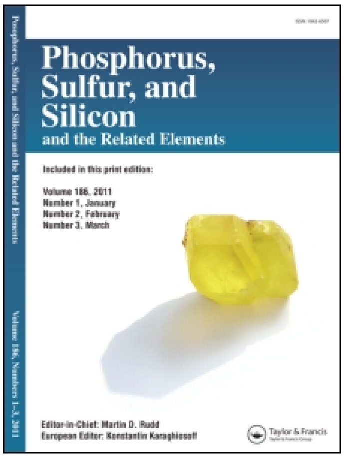

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ABOUT THE COORDINATION CHEMISTRY OF THE PHOSPHORUS-NITROGEN ENTITY

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To cite this Article Riess, Jean G.(1986) 'ABOUT THE COORDINATION CHEMISTRY OF THE PHOSPHORUS-NITROGEN ENTITY', Phosphorus, Sulfur, and Silicon and the Related Elements, 27: 1, 93 — 107
To link to this Article: DOI: 10.1080/03086648608072762
URL: http://dx.doi.org/10.1080/03086648608072762

Phosphorus and Sulfur, 1986, Vol. 27, pp. 93–107
0308-664X/86/2702-0093/$20.00/0

ABOUT THE COORDINATION CHEMISTRY OF THE PHOSPHORUS-NITROGEN ENTITY*

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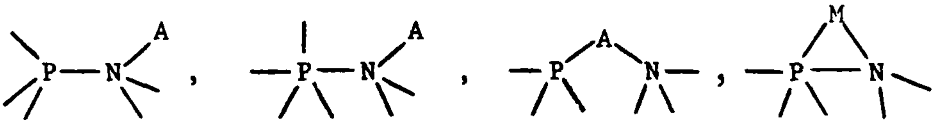
Triply coordinated trivalent nitrogen atoms are known to lose most or all of their Lewis donor capacity when bonded to a third or higher row element. It is shown here, in the case of P-bonded nitrogen atoms, that structural constraints which maintain the nitrogen atom in a pyramidal configuration can contribute much in preserving their basicity and/or nucleophilic character. In particular, nitrogen atoms apically bonded to 5-coordinated formally penta- or trivalent phosphorus atoms can display definite basicity. Examples of metal- and base-induced opening and closing of P—N bonds are also presented. The following unusual coordination modes and/or reaction issues are exemplified:



where A can be—depending on the case—H^+, CH_3^+, BH_3, BF_3 or a transition metal moiety, as for example $CpMo(CO)_2Cl$ or $CpMo(CO)_2$, etc. The factors that affect the rather variable P—N bond length are discussed.

INTRODUCTION

It is generally known that a tricoordinated nitrogen atom when bonded to third or higher row elements loses most or all of the donor character normally associated with the presence of a free valence electron pair.[1] Correlatively, the donor capacity of the third row element, when it has a lone pair, is then enhanced. A few text book examples will illustrate this situation (Scheme 1).

At the same time the nitrogen atom tends to become co-planar with its substituents, and its bonds to them to become shorter than the sum of Pauling-type single-bond covalent radii, as extracted, in the case of nitrogen, from the common pyramidal aliphatic amines ($r_c = 0.70$ Å). When homogeneous series are considered it is usually found that there exists an inverse linear relationship between these bond lengths and the degree of planarity of the nitrogen atoms, as expressed by the sum, ΣN, of the angles they form with their substituents.[6]

It is customary to recognize in these various phenomena (Scheme 2) the revelation of some p_π-d_π contribution through which the lone pair electrons of the nitrogen are drained into the higher row element's empty d orbitals. This is particularly the case with bond lengths: bond "shortening" below 1.77 Å (the sum of Pauling's radii,

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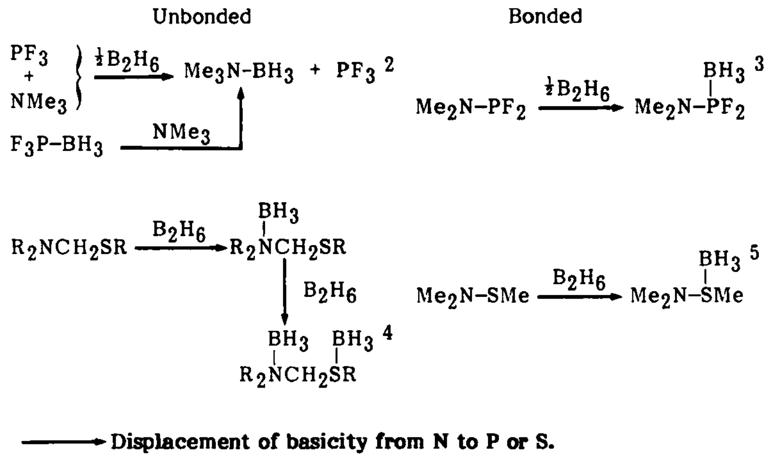
*Presented as part of a lecture given at the Conference on Phosphorus, Silicon and Sulfur—Common Aspects, at Sulejov, Poland, Mai 1985.



→ Displacement of basicity from N to P or S.

SCHEME 1 Lewis basicity of N when, bonded to 3rd row elements.

Symptoms :

loss of basicity of N
or short P–N bond
or planar N configuration
or low energy lone pair on N (from PES)
or increased s character (from J)

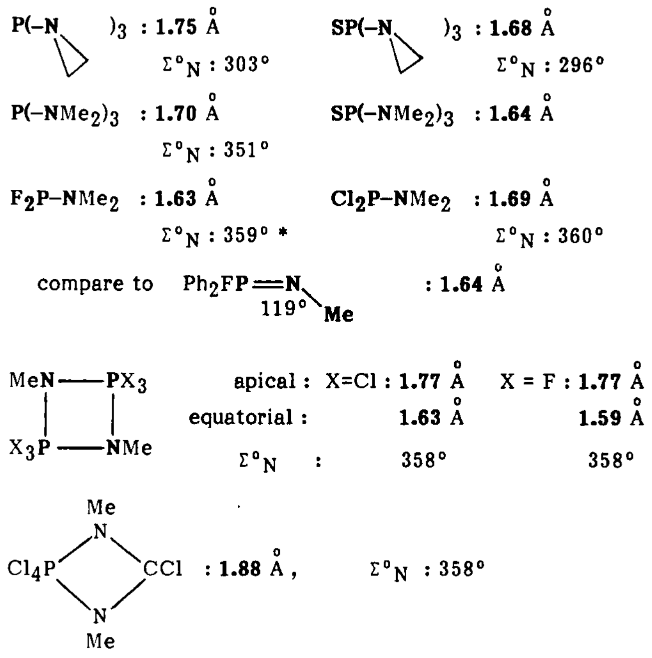
Diagnosis : **Np_π - Pd_π** character

Prognosis : lone pair not available for donation → **low coordination ability**

SCHEME 2 Phenomena experienced by P-bound N atoms.

1.80 Å, corrected according to Schomacker and Stevenson for the electronegativity difference) is usually done away with by invoking p_π-d_π character. The data collected in Scheme 3[7] should make us more cautious:[8] quite evidently the P—N distance is sensitive to many factors, and in particular to the nature of the substituents of phosphorus and to its oxidation state (Scheme 4), and these factors are all closely interdependent—and usually inextricable. For example, the mere change of hybridization from sp^3 to sp^2 associated with the nitrogen's configuration becoming planar is already expected to result in a shortening of 0.3–0.4 Å, which in turn will tend to reinforce the overlap of the π-orbitals, and this will also tighten the σ-frame and contribute to rendering individual contributions inseparable. An example of the effect of crystal packing forces is shown in Scheme 5: in this "soft" molecular structure[8] the lengths of the 12 chemically equivalent P—N bonds range from 1.59 ± 0.02 to 1.75 ± 0.02 Å![9]

Clearly the two atoms can no longer be expected to behave as independent donor sites, and the P—N entity must be taken as a whole.



* from X-ray diffraction ; pyramidal from electron diffraction.

SCHEME 3 Variability in P—N "single" bond lengths.[7]

"single" bond length.

$|O_3P{-}NH_3|^-$ "standard" : 1.77 Å

$\Sigma r_{\text{Pauling}}$: 1.80 Å

Schomaker & Stevenson : -0.04 Å

N $sp^3 \longrightarrow sp^2$: -0.03 -0.04 Å

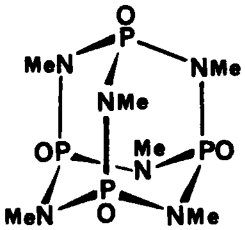
P(III) ⟶ P(V) : up to -0.08 Å

packing forces : up to 0.13 Å !

+ steric effects, solvation effects, etc...

SCHEME 4 Some factors affecting P—N "single" bond length.

This paper will present some examples of unusual coordination behavior of this P—N entity that have been observed in our Laboratory, especially when cyclic constraints, which prevented the nitrogen atom from adopting a planar configuration, were introduced. The polycyclic species **1** to **4** shown in Scheme 6 have provided privileged substrates[10-12] for these investigations. The coordination modes that were established in isolated adducts and will be discussed here are collected in Scheme 7.



$P2_1/m$ Z = 8

4 independent molecules in asymmetric unit

⟶ 48 independent P-N measurements

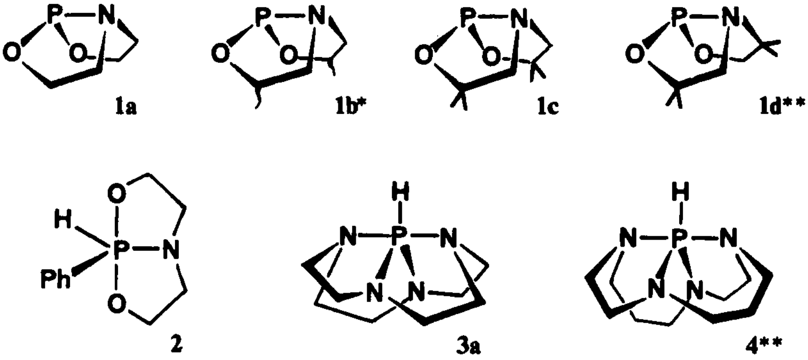
molecule of Td symmetry

12 equiv. P-N bonds

$\overline{av}$ P-N : 1.667 ± 0.02 Å

Spread : 1.591(9) - 1.760(8) Å !

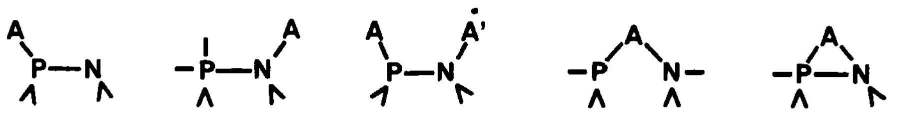
SCHEME 5 Effect of crystal forces on P—N bond length.[9]



* as a mixture of diastereoisomers (meso and racemie).

** as a mixture of enantiomers.

SCHEME 6 Some polycyclic ligands and precursors of polycyclic ligands.[10-12]



A = BH_3
$Mo(CO)_5$
$CpMo(CO)_2Cl$
$CpFe(CO)Ph$
$W(O)Cl_4$
etc

A = BH_3
BF_3
CH_3^+
H^+

A = $CpMo(CO)_2Cl$
A' = H^+
A = BH_3
A' = $W(O)(OMe)_4$
A = $CpMo(CO)_2Cl$
A' = $Fe(NO)_2I$ (?)

A = $CpMo(CO)_2$
$CpFe(CO)$
etc

A = $CpMo(CO)_2$
$CpW(CO)_2$
$CpFe(CO)$
$CpRu(CO)$

SCHEME 7 Coordination modes of the P—N entity.

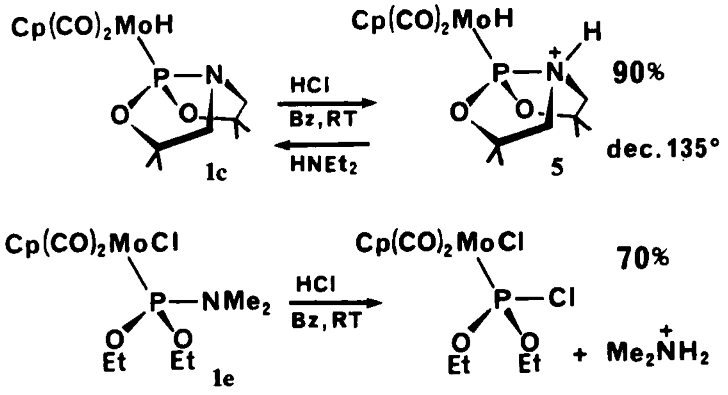
COORDINATION OF PHOSPHORUS-BONDED NITROGEN ATOMS

Protonation and Alkylation

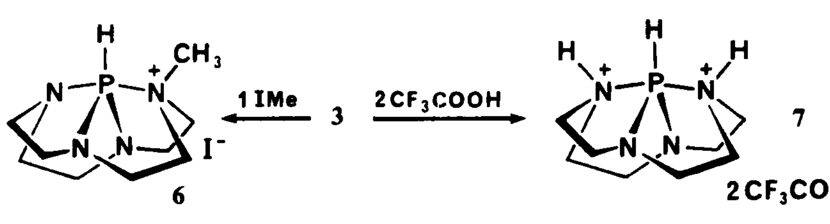
The proton affinity of P-bonded tricoordinated N atoms is scarcely documented just because, as a rule, P—N "single" bonds are readily cleft by hydracids to give the corresponding halophosphorus derivatives and ammonium halides.[13,14] Coordination of the phosphorus atom to a transition metal does not change this issue. Protonated P-bonded nitrogen species have often been postulated to occur as reaction intermediates, but no direct evidence for their formation could be produced.

It is therefore noteworthy that an unexpectedly stable (dec. ~ 135°) compound, **5**, having such a protonated P-bonded nitrogen could be isolated in close to quantitative yields when the constrained bicyclic aminophosphane **1c** was subjected to the action of HCl (Scheme 8), a process which can be reversed under the action of diethylamine.[13] By contrast, the adduct of the non-cyclic ligand **1e** with comparable environments at P and N, when treated in similar conditions, immediately underwent P—N bond cleavage. No phosphorammonium species could however be isolated with the non-methylated bicyclic phosphane **1a** which gave a complex reaction; this may however be related to the tendency of **1a** to undergo dimerization.[10]

The action of IMe on cyclenophosphorane **3** yielded quasi-quantitatively the phosphorammonium salt **6**, establishing the nucleophilic character of the apical nitrogen in this polycyclic compound (Scheme 9). Cyclenphosphorane also readily



SCHEME 8 Basicity of P—N towards H^+.[13,29]



SCHEME 9 Protonation and alkylation of cyclenphosphorane.[18]

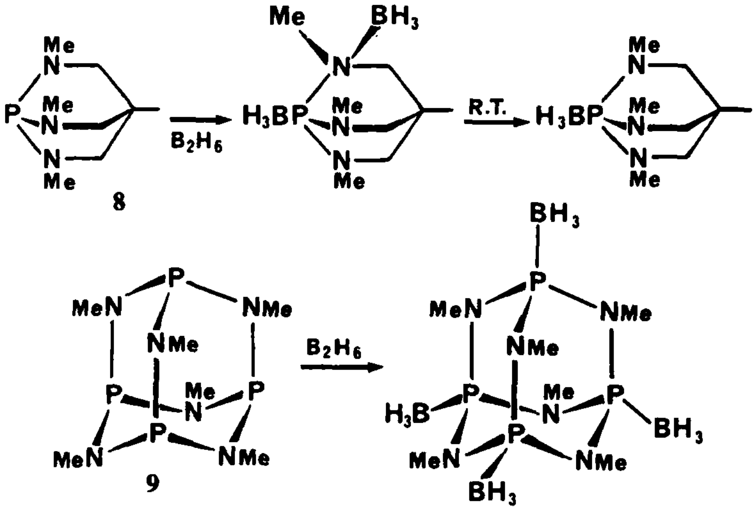
reacts with two equivalents of CF_3COOH; the ^{31}P and ^{31}C NMR spectra of the hygroscopic compound isolated indicate deprotonation of the preserved five-coordinated phosphorane structure 7.[18]

Coordination of P-bonded Nitrogen Atoms to BH_3 or BF_3

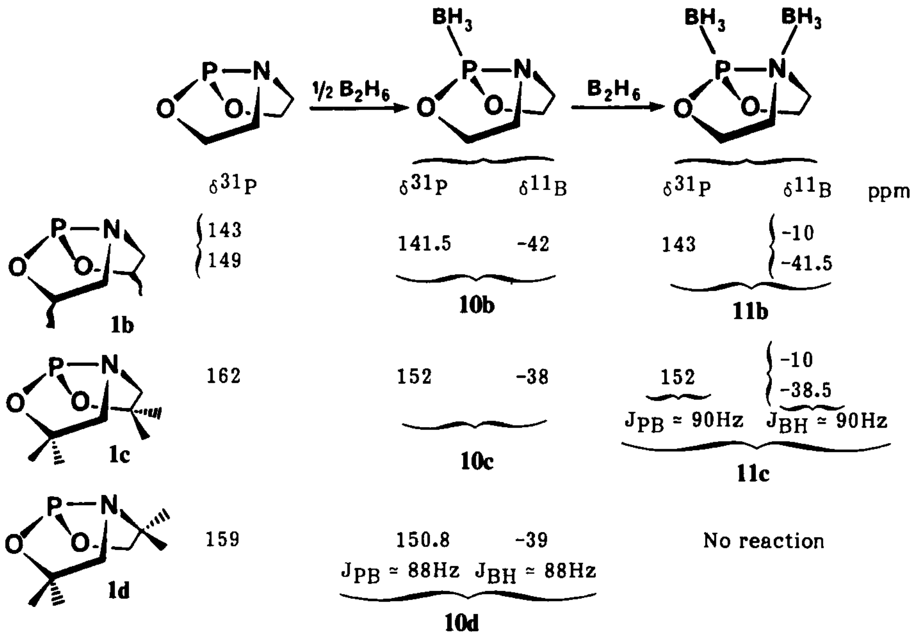
P-bonded nitrogen atoms usually show little inclination for Lewis acids. Examples of coordination are scarce (Scheme 10) and the few adducts known, generally with BH_3, are rather unstable.[19] An adduct with a BH_3 group on one of the N atoms of **8** was obtained by Verkade, but only after a first BH_3 group had been coordinated to the phosphorus site; however, it loses the N-coordinated borane group on attaining room temperature.[20] In **9**, all the four P-sites readily accept BH_3 or $Ni(CO)_3$, while the coordination of the N sites was never observed.[8] A forced pyramidal configuration at nitrogen does not guarantee obtaining a stable adduct at nitrogen.[21]

The behavior of the bicyclic aminophosphanes **1** (Scheme 11) is therefore of interest. Although the P-adduct **10** is still the first to form, dicoordination to yield **11** readily takes place when a second equivalent of BH_3 is added (unless there is, as in **1d**, steric hindrance at nitrogen).[19,22]

The most remarkable feature of these white crystalline adducts is their thermal stability: they can be stored under nitrogen for several months at room temperature without noticeable changes, and their decomposition points, close to or above 110°, are higher than those of the mono adducts. This stability is further illustrated by the observation of the molecular peak in the mass spectra, and permitted X-ray diffraction patterns to be recorded on **11c**. The N—B bond (1.655(8) Å) falls within the range, though at the higher limit, of those measured for BH_3 adducts of non-P-bonded nitrogens. The rather short P—B bond (1.873(7) Å) is consistent with the phosphorus bearing electronegative substituents. The NMR data clearly establish that the coordination bonds are preserved in solution.



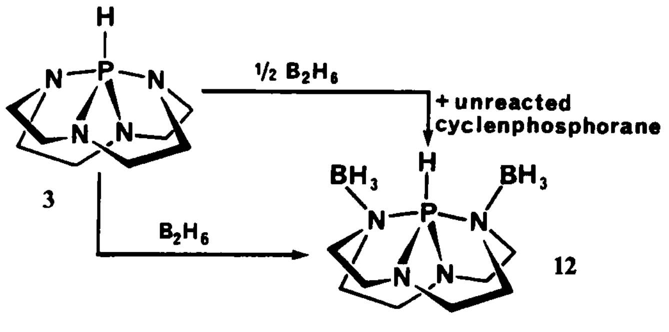
SCHEME 10 Addition of B_2H_6 on $>P—N<$.[8,20]



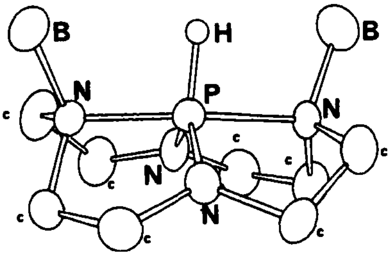
SCHEME 11 Coordination of P and N in bicyclic aminophosphanes.[22]

The harder BF_3 acid was a priori expected to be more inclined to coordinate to the nitrogen than to the phosphorus site, and N-bonded-only BF_3 adducts have indeed been reported to form with F_2P—NMe_2 (unstable)[3] and $FPN(Me)CH_2CH_2NMe$.[24] Similarly, stable sublimable monoadducts (meso and racemic) were obtained with **1b**, in which N-coordination was established by NMR. No further addition was observed with excess BF_3, and no evidence was found for an exchange of BF_3 groups between the two potential donor sites.[23]

Another unusual example of coordination of borane groups to P-bonded nitrogens is provided by the cyclenphosphorane adduct **12** (Scheme 12) in which two BH_3 groups are affixed to the apical nitrogen sites, which results in an original B-N-P-N-B



SCHEME 12 A unique stable adduct with two BH_3 groups on two P-bond N atoms.[25]



SCHEME 13 ORTEP view of the cyclenphosphorane bis(borane) adduct **12**.[25]

sequence (Scheme 13).[25] It is notable that the N—B bond lengths (1.597 and 1.604 Å) lie well within the usual range reported for N—BH_3 bonds (1.56–1.66 Å) in spite of the nitrogen atom's being bonded to a third-row element. The outstanding stability of **12** is illustrated by its high melting/decomposition point around 200°C, absence of air sensibility, and absence of evolution of diborane upon dissolution. It is also noteworthy that the di-adduct is the only compound formed, in addition to cyclenphosphorane, when there is a shortage of B_2H_6.

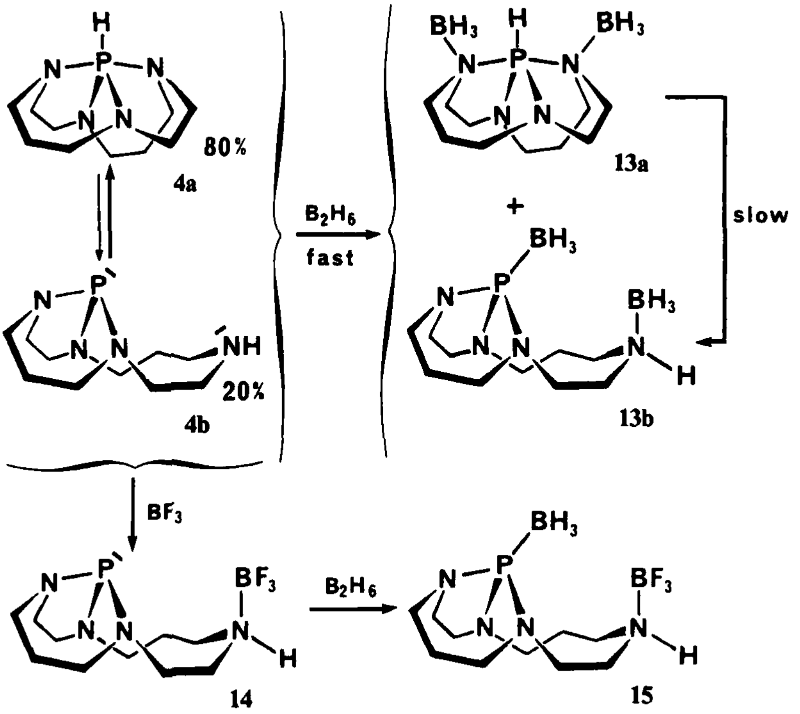
The formation and stability of **12** establishes that apically P-bonded N-sites may display definite basicity. The p_π-d_π rationale leads indeed to the expectation that the apical nitrogen's lone pair should be more available for donation than the equatorial ones,[26] especially here where polycyclic constraints contribute to conferring some pyramidal character to the former. In keeping with this rationale, **12** exhibits unusually short equatorial (av. 1.649 Å) and long apical (av. 1.868 Å) P—N bonds. The latter are longer than all those yet reported for phosphorane structures with apical nitrogens. As these nitrogens have no electrons left for donation, no π-contribution can be envisaged, and the distance measured of 1.87 Å can be proposed as representative of an apical single bond between a bipyramidal P(V) and a tetrahedral N(III). In compensation, maximum Pd_π-Np_π bonding is achieved with the planar equatorial nitrogen atoms, with their substituents favorably oriented perpendicular to the equatorial plane (Scheme 13).

In the case of the less strained, dissymetrical cyclamphosphorane, which occurs in solution as a mixture of tautomers, **4a** + **4b**, the formation of the adducts of both the open and the closed isomers is observed[27] (Scheme 14). Both adducts can be stored in the solid state for months without noticeable changes, but **13a** was shown to convert slowly into **13b** at room temperature in solution.

If one equivalent of BF_3 is allowed to react with **4**, the open N-coordinated adduct **14** is readily formed; this, under the action of diborane, yields the mixed adduct **15**,[27] while an excess of BF_3 leads to a mixture containing ionic compounds with the ^{11}B and ^{19}F identified > $BF_3^+BF_4^-$ pattern.[18]

Coordination of P-bonded Nitrogen Atoms to Transition Metals

The only well established case of transition metal-coordinated P-bonded tricoordinated nitrogen appears for long to have been that in which a tetracarbonyltungsten (0) moiety is coordinated to an amino group exocyclic to a phosphazene ring.[17]



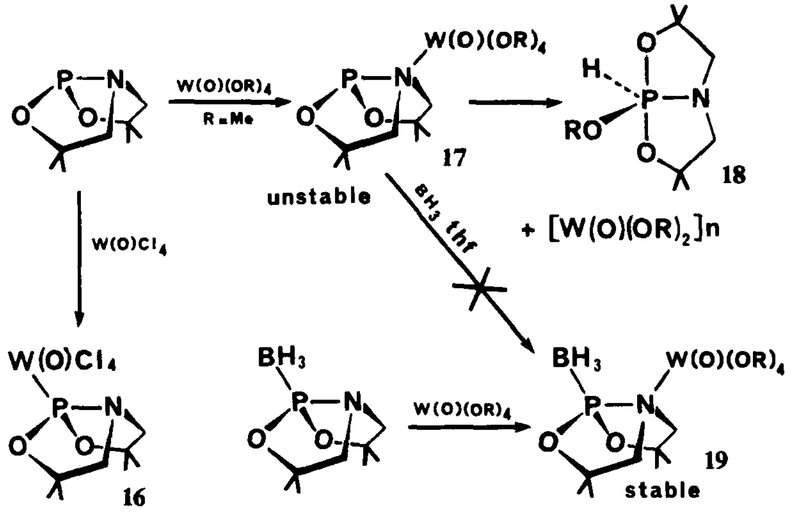
SCHEME 14 The reactions of cyclamphosphorane with B_2H_6 and B_2F_3.[27]

In most cases even ligands **1** act as monodentate P-donors only, as for example towards Mo(0), W(0)[28], Mo(II)[29], Fe(II)[30], Ni(II), Pd(II) and Rh(I)[31] derivatives. Even the tungsten (VI) oxychloride $WOCl_4$ only led to the P-coordinated adduct **16** $WOCl_4$ (**1c**)$_2$ (Scheme 15)[32]. It required the still harder oxyalkoxide $WO(OMe)_4$ to obtain a N-coordinated 1 : 1 adduct **17**. Although **17** was unambiguously identified in solution, it was not possible to isolate it, as a result of a redox process which, in protic solvents, led to the alkoxyphosphorane **18** plus $|W(O)(OR)_2|_n$. Stabilization of a nitrogen-coordinated metal adduct **19** could however be achieved by coordinating the P-site of ligand **1** to a borane group prior to the addition of the tungsten alkoxide; adduct **19** could then be isolated and fully characterized.[32]

Another adduct in which both N and P sites are likely to be coordinated resulted from the addition of half an equivalent of $|Fe(NO)_2I|_2$ to the P-coordinated (η^5-Cp)$Mo(CO)_2Cl$(**1c**) complex.[31] Its infrared (ν(NO) 1755 and 1670 cm^{-1}; ν(FeI) 265 cm^{-1}) and mass spectra ($|1cH|^+$, $|M—Fe(NO)_2I|^+$, but no molecular ion) are consistent with such a formulation with a M—P—N—M′ sequence, but no single crystal could be grown to allow conclusive characterization.

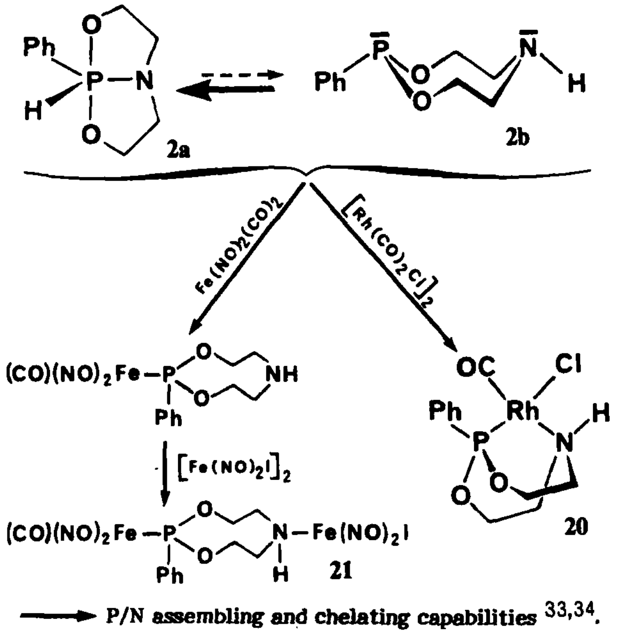
A further interesting situation has been met where both phosphorus and nitrogen became coordinated to transition metals *after* the P—N bond had been opened, so as to create two essentially independent donor sites.

This was consistently observed with aminophosphoranes of type **2**, which as such are expected to have very little donor capacity at the close-to-planar equatorial



SCHEME 15 Coordination of a P-bound N to a transition metal.[32]

nitrogen, and none at phosphorus which has no free electrons available. But these compounds, under the action of transition metal derivatives, were shown to yield adducts of their open form tautomers **2b** (Scheme 16).[33] Such a behavior hence requires that the P—N compound is structurally fit to convert into an open tautomeric species with unbonded phosphane and amine sites. The latter species can then behave as a mono- or as a bidentate, chelating (as in **20**) or bridging (as in **21**)



→ P/N assembling and chelating capabilities [33,34].

SCHEME 16 Coordination chemistry of bicyclic hydroaminophosphoranes.

ligand (Scheme 16) with a variety of metal derivatives, including for example Mo and W, Fe and Ru, Rh, and Pd species.[33,34,30] Cyclamphosphorane **4**, but not cyclenphosphorane **3**, exhibits comparable coordination chemistry.[35]

Effects of the Nitrogen Atom on the Donor Character of the Phosphorus Atom

The maintenance of the pyramidal configuration at a P-bonded nitrogen as a result of cyclic strians is obviously not without repercussion on the phosphorus site's donor character. When for example the frequency of the ν(CO) vibrations of $M(CO)_5L$ adducts are measured—a commonly used approach to probe the π-accepting ability of a ligand L—one observes that these frequencies are significantly higher than L = **1** than with related but acyclic phosphorus ligands reputed to be strongly π-acid (Scheme 17).[22,28,29]

This again is in line with the p_π-d_π rationale: the overlap of the orbitals concerned being expected to be less effective when nitrogen is pyramidal, the π-acid character of the phosphorus with respect to the metal should be enhanced; but the strain imposed on the angles at phosphorus is also expected to influence this character.

Interestingly, other data can be interpreted to contradict this picture. $^1J_{P-B}$ values have been considered to reflect Lewis π-acidity of a P-site.[36] Here however it is found that these coupling constants are not significantly affected when adducts of the bicyclic species are compared to acyclic adducts with comparable substitutions at phosphorus, or when the di-borano adducts **11** are compared to the mono adducts **10** (Scheme 18), which, accordingly, would mean that the extent of Np_π-Pd_π bonding is the same in both mono and di-adduct, i.e. effectively zero, since in the latter case the nitrogen's lone pair is no longer available for π-bonding.[22] But how will one then

$Mo(CO)_5L$:

L = 1b	: 2098, 2006, 1976, 1966 cm^{-1}
$P(OEt)_3$	: 2080, 1995, 1966, 1952
$P(NMe_2)_3$	: 2073, 1986, 1949, 1942
PPh_3	: 2076, 1922, 1943

$Mo(CO)_3L_3$:

L = 1b	: 2020, 1923
PF_2NMe_2	: 2000, 1923
PPh_3	: 1949, 1835
dien	: 1883, 1723

⟶ High π -accepting character of P in 1b.

SCHEME 17 ν(CO) stretching frequencies in $Mo(CO)_5L$ and $Mo(CO)_3L_3$.

Compound	$^1J_{P-B}$(Hz)
(1 b,c,d)BH_3 (or 10)	92 - 93
Me_2OPBH_3	97.2
$Me_2N(^+BuO)_2PBH_3$	99
(1 b,c)$2BH_3$ (or 11)	89 - 90
(1c)[$W(O)(OMe)_4$]BH_3	89

no significant effect of NP_π-Pd_π bonding ?

SCHEME 18 Some $^1J_{N)P-B}$ couplings.[22,37]

conciliate this with the large decrease in P—N bond length (0.07 Å) observed between **11c** and the solely P-coordinated complex **22**? It is also difficult to reconcile the total absence of Np_π-Pd_π interaction with the low coordination ability of this pyramidal nitrogen towards transition metals, even in their high oxidation states.

TRANSITION METAL-BRIDGED P—N BONDS

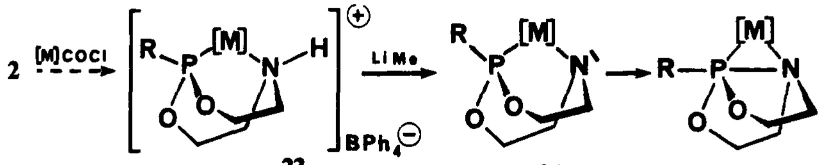
A series of complexes having the structural "motif" $\overset{M}{P\text{—}N}$ has recently been obtained. These display a transition-metal-bridged P—N bond, and the phosphorus atom is here best described as being in a 5-coordinated trivalent phosphoranide state.[38-40]

It is remarkable that not only did several of these compounds turn out to be highly stable, with melting or decomposition points up to 200°C, but also that the formation of the P—N bond was actually achieved in the metal's coordination sphere only *after* both the phosphorus and nitrogen atoms were coordinated to this metal.

Scheme 19 exemplifies this synthetic approach: a cationic phosphorus- and nitrogen-bonded metal chelate, **23**, is first derived from the bicyclic aminophosphorane **2**. A base, LiMe, is then used to abstract a proton from **23** and convert it into the unstable amido/phosphane complex **24**, which, in the example shown in Scheme 19, converts into the metal-bridged aminophosphoranide **25** at room temperature in solution. In the latter reaction, the nitrogen's lone pair can formally be considered as responsible for the creation of the new N—P bond. These reactions are close-to-quantitative, and the overall yields depend primarily on the procedure to be used for their isolation, hence on the nature of the counter-ion; with BPh_4^- these yields can attain 90%. The formation of **25** is characterized in the ^{31}P NMR by a remarkable upfield shift of some 130 to 160 ppm with respect to **23** or **24**.[41] Further examples of such metal-bridged P—N bonds have been obtained from cyclamphosphorane.[35]

Scheme 20 represents an ORTEP view of one of these compounds (**25**: R = Ph; |M| = $CpMo(CO)_2$), with its unusual $\overset{M}{P\text{—}N}$ cycle and a close-to-pyramidal arrangement of the substituents around the 5-coordinated phosphorus atom.[39]

It is notable that the N—M bond-length (2.227(10) Å) falls well into the range found for the common Mo(II)-amine adducts; the P—M bond (2.382(4) Å) is short, but the P—N bond (1.980(12) Å) is unusually long.

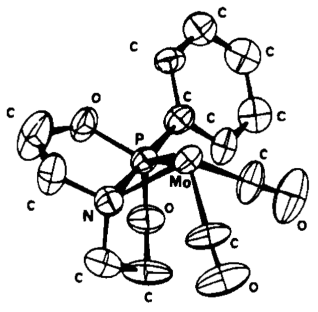


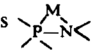
23 **24** **25**

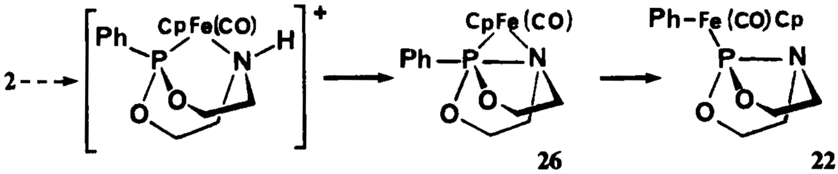
$[M] = CpMo(CO)_2, CpW(CO)_2$

a transition metal induced opening and closing of a P–N bond.

SCHEME 19 Access to metal-bridged aminophosphoranides.[39]



SCHEME 20 An ORTEP view of the molybdenum phosphoranide 25 with its  motif.[39]



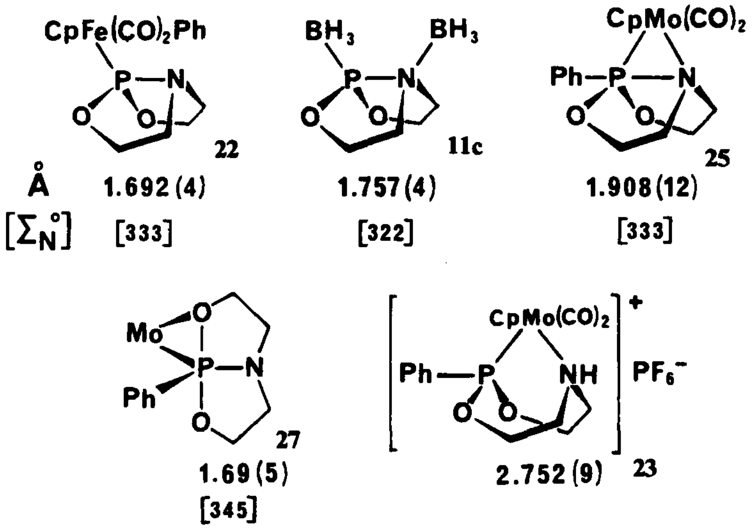
26 **22**

SCHEME 21 From a bicyclic aminophosphorane to an iron aminophosphoranide to an iron aminophosphane adduct.[30]

In the case of the iron analogue **26** (Scheme 21), an unexpected transformation was observed to occur in which the three-membered $\overset{Fe}{\text{P—N}}$ ring, which resulted from the P—N bond formation, opens again, but at the Fe—N bond, while the phenyl group, initially borne by the phosphorus atom, is transferred onto the iron atom. The P-bonded amine/phosphane adduct **22** is formed by this process.

Scheme 22 compares the lengths of a collection of P—N bonds taken in related environments. In the absence of electrons available for donation, the P—N bond in the diborane adduct **11c** can be taken as representative of a single bond. With respect to this bond, one observes a considerable (0.1 Å) shortening of the bond, when only the phosphorus atom is coordinated in **22** in spite of the marked pyramidal character of the nitrogen atom. That this P—N bond is as short as in **27**, with its close-to-planar nitrogen, shows that the mechanism(s) which cause(s) the bond-shortening is(are) not hindered by this pyramidal character of the nitrogen atom; this is particularly notable, since further contributions to bond shortening are expected in the case of **27** from the rehybridization of both N (increase in s character) and P (equatorial bond) atoms. The P—N bond in **25** is one of the longest known, probably as a combined result of its apical nature, electron donation to the metal and steric strain.

The few examples reported in this paper show that, while the decrease and virtual disappearing of the nitrogen's Lewis donor character when bonded to phosphorus certainly remains the most frequent situation, this can be profoundly changed when structural constraints are introduced. Definite basicity can then appear at such third-row-element-bonded nitrogen atoms. Moreover, these constraints can induce original reactivity and lead to new structural arrangements.



SCHEME 22 An extensive range of P—N bond length.

ACKNOWLEDGMENTS

Thanks are due to my coworkers whose names are cited in the references, to Bunty Lepage for the typing, to Colette Onteniente for the artwork, to the CNRS, French and Polish Academies of Sciences for support, and to Pr. Jan Michalski and his Staff for their friendly reception in Poland.

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14. Cyclophosphonitriles provide some interesting exceptions to this rule: Although alkylation usually occurs at the intracyclic nitrogens, evidence has been reported for exocyclic alkylation by Me_3O^+/BF_4^- of the dimethylamino-substituted compounds $N_3P_3Cl_{6-n}(NMe_2)_n$.[15] In these structures there appears however to be much intracyclic π-bonding with the electron-rich dicoordinated nitrogens, and consequently little with the tricoordinated, exocyclic ones.[16] A remarkable and unique example of coordination of a soft transition metal moiety, $W(CO)_4$ (further coordinated to a phosphorus atom), to a dimethylamino group exocyclic to a tetracyclophosphonitrile has also been reported.[17]

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