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Palladium(II) Chloride Complexes of Bis(pyrazolyl)cyclotriphosphazenes[1]

A. Chandrasekaran, Setharampattu S. Krishnamurthy,* and Munirathinam Nethaji

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

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Reactions of the bis(3,5-dimethylpyrazolyl)cyclotriphosphazene derivatives *gem*-$N_3P_3(MeNCH_2CH_2O)_2(dmp)_2$ (**1**) and nongeminal *cis*-$N_3P_3(OPh)_4(dmp)_2$ (**2**) with $PdCl_2$ afford complexes of the type [$PdCl_2$·(L)] (L = **1** or **2**). In these complexes, the phosphazenes act as bidentate NN-donor ligands with the two pyrazolyl pyridinic nitrogen atoms bonded to the metal, thus forming a six- and an eight-membered chelate ring, respectively. The structures of **2** and [$PdCl_2$·(**2**)] (**4**) have been confirmed by single-crystal X-ray diffraction. Crystal data for **2**: $a = 16.759(2)$ Å, $b = 10.788(3)$ Å, $c = 19.635(9)$ Å, $\beta = 101.61(3)°$, $P2_1/c$, $Z = 4$, $R = 0.038$ for 4688 reflections with $F > 5\sigma(F)$. Crystal data for **4**: $a = 9.701(3)$ Å, $b = 24.853(4)$ Å, $c = 15.794(4)$ Å, $\beta = 101.46(2)°$, $P2_1/n$, $Z = 4$, $R = 0.030$ for 5416 reflections with $F > 5\sigma(F)$.

The versatile coordination chemistry of pyrazole derivatives[2] and that of cyclophosphazenes[3] are well documented. The use of (pyrazolyl)cyclophosphazenes as ligands in transition metal chemistry was first investigated by Paddock and co-workers.[4] The (pyrazolyl)cyclotriphosphazenes were found to act as bidentate ligands toward palladium and platinum chlorides via their pyrazolyl pyridinic nitrogen atoms. In these complexes, the phosphazene ring nitrogen–metal interaction was not considered though the ^{31}P NMR spectral data would suggest such a possibility. The involvement of a phosphazene ring nitrogen in bonding to transition metals was confirmed recently in the structurally characterized metal carbonyl complexes[1,5] of *gem*-$N_3P_3Ph_4(dmp)_2$ (dmp = 3,5-dimethyl-1-pyrazolyl) and $N_3P_3(MeNCH_2CH_2O)_2(dmp)_2$ (**1**) and the copper(II) chloride complex[6] of $N_3P_3(dmp)_6$. The bonding to the metal occurs via the pyridinic nitrogen atoms of the pyrazolyl groups on the same phosphorus (as in the former[1]) or on different phosphorus atoms with *cis* disposition (as in the latter[6]) and a phosphazene ring nitrogen atom. In this paper, we report the synthesis of a new *cis*-bis(dmp)cyclotriphosphazene, 2-*cis*-4,6,6;2,4-$N_3P_3(OPh)_4(dmp)_2$ (**2**) and the palladium chloride complexes of **1** and **2**. Our aim is to compare the complexing abilities of geminal and *cis*-(pyrazolyl)phosphazenes (which would give a six- and an eight-membered chelate complex, respectively) and to study the possible fifth coordination to the metal via the phosphazene ring nitrogen.

Experimental Section

The cyclotriphosphazenes $N_3P_3(MeNCH_2CH_2O)_2(dmp)_2$ (**1**) and $N_3P_3(OPh)_4Cl_2$ (*cis* and *trans* mixture) were synthesized according to the literature methods.[1,7a] The NMR spectra were recorded using a Bruker ACF-200 spectrometer [^1H, ^{31}P (81.1 MHz; 85% H_3PO_4 as external standard) and ^{13}C (50.0 MHz; TMS standard)]. The spectra were recorded using $CDCl_3$ (^1H) and CH_2Cl_2 (^{31}P and ^{13}C) as solvents. Positive chemical shifts are downfield of the standard.

Synthesis of *cis*-$N_3P_3(OPh)_4(dmp)_2$ (2). A solution of $N_3P_3(OPh)_4Cl_2$ (*cis–trans* mixture) (5.0 g, 8.65 mmol), dmpH (2.0 g, 21 mmol), and triethylamine (5 mL) in toluene (50 mL) was heated under reflux for 2 days. The solution was passed through a short column of silica gel to remove the dissolved amine hydrochloride. Solvent was removed from the solution and the residue dissolved in a hot petroleum ether–benzene (1:1) mixture. The solution was cooled to 0 °C. Prolonged cooling of the solution (>10 days) led to deposition of the crystals of the title compound: yield 1.0 g (17%); mp 115 °C. Anal. Calcd for $C_{34}H_{34}N_7O_4P_3$: C, 58.6; H, 4.9; N, 14.0. Found: C, 59.4; H, 4.9; N, 14.2. The ^{31}P NMR spectrum of the mother liquor showed a broad peak at 6.3 ppm arising from **2** and overlapping resonances which presumably arise from the *trans* isomer of **2**. Attempts to separate the components of this mixture further were unsuccessful.

Table I. Crystal Data and Final Refinement Parameters

	2	**4**
mol formula	$C_{34}H_{34}N_7O_4P_3$	$C_{34}H_{34}Cl_2N_7O_4P_3Pd$
mol wt	697.4	874.9
cryst size, mm	0.18 × 0.38 × 0.42	0.12 × 0.15 × 0.30
space group	$P2_1/c$	$P2_1/n$
a, Å	16.759(2)	9.701(3)
b, Å	10.788(3)	24.853(4)
c, Å	19.635(9)	15.794(4)
β, deg	101.61(3)	101.46(2)
V, Å^3	3477	3732
Z	4	4
d(calc), g cm^{-3}	1.332	1.557
μ, cm^{-1}	1.75	8.07
temp, °C	20	20
wavelength, Å	0.7107	0.7107
no. of obsd reflns ($F > 5\sigma(F)$)	4688	5416
final R[a]	0.038	0.030
final R_w[b]	0.043	0.035
k; *g*[b]	3.6153; 0	1; 0

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

Synthesis of Complex 3. A mixture of phosphazene **1** (0.4 g, 0.85 mmol) and palladium chloride (0.15 g, 0.85 mmol) in acetonitrile (40 mL) was heated under reflux for 5 h. Solvent was removed under reduced pressure, the residue was extracted with petroleum ether–dichloromethane (1:1) (40 mL), and the extract was filtered. Addition of petroleum ether (100 mL) to the filtrate gave a yellow precipitate of **3**: yield 0.4 g (73%); mp >200 °C dec. Anal. Calcd for $C_{16}H_{28}Cl_2N_9O_2P_3Pd$: C, 29.5; H, 4.6; N, 19.4. Found: C, 29.4; H, 4.3; N, 19.1. ^{13}C NMR (ppm): 156.7, 148.4 (dmp quaternary carbons); 110.9 (dmp tertiary carbons); 65.2 64.9 (OCH_2 carbons); 49.37 (d, 14 Hz), 49.09 (d, 14 Hz) (NCH_2 carbons); 31.0 (NMe carbons); 14.65, 13.53 (dmp methyl carbons).

Synthesis of Complex 4. A mixture of phosphazene **2** (0.1 g, 0.14 mmol) and palladium chloride (0.025 g, 0.14 mmol) in acetonitrile (30 mL) was heated under reflux for 8 h. The reaction mixture was worked up as described above to isolate the title compound as a yellow solid: yield 0.1 g (80%); mp 233 °C. Anal. Calcd for $C_{34}H_{34}Cl_2N_7O_4P_3Pd$: C, 46.8; H, 3.9; N, 11.2. Found: C, 46.4; H, 4.2; N, 11.5.

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10^4$ Å^2) for Non-Hydrogen Atoms of **2**

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
P1	1463.5(3)	1234.5(5)	3576.9(3)	340(2)
N1	2028(1)	278(1)	4058(1)	367(6)
P2	2697.5(3)	711.9(5)	4697.3(3)	324(2)
N2	2708(1)	2121(2)	4913(1)	381(5)
P3	2194.8(3)	3125.6(5)	4430.9(3)	365(2)
N3	1625(1)	2657(2)	3740(1)	393(6)
O1	1456(1)	988(1)	2780(1)	428(5)
C11	2121(1)	1221(2)	2466(1)	401(7)
C12	2065(2)	2197(2)	2011(1)	605(10)
C13	2673(2)	2359(3)	1640(2)	855(15)
C14	3307(2)	1556(4)	1727(2)	947(15)
C15	3373(2)	601(4)	2199(2)	859(15)
C16	2762(2)	417(3)	2567(1)	602(10)
O2	558(1)	831(1)	3583(1)	416(5)
C21	−114(1)	1261(2)	3086(1)	382(7)
C22	−337(1)	2477(2)	3076(1)	570(9)
C23	−1004(2)	2850(3)	2577(2)	829(13)
C24	−1432(2)	2012(4)	2121(2)	857(14)
C25	−1208(2)	808(4)	2149(1)	807(13)
C26	−540(1)	401(3)	2642(1)	580(9)
O3	3586(1)	413(1)	4604(1)	380(4)
C31	3874(1)	−636(2)	4311(1)	362(7)
C32	4624(1)	−503(2)	4139(1)	505(8)
C33	4948(1)	−1496(3)	3850(2)	709(11)
C34	4531(2)	−2597(3)	3733(2)	775(11)
C35	3784(2)	−2718(2)	3913(2)	656(10)
C36	3449(1)	−1732(2)	4208(1)	483(8)
N41	2599(1)	−187(2)	5382(1)	407(6)
N42	3293(1)	−508(2)	5860(1)	484(7)
C43	3012(2)	−1002(2)	6378(1)	553(8)
C44	2161(2)	−991(2)	6257(1)	609(10)
C45	1906(1)	−468(2)	5626(1)	540(9)
C46	3580(2)	−1493(4)	7001(2)	999(16)
C47	1057(2)	−180(4)	5244(2)	928(14)
O5	2771(1)	4198(1)	4261(1)	466(5)
C51	3505(1)	3905(2)	4051(1)	489(9)
C52	3509(2)	3853(3)	3366(2)	868(14)
C53	4270(3)	3627(4)	3174(3)	1288(23)
C54	4947(3)	3489(4)	3682(4)	1330(27)
C55	4919(2)	3536(4)	4365(3)	1203(22)
C56	4187(2)	3747(3)	4549(2)	834(14)
N61	1649(1)	3977(2)	4892(1)	485(6)
N62	989(1)	3327(2)	5033(1)	619(9)
C63	749(2)	3988(3)	5526(1)	710(11)
C64	1237(2)	5025(3)	5697(2)	792(12)
C65	1808(2)	5013(2)	5308(1)	605(10)
C66	52(2)	3562(4)	5831(2)	1107(16)
C67	2475(2)	5909(3)	5296(2)	993(17)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*b_j^*\vec{a}_i\cdot\vec{b}_j$.

X-ray Crystallography. Data Collection. Single crystals suitable for the crystallographic studies were obtained by slow evaporation of solvent from a benzene solution (for compound **2**) or from an acetonitrile solution (for complex **4**). The crystals were mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The cell dimensions were obtained using 25 randomly selected well-centered reflections. The intensity data were collected using the $\omega/2\theta$ 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), and three standard reflections were used to check the decay (checked after every 3600 s of exposure). No significant decay was observed for either compound. The data were corrected for Lorentz and polarization effects. The crystal data for **2** and **4** and some details pertinent to the data collection are given in Table I.

Structure Solution and Refinement. The structures were solved by the Patterson heavy-atom method using SHELX-76 (for complex **4**) or by direct methods (MULTAN-82 for ligand **2**) and by subsequent difference Fourier syntheses using SHELX-76. The scattering factors for H, C, N, O, P, and Cl were those included in the above programs; for palladium, the values were taken from ref 7b. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms, located from the difference map, were refined once isotropically. The final refinement parameters are also given in Table I. The fractional atomic coordinates with equivalent temperature factors for the non-hydrogen atoms are given in Tables II and III.

Table III. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10^4$ Å^2) for Non-Hydrogen atoms of **4**

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Pd1	5995.8(3)	3142.7(1)	3493.9(1)	295(1)
Cl1	7452(1)	2865.7(4)	4729.9(6)	499(3)
Cl2	4073(1)	2989.4(4)	4089.5(7)	517(3)
P1	6950.1(9)	4775.2(3)	1478.2(5)	323(3)
N1	8162(3)	4590(1)	2239(2)	358(9)
P2	7877.2(9)	4329.7(3)	3099.0(5)	304(3)
N2	6294(3)	4268(1)	3202(2)	296(8)
P3	5047.5(8)	4408.1(3)	2432.2(5)	289(2)
N3	5391(3)	4702(1)	1615(2)	356(10)
O1	7146(3)	4502(1)	602(1)	428(9)
C11	6985(4)	3942(1)	501(2)	431(12)
C12	5698(5)	3741(2)	112(3)	716(20)
C13	5580(7)	3184(2)	−34(4)	904(26)
C14	6732(8)	2857(2)	198(4)	890(26)
C15	7980(7)	3074(2)	596(4)	805(24)
Cl6	8133(5)	3614(2)	761(3)	596(17)
O2	7106(3)	5384(1)	1242(1)	425(8)
C21	8351(4)	5659(1)	1215(1)	389(11)
C22	8245(5)	6215(2)	1198(3)	525(14)
C23	9422(5)	6511(2)	1136(3)	636(18)
C24	671(5)	6273(2)	1107(3)	642(16)
C25	750(5)	5719(2)	1110(3)	643(18)
C26	9589(4)	5407(2)	1161(3)	521(14)
O3	8805(2)	4607(1)	3908(1)	389(8)
C31	8885(4)	5179(1)	3972(2)	405(11)
C32	56(5)	5428(2)	3819(4)	690(20)
C33	192(6)	5981(2)	3937(5)	931(28)
C34	9150(6)	6262(2)	4190(4)	796(22)
C35	7976(6)	6009(2)	4331(4)	764(21)
C36	7823(5)	5455(2)	4218(3)	580(16)
N41	8638(3)	3710(1)	3217(2)	357(9)
N42	7797(3)	3256(1)	3011(2)	380(10)
C43	8662(4)	2868(2)	2861(3)	490(15)
C44	29(4)	3058(2)	2954(3)	591(16)
C45	5(4)	3589(2)	3163(3)	474(13)
C46	8129(6)	2311(2)	2648(4)	782(23)
C47	1148(4)	3991(2)	3294(3)	620(17)
O5	3828(2)	4713(1)	2767(1)	368(8)
C51	3995(4)	5238(1)	3121(2)	418(12)
C52	3938(5)	5286(2)	3980(3)	605(16)
C53	4024(6)	5797(3)	4344(4)	858(25)
C54	4149(6)	6232(3)	3843(5)	959(26)
C55	4208(6)	6181(2)	3005(4)	831(25)
C56	4131(5)	5671(2)	2604(3)	587(16)
N61	4128(3)	3835(1)	2106(2)	313(8)
N62	4633(3)	3328(1)	2364(2)	368(9)
C63	3778(4)	2983(2)	1871(2)	461(12)
C64	2736(4)	3254(2)	1297(2)	466(13)
C65	2968(4)	3792(1)	1444(2)	380(11)
C66	3963(6)	2392(2)	1972(3)	771(20)
C67	2183(4)	4266(2)	1021(4)	506(13)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*b_j^*\vec{a}_i\cdot\vec{b}_j$.

Results and Discussion

Synthesis. The geminal bis(dmp)phosphazene $N_3P_3(MeNCH_2CH_2O)_2(dmp)_2$ (**1**) is obtained from the reaction of $N_3P_3(MeNCH_2CH_2O)_2Cl_2$ with dmpH in the presence of triethylamine.[1] *cis*-$N_3P_3(OPh)_4(dmp)_2$ (**2**) has been synthesized by the reaction of a *cis* and *trans* mixture of $N_3P_3(OPh)_4Cl_2$ with dmpH in the presence of triethylamine in boiling toluene followed by fractional crystallization of the product from petroleum ether–benzene. The yield of **2** is only 17%. It has the lowest melting point (115 °C) among a dozen (pyrazolyl)cyclophosphazenes which are hitherto known and which have melting points of >200 °C. Compound **2** has been characterized by CHN elemental analyses and by NMR spectroscopy. The *cis* disposition of the pyrazolyl substituents has been established by X-ray crystallography.

The reactions of **1** and **2** with palladium chloride in boiling acetonitrile give the complexes [$PdCl_2$·(**1**)] (**3**) and [$PdCl_2$·(**2**)] (**4**) in good yields (73 and 80%, respectively) (Scheme I). In these complexes the two pyrazolyl pyridinic nitrogen atoms are

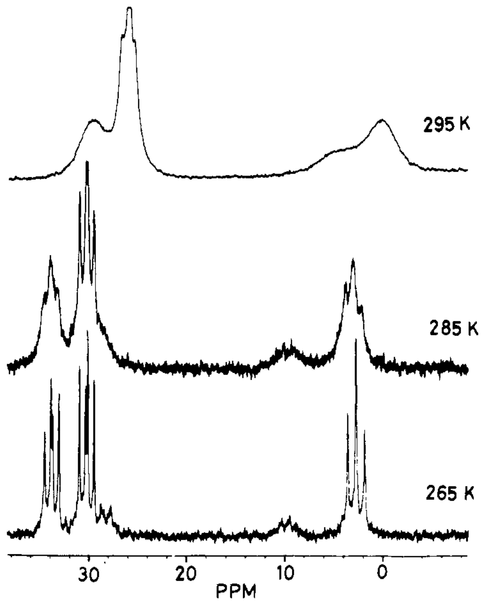
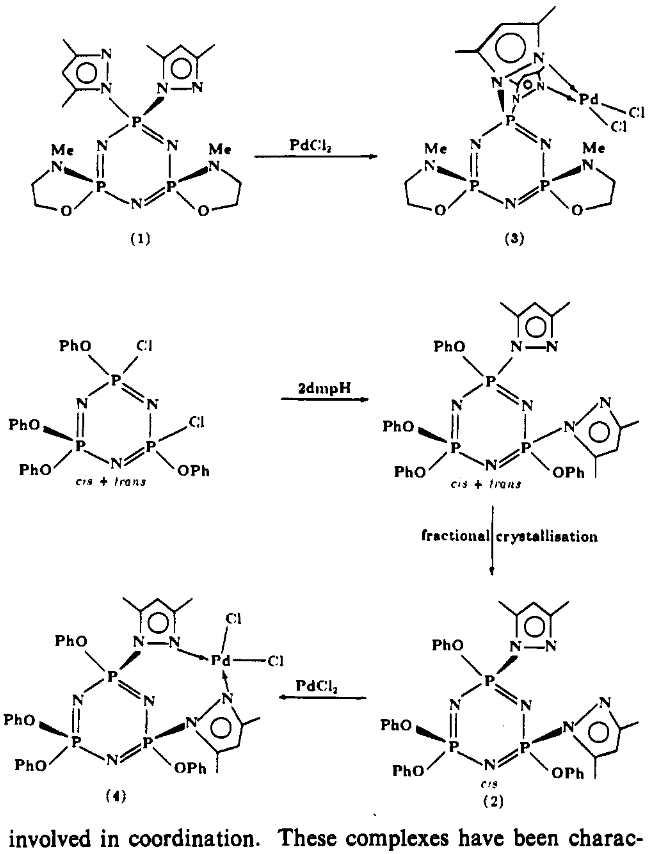


Figure 1. Variable-temperature ^{31}P NMR spectrum of 3.

Scheme I



involved in coordination. These complexes have been characterized by CHN elemental analyses and by ^1H and ^{31}P NMR spectroscopic data. The structure of 4 has been confirmed by single-crystal X-ray diffraction.

NMR Spectroscopy. The ^1H and ^{31}P NMR spectroscopic data for the ligands and their complexes are given in Table IV. The ^{31}P NMR spectrum[1] of 1 shows an A_2X pattern with resonances at 31.2 (A) and 6.0 (X) ppm with a $^2J_{PP}$ coupling constant of 68 Hz. The ^{31}P NMR spectrum of 3 at 295 K shows broad resonances around 33.1, 30.1, and 4.5 ppm; below 265 K, the spectrum changes to a sharp ABX pattern with chemical shifts of 33.4 (A), 30.2 (B), and 2.0 (X) ppm. The spectra recorded at various temperatures are shown in Figure 1. Evidently, the two phosphorus nuclei bearing the spiro rings are not equivalent. The downfield resonance can be assigned to the phosphorus closer to the metal. The coupling constants of the $P(dmp)_2$ phosphorus with P(B) is 73 Hz and with P(A) is 67 Hz. This difference in coupling constant suggests that there is an interaction between the ring nitrogen flanking the $P(dmp)_2$ and P(A) phosphorus atoms and the metal. The ^1H NMR spectrum of 3 shows broad resonances at ambient temperature which could not be fully resolved even at 211 K. The chemical shifts are close to those obtained for the molybdenum and tungsten tricarbonyl complexes[1] of 1. A possible reason for this fluxional behavior is discussed later.

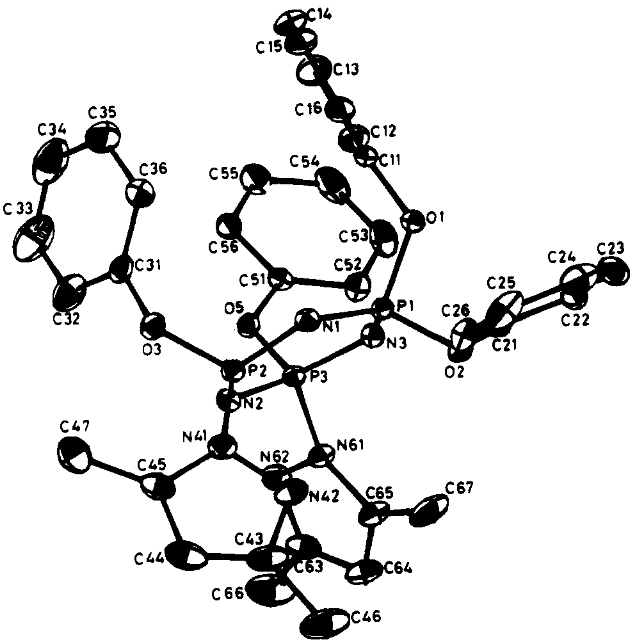


Figure 2. ORTEP diagram of *cis*-$N_3P_3(OPh)_4(dmp)_2$ (2).

Unlike the ^1H and ^{31}P NMR spectra of 3, its ^{13}C NMR spectrum shows sharp lines even at ambient temperature.[8] All the carbon nuclei of the pyrazolyl substituents are deshielded in the complex as compared to the ligand. The OCH_2 and NCH_2 carbon atoms of the two *N*-methylethanolamino groups are nonequivalent.

The ^{31}P NMR spectrum of 2 shows a single broad resonance centered at 6.3 ppm. There is thus an accidental coincidence of the ^{31}P chemical shifts of $P(OPh)_2$ and P(OPh)(dmp) phosphorus nuclei.[9] However, the spectrum of 4 shows an AB_2 pattern with chemical shifts of 5.4 and 4.4 ppm and a coupling constant of 81 Hz. In contrast to the slight shielding of the phosphorus nuclei upon complexation, the chemical shifts of the pyrazolyl group protons of complex 4 were deshiedled appreciably compared to the corresponding values of the ligand.

Crystal Structures of 2 and 4. Perspective views of the structures of 2 and 4 along with the numbering scheme are shown in Figures 2 and 3, respectively. Selected bond lengths and bond angles are given in Table V.

The crystal structure of 2 shows that the two pyrazolyl groups are on the same side of the P_3N_3 ring (*cis* orientation). The structural features are very similar to those observed for $N_3P_3(OPh)_6$.[11] As observed in the structure of 1,[1] there is not much change in the phosphazene ring shape or its dimensions as a result of the introduction of the pyrazolyl groups.

The P–N bond lengths within the P_3N_3 ring lie in a narrow range (1.577(2)–1.586(2) Å), and the exocyclic P–N(dmp) bond

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(8) This observation indicates that the rate of the fluxional process is between the time scales associated with ^{31}P and ^{13}C NMR.

(9) The chemical shifts of $P(OPh)_2$ and $P(dmp)_2$ phosphorus in cyclophosphazenes lie in the ranges 6.3 to 8.3 and –6.1 to 6.0 ppm, respectively.[10]

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Table IV. ^1H and ^{31}P NMR Data for the Complexes (**3** and **4**) and Ligands (**1** and **2**) (δ, ppm; *J*, Hz)

compd	NMe	*J*(PH)	NCH_2	OCH_2	CH_3(dmp)	CH(dmp)	P(A)	P(B)	P(X)	*J*(AB)	*J*(AX)	*J*(BX)
1	2.62	12	3.3 (m)	4.3 (m)	2.36, 2.21 2.17, 2.08	5.88, 5.87	31.2		6.0[a]		68	
3	2.71; 2.67	br; br	3.8; 3.4	4.8; 4.3	2.57, 2.53	5.96, 5.93						
3[b]	2.83; 2.77		3.8; 3.4	4.6; 4.3	2.65, 2.62 2.58, 2.52	6.03, 5.98[c]	33.4[d]	30.2	2.0[a]	48	67	73
2[e]					2.23, 2.19	5.80	6.3[f]					
4[g]					3.02, 2.51	6.05	5.4	4.4		81		

[a] *P*$(dmp)_2$ phosphorus. [b] ^1H at 220 K and ^{31}P at 211 K. [c] Both doublets (*J* = 4 Hz). [d] Resonance for the phosphorus near the coordination site. [e] Phenyl protons appear in the range 7.24–6.86 ppm. [f] Broad resonance. [g] Phenyl protons appear in the range 7.5–6.2 ppm; the ^{31}P NMR spectrum is of A_2B type.

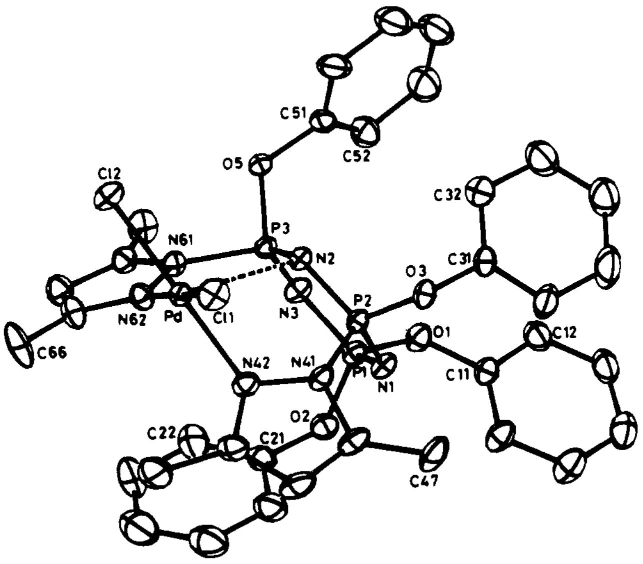

Figure 3. ORTEP diagram of $[PdCl_2\cdot\{cis\text{-}N_3P_3(OPh)_4(dmp)_2\}]$ (**4**).

Table V. Selected Bond Distances (Å) and Bond Angles (deg) Involving Non-Hydrogen Atoms of **2** and **4**

	dist			dist	
atoms	**2**	**4**	atoms	**2**	**4**
P1–N1	1.585(2)	1.574(3)	P2–N41	1.691(2)	1.702(3)
P1–N3	1.580(2)	1.580(3)	N2–P3	1.581(2)	1.574(3)
P1–O1	1.585(2)	1.586(2)	P3–N3	1.586(2)	1.575(3)
P1–O2	1.580(2)	1.573(3)	P3–O5	1.582(2)	1.582(2)
N1–P2	1.585(2)	1.578(3)	P3–N61	1.678(2)	1.705(3)
P2–N2	1.577(2)	1.584(3)	O2–C21	1.420(2)	1.396(5)
P2–O3	1.569(2)	1.569(2)	O3–C31	1.397(3)	1.426(4)
Pd1–Cl1		2.277(1)	Pd1–N42		2.060(3)
Pd1–Cl2		2.282(1)	Pd1–N62		2.051(3)

	angle			angle	
atoms	**2**	**4**	atoms	**2**	**4**
O1–P1–O2	97.7(1)	99.9(1)	P1–N3–P3	122.4(2)	122.0(2)
N1–P1–N3	116.9(1)	116.9(2)	P1–O1–C11	123.4(2)	119.5(2)
P1–N1–P2	122.1(1)	123.0(2)	P1–O2–C21	122.8(2)	127.1(2)
N1–P2–N2	117.9(1)	117.9(2)	P2–O3–C31	128.7(2)	120.7(2)
O3–P2–N41	102.3(1)	98.2(2)	P2–N41–N42	118.9(2)	119.1(2)
P2–N2–P3	121.5(2)	120.7(2)	P3–O5–C51	120.1(2)	122.6(2)
N2–P3–N3	117.6(2)	118.7(2)	P3–N61–N62	111.7(2)	122.6(3)
O5–P3–N61	97.6(1)	96.9(2)			
N42–Pd1–N62		95.4(1)	Cl1–Pd1–Cl2		90.95(5)
Cl2–Pd1–N42		176.8(1)	Pd1–N42–N41		121.7(2)
Cl1–Pd1–N62		175.3(1)	Pd1–N62–N61		126.2(2)

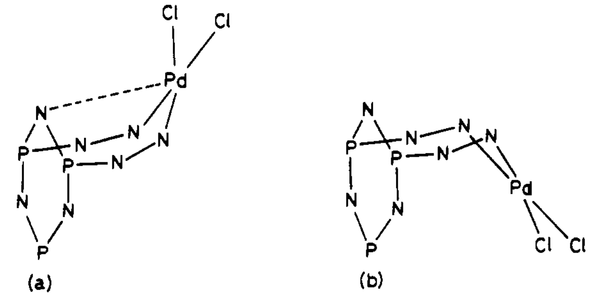

Figure 4. The two possible [(a) boatlike and (b) chairlike] conformations for the eight-membered chelate ring of **4**. Only the phosphazene ring and chelate ring atoms are shown.

lengths are longer (1.678(2), 1.691(2) Å). The ring angles at P span a narrow range (1.0°); so do the angles at nitrogen (0.9°). In contrast, the exocyclic angles at the phosphorus atoms differ considerably (97.7(1), 102.3(1), 97.6(1)°). Though the substituents at P2 and P3 are the same, the angles at these phosphorus atoms deviate by 4.7°. In $N_3P_3(OPh)_6$, a difference of 6.0° is observed in the exocyclic angles at the phosphorus atoms.[11] These deviations can be attributed to the relative orientations of the phenoxy and pyrazolyl groups. The phosphazene ring is almost planar, with a maximum deviation of 0.15 Å for N3, which is comparable to that of $N_3P_3(OPh)_6$ (maximum deviation is 0.17 Å).[11]

The phosphazene ring P–N bond lengths in **4** vary over a narrow range (1.574(3)–1.584(3) Å) and are close to those of the ligand. Evidently, the phosphazene ring is not affected appreciably as a result of complexation. The exocyclic P–N bond lengths are 1.702(3) and 1.705(3) Å, which are slightly longer (~0.02 Å) when compared to those of ligand **2**. The exocyclic angle at the phosphorus atoms, unlike in the lignad, lie in a narrow range (96.9–99.9°) presumably because the orientations of the pyrazolyl groups are restricted as a result of chelation. The phosphazene ring in complex **4** is nearly planar, more so than that in the ligand **2**; the sum of moduli of ring torsion angles in **4** is 35.1° whereas in **2** it is 47.8°.

The geometry around the metal in **4** is nearly planar; one of the pyrazolyl nitrogen (N62) atoms deviates from planarity by 0.12 Å. The Pd–Cl and Pd–N distances are similar. The Cl–Pd–Cl angle is close to 90°, but the N–Pd–N angle is 95.4(1)°, which can be attribted to the formation of an eight-membered chelate ring. The eight-membered chelate ring has a nearly saddle type conformation, with the phosphazene ring nitrogen (N2) and the metal deviating from the mean plane formed by the other six atoms by 0.75 and 1.39 Å, respectively (see Figure 4a).

The Phosphazene Ring Nitrogen–Metal Interaction. The distance between the metal and the phosphazene ring nitrogen (N2) in **4** is 2.86 Å, which is much less than the sum of van der Waals radii of Pd (2.1 Å) and N (1.5 Å). There are two possible orientations for the eight-membered ring—a boatlike (saddle) form in which the metal is close to the phosphazene ring nitrogen (N2) or a chairlike conformation in which the metal is far from N2 (Figure 4). The observed boatlike conformation (Figure 4a) suggests that the Pd--N2 short contact might be energetically favored.

In contrast to complex **4**, the $PdCl_2$ complexes of **1** and $N_3P_3Ph_4(dmp)_2$ contain six-membered chelate rings. The ^1H, ^{13}C, and ^{31}P NMR spectral data for the complexes show the nonequivalence of the two phosphorus nuclei not bearing the pyrazolyl groups. Also, in the ^{31}P NMR spectra, the coupling constant involving the *P*$(dmp)_2$ phosphorus and one of the other phosphorus atoms is much less than the coupling constant involving third phosphorus. These data are similar to the features observed for the molybdenum–tricarbonyl complexes of the corresponding ligands in which a phosphazene ring nitrogen is also coordinated to the metal.[1] Since the phosphazene ring nitrogen atoms of **1** are more basic than those of **2** (in view of the greater electron-releasing ability of amino substituents), a stronger ring nitrogen–metal interaction can be envisaged in **3**. The fluxional process revealed by ^{31}P NMR studies of **3** may be attributed to an equilibrium between a four- and a five-coordinated species in solution. A definite conclusion regarding the phosphazene ring nitrogen–metal interaction must await structural studies on a series of palladium chloride complexes of *gem*-bis(pyrazolyl)-cyclophosphazenes with varying basic character of the phosphazene ring nitrogen atoms.

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Supplementary Material Available: Tables of crystallographic data, hydrogen coordinates and isotropic thermal parameters, and anisotropic thermal parameters, bond lengths and bond angles for non-hydrogen atoms of **2** and **4** (10 pages). Ordering information is given on any current masthead page.