THE PREPARATION, STRUCTURES, AND REACTIONS OF TWO-COORDINATE PHOSPHORUS CATIONS

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Abstract - The synthesis of a variety of two-coordinate phos-
phorus cations (phosphenium ions) has been achieved via halide
ion abstractions from precursor halophosphines. At least one
dialkylamino group is necessary for the detection or isolation
of a phosphenium ion, thus implying the importance of thermo-
dynamic stabilization of these species by N→P conjugation.
The structure of the salt, $[(^iPr_2N)_2P]^+[AlCl_4]^-$, has been
determined by X-ray crystallography. Significant features of
the structure are the rather short N-P bond lengths (1.613 Å),
the near planarity of the $(C_2N)_2P$ skeleton, and the trigonal
planar geometries at both nitrogen centers. Other phosphenium
ions have been characterized primarily on the basis of ^{31}P NMR
chemical shifts which fall in the range +260 to +510 ppm.
Many of the phosphenium ions exhibit fluxional behavior at
ambient temperature. Dynamic NMR studies and molecular orbital
calculations have established that the stereochemical non-
rigidity is due to rotation around the N-P bonds. The versatility
of phosphenium ions as reagents has been demonstrated by the
fact that they react with both electron pair donors such as
phosphines and electron pair acceptors such as metal carbonyls.

INTRODUCTION

Our interest in two-coordinate phosphorus cations represents part of a more
general concern with the cationic chemistry of several main group elements.
Two-coordinate phosphorus cations, or phosphenium ions, constitute one member
of a family of silicon, phosphorus, and sulfur cations featuring six valence
electrons at the central atom. It will be demonstrated that the synthesis of
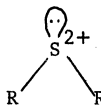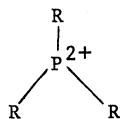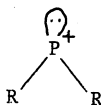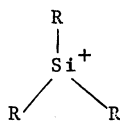
phosphenium ions has raised a number of interesting questions about their
bonding and stereochemistry. Furthermore, these species are showing promise
as versatile and useful reagents. The reactivity patterns of phosphenium
ions will be illustrated by discussing their reactions with both electron
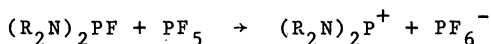pair donors and electron pair acceptors.

SYNTHESIS OF PHOSPHENIUM IONS

So far the most viable approach to phosphenium ion synthesis involves halide
ion abstraction reaction from precursor halophosphines, typically

$$R_2N \!\!\! > \!\!\! P - Cl + 1/2\ Al_2Cl_6 \rightarrow R_2N \!\!\! > \!\!\! P^+ + AlCl_4^- \qquad (1)$$
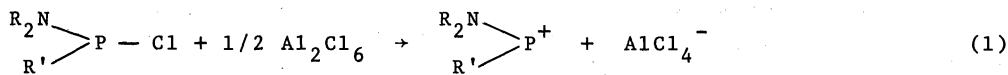
$$R = \text{alkyl}, Me_3Si$$
$$R' = R_2N, (Me_3Si)_2N, Cl, {}^tBu \qquad (2)$$

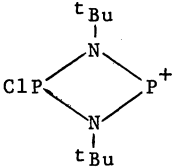$$(R_2N)_2PF + PF_5 \rightarrow (R_2N)_2P^+ + PF_6^-$$

$$R = \text{alkyl}$$

This approach has its origins in the work of Fleming, Lupton, and Jekot (1), and Hutchins and Maryanoff (2) who concluded independently that the treatment of cyclic haloaminophosphines with halide ion abstractors resulted in cyclic phosphenium ions.

As noted by Parry and co-workers (3,4), ^{31}P NMR spectroscopy is an invaluable tool both for the identification of phosphenium ions and for the elucidation of subsequent reactions. The data in Table 1 demonstrate that the ^{31}P NMR chemical shifts of phosphenium ions encompass the range +260 to +510 ppm. In fact, the ^{31}P chemical shift of $[{}^tBu(Me_2N)P]^+$ appears to be the largest ever measured (5). The pronounced deshielding in this case is attributed to (i) the inability of the t-butyl group to conjugate with the P^+ center, and (ii) the possibility that dative π-bonding from the Me_2N group is attenuated by sterically induced twisting of this moiety (vide infra). Another conspicuous feature of the data in Table 1 is the fact that in all experiments to date at least one dialkylamino must be appended to the cationic center to permit detection or isolation of a phosphenium ion. This observation leads us to imply that thermodynamic stabilization of the cations by N→P π-bonding is more important than kinetic stabilization by bulky substituents.
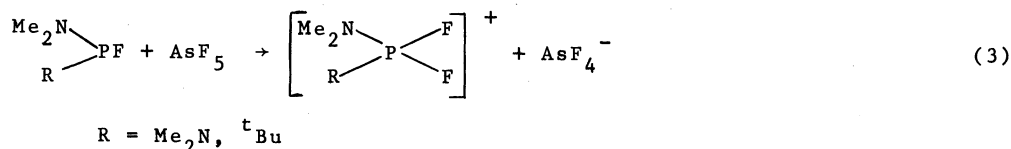
TABLE 1. ^{31}P NMR chemical shifts of phosphenium ions

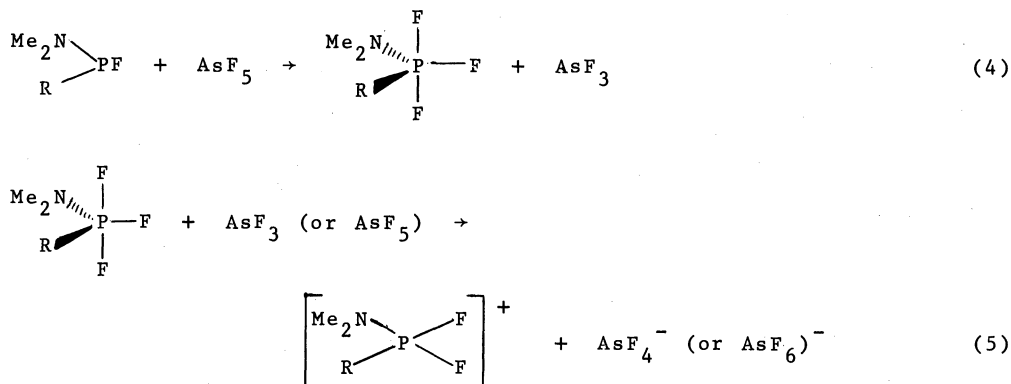| Cation	^{31}P Chemical Shift[a]
$(Me_2N)_2P^+$	264[b]
$(Me_2N)({}^iPr_2N)P^+$	290
$({}^iPr_2N)_2P^+$	313
$Cl(Me_2N)P^+$	325[b]
$(Me_2N)[(Me_3Si)_2N]P^+$	354
(cyclic structure: ClP and P⁺ bridged by two N–ᵗBu groups)	363
$[(Me_3Si)_2N]_2P^+$	451
${}^tBu(Me_2N)P^+$	510

[a] In ppm downfield from 85% H_3PO_4.
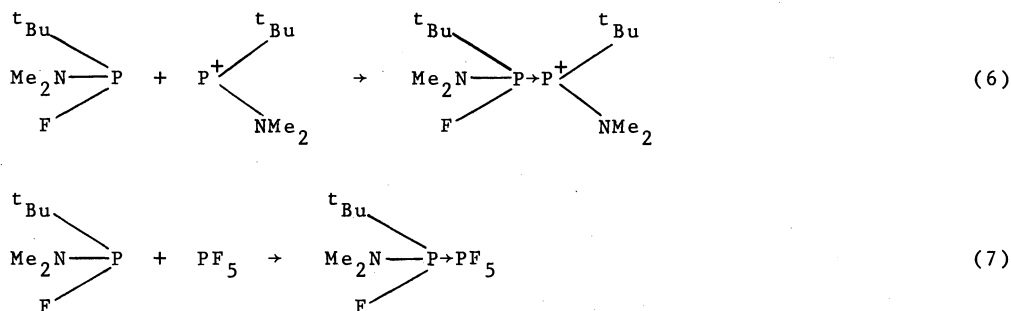
[b] Data from reference 4.

The interaction of a halophosphine with a halide ion acceptor is not always straightforward. Consider, as a first example, the reaction of fluorophosphines with AsF_5 (5,6). Rather than producing phosphenium cations this reaction results in the formation of four-coordinate fluorophosphonium cations.

$$\begin{array}{c}Me_2N\\ \diagdown\\ \diagup\\ R\end{array}PF \;+\; AsF_5 \;\rightarrow\; \left[\begin{array}{c}Me_2N\\ \diagdown\diagup F\\ P\\ \diagup\diagdown F\\ R\end{array}\right]^+ \;+\; AsF_4^- \qquad\qquad (3)$$

$$R = Me_2N, {}^tBu$$

While the mechanism of this net transfer of F^+ is not known, it is speculated that at least two steps are involved. The first step presumably involves oxidative fluorination of the fluorophosphine forming a trifluorophosphorane followed by fluoride ion abstraction by AsF_3 or AsF_5.

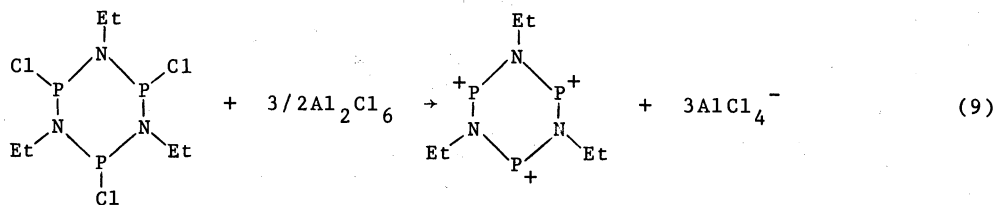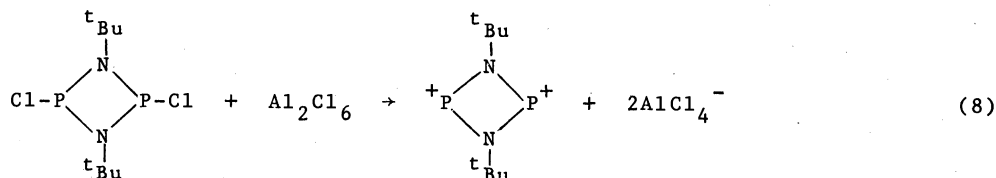$$\begin{array}{c}Me_2N\\ \diagdown\\ \diagup\\ R\end{array}PF \;+\; AsF_5 \;\rightarrow\; \begin{array}{c}F\\ Me_2N_{/\!/\!/\!\!,}\;|\\ P-\!\!\!-F\\ R\blacktriangleleft\;|\\ F\end{array} \;+\; AsF_3 \qquad\qquad (4)$$

$$\begin{array}{c}F\\ Me_2N_{/\!/\!/\!\!,}\;|\\ P-\!\!\!-F\\ R\blacktriangleleft\;|\\ F\end{array} \;+\; AsF_3 \;(or\; AsF_5) \;\rightarrow$$

$$\left[\begin{array}{c}Me_2N\\ \diagdown\diagup F\\ P\\ \diagup\diagdown F\\ R\end{array}\right]^+ \;+\; AsF_4^- \;(or\; AsF_6)^- \qquad\qquad (5)$$

As a second example consider the reaction of $Me_2N({}^tBu)PF$ with PF_5 (5). This results in a highly complex ^{31}P NMR spectrum, first-order analysis of which indicates that the following two side reactions occur in addition to production of the $[Me_2N({}^tBu)P]^+$ cation.

$$\begin{array}{c}{}^tBu\\ \diagdown\\ Me_2N-\!\!\!-P\\ \diagup\\ F\end{array} \;+\; \begin{array}{c}{}^tBu\\ \diagup\\ P^+\\ \diagdown\\ NMe_2\end{array} \;\rightarrow\; \begin{array}{c}{}^tBu\\ \diagdown\\ Me_2N-\!\!\!-P\rightarrow P^+\\ \diagup\\ F\end{array}\begin{array}{c}{}^tBu\\ \diagup\\ \\ \diagdown\\ NMe_2\end{array} \qquad (6)$$

$$\begin{array}{c}{}^tBu\\ \diagdown\\ Me_2N-\!\!\!-P\\ \diagup\\ F\end{array} \;+\; PF_5 \;\rightarrow\; \begin{array}{c}{}^tBu\\ \diagdown\\ Me_2N-\!\!\!-P\rightarrow PF_5\\ \diagup\\ F\end{array} \qquad\qquad (7)$$

Equation (6) exemplifies the reaction of a phosphenium ion with a Lewis base. Presumably the interaction occurs by donation of the electron pair on the phosphine to the formally vacant P(3p) orbital on the phosphenium ion. The fact that the reaction of $Me_2N({}^tBu)PF$ with $[Me_2N({}^tBu)P]^+$ is so facile indicates the very electrophilic nature of the cationic center. This conclusion is consistent with the very large positive (i.e. deshielded) chemical shift for this cation. Reactions of the type shown in Equation (7) have been observed previously for methylated phosphines (7).

Attempts have been made to synthesize phosphorus polycations using the compounds shown below (8).

$$\underset{\underset{\displaystyle{}^tBu}{\overset{\displaystyle{}^tBu}{\text{Cl-P}}\diagup\!\!\!\diagdown\text{P-Cl}}}{} \quad + \quad Al_2Cl_6 \quad \rightarrow \quad \text{(dication)} \quad + \quad 2AlCl_4^- \tag{8}$$

$$\text{(ring with Cl)} \quad + \quad 3/2\,Al_2Cl_6 \quad \rightarrow \quad \text{(trication)} \quad + \quad 3AlCl_4^- \tag{9}$$

The di- and trications shown above are intriguing because of their similarity to carbocyclic π–systems. Thus, neglecting the orthogonal phosphorus lone pair electrons, the di- and trications should be π–isolectronic with cyclobutadiene and benzene respectively. We find, however, that treatment of the diazadiphosphetidine with an excess of aluminum chloride results in the abstraction of only one chloride ion as evidenced by the AB pattern ^{31}P NMR spectrum (Figure 1 and Table 1) (9).
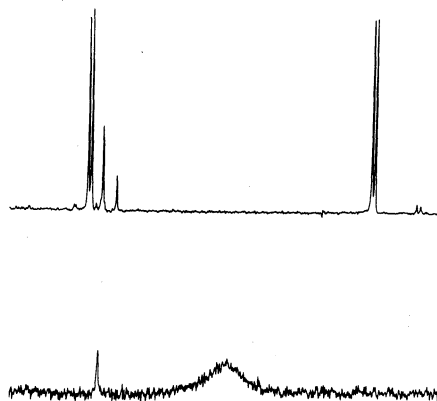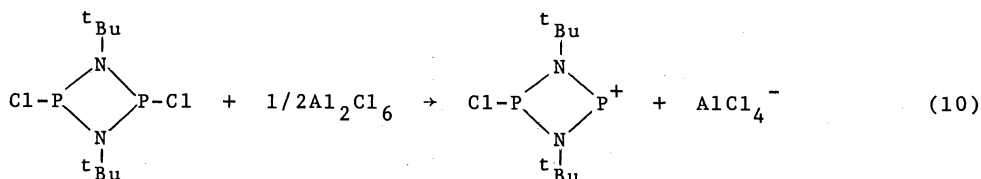
$$\underset{}{\text{Cl-P}\diagup\!\!\!\diagdown\text{P-Cl}} \quad + \quad 1/2\,Al_2Cl_6 \quad \rightarrow \quad \text{Cl-P}\diagup\!\!\!\diagdown\text{P}^+ \quad + \quad AlCl_4^- \tag{10}$$

Fig. 1. ^{31}P NMR spectrum of mixtures of $(^tBuNPCl)_2$ and Al_2Cl_6 in CH_2Cl_2 at $-40°$ (upper spectrum) and $+70°$ (lower spectrum). The lower intensity peaks are due to impurities.

Warming the system from $-40°$ to $+70°$ results in collapse of the AB spectrum and the production of a broad resonance with the same chemical shift. Possibly this observation is due to an intramolecular transfer of Cl^- between the two phosphorus sites; however, this speculation needs to be verified.

MOLECULAR AND ELECTRONIC STRUCTURES OF PHOSPHENIUM IONS

The two-coordinate geometry of phosphenium ions, $(R_2N)_2P^+$, suggested by Parry et al. (4) has been confirmed in our laboratory by X-ray diffraction experiments on $[(^iPr_2N)_2P]^+[AlCl_4]^-$ (10). The conformation of $(^iPr_2N)_2P^+$ in the solid state is shown in Figure 2, and a summary of pertinent bond lengths and angles appears in Table 2.

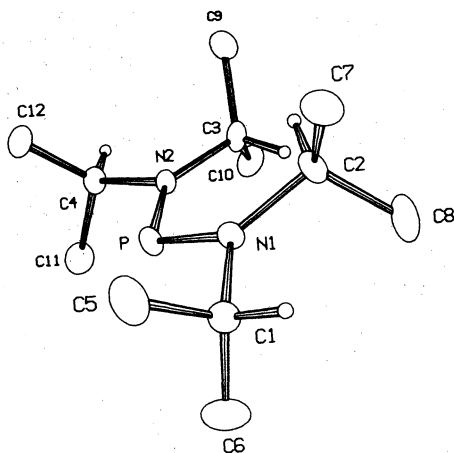Fig. 2. ORTEP drawing of [(^{i}Pr$_2$N)$_2$P]$^+$. The thermal ellipsoids
are drawn at the 20% probability level. The methyl hydrogens
are omitted. (Reproduced by permission of the American Chem-
ical Society).

TABLE 2. Bond lengths and angles for the dicoordinate phos-
phorus cation, [(^{i}Pr$_2$N)$_2$P]$^+$

Bond Lengths (Å)	
P-N(1)	1.611 (0.004)
P-N(2)	1.615 (0.004)
N(1)-C(1)	1.530 (0.006)
N(1)-C(2)	1.500 (0.006)
N(2)-C(3)	1.497 (0.006)
N(2)-C(4)	1.526 (0.005)

Bond Angles (degrees)	
N(1)-P-N(2)	114.8 (0.2)
P-N(1)-C(1)	112.3 (0.3)
P-N(1)-C(2)	132.9 (0.3)
C(1)-N(1)-C(2)	114.7 (0.3)
P-N(2)-C(3)	132.1 (0.3)
P-N(2)-C(4)	112.5 (0.3)
C(3)-N(2)-C(4)	115.4 (0.3)

The geometry at the cationic center can be understood in terms of approximate
trigonal planar hybridization at phosphorus, diminution of the N(1)-P-N(2)
bond angle from 120 to 114.8° being caused by lone pair-bond pair repulsions.
Within experimental error the sum of the bond angles around each of the nitro-
gen atoms is 360°, thus indicating planar nitrogen geometries for both ^{i}Pr$_2$N
groups. Such an arrangement is expected on the basis of optimization of the
conjugation between the nitrogen lone pairs and the formally vacant phosphorus
3p orbital. The approximately planar conformation of the sub-unit C(1)C(2)N(1)-
PN(2)C(3)C(4) is understandable on the same basis. The average N-P bond length
of 1.613Å in [(^{i}Pr$_2$N)$_2$P]$^+$ is slightly shorter than those found in neutral
aminophosphines (11). This bond shortening is presumably due a combination of
the formal positive charge at phosphorus and the N→P dative π-bonding discussed
above. The fact that the dihedral angle between the two C$_2$NP planes is approx-
imately 18° suggests that the cation geometry is influenced by steric strain.

Initially it was thought that steric strain was also responsible for the fact
that within each C_2NP moiety the endo C-N-P angle is appreciably larger than
the other two angles.

                                          <NPN = 114.8°
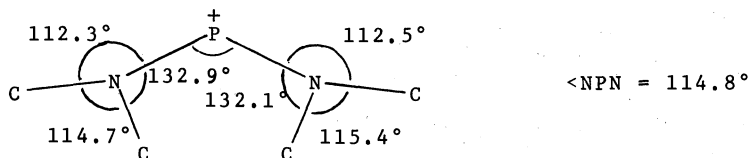
However, the geometry-optimized structure emerging from ab initio (GAUSSIAN 76)
molecular orbital (MO) calculations on the virtually strain-free model cation,
$(H_2N)_2P^+$, displayed the same trends in the bond angles at nitrogen (12).

                                          <NPN = 102.9°
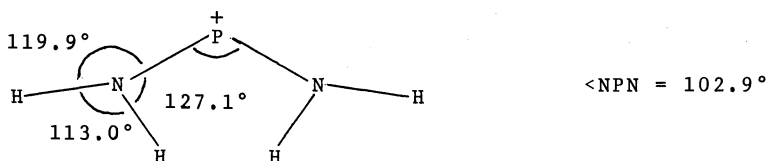
It is interesting to note that the same trend in angles is apparent in the
X-ray structure of the N,N,N',N'-tetramethylformamidinium cation (13). It

                                          <NCN = 131.4°
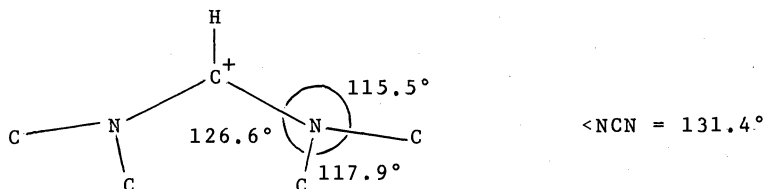
seems that the foregoing structural features are due to the operation of
subtle electronic effects.

The ab initio MO calculations (12) have also provided valuable insights into
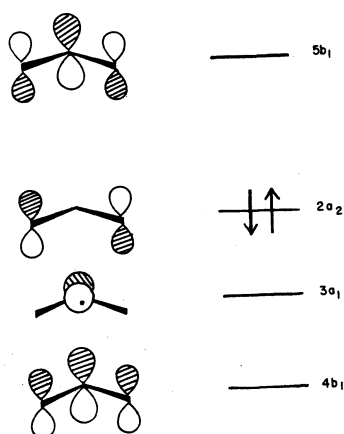the electronic structures of phosphenium ions. As shown in Figure 3, the

Fig. 3. Some molecular orbitals for the model cation,
$[(H_2N)_2P]^+$.

highest occupied MO of the model system, $(H_2N)_2P^+$, possesses a_2 symmetry and consists of an out-of-phase combination of N(2p) AO's. The second occupied MO is essentially phosphorus lone pair in character and is directed perpendicular to the N(2p) AO's. It is this $3a_1$ MO which is responsible for the donor action of phosphenium ions (<u>vide infra</u>). The $4b_1$ MO is best described as N–P π–bonding. Conjugation of this type from the filled N(2p) AO's to the vacant P(3p) AO appears to play a pivotally important role in stabilizing phosphenium ions and explains why it is necessary to have at least one dialkylamino group attached to the cationic center. The lowest-lying virtual orbital, $5b_1$, is N–P π–antibonding in character and is expected to play an important role in the binding of phosphenium ions to transition metals.

DYNAMIC STEREOCHEMISTRY OF PHOSPHENIUM IONS

Dynamic NMR studies have shown that acyclic phosphenium ions are stereochemically non-rigid. For a typical cation distinct R_a and R_b resonances are
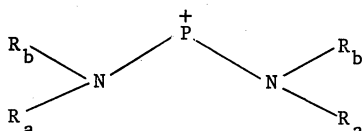
detectable at lower temperatures in accordance with the X-ray crystal structure of $[(^iPr_2N)_2P]^+$. Equivalencing of the R_a and R_b environments could, in principle, arise from N–P bond rotation and/or inversion at the P^+ center becoming rapid on the NMR time scale. To probe this question we prepared the "mixed" cation, $[(^iPr_2N)(Me_2N)P]^+$, and examined its fluxional behavior by ^1H dynamic NMR. Interestingly it was found that $[(^iPr_2N)(Me_2N)P]^+$ exhibits two coalescence phenomena (Figure 4), the barriers pertaining to which are 11.9 and 14.1 kcal/mol.
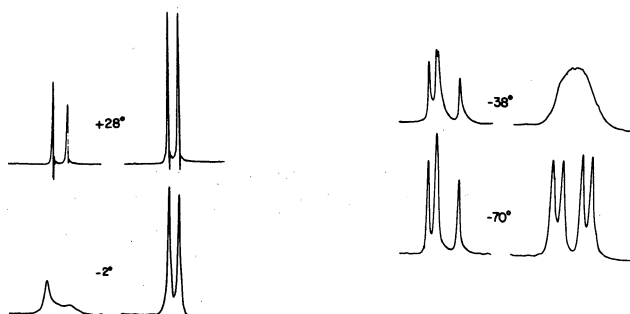

Fig. 4. ^1H NMR spectra of $[(^iPr_2N)(Me_2N)P]^+$ at various temperatures.

The 11.9 and 14.1 kcal/mol barriers are assigned to the $^iPr_2N$ and Me_2N moieties of the "mixed" cation by virtue of their similarity to the barriers in the symmetrical cations (Table 3).

TABLE 3. N–P torsional barriers for phosphenium ions

Cation	Barrier (kcal/mol)
$(Me_2N)_2P^+$	14.6
$(^iPr_2N)_2P^+$	11.1
$\begin{matrix} Me_2N \\ ^iPr_2N \end{matrix} {>} P^+$	11.9 (^iPr); 14.1 (Me)
$\begin{matrix} Me_2N \\ (Me_3Si)_2N \end{matrix} {>} P^+$	16.4 (Me)

The observation of two barriers for $[(^iPr_2N)(Me_2N)P]^+$ indicates that the dynamic NMR observations are due to N-P rotational effects since inversion at the P^+ center would require both dialkylamino groups to undergo coalescence simultaneously. This conclusion agrees with MNDO calculations on $[(Me_2N)_2P]^+$ which indicate that the barriers for single N-P rotation, double N-P rotation, and inversion at P^+ are 8.5, 40.0 and 62.2 kcal/mol, respectively. The computed rotational transition state is thus
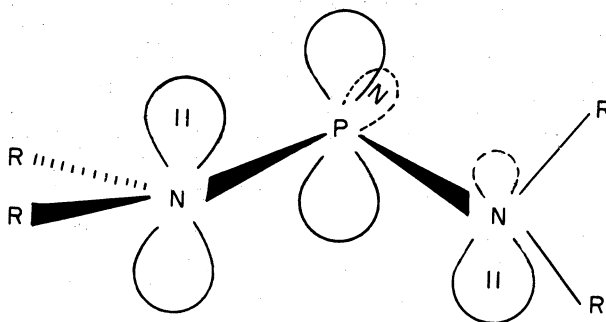
It is clear that as rotation proceeds around a given N-P bond the rest of the cation remains fixed in order to minimize the loss of $p\pi$-$p\pi$ conjugation.

REACTIONS OF PHOSPHENIUM IONS

Phosphenium ions promise to be versatile reagents and interesting ligands because of the presence of both a lone pair of electrons and a vacant p orbital at the cationic center.

Essentially, two approaches have been taken to the preparation of transition metal derivatives of phosphenium ions (14, 15). One approach involves direct interaction of the cation with e.g., metal carbonyls; the other involves coordination of a suitable halogen-containing precursor, such as R_2PCl, followed by halide ion abstraction. X-ray crystallographic studies are in progress on representative $[(R_2N)_2PFe(CO)_4]^+$ species to determine the geometry of ligated phosphenium ions and to assess the π-acceptor capabilities of these ligands by measurement of e.g., the P-Fe, Fe-C, and C-O bond lengths. At the present time the formulation of these materials as phosphenium ion complexes is based on the positive ^{31}P chemical shifts (Table 4).

TABLE 4. ^{31}P NMR chemical shifts for free and complexed phosphenium ions

	$\delta(^{31}P)$ Complexed	$\delta(^{31}P)$ Free
$\begin{bmatrix} Me_2N \\ Cl \end{bmatrix} P \cdot Fe(CO)_4 \end{bmatrix}^+$	287	325
$\begin{bmatrix} Me_2N \\ Me_2N \end{bmatrix} P \cdot Fe(CO)_4 \end{bmatrix}^+$	311	264
$\begin{bmatrix} (Me_3Si)_2N \\ (Me_3Si)_2N \end{bmatrix} P \cdot Fe(CO)_4 \end{bmatrix}^+$	341	451

The π-acceptor nature of the phosphenium ligands has been inferred from interesting work by Bennett and Parry (16) in which they demonstrated that in contrast to the fluorophosphine precursor, the phosphenium complex $[(Me_2N)_2P \cdot Fe(CO)_4]^+$ readily undergoes exchange with labelled CO.

Paine et al. (17,18) have reported the synthesis of coordinated R_2P moieties by treatment of fluorophosphines with organometallic anions such as $[(h^5-C_5H_5)Mo(CO)_3]^-$. However, these compounds are probably best regarded as σ-bonded metal-substituted phosphines like $(h^5-C_5H_5)(CO)_3MPCl_2$, M=Cr, Mo, W (19) rather than phosphenium ion complexes. Structural data are clearly needed to resolve the question of the bonding.

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