
Cl1–Pd1–N1′	97.1(1)	N41–P3–N51	104.6(4)
O1–P1–N11	102.6(2)	P1–N3–P3	125.1(3)
N1–P1–N3	113.4(3)	Pd1–N11–P1	117.8(2)

(1.563(5) and 1.569(5) Å). The lengths of the P–N bonds farther from N1 lie between these two sets (1.590(5) and 1.594(5) Å). The short P1–N11 and Pd–N11 bond lengths suggest that nitrogen N11 is in an anionic form. The chelating five-membered ring (formed by the ethanediamino moiety) is highly puckered.

Scheme 1. Proposed Mechanism for the Formation of **5** and **6** from **1**



The metal is coordinated to four different kinds of donors: an anionic nitrogen (N11), an amino nitrogen (N14), a phosphazene ring nitrogen (N1), and a chloride ion with distances 2.012(4), 2.043(4), 2.081(4), and 2.358(2) Å. The two anionic donors are *trans* to each other rather than being in the more common *cis* mode of coordination. The geometry around palladium is planar; the maximum deviation is only 0.02 Å. The planes of the coordination spheres of the two palladium atoms of the molecule have a dihedral angle of 9.1°, and the distance between the two metal atoms is 2.998(1) Å.

There is an intramolecular H-bond between one of the NH$_2$ hydrogen atoms and the chlorine atom of the other half of the molecule. The two phosphazene moieties are bridged by all possible bonds: a covalent linkage through the bridging oxygen atom, two coordinate linkages through the palladium atoms, and two "intermoiety" hydrogen bonds (using NH and Cl atoms of each moiety). Intermolecular N–H···Cl hydrogen bonds extend the structural motif along the *z* axis (see Figure 5).

Hydrolysis Studies of 1. The hydrolyzed complex **5** is formed even when the reaction is carried out in acetonitrile distilled over CaH$_2$. Apparently the hydrolysis is very facile in the presence of palladium chloride and is brought about by even traces of water present in the solvent or adsorbed on the glass vessel. In order to throw further light on this aspect, the hydrolysis of the spirocyclic phosphazene, **1**, has been monitored by ^{31}P NMR spectroscopy in both the presence and the absence of PdCl$_2$.

Compound **1** does not hydrolyze in aqueous solution over a period of 24 h, as shown by ^{31}P NMR spectroscopy. However, heating the solution at 80 °C for 2 days results in 20% hydrolysis of **1**. The ^{31}P NMR spectrum of the hydrolyzed product is of an A$_2$X type with resonances at 23.6 and 4.8 ppm ($^2J_{PP}$ = 28 Hz) and can be assigned to the oxophosphazadiene $HN_3P_3(O)(NMe_2)_4(NHCH_2CH_2NH_2)$.[13]

The course of the reaction of $PdCl_2$ and **1** in CH_3CN was monitored by ^{31}P NMR spectroscopy. The spectra recorded at various time intervals are shown in Figure 6. Within 20 min, a new set of resonances at 42.6, 25.0, and 20.9 ppm consisting of an unresolved AMX pattern was observed in addition to the resonances arising from unreacted **1**. This result indicates the formation of an intermediate for which a chelate structure (as shown in Scheme 1) is assigned on the basis of the ^{31}P chemical shifts observed for **4** and the chelate complex $[W(CO)_4 \cdot \mathbf{1}]$ (42.1, 25.7, 22.4 ppm).[14] The chelate complex **3**, unlike **4**, was a highly strained structure as the phosphorus atom is part of a six-membered phosphazene ring, a five-membered PN_2C_2 ring, and a four-membered PN_2M chelate ring. Hence, it undergoes facile hydrolytic cleavage[15] of the five-membered PN_2C_2 ring.

A plausible mechanism for the formation of **5** and **6** from **1** is shown in Scheme 1. From the structure of **4** it can be seen that the P–N bond involving the nitrogen coordinated to the metal is the weakest among all the P–N bonds. Hence, we propose that the P–N bond involving the nitrogen coordinated to palladium in **3** is cleaved. The cleavage followed by rearrangement of the P_3N_3 ring nitrogen–metal bond gives the "hydroxy" species **A**, which further rearranges to the oxophosphazadiene form (**5**). The intermediate **3** reacts with **A** (when there is no further water) to give **B**, which on dehydrohalogenation (owing to the strong basicity of the ligand **1**) yields **6**. Neither species **A** nor **B** could be detected by ^{31}P NMR spectroscopy. However, formation of P–O–P bridged bis(cyclotriphosphazenes) from "hydroxy" phosphazenes has been reported previously.[16]

There is only one report so far on the hydrolysis of a five-membered λ^5-diazaphospholane ring using dilute HCl.[17] In the present study, for the first time, a metal-assisted hydrolysis of a λ^5-diazaphospholane ring has been observed under neutral and nonaqueous conditions, and this approach may lead to unusual complexes with unprecedented structural features.

Acknowledgment. The authors thank the Council of Scientific and Industrial Research (CSIR), New Delhi, for financial support.

Supplementary Material Available: Tables of crystallographic data, anisotropic thermal parameters, bond lengths, and bond angles for non-hydrogen atoms and coordinates and isotropic thermal parameters for hydrogen atoms for **4**–**6** (15 pages). Ordering information is given on any current masthead page.

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[13] The ^{31}P NMR spectra of the oxophosphazadiene displays resonances at 19.0 (d) and 5.0 ppm (t) with $^2J_{PP} = 15$ Hz in aqueous HCl and at 27.5 (d) and 12.5 ppm (t) ($^3J_{PH} = 9$; triplet) with $^2J_{PP} = 37$ Hz in aqueous KOH.

[14] Krishnamurthy, S. S.; Reddy, V. S.; Chandrasekaran, A.; Nethaji, M. *Phosphorus, Sulfur Silicon* **1992**, *64*, 99.

[15] Monitoring of the reaction by ^{31}P NMR spectroscopy shows that the intensity of the resonance at 42.6 ppm (arising from **3**) decays exponentially with time.

[16] Katti, K. V.; Krishnamurthy, S. S.; Woods, M. *Phosphorus Sulfur* **1985**, *25*, 167 and references therein.

[17] Anson, M. S.; McGuigan, C. *J. Chem. Soc., Perkin Trans. 1* **1989**, 715.