# 1-Pyrazolyl phosphazenes and their complexes with palladium(II) chloride and platinum(II) chloride

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The chlorophosphazenes $(NPCl_2)_{3-6}$ and the phenylchlorophosphazenes *gem*-$N_3P_3Ph_4Cl_2$ and *gem*-$N_3P_3Ph_2Cl_4$ react with pyrazole, 3-methylpyrazole, and 3,5-dimethylpyrazole to give $(NPpz_2)_{3-6}$, $[NP(Mepz)_2]_{3-5}$, $[NP(Me_2pz)_2]_{3,4}$, $N_3P_3Ph_4(Mepz)_2$, $N_3P_3Ph_4(Me_2pz)_2$, and $N_3P_3Ph_2(Me_2pz)_4$. Infrared and nmr spectroscopy show the pyrazolyl group to be an electron-withdrawing substituent on the phosphazene ring, resembling a halogen rather than an amino-group. The pyrazolyl group also acts as a donor through its pyridinic nitrogen atom, both intramolecularly and in the formation of the complexes *gem*-$N_3P_3Ph_4(Me_2pz)_2 \cdot PdCl_2$, *gem*-$N_3P_3Ph_2(Me_2pz)_4 \cdot PdCl_2$, $N_3P_3(Me_2pz)_6 \cdot 2PdCl_2$, $N_3P_3(Me_2pz)_6 \cdot 2PtCl_2$, and $N_3P_3(Me_2pz)_6 \cdot 3PdCl_2$. No bonding between the metal and a nitrtogen atom in the ring was detected.

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Les chlorophosphazènes $(NPCl_2)_{3-6}$ et les phénylchlorophosphazènes *gem*-$N_3P_3Ph_4Cl_2$ et *gem*-$N_3P_3Ph_2Cl_4$ réagissent avec le pyrazole, le méthyl-3 pyrazole et le diméthyl-3,5 pyrazole pour donner les composés suivants: $(NPpz_2)_{3-6}$, $[NP(Mepz)_2]_{3-5}$, $[NP(Me_2pz)_2]_{3,4}$, $N_3P_3Ph_4(Mepz)_2$, $N_3P_3Ph_4(Me_2pz)$ et $N_3P_3Ph_2(Me_2pz)_4$. La spectroscopie infrarouge et la RMN montrent que le groupe pyrazolyle est un substituant électroattracteur du cycle phosphazène ressemblant plutôt à un halogène qu'à un groupe amino. Le groupe pyrazolyle agit également comme donneur par l'intermédiaire de son atome d'azote à la fois de façon intramoléculaire et lors de la formation des complexes *gem*-$N_3P_3Ph_4(Me_2pz)_2 \cdot PdCl_2$, *gem*-$N_3P_3Ph_2(Me_2pz)_4 \cdot PdCl_2$, $N_3P_3(Me_2pz)_6 \cdot 2PdCl_2$, $N_3Pe(Me_2pz)_6 \cdot 2PtCl_2$ et $N_3P_3(Me_2pz)_6 \cdot 3PdCl_2$. On n'a pas décelé de liaison entre le métal et l'atome d'azote dans le cycle.

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## Introduction

The phosphazene ring normally acts as an acceptor to substituent groups with unshared electrons. The electron transfer from such ligands as the dimethylamido-group shortens the exocyclic bonds, makes the phosphorus atom to which they are attached less electrophilic, and accentuates the donor properties of the nitrogen atoms in the phosphazene ring. The properties of the pyrazolyl group as a substituent (Fig. 1*a*) are different, in that the formally unshared electrons on nitrogen form part of the aromatic sextet, and their reduced availability for transfer to the phosphazene ring is diminished still further by an adjacent pyridinic nitrogen atom, which is more electronegative than carbon. The same conclusion applies to other heteroaromatic rings, and the validity of the basic concepts is confirmed by a study of the rates of hydrolysis of *N*-acylazoles (1), which increase both with the number of nitrogen atoms in the ring and with their separation, as expected theoretically.

One object of the present work was to compare the general properties of the pyrazolylphosphazenes with those of other phosphazene series, so as to clarify the electronic interactions between azole and phosphazene rings. A second object was to examine their coordination behaviour, to see how far the concentration of charge within the azole ring might shift the donor site from the phosphazene ring to the exocyclic groups. Among heteroaromatic rings, pyrazole is particularly appropriate, because of the stability conferred by chelation in its most usual coordination (Fig. 1*b*). We give below details of the preparation of the series of 1-pyrazolylphosphazenes shown in Fig. 2. The complexes *gem*-$N_3P_3Ph_4(Me_2pz)_2 \cdot PdCl_2$ (**7***a*) and *gem*-$N_3P_3Ph_2(Me_2pz)_4 \cdot PdCl_2$ (**7***b*) were prepared from $PdCl_2$ and **6***b* and **5** respectively, **1***c* gave $N_3P_3(Me_2pz)_6 \cdot 2PtCl_2$ (**8***b*) with $PtCl_2$ and $N_3P_3(Me_2pz)_6 \cdot 2PdCl_2$ (**8***a*) and $N_3P_3(Me_2pz)_6 \cdot 3PdCl_2$ (**9**) with $PdCl_2$. The spectroscopic results confirm the conclusion of a preliminary report (2), and show (*i*) that the pyrazolyl group is an electron-withdrawing substituent, and (*ii*) that coordination occurs exclusively at the pyrazolyl groups, as in Fig. 1*b*.

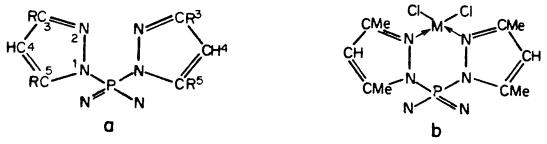


FIG. 1. (*a*) Numbering scheme of pyrazolyl group L. (*b*) Coordination scheme.

## Results and Discussion

All the pyrazolylphosphazenes are crystalline

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TABLE 1. Nuclear magnetic resonance parameters[a] and vibrational frequencies[b] of pyrazolylphosphazenes

| Compound | ν(P=N) (cm$^{-1}$)[j] | Proton shifts, $\delta_H$ (ppm) R(3) | H(4)[c] | R(5) | Coupling constants (Hz) $J_{3,4}$ | $J_{4,5}$ | $\delta_P$ (ppm)[i] |
|---|---|---|---|---|---|---|---|
| pzH[d] | — | 7.61 | 6.31 | 7.61 | 1.9 | 1.9 | — |
| **1***a*[k] | 1238 | 7.82[c] | 6.37 | 8.04 | 1.5 | 1.9 | −111.9 |
| **2***a*[e] | 1428 | 7.75[c] | 6.28 | 8.49 | 1.4 | 2.8 | −137.8 |
| **3***a* | 1425, 1447 | 7.56[c] | 6.18 | 8.22 | 1.5 | 2.7 | −137.1 |
| **4***a*[f] | 1356 | 7.61[c] (7.52)[g] | 6.21 (6.24) | 8.06 (7.52) | 1.5 (2.1) | 2.9 (2.1) | −136.9 |
| MepzH[d] | — | 2.32 | 6.06 | 7.48 | — | 1.7 | — |
| **1***b*[k] | 1234 | 2.22 | 6.10 | 7.90 | — | 2.8 | −112.8 |
| **2***b* | [h] | 2.21 | 6.02 | 8.34 | — | 2.7 | −137.6 |
| **3***b* | [h] | 2.13 | 5.98 | 8.21 | — | 2.6 | −137.2 |
| $Me_2$pzH[d] | — | 2.21 | 5.76 | 2.21 | — | — | — |
| **1***c*[k] | 1228 | 2.09 | 5.81 | 2.19 | — | — | −114.3 |
| **2***c* | [h] | 2.02 | 5.67 | 2.16 | — | — | −131.1 |

[a]Dilute solutions in $CDCl_3$, $\delta_H$, internal TMS, $\delta_P$, negative shifts to high field of external $P_4O_6$.
[b]From mulls in Nujol or hexachlorobutadiene.
[c]$J_{PH} < 1.0$ Hz.
[d]Reference 3.
[e]$J_{3,5} \sim 0.5$ Hz.
[f]$J_{3,5} \sim 0.7$ Hz.
[g]Parenthesised numbers refer to solution in $CCl_4$.
[h]Obscured.
[i]Cf. $\delta_P$ for $(NPF_2)_{3,4}$ = −98.6, −129.5 (4), $(NPCl_2)_{3,4}$ = −92.5, −119.5 (5), $(NPBr_2)_{3,4}$ = −162.0, −184.3 (6), $[NP(NMe_2)_2]_{3,4}$ = −87.7, −102.9 (7), $(NPMe_2)_{3,4}$ = −80.6, −86.2 (8).
[j]Cf. ν(P=N) for $(NPF_2)_{3,4}$ = 1305, 1425/1445 (32), $(NPCl_2)_{3,4}$ = 1218, 1315 (33), $(NPBr_2)_{3,4}$ = 1126/1175, 1272 (6), $[NP(NMe_2)_2]_{3,4}$ = 1195, 1265 (34), $(NPMe_2)_{3,4}$ = 1180, 1220 (9).
[k]Pyrazole ring frequency almost independent of ring size of phosphazene: **1***a*–**4***a*, ~ 1520; **1***b*–**3***b*, ~ 1540; **1***c*, **2***c*, ~ 1570 cm$^{-1}$.

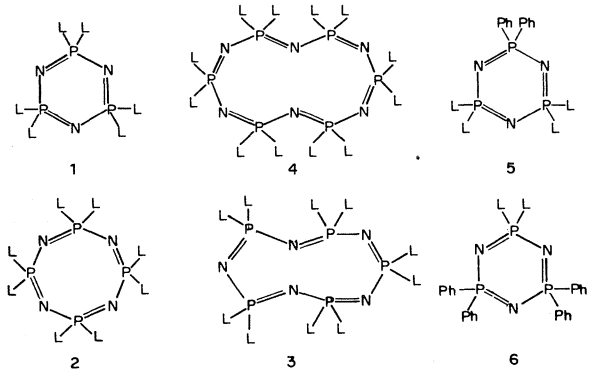



FIG. 2. L is the pyrazolyl group (Fig. 1*a*); **1***a*–**4***a*, $R^3 = R^5 =$ H; **1***b*–**3***b*, **6***a*, $R^3$ = Me, $R^5$ = H, **1***c*, **2***c*, **5**, **6***b*, $R^3 = R^5$ = Me. The following abbreviations are used throughout: pz = 1-pyrazolyl, Mepz = 1-(3-methylpyrazolyl), $Me_2$pz = 1-(3,5-dimethylpyrazolyl).

white solids, that either melt or decompose above 200°C. They are stable to moist air, insoluble in acetonitrile and acetone, increasingly soluble (especially the methyl derivatives) in tetrahydrofuran, diethyl ether, benzene, and chloroform. The pyrazolylphenylphosphazenes are soluble in aromatic solvents.

Spectroscopic information on **1**–**6** is given in Tables 1 and 2. The proton nmr spectra show that the pyrazolyl groups on a particular phosphorus atom are magnetically equivalent. The 3- and 5-positions are differentiated. If $R^3$ and $R^5$ are identical, and contain protons which couple to $H^4$, $R^5$ is identified through the larger coupling constant $J_{4,5}$, arising from the greater double bond character of $C^4$—$C^5$. In the series **1***a*–**4***a*, the order H(5) > H(3) > H(4) for $\delta_H$ was confirmed by comparing the $^{31}$P-decoupled spectra to those of the corresponding methylpyrazolyl compounds (Table 1). The same order is found in $Ppz_3$ and $PhPpz_2$ (11); in $(Me_2N)_2Ppz$ (12) the H(3) resonance is at low field. The methyl signals themselves appear as sharp singlets. The lower-field methyl resonance in **1***c*, **2***c* is arbitrarily assigned to Me(5) by analogy with **1***a*–**4***a*. The peak separation $\Delta = \delta_H R(5) - \delta_H R(3)$ varies with solvent and temperature. Some typical results for **5** are shown in Table 3. Similar phenomena are observed in the spectra of (trimethylsilyl)pyrazoles (13) and in phosphino- and phosphinato-azoles (11). In the former, an intramolecular migration of the $Me_3Si$ group has been suggested to account for the coalescence of the 3- and 5-substituent resonances upon increasing the temperature. The behaviour of the pyrazolylphosphazenes is evidently different, because the coalescence is unsymmetrical, and in $CCl_4$ the bands separate when the temperature is increased. The significantly larger separations found for aromatic

TABLE 2. Nuclear magnetic resonance parameters[a] and vibrational frequencies[b] of phenylpyrazolylphosphazenes

| Compound | ν(P=N) (cm$^{-1}$) | Proton shifts $\delta_H$ (ppm) | | | Phosphorus: $\delta_P$ (ppm) | | J(PP) (Hz) |
|---|---|---|---|---|---|---|---|
| | | R(3) | H(4) | R(5) | $Ppz_2$ | $PPh_2$[e] | |
| **5** | 1219, 1231 | 2.04 | 5.77 | 2.11 | −115.8 | −90.6 | 25 |
| **6***b*[c] | 1214–1224 | 2.12 | 5.81 | 2.18 | −117.5 | −94.1 | 19.9 |
| **6***a*[d] | 1212, 1188 | 2.28 | 6.04 | 7.88 | −118.4 | −93.2 | 19.9 |

[a]Dilute solutions in $CDCl_3$, $\delta_h$, internal TMS, $\delta_P$, negative shifts to high field of external $P_4O_6$.
[b]From mulls in Nujol or hexachlorobutadiene.
[c]$J_{PH(4)}$ = 2.8 Hz.
[d]$J_{PH(4)}$ = 2.7 Hz; $J_{PH(5)}$ = 1.7 Hz, $J_{H(4)H(5)}$ = 2.7 Hz.
[e]Cf. −98.2 ppm in $N_3P_3Ph_6$ (10).

TABLE 3. Peak separation Δ (Hz) of **5** in different solvents[a]

| $CDCl_3$ | | $C_6H_5NO_2$ | | $C_6D_5CD_3$ | | $CS_2$ | | $CCl_4$ | |
|---|---|---|---|---|---|---|---|---|---|
| *T* | Δ | *T* | Δ | *T* | Δ | *T* | Δ | *T* | Δ |
| −30 | 14 | Amb | 19.5 | Amb | 27 | −75 | 3.3 | Amb | 0 |
| Amb | 7.0 | 50 | 20.5 | | | Amb | 0 | 55 | 3.2 |
| 55 | 4.5 | 70 | 21.4 | | | | | 70 | 4.4 |

[a]Amb for ambient.

solvents is probably a result of the interaction of the induced magnetic fields of the solvent and the pyrazole ring.

The $^{31}P$ chemical shifts (Table 1) vary with ring size in qualitatively the same way as in other phosphazene series; shielding is greater in the tetramer than in the trimer, and is greater for compounds with the more electronegative ligands. A similar statement applies to $\nu_{as}$ (P=N). Both criteria suggest that the pyrazolyl group resembles the more electronegative ligands F, Cl, Br, in withdrawing electrons from the phosphazene ring, rather than the methyl- or dimethylamido-groups which release them. Table 2 shows that the introduction of $PPh_2$ groups increases the shielding of neighbouring $Ppz_2$ groups, as expected.

The mass spectra of the trimeric pyrazolyl derivatives are similar to those of the halogen-derivatives, in that the parent ion is dominant; the appearance of metastable peaks shows that $R_2pz$ groups are lost consecutively. The significant difference is that the intensity of the parent peak of the pyrazolyls decreases rapidly with increase in ring size; no parent ion was found in the spectrum of **4***a* (Fig. 3). It is probable that the transannular attack, suggested as an explanation for the formation of $N_3P_3$ fragments from $N_6P_6Cl_{12}$ (14), would be facilitated by the good donor properties of the pyrazolyl groups. A similar interaction could account for the low yield obtained in the preparation of the pyrazolylphosphazenes, as discussed below.

All the pyrazolylphosphazenes, **1–6** were prepared from the chlorophosphazene and an excess of the pyrazole in THF or benzene, triethylamine

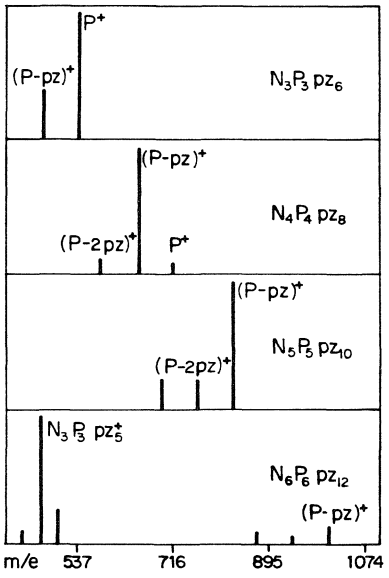
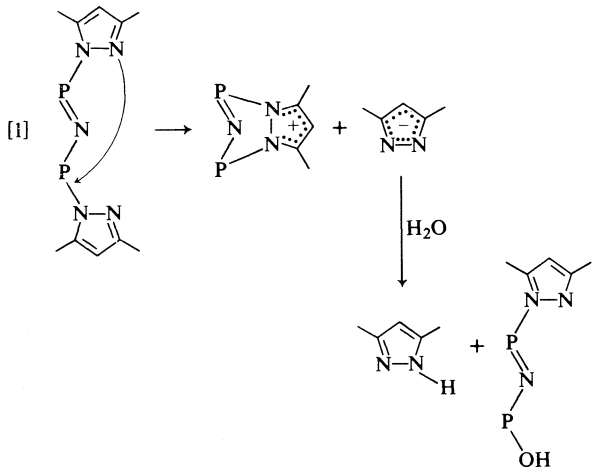



FIG. 3. The mass spectra of **1***a*–**4***a*. The mass numbers of the parent ions are marked; the individual base peaks are given the same intensity. Fragments less abundant than 5% of the base peak are omitted.

being used as an acceptor for hydrogen chloride. Triethylamine hydrochloride was precipitated almost quantitatively, and was variably contaminated by unidentified by-products. The yields of pyrazolylphosphazenes were also variable. They decreased with increase in the size of the phosphazene ring, and with the excess of the pyrazole and triethylamine; broadly speaking, by those changes in reaction conditions which would facilitate parasitic attack of a pyrazolyl group, free or combined, on phosphorus. In agreement, and with the exception of the trimeric derivatives (in which the ring is too small to allow transannular attack), methylation of the pyrazole ring also reduces the yield. Within the same molecule (reaction [1]), nucleophilic attack is made easier by an increase in electron density at the pyridinic nitrogen atom, the greater flexibility of the larger rings, and the partial




positive charge on phosphorus induced by the substituent. A similar intermolecular reaction is clearly also possible; either would account for the large amounts of $Me_2pzH$ and MepzH recovered (with near-quantitative formation of $Et_3N{\cdot}HCl$) in their reactions with $(NPCl_2)_{5,6}$. In the later stages of this investigation, it was found that benzene was a better solvent than tetrahydrofuran, in that smaller amounts of by-products were formed and yields were improved. Such compounds as $[NP(Me_2pz)]_5$ could probably be obtained by using it.

The reaction appears to resemble that of catechol with the chlorophosphazenes (15), in which, also, the precipitation of $Et_3N{\cdot}HCl$ in high yield is accompanied by ring degradation; in this case no cyclic derivative of larger size than the trimer could be obtained. No such difficulties are found with the reaction of the phenylchlorophosphazenes with the pyrazoles, in which the reactivity of $PCl_2$ groups to nucleophiles is drastically reduced. The reactions of *gem*-$N_3P_3Ph_2Cl_4$ and *gem*-$N_3P_3Ph_4Cl_2$ are slow, those of the latter especially so, but by-products are absent and the yields are excellent.

The chemical properties of the pyrazolylphosphazenes are consistent with the general concepts developed above. As reported earlier (2), and confirmed here for **2***b*, they are cleaved by HCl more easily than are the dimethylamidophosphazenes, but qualitatively appear to be more stable to hydrolysis than is the trimeric imidazolide $N_3P_3Im_6$ (16); similarly, *N*-acetylimidazole is hydrolysed faster than *N*-acetylpyrazole (1). Since, also, pyrazolylphosphines are hydrolysed faster than are pyrrolylphosphines (17), it is likely that the first stage in the reaction is the protonation of the pyridinic nitrogen (16, 17). For the pyrazolylphosphazenes, its completion is aided by both the induced partial positive charge on phosphorus, and the slight extension (relative to dimethylamidophosphazenes) of the exocyclic P—N bond (2).

The donor sites of phosphazenes are almost always the nitrogen atoms in the ring, whether the acceptor group is a proton (18) or a metal ion (19), even when the use of other sites might reduce steric strain (20). Exceptionally, quaternisation of dimethylamidophosphazenes can occur exocyclically (21), and one tungsten carbonyl complex is known in which the metal is bound to ring and exocyclic nitrogen atoms (22). The structures of the five complexes reported here (Fig. 4) have been established spectroscopically, the numerical detail being given in Table 4.

The low electrical conductivities of **7***a*, *b*; **8***a*, *b* in nitromethane reported in the Experimental part show that ionisation plays no important part in determining the stereochemistry. The ν(Pd—Cl) frequencies in **7***a*, **7***b* are assigned to the $A_1$ (sym) and $B_1$ (asym) vibrations of a *cis*-coordinated $PdCl_2$ group of symmetry $C_{2v}$, by comparison with the spectra of *cis*-$PdCl_2(py)_2$ (23), *cis*-$PdCl_2(im)_2$ (24), and *cis*-$PdCl_2(Me_2pzH)_2$ (25), and the broad lines found in the spectra of **8***a*, **8***b*, and **9** are also more in accord with this type of coordination than with a *trans*-configuration, for which a single sharp line would be expected. Coordination at the nitrogen atoms of the phosphazene ring of **7***a* is ruled out by the magnetic equivalence of the two $Me_2pz$ groups. The $^{31}P$ spectrum of **7***a* is of the ABX type, the two $PPh_2$ phosphorus atoms being distinguished. The molecule is therefore stereochemically rigid, in the form shown in Fig. 4; the more downfield $PPh_2$ resonance is assigned to the phosphorus atom $P_A$ closest to the $PdCl_2$ unit. Compound **7***b* introduces a new feature, in that it contains four pyrazolyl groups and coordination might occur at two pyrazolyl groups on the same, or different, phosphorus atoms. The $^1H$ nmr spectrum shows two sets of pyrazolyl groups, consistent with both possibilities. The ABX pattern of the $^{31}P$ spectrum excludes the second possibility, which would require an $A_2X$

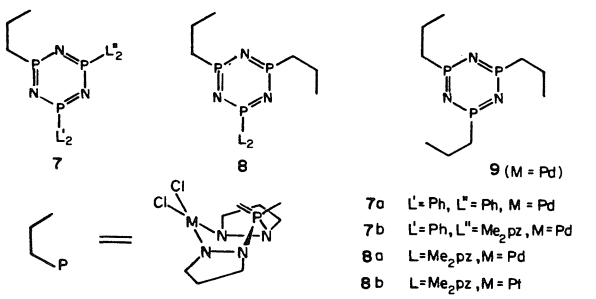



FIG. 4. Schematic stereochemistry of pyrazolylphosphazene complexes.

TABLE 4. Nuclear magnetic resonance parameters[a] and vibrational frequencies[b] of Pd and Pt complexes of pyrazolylphosphazenes

| Compound | ν(P=N) ($cm^{-1}$) | ν(M—Cl) ($cm^{-1}$) | Proton shifts $\delta_H$ (ppm)[c] H(4) | Me | Phosphorus shifts $\delta_P$ (ppm) $PPh_2$ | $P(Me_2pz)_2$ | $J_{PP}$(Hz)[d] |
|---|---|---|---|---|---|---|---|
| *7a* | 1230 | 325, 329 | 5.74 (~ 4.0) | 2.04[e] | $1P_A$, −93.0 | $1P_X$, − 122.7 | 0.0 (AB) |
| | 1197 | 341 | | 2.68 | $1P_B$, −95.0 | | 14.2 (AX) |
| | 1180 | | | | | | 27.3 (BX) |
| *7b* | 1200 | 332 | 5.83 (~ 4.0) | 2.16[f] | $1P_X$, −91.5 | $1P_A$, −113.8 | 49.7 (AB) |
| | 1246 | 347 | | 2.38 | | $1P_B$, −118.1 | 18.1 (AX) |
| | | | 6.02 (~ 4.0) | 2.70 | | | 32.7 (BX) |
| *8a* | 1212 | 344 br | 5.92 (4.8) | 2.05, 2.32 | | | |
| | 1225 sh | | 5.98 (4.0) | 2.35, 2.61 | | | |
| | | | 6.03 (4.8) | 2.63, 2.72 | | | |
| *8b* | 1212 | 344 br | 6.02 (5.0) | 2.10, 2.27 | | | |
| | 1225 sh | | 6.12 (5.0) | 2.35, 2.61 | | | |
| | | | | 2.63, 2.70 | | | |
| **9** | 1227 | 344 br | 6.19 br | 2.52, 2.73 | | 3P, −123.8 | |

[a] $CDCl_3$ or $CD_2Cl_2$ (**9**) solutions. Referred to internal TMS or external $P_4O_6$. Negative shifts to high field of reference.
[b] From Nujol mulls; br = broad.
[c] Coupling constants in parentheses.
[d] AX = $P_AP_X$, BX = $P_BP_X$, AB = $P_AP_B$.
[e] Cf. 1.93, 2.69δ in $PdCl_2(Me_2PzH)_2$ (25)
[f] Successive relative intensities 2:1:1.

pattern. The nmr evidence does not distinguish between the two isomers shown (Fig. 5).

Apart from the substitution of platinum for palladium, the empirical formulae of **8***a* and **8***b* are the same, and their $^1H$, $^{31}P$, and infrared spectra suggest that they are isostructural. The $^{31}P$-decoupled $^1H$ nmr spectrum of **8***a* shows six singlets of equal intensity in the methyl region and three singlets of equal intensity in the H(4) region, corresponding to three non-equivalent sets containing two $Me_2pz$ groups each. The $^{31}P$ nmr spectrum of **8***a* is of the ABC type (Fig. 6), which is uniquely consistent with the schematic stereochemistry of Fig. 4. If the boat-shaped complexed pyrazolyl groups were turned towards one another, the two sets of $Me_2pz$ groups would be magnetically equivalent; a doublet and a triplet would be seen in the $^{31}P$ spectrum, and there would be two resonances of intensity ratio 2:1 for H(4), and at most four methyl resonances.

The introduction of a third metal atom simplifies the spectra. The infrared spectrum of **9** is almost identical to that of the ligand, particularly in the region of 1200 $cm^{-1}$, where $\nu_{as}$(P=N) remains

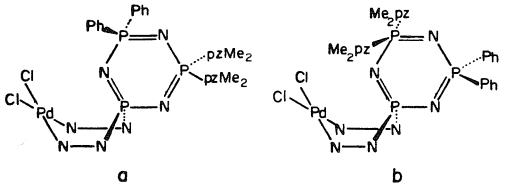



FIG. 5. Alternative structures of **7***b*.

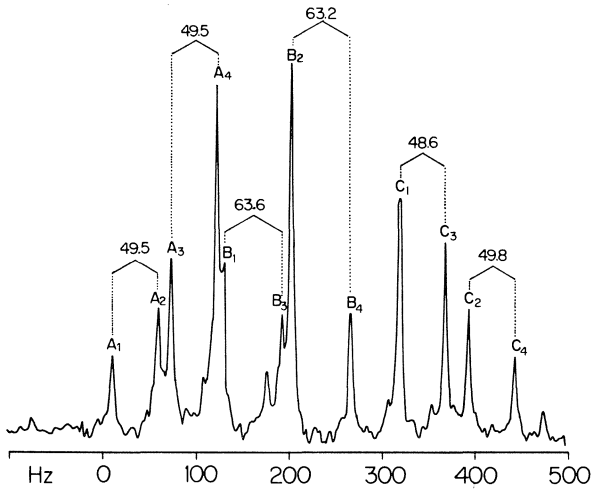



FIG. 6. The $^1H$-decoupled $^{31}P$ nmr spectrum of **8***a* (40.5 MHz, $CDCl_3$). Analysis, by method of ref. 35, in Table 4.

single, suggesting that the complex has a high symmetry. The symmetrical nature of the coordination is confirmed by the pair of singlets in the methyl region of the proton spectrum and by the singlet in the $^{31}P$ spectrum. The H(4) resonance remains as a broad unresolved band, in contrast to the observable couplings of ~ 4.0 Hz apparent in the spectra of the other palladium derivatives. The schematic stereochemistry is therefore that shown in Fig. 4.

We can conclude that in all the complexes, as in other pyrazolyl complexes of the same metals (26), the palladium or platinum has its normal square

planar coordination, that coordination occurs through two pyrazolyl groups on the same phosphorus atom, and that, where there is more than one coordination group in the same molecule, the boat-shaped groups are oriented in the same direction; successive addition of metal halides takes place in the sense **7** → **8** → **9** of Fig. 4. The infrared spectra show no evidence of additional coordination of the metal to the nitrogen atoms of the phosphazene ring, which would be expected to lower ν(M—Cl) by 15–20 $cm^{-1}$ (27). Such a lowering is in fact found in the complexes of **5** with $ZnCl_2$ and with $CoCl_2$, to be reported later in detail. The coordination chemistry of the Pd, Pt complexes confirms the spectroscopic results on the ligands, that the pyrazolyl group is an electronegative substituent on the phosphazene ring, which withdraws electron density sufficiently strongly to overcome the normal coordination properties of the phosphazene ring.

## Experimental

The chlorophosphazenes $(NPCl_2)_{3-6}$ (5) and the phenylchlorophosphazenes *gem*-$N_3P_3Ph_4Cl_2$ (28) and *gem*-$N_3P_3Ph_2Cl_4$ (29) were prepared as described in the literature. Pyrazole, 3-methylpyrazole, and 3,5-dimethylpyrazole (Aldrich) were purified by sublimation or distillation. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone, benzene and xylene from $LiAlH_4$, and dichloromethane from $P_2O_5$. Methanol was dried over 4A molecular sieves, and acetonitrile and triethylamine over $CaH_2$. Standard methods (30) were used to make *cis*-bis(benzonitrile)dichloroplatinum (II) and *trans*-bis(benzonitrile)dichloropalladium (II). The pyrazolylphosphazenes were dried at 110°C.

Infrared spectra, calibrated against polystyrene, were obtained from Nujol or hexachlorobutadiene mulls on CsI or polyethylene plates, using Perkin-Elmer 457 or 225 spectrophotometers. Mass spectra were recorded at 70 eV on Varian (Atlas) CH 4-B and (for compounds with m.w. > 1000) Kratos AEI MS-902 mass spectrometers. Nuclear magnetic resonance spectra were run on Varian XL-100 ($^1H$, 100 MHz; $^{31}P$, 40.5 MHz), HA-100 ($^1H$, 100 MHz), and Nicolet-Oxford H-270 ($^1H$, 270 MHz) spectrometers. Double resonance techniques were used for $^{31}P$–$^1H$ decoupling (31). Conductance measurements were made with a Wayne Kerr Universal Bridge, Model B221A on solutions in nitromethane, ~ $10^{-3}$ *M*.

*$N_3P_3(pz)_6$ (1a)*

A solution of pyrazole (1.62 g, 23.8 mmol, 25% excess) and triethylamine (2.11 g, 20.9 mmol, 10% excess) in 50 mL THF was added dropwise to a stirred solution of $N_3P_3Cl_6$ (1.10 g, 3.16 mmol) in 60 mL THF. After heating under reflux for 24 h, the white precipitate (3.32 g) was filtered off, and the part soluble in chloroform (2.50 g) was identified as $Et_3N{\cdot}HCl$ (96%). Some of the product (0.15 g) was crystallised from the concentrated and cooled filtrate. The solvent was removed, and the residual white solid was heated at 110°C/0.1 Torr for 2 h, to remove traces of $Et_3N{\cdot}HCl$ and the excess of pyrazole. Crystallisation from acetonitrile yielded a further 0.15 g, of **1***a* (total 18%) as colourless prismatic needles, decomp. 268°C. *Anal.* calcd. for $C_{18}H_{18}N_{15}P_3$: C 40.2, H 3.4, N 39.1; found: C 40.1, H 3.3, N 39.2.

*$N_4P_4(pz)_8$ (2a)*

In a similar but faster reaction, 1.06 g of $N_4P_4Cl_8$ gave $Et_3N{\cdot}HCl$ (2.30 g, 92%), insoluble by-products (1.318 g) and **2***a* (0.30 g, 20%), which was recrystallised from acetonitrile/1,2-dichloroethane; decomp. 361°C. *Anal.* found: C 40.6, H 3.3, N 39.4.

*$N_5P_5(pz)_{10}$ (3a)*

By a similar method, but with a reduced excess of pyrazole (10%) and triethylamine (5%), $N_5P_5Cl_{10}$ (3.89 g, 6.7 mmol) gave a clear colourless oil, which was dissolved in 100 mL 1:1 acetonitrile/toluene and passed through a column of alumina. Slow evaporation of the solvent yielded colourless crystals (2.71 g, 45%) of **3***a*; decomp. 249°C. *Anal.* found: C 40.5, H 3.4, N 38.8.

*$N_6P_6(pz)_{12}$ (4a)*

The reaction product from $N_6P_6Cl_{12}$ (2.13 g, 3.1 mmol) was crystallised from acetonitrile/1,2-dichloroethane as **4***a* (0.692 g, 21%); decomp. 316°C. *Anal.* found: C 40.4, H 3.3, N 38.9.

*$N_3P_3(Mepz)_6$ (1b)*

3-Methylpyrazole (2.40 g, 29.2 mmol, 6% excess) and triethylamine (3.08 g, 30.4 mmol, 10% excess) were heated under reflux with $N_3P_3Cl_6$ (1.60 g, 4.6 mmol in 110 mL THF for 24 h. The $Et_3N{\cdot}HCl$ and by-products were filtered off, and the solvent removed *in vacuo*. The semisolid residue was washed with acetonitrile and crystallised from acetonitrile/1,2-dichloroethane as **1***b* (0.87 g, 30%); mp 213–218.5°C. *Anal.* calcd. for $C_{24}H_{30}N_{15}P_3$: C 46.4, H 4.9, N 33.8; found: C 46.7, H 4.9, N 33.9.

*$N_4P_4(Mepz)_8$ (2b)*

In a similar reaction, the product from $N_4P_4Cl_8$ (1.52 g, 3.3 mmol) was recrystallised from acetonitrile as **2***b* (1.60 g, 59%); mp 253.5–255°C. *Anal.* found: C 46.5, H 4.8, N 33.5. Hydrogen chloride was bubbled into a benzene solution of **2***b* (0.12 g, 0.15 mmol) for 10 min. The clear colourless solution was heated under reflux for 10 min and the solvent removed. The product was a mixture of $N_4P_4Cl_8$ and MepzH·HCl.

*$N_5P_5(Mepz)_{10}$ (3b)*

In a similar preparative experiment with $N_5P_5Cl_{10}$, the colourless oily product was identified by $^1H$ nmr spectroscopy as a mixture of 3-methylpyrazole and **3***b*. The pure compound was not isolated.

*$N_3P_3(Me_2pz)_6$ (1c)*

From $N_3P_3Cl_6$ (1.66 g, 4.8 mmol), 3,5-dimethylpyrazole (3.21 g, 33.3 mmol), and triethylamine (3.18 g, 31.4 mmol) in 115 mL THF, a white solid product (1.92 g) was obtained, which was crystallised from acetonitrile/1,2-dichloroethane as colourless blocks of **1***c*, 58%; mp 253.5–254.5°C. *Anal.* calcd. for $C_{30}H_{42}N_{15}P_3$: C 51.1, H 6.0, N 29.8; found: C 51.1, H 5.9, N 29.7. The product was also obtained in 91% yield by using benzene as a solvent, and a 5% excess of both triethylamine and 3,5-dimethylpyrazole. No by-products were found.

*$N_4P_4(Me_2pz)_8$ (2c)*

From $N_4P_4Cl_8$ (1.86 g, 4.0 mmol), 3,5-dimethylpyrazole (3.50 g, 36.4 mmol, 13% excess) and triethylamine (3.58 g, 35.4 mmol) in 115 mL THF, a colourless product was obtained, which was crystallised from benzene as **2***c*, 0.303 g; 8%, mp 222.5°C (gels). *Anal.* found: C 51.3, H 6.1, N 29.7. The yield was improved (to 17%) and the quantity of by-products diminished, by using the theoretical quantity of the pyrazole.

gem-*$N_3P_3Ph_2(Me_2pz)_4$ (5)*

A solution of 3,5-dimethylpyrazole (0.85 g, 8.9 mmol) and triethylamine (0.99 g, 9.8 mmol) in 50 mL THF was added to a

stirred solution of *gem*$N_3P_3Ph_2Cl_4$ (0.96 g, 2.2 mmol) in 70 mL THF, and the mixture heated under reflux for 8 days. The white precipitate consisted solely of $Et_3N{\cdot}HCl$. The solvent was evaporated from the filtrate, leaving a clear pale yellow oil which solidified on standing. Residual $Et_3N{\cdot}HCl$ and 3,5-dimethylpyrazole were removed by sublimation *in vacuo*, and the residue crystallised from acetonitrile/1,2-dichloroethane as colourless needles of **5** (1.34 g, 90%); mp 217.5–219°C. *Anal.* calcd. for $C_{32}H_{38}N_{11}P_3$: C 57.4, H 5.7, N 23.0; found: C 57.1; H 5.6, N 22.8.

gem-$N_3P_3Ph_4(Me_2pz)_2$ (**6***b*)

In a similar but slower reaction, *gem*-$N_3P_3Ph_4Cl_2$ (1.50 g, 2.9 mmol), 3,5-dimethylpyrazole and triethylamine (both in 10% excess) in 120 mL xylene were heated under reflux for 8 days, when 81% of the pyrazole had reacted. The product was crystallised from acetonitrile/1,2-dichloroethane as colourless blocks of **6***b* (1.10 g, 73%); mp 211–212.5°C. *Anal.* calcd. for $C_{34}H_{34}N_7P_3$: C 64.5, H 5.4, N 15.5; found: C 64.7, H 5.4, N 15.5.

gem-$N_3P_3Ph_4(Mepz)_2$ (**6***a*)

The product from a similar reaction of *gem*-$N_3P_3Ph_4Cl_2$ in 80 mL xylene was obtained as an adduct with acetonitrile. The acetonitrile was removed by heating the powdered crystals at 100°C/0.1 Torr for 3 h, giving **6***a* (0.77 g, 71%) mp 203–208°C. *Anal.* calcd. for $C_{32}H_{30}N_7P_3$: C 63.5, H 5.0, N 16.2; found: C 63.4, H 5.0, N 16.0.

gem-$N_3P_3Ph_4(Me_2pz)_2{\cdot}PdCl_2$ (**7***a*)

A solution of $PdCl_2(PhCN)_2$ (0.045 g, 0.12 mmol) in 10 mL dichloromethane was filtered into a stirred solution of **6***b* (0.070 g, 0.11 mmol) in 5 mL dichloromethane. The solution gradually became orange, and deposited a yellow precipitate during 24 h at room temperature. The precipitate was crystallised from chloroform as **7***a* (0.081 g, 90%); decomp. 250°C. *Anal.* calcd. for $C_{34}H_{34}Cl_2N_7P_3Pd$: C 50.4, H 4.2, N 12.1; found: C 51.0, H 4.1, N 11.6. $\Lambda_M$(nitromethane) = 1.21 $cm^2$ $ohm^2$ $mol^{-1}$.

gem-$N_3P_3Ph_2(Me_2pz)_4{\cdot}PdCl_2$ (**7***b*)

In a similar experiment, in which benzene was used as a solvent, **5** with an excess of $PdCl_2(PhCN)_2$ yielded an orange solid, which was recrystallised from chloroform as orange needles of **7***b* (34%); decomp. 225°C, *Anal.* calcd. for $C_{32}H_{38}Cl_2N_{11}P_3Pd$: C 45.4, H 4.5, Cl 8.4, N 18.2; found: C 45.2, H 4.4, Cl 8.1, N 17.9. $\Lambda_M$(nitromethane) = 3.41 $cm^2$ $ohm^{-1}$ $mol^{-1}$.

$N_3P_3(Me_2pz)_6{\cdot}2PtCl_2$ (**8***b*)

In a slower reaction, a suspension of **1***c* (0.101 g, 0.14 mmol) in 30 mL benzene was heated under reflux with $PtCl_2(PhCN)_2$ (0.203 g, 0.43 mmol) for 7 days. The yellow precipitate was filtered off, washed with 50 mL benzene, and crystallised from chloroform/benzene as **8***b* (0.076 g, 43%); mp 275–280°C. *Anal.* calcd. for $C_{30}H_{42}Cl_4N_{15}P_3Pt_2$: C 29.1, H 3.4, N 17.0; found: C 29.5, H 3.4, N 15.7. The sample contained traces of benzene which could not be removed by heating it *in vacuo*. $\Lambda_M$(nitromethane) = 1.68 $cm^2$ $ohm^{-1}$ $mol^{-1}$.

$N_3P_3(Me_2pz)_6{\cdot}2PdCl_2$ (**8***a*)

The similar reaction of **1***c* with $PdCl_2(PhCN)_2$ was complete after 4 days. The dull yellow solid was crystallised from chloroform/benzene as orange blocks of **8***a* (80%); decomp. 250°C. *Anal.* calcd. for $C_{30}H_{42}Cl_4N_{15}P_3Pd_2$: C 34.0, H 4.0, Cl 13.4, N 19.8; found: C 34.1, H 4.8, Cl 13.8, N 19.5. Alternatively, the reaction was carried out in dichloromethane (**1***c*:Pd = 1:2) for 16 h. The orange solution was concentrated and added to a large volume of hexane. The yellow solid was filtered off and washed with benzene: yield 99%. $\Lambda_M$(nitromethane) = 2.26 $cm^2$ $ohm^{-1}$ $mol^{-1}$.

$N_3P_3(Me_2pz)_6{\cdot}3PdCl_2$ (**9**)

In the above reactions, no more than two $MCl_2$ groups could be introduced because the complexes were insoluble in benzene. The better solvent dichloromethane allowed further reaction. A solution of $PdCl_2(PhCN)_2$ (0.145 g, 0.38 mmol) in 30 mL dichloromethane was filtered into a solution of **1***c* (0.085 g, 0.12 mmol) in 3 mL dichloromethane. The orange solution was heated under reflux for 24 h, concentrated to 3 mL, and added dropwise to a large volume of hexane. The orange–yellow solid was filtered off and crystallised from dichloromethane as **9** (0.143 g, 96%); decomp. 250°C. *Anal.* calcd. for $C_{30}H_{42}Cl_6N_{15}P_3Pd_3$: C 29.1, H 3.4, N 17.0; found: C 29.9, H 3.8, N 16.6.

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