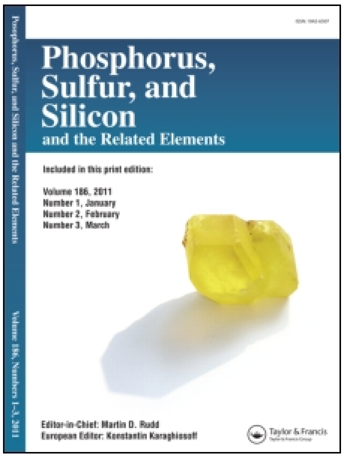

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Phosphazenes and Phosphazanes—The Nature of the P-N Bond

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PHOSPHAZENES AND PHOSPHAZANES–THE NATURE OF THE P-N BOND

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Abstract Synthetic, spectroscopic and X-ray structural studies on linear and cyclic λ^3-diphosphazanes, λ^3-cyclotriphosphaz*anes*, λ^5-cyclotriphosphaz*enes* and a bicyclic P_4N_5 derivative are summarised. Transition metal organometallic chemistry of linear and cyclic λ^3-phosphazanes and suitably functionalised λ^5-cyclotriphosphaz*enes* is also investigated. Novel mono- and dinuclear palladium complexes have been isolated from spirocyclic λ^5-cyclotriphosphazenes by facile hydrolytic cleavage of a λ^5-diazaphospholane ring. The structural data on P-N compounds and their complexes and *ab initio* molecular orbital calculations on selected model systems provide strong evidence for "negative hyperconjugation" as a dominant feature of multiple bonding between phosphorus and nitrogen.

Key words : Linear and cyclic phosphazanes, cyclotriphoshazenes, transition metal complexes, negative hyperconjugation

INTRODUCTION

Phosphorus and nitrogen are unique among any pair of adjacent elements of the same group of the Periodic Table in forming a myriad range of linear and cyclic compounds.[1,2] The two most widely used synthetic routes for generating a P-N bond are the reactions of halophosphorus compounds (in particular chloro derivatives) with ammonia, amines or silylamines (named as Kirsanov reaction when applied to specific P^V systems) and the reactions of P^{III} compounds with azides (known as Staudinger reaction). The important types of P-N compounds are shown in Figure 1. We have carried out extensive investigations on several of these systems. A brief account of our recent work on phospha*zanes* and phospha*zenes* as well as their organometallic chemistry and the implications of the structural data for an understanding of the nature of the P-N bond is presented in this talk.

UNSYMMETRICALLY SUBSTITUTED λ^3-DIPHOSPHAZANES

Continuing our interest in the organometallic chemistry of λ^3-diphosphazanes,[3,4] we have synthesised a series of unsymmetrically substituted diphosphazanes of the type $X_2PN(R)PYY'$(**1**) (Scheme 1). Some of these diphosphazanes (*e.g.* **1h** and **1i**) feature an additional hard nitrogen donor site in addition to the two phosphorus

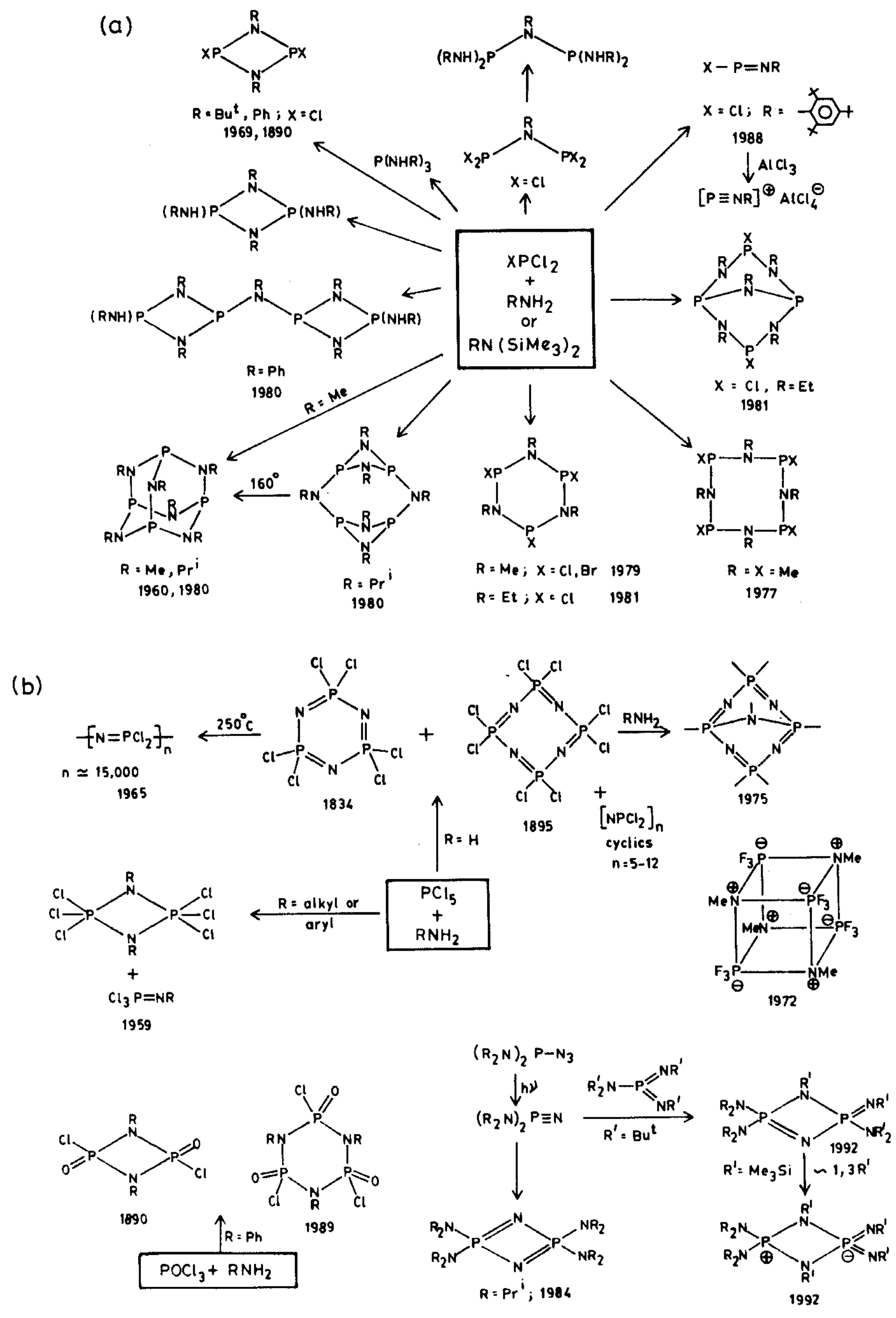
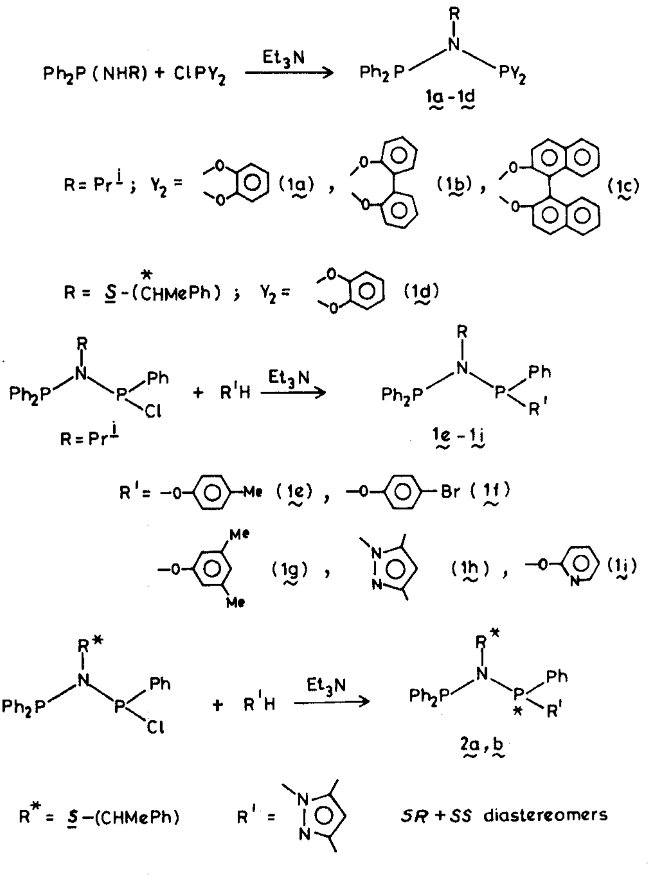


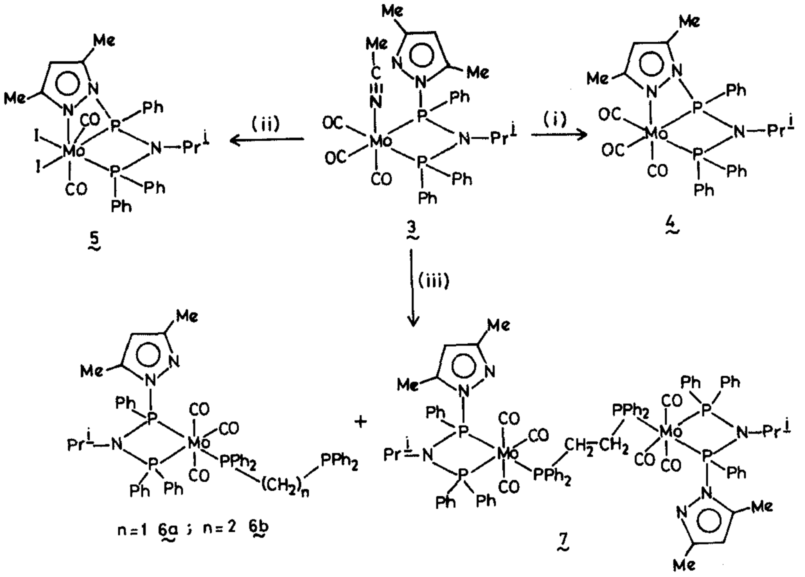
Figure 1. Important types of (a) P^{III}-N and (b) P^{V}-N compounds (year of discovery shown underneath each compound type)

centres and can be potential tridentate ligands (see below). This synthetic methodology can be conveniently employed to prepare chiral diphosphazanes (*e.g.* **1d**, **2**). There is a chiral induction in the reaction leading to **2a,b** as these two diastereomers are formed in the ratio 2:3 (^{31}P NMR evidence). One of these diastereomers has been separated by fractional crystallization from petrol; X-ray crystal structure determination reveals it to be the *S,R*-diastereomer.[5] Variable temperature ^{31}P NMR studies on **1a**, **1e** and **1h** show that atleast two conformers are present in solution.[5,6]



Scheme 1

We had earlier reported that the treatment of **1h** with [Mo(CO)$_3$(MeCN)$_3$] gives the chelate complex **3** containing a labile MeCN ligand.[4] Pyrolysis of **3** in heptane gives **4** in which the diphosphazane ligand acts as a PPN tridentate ligand (Scheme 2). Treatment of **3** with iodine in toluene gives the Mo(II) diiodo complex **5** whose structure has been confirmed by X-ray crystallography. The geometry around molybdenum is capped octahedral. A similar PPN coordination has been realised in the molybdenum tricarbonyl complex formed from [Mo(CO)$_3$(MeCN)$_3$]

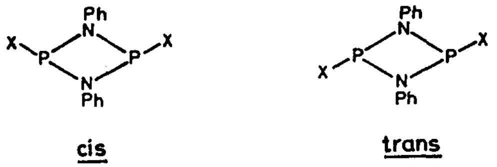


Scheme 2 : (i) heptane, 96°C, 1 h; (ii) I_2, benzene, 30°C, 1 h; (iii) dppm or dppe (1:1 or 2:1)

and **1i**. Reaction of **3** with with dppm or dppe affords **6** in which the diphosphinoalkane ligand exhibits η^1-mode of coordination; with dppe, the bimetallic complex **7** is also obtained.[5] (Scheme 2). The reaction of **1h** with $[Pd_2(dba)_3]$ (dba = dibenzylidine acetone) in the presence of methyl iodide affords the diiodo chelate complex $[PdI_2\{Ph_2PN(Pr^i)PPhMe\text{-}PP'\}]$ (**8**) whose structure has been confirmed by X-ray crystallography. The pyrazolyl group on the phosphorus is replaced by a methyl group.

λ^3-CYCLODIPHOSPHAZANES AND THEIR TRANSITION METAL COMPLEXES

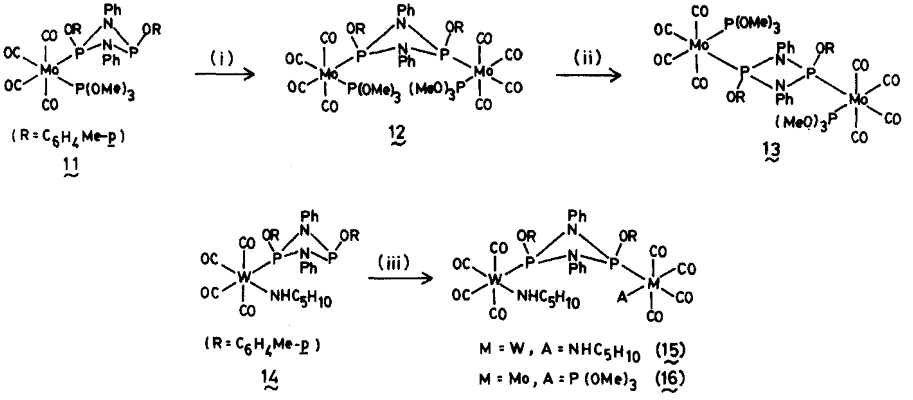
Whereas both the aryloxy and trifluoroethoxy derivatives **9** and **10** exist in solid state in their *trans* isomeric form, in solution they exist as a mixture of both *cis* and *trans* isomers (ratio 3:1 for **9** and 9:1 for **10**) (^{31}P NMR evidence).[7] Reactions of **9** and **10** with Group 6 metal carbonyl moieties give both mono- and di-nuclear complexes in which the cyclodiphosphazane in its *cis* or *trans* form exhibits η^1- or μ-bidentate mode of coordination of the phosphorus centres (Scheme 3). The mononuclear molybdenum complex **11** on treatment with $[Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})]$ yields at first the dinuclear complex **12** which isomerizes to **13**. Although **12** could not be isolated, its intermediacy has been established by ^{31}P NMR spectroscopy. In sharp contrast to the behaviour of **11**, the tungsten complex **14** gives **15** and **16** in which the cyclodiphosphazane retains its *cis*-configuration. However the reaction of $[Mo(CO)_4(NHC_5H_{10})_2]$ with **10** gives the dinuclear complex $[\{Mo(CO)_4(NHC_5H_{10})\}_2(\mu\text{-}\mathbf{10})]$ in which the cyclodiphosphazane adopts the *trans*-configuration. No *cis* → *trans* isomerization is observed even when **15** or **16** is heated in toluene for several hours. The structures of both **13** and **16** have been confirmed by X-ray crystallography.[8] The P_2N_2 ring in **13** is planar whereas in **16**, the ring is slightly puckered. Puckering in **16** is, however, less-pronounced than in the η^1-coordinated complex **14**.[7]



cis trans

X = OC_6H_4Me-p **9a** **9b**

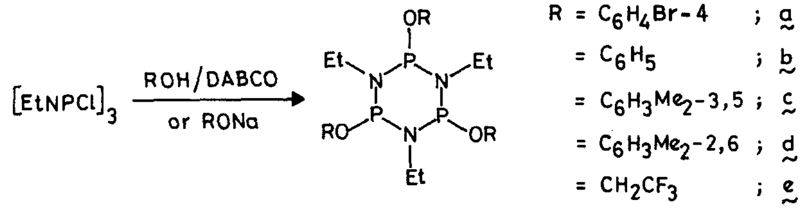
X = OCH_2CF_3 **10a** **10b**



Scheme 3: (i) $Mo(CO)_4\{P(OMe)_3\}(NHC_5H_{10})/CDCl_3$, 45°C, 10 min; (ii) after 60 min; (iii) $M(CO)_4(A)(NHC_5H_{10})/CH_2Cl_2$ ($M = Mo$, $A = P(OMe)_3$; $M = W$, $A = NHC_5H_{10}$)

λ^3-CYCLOTRIPHOSPHAZANES AND THEIR TRANSITION METAL COMPLEXES

Unlike λ^3-cyclodiphosphazanes, λ^3-cyclotriphosphazanes are of recent vintage.[9] Little information is available on the conformations of the six-membered P_3N_3 ring in λ^3-cyclotriphosphazenes. We have prepared a series of λ^3-cyclotriphosphazanes $[EtNP(OR)]_3$ (**17**) from the chloro precursor, $(EtNPCl)_3$ (Scheme 4). Compounds **17a-c** and **17e** are formed as a mixture of *cis-trans* isomers whereas **17d** is formed exclusively as its *trans*-isomer (^{31}P NMR evidence). The *cis-* and *trans-* isomers of **17a** can be conveniently separated by fractional crystallization and their structures determined by X-ray crystallography. The *cis*-isomer exhibits a flattened chair conformation while the *trans*-isomer adopts a boat conformation. The exocyclic substituents in both the isomers occupy axial positions and the geometry around all the nitrogen atoms is trigonal planar (see below). Unlike cyclodiphosphazanes, cyclotriphosphazanes are rigid and do not show any isomerization in solution even when heated to 100°C in toluene.[10]

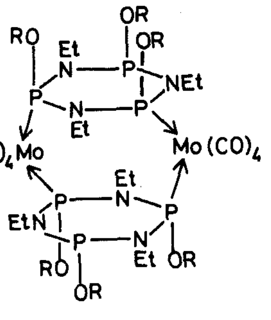


R = C_6H_4Br-4 ; a
= C_6H_5 ; b
= $C_6H_3Me_2$-3,5 ; c
= $C_6H_3Me_2$-2,6 ; d
= CH_2CF_3 ; e

Scheme 4

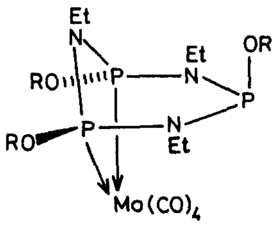
17a-17e

The presence of three tricoordinate phosphorus centres in λ^3-cyclotriphosphazanes would make them interesting ligands in organometallic chemistry. Preliminary studies with the *cis*-isomer of **17e** and the *trans*-isomer of **17d** unfold interesting differences in the coordination modes of the two ligands.[11] The reaction of *cis*-**17e** with [$M(CO)_4$(norbornadiene)] gives the dinuclear complex **18**; on the other hand, *trans*-**17d** affords the mononuclear chelate complex **19**. Both the complexes have been subjected to X-ray crystal structure analysis. It is interesting to note that in the chelate complex **19**, the nitrogen flanking the coordinated phosphorus centres displays pyramidal geometry while the other nitrogens (and also the nitrogens in **18**) are strictly trigonal planar.



R = CH_2CF_3

18

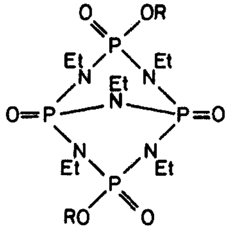


R = $C_6H_3Me_2$-2,6

19

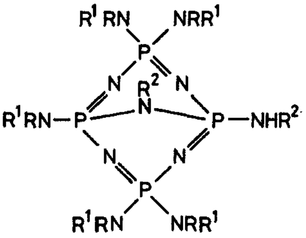
λ^5-BICYCLIC P_4N_5 SYSTEMS

The reaction of PCl_3 with ethylamine hydrochloride gives not only the λ^3-cyclotriphosphazane, $(EtNPCl)_3$ but also the bicyclic phosphazane[9] $Cl_2P_4(NEt)_5$ from which we have synthesised the tetraoxo derivative **20**. X-ray structure analysis of **20** reveals that the two six-membered ring segments are inclined at an angle of 120°. The geometry around the bridging nitrogen deviates from planarity only slightly (sum of the bond angles = 355.4°)[12] in contrast to the λ^5-bicyclic phosphazenes (**21**)[13] in which the bridging nitrogen exhibits a pronounced pyramidal character $\Sigma\hat{N} = 330°$) (see below).



R=$C_6H_3Me_2$-2,6

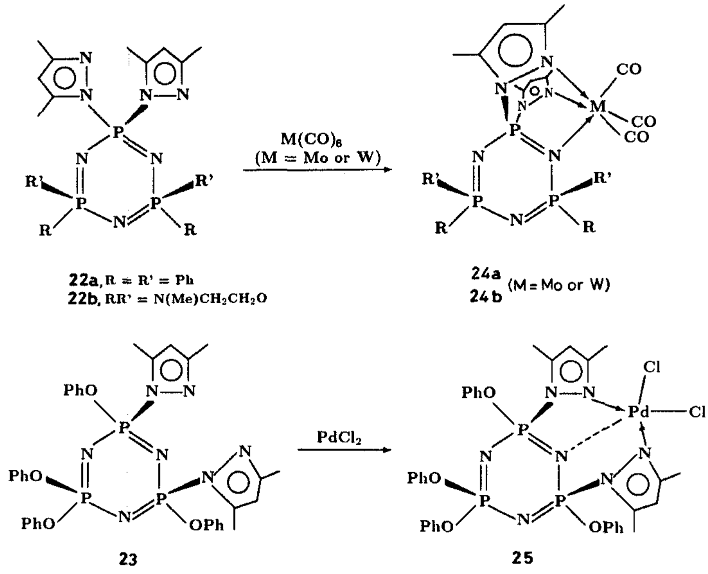
20



21

TRANSITION METAL COMPLEXES OF λ^5-CYCLOTRIPHOSPHAZENES

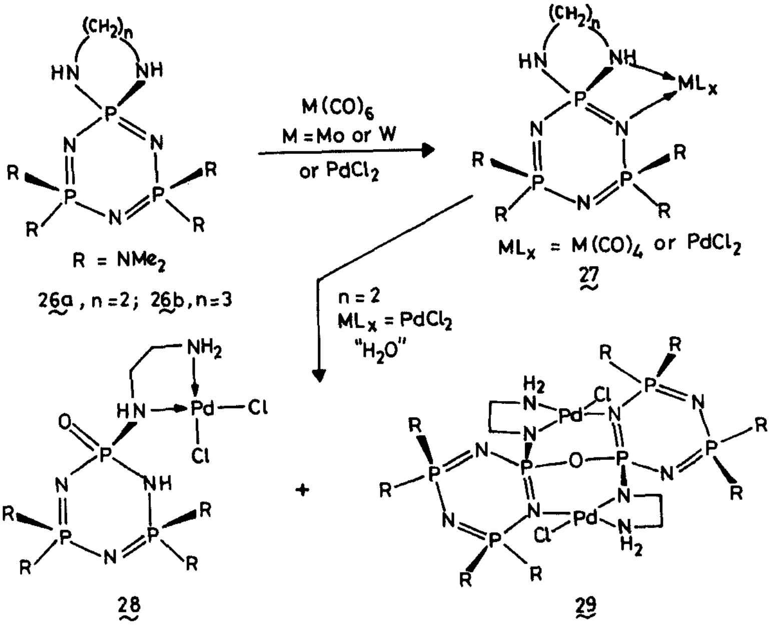
The successful symbiosis of P-N chemistry and organometallic chemistry using λ^3-phosphazanes as ligands prompted us to explore the transition metal chemistry of suitably functionalized cyclotriphosphazenes with a view to developing new synthetic strategies for anchoring transition metal moieties to P-N polymers. Two types of cyclotriphosphazenes have been chosen for the study. The first type comprises pyrazolyl phosphazenes such as **22** and **23** in which the pyrazolyl groups reside on the same or on two different phosphorus centres (Scheme 5). The metal tricarbonyl complexes **24** represent the first structurally characterized zerovalent complexes of



Scheme 5

cyclotriphosphazenes. The σ-donor ability of the phosphazene ring nitrogen atom can be modulated by changing the substitutents on the phosphorus as shown by the M-N bond distances in the two complexes [Mo(CO)$_3$·**22a**] (2.391 Å) and [W(CO)$_3$·**22b**] (2.309 Å)[14]. In the palladium chloride complex (**25**) of the nongeminal pyrazolyl derivative, the interaction of the phosphazene ring nitrogen with the metal is much weaker as can be discerned from the M···N distance (2.858 Å).[15]

The second type of cyclotriphosphazene ligands that we have investigated are the spirocyclic derivatives, **26a** and **26b** with varying size of the ring exocyclic to the P_3N_3 ring.[15] The reaction of **26b** with $PdCl_2$ gives a stable chelate complex **27** (n = 3; ML_x = $PdCl_2$) whose structure has been confirmed by X-ray crystallography. The ^{31}P NMR spectrum of [$PdCl_2$·**26b**] is of the AMX type; the chemical shift of the *spiro* phosphorus (δ_p 43.1) moves considerably downfield compared to that in the free ligand [δ_p (*spiro*) 17.8]. More interesting is the reaction of **26a** with $PdCl_2$; the diazaphospholane ring undergoes a facile hydrolytic cleavage even when apparently anhydrous MeCN (distilled over CaH_2) is used as the solvent to give novel mono- and bi-metallic complexes **28** and **29**. X-ray crystallography reveals that in **28**, an (oxophosphazadienyl)ethylenediamine is chelated to the metal *via* its two exocyclic nitrogen atoms whereas in **29**, an oxobridged bi(cyclotriphosphazene) acts as a hexadentate NNNNNN donor ligand in its dianionic form. The intermediacy of a four-membered chelate complex [$PdCl_2$·**26a**] (analogous to that formed by **26b**) is inferred from ^{31}P NMR spectral monitoring of the course of the reaction. Group 6 metal tetracarbonyl complexes (**27**) have also been isolated (scheme 6).



Scheme 6

STRUCTURAL DATA FOR PHOSPHAZANES AND PHOSPHAZENES AND THE NATURE OF THE P-N BOND

A wide variety of P-N compounds and their metal complexes were described in the previous sections and some salient features of their structures pointed out. What insight do these structural data provide into the nature of the P-N bond? Greenwood and Earnshaw[16] in their monumental book "Chemistry of the Elements" comment: "The P-N bond is one of the most intriguing in chemistry and many of its more subtle aspects still elude a detailed and satisfactory description". Almost a decade later it would appear that a better understanding of the P-N bond can be gleaned from a careful analysis of the structural data and application of new theoretical ideas invoked to explain bonding in compounds of heavier main group elements.

Conventional bonding models of formally unsaturated phosphazene systems involve the overlap of nitrogen *p*-orbitals with phosphorus d-orbitals (p_π-d_π bonding).[17] Even in formally saturated P-N systems, there is the possibility of the interaction of the lone pair of electrons on the nitrogen with phosphorus d-orbitals introducing multiple bonding character in the P-N bond and thereby shortening it compared to the normally accepted value for a P-N single bond (1.77 - 1.80 Å).[18] The data for a few typical P-N systems are shown in Figure 2. Dramatic differences are observed when the double bonds are within or exocyclic to the P-N ring (e.g. VII, VIII and IX; XVII and XVIII). The P-N-P angle in diphosphazanes and their transition metal complexes vary over a wide range (97-131°); yet trigonal planarity at the nitrogen is maintained. When a ring nitrogen atom of a cyclophosphazene is protonated or coordinated to the metal, its lone pair is no longer available for interaction with phosphorus orbitals and the P-N bonds at the site of protonation or metallation are appreciably lengthened compared to those away from it (XIV-XVI).

In order to gain a better understanding of the above structural features and the conformational preferences of the P-N rings, we have carried out semi-empirical MNDO and *ab initio* molecular orbital calculations on the model six-membered P_3N_3 systems $(XPNH)_3$ (X = H or F). The calculations indicate that the observed structural data can be readily explained on the basis of "negative hyperconjugative" model[19] involving the overlap of the lone pair on the nitrogen (which resides on an orbital of π-symmetry) with antibonding σ^* orbitals of the P-X bond. The more electronegative the substituent X, the more efficient is this overlap and greater is the shortening of the P-N bond. Incidentally, this idea to explain bonding in phosphorus compounds was put forth by Lehn and Wipff[20] for phosphate esters in 1975 and was later invoked by Shaw and coworkers[21] to explain the conformations of (triphenyl phosphazenyl)cyclophosphazenes. For "negative hyperconjugation" to be most effective, there must be a parallel arrangement between the P-X bond and the nitrogen lone pair. In this respect, the conformational constraints imposed by "negative hyperconjugation" would be different from those expected for d_π-p_π bonding. Further, this kind of interaction seems to be ineffective when the nitrogen lone pair is parallel

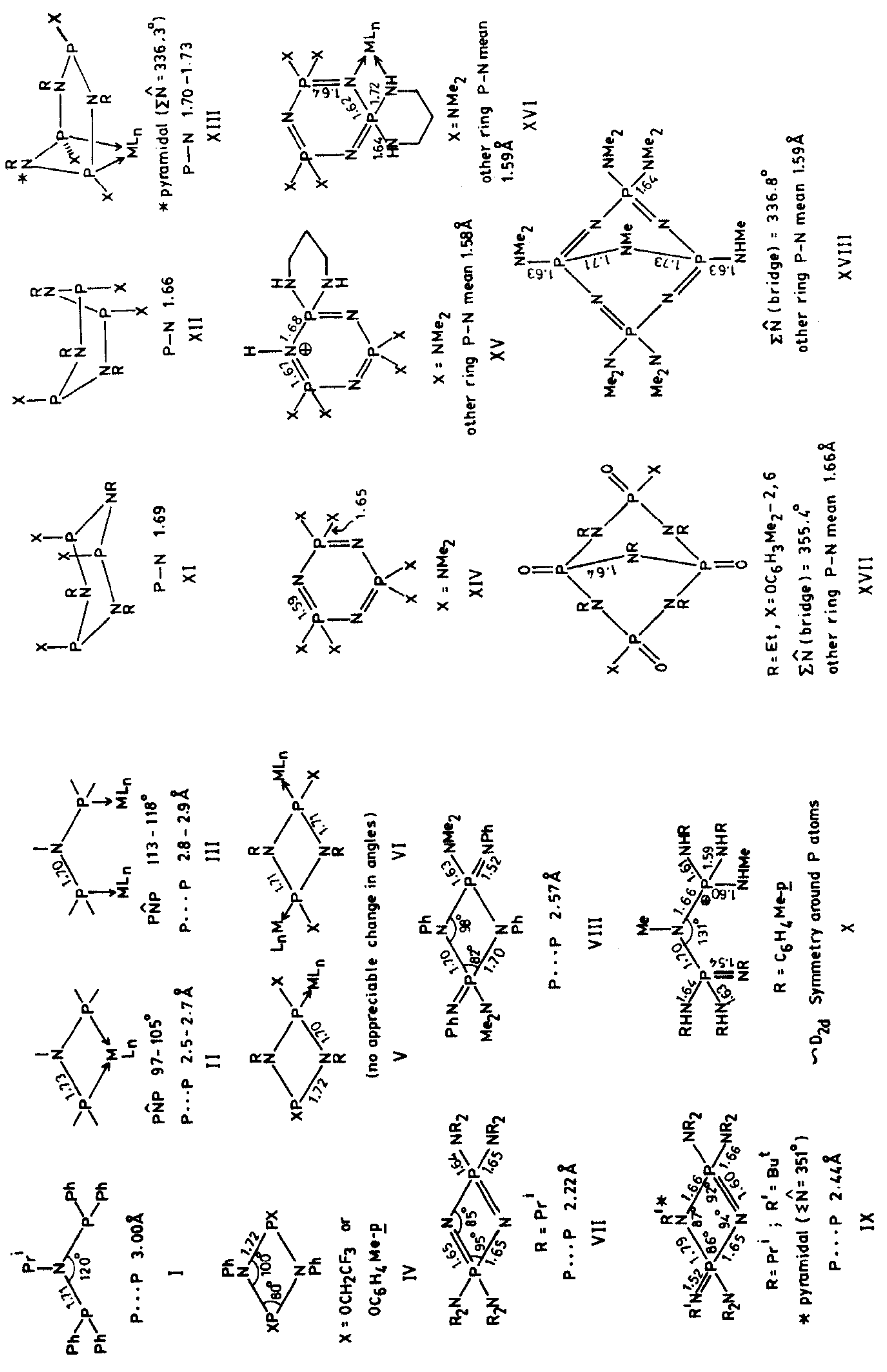


Figure 2 Structural data for some selected P–N compounds and their transition metal complexes

to a P=X unit. The observed conformations of *cis*- and *trans*-[EtNP(OC_6H_4Br-*p*)]$_3$ and the λ^5-bicyclic phosphazane **20** provide convincing evidence in support of these arguments.[10,12] Since the lone pair on the bridging nitrogen in the λ^5-bicyclic phosphazenes **21** cannot orient itself parallel to a P-X σ^* orbital, it assumes a pyramidal geometry in contrast to the bicyclic phosphazane **20**. The pyramidal geometry at one of the ring nitrogen atoms of the chelate complex **19** (XIII in Figure 2) can also be explained in a similar way; upon complexation, the P_3N_3 ring in **19** undergoes a conformational change with the substituents at the coordinated phosphorus centres occupying equatorial positions. Hence the lone pair on the nitrogen flanked by these two phosphorus atoms cannot have a parallel orientation to a P-X σ^* orbital and this circumstance forces the nitrogen to assume a pyramidal geometry.[11]

The reactions of hexachlorocyclodiphosphazane [$MeNPCl_3$]$_2$ with primary aromatic amines give bisphosphinimine hydrochlorides of the type X (Figure 2) in which two sets of C-N-P-N' dihedral angles around each phosphorus atom are close to 180°. This geometry is ideal for interaction between each of the nitrogen lone pair orbitals and an adjacent P-N σ^* orbital of appropriate symmetry. The P-N single bonds are remarkably short (mean 1.655 and 1.621 Å in the phosphinimine and phosphonium units) as a result of cumulative "negative hyperconjugative" interactions. *Ab initio* calculations on $(NH_2)_3P{=}NH$ and $[P(NH_2)_4]^+$ reproduce the observed bond lengths and bond angles at the phosphinimine and the phosphonium ion parts of the molecule.[22]

Structural data on a range of P-N compounds and their complexes and theoretical calculations on model systems (though admittedly limited) lend strong support for "negative hyperconjugation" as a key factor that contributes to multiple bonding between phosphorus and nitrogen.

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