

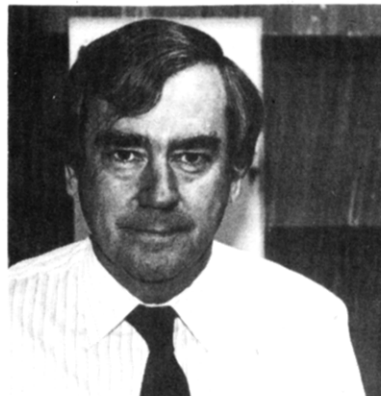
Synthesis and Reaction Chemistry of Stable Two-Coordinate Phosphorus Cations (Phosphenium Ions)

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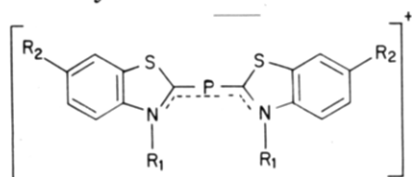
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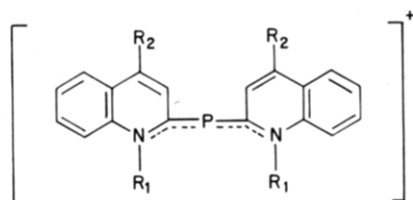
Alan H. Cowley was born in Manchester, England. He received B.Sc., M.Sc., and Ph.D. degrees from the Victoria University of Manchester. Graduate study was conducted under the supervision of the late Professor F. Fairbrother. After postdoctoral study with Professor H. H. Sisler at the University of Florida and a brief sojourn with Imperial Chemical Industries, he joined the faculty of the University of Texas at Austin where he is presently the George W. Watt Centennial Professor of Chemistry. He is the author of approximately 200 publications in the areas of main-group and organometallic chemistry. Honors include a Guggenheim Fellowship and the Royal Society of Chemistry Award for Main-Group Chemistry. He has been named 1986-1987 Centenary Lecturer by the Royal Society of Chemistry.

I. Introduction and Scope of the Review

The first dicoordinate phosphorus cations **1** and **2** were reported by Dimroth and Hoffmann¹ in 1964.

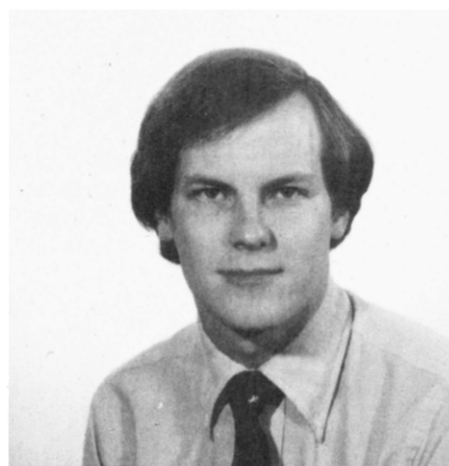


1, R₁ = Me, Et; R₂ = H, OMe



2, R₁ = Et; R₂ = H, Me

Since that time, many other so-called phosphamethine cyanines have been prepared and this exciting field has been reviewed.² However, the ³¹P NMR chemical shifts and patterns of reactivity of these cations suggest ex-

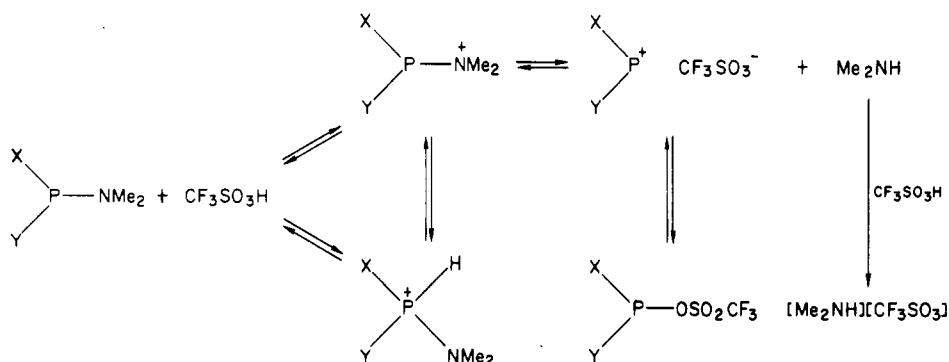


Richard A. Kemp, a native Texan, was born in 1956 and after graduation from high school entered Texas Tech University in Lubbock where he received the Bachelor of Science degree in Chemistry in 1978. He then entered the Graduate School of The University of Texas in Austin, choosing to work with Professor Alan H. Cowley. The topic chosen for study involved the interactions of low-coordinate phosphorus compounds with transition-metal complexes. After receiving the Ph.D. degree in 1981, he spent 2 years as a Research Chemist for Gulf Oil working on new polymerization catalysts. Presently, he is a staff member in the Catalysis Department at Shell's Westhollow Research Laboratory pursuing research on hydroprocessing catalysts. Current interests involve computer applications to chemistry, homogeneous catalysis, and heterogeneous catalysis.

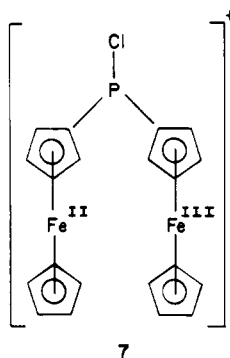
tensive charge delocalization as exemplified by canonical forms **3a,b**. Since the positive charge is not located

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SCHEME I

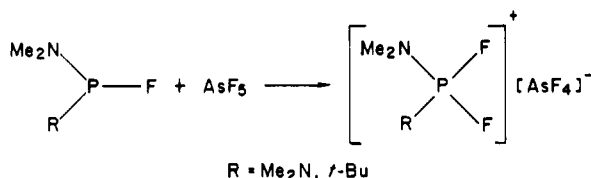


product of the reaction of $\text{Fc}_2\text{P}\text{Cl}$ with Al_2Cl_6 revealed that it is the phosphenium ion Fc_2P^+ , and not **5**.



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Fluoride ion abstraction from P-F bonds also represents a very useful approach to phosphenium ion synthesis, PF_5 and BF_3 being particularly effective in this regard.^{10,12} Caution should be exercised with this technique, however, when AsF_5 is used because of the oxidizing ability of As^{5+} . Thus, the reaction of $(\text{Me}_2\text{N})(\text{R})\text{PF}$ ($\text{R} = \text{Me}_2\text{N}$, *t*-Bu) with AsF_5 results in the formation of four-coordinate difluorophosphonium cations rather than a phosphenium ion.^{5b}



$\text{R} = \text{Me}_2\text{N}, t\text{-Bu}$

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

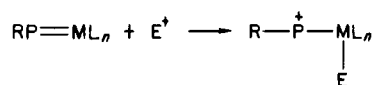
B. Protic Attack of Phosphorus-Nitrogen Bonds

Cleavage of P-N bonds with strong acids represents a promising new approach to phosphenium ion synthesis.³⁵ Trifluoromethanesulfonic acid was selected as the proton source because of the low nucleophilicity of the $[\text{CF}_3\text{SO}_3]^-$ anion. However, even with this anion, covalent products are formed unless the phosphenium ion is stabilized extensively by delocalization, e.g., $\text{X} = \text{Y} = \text{Me}_2\text{N}$. A complex set of equilibria appear to be involved as shown in Scheme I.

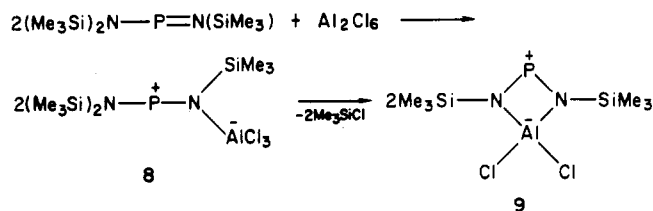
C. Electrophilic Attack of Element-Phosphorus Double Bonds

In principle, the electrophilic attack of element-

phosphorus double bonds should represent a general synthetic pathway to phosphenium ions, viz.

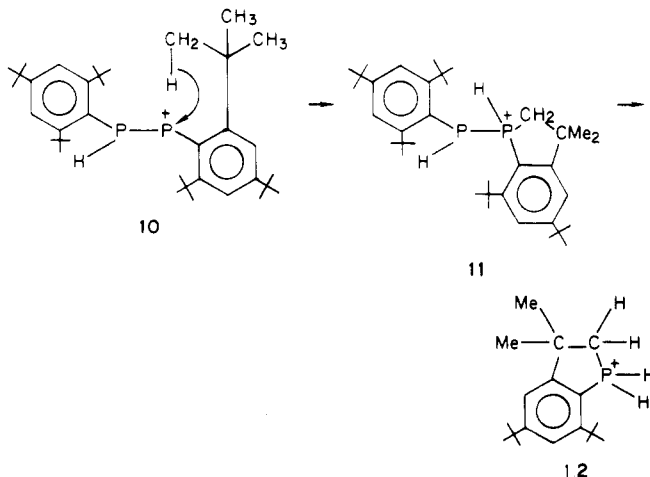


However, at the present time there are only two examples of this approach. Thus, Niecke and Kröher²⁶ prepared the acyclic zwitterion **8** by Al_2Cl_6 attack of a phosphorus-nitrogen double bond as shown. In turn,



8 was converted to the cyclic zwitterion **9** upon thermolysis at 70°C . Although zwitterionic, it is clear from the ^{31}P NMR chemical shift data (vide infra) that both **8** and **9** involve considerable localization of positive charge at phosphorus.

In a second example, it is believed that protic attack of the phosphorus-phosphorus double bond of $(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2\text{P}=\text{P}(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2))$ resulted in the phosphenium ion **10**³⁶ as the initial product. It was proposed further that labile **10** forms **11** via intramolecular C-H oxidative addition of an *o*-*t*-Bu group to the P^+ center. Although **11** is detectable by multinuclear NMR experiments at -78°C , the isolated product is the monophosphenium salt **12**· BF_4 .



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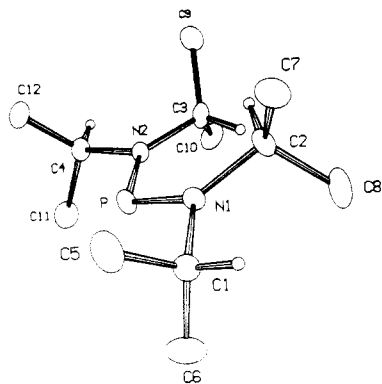
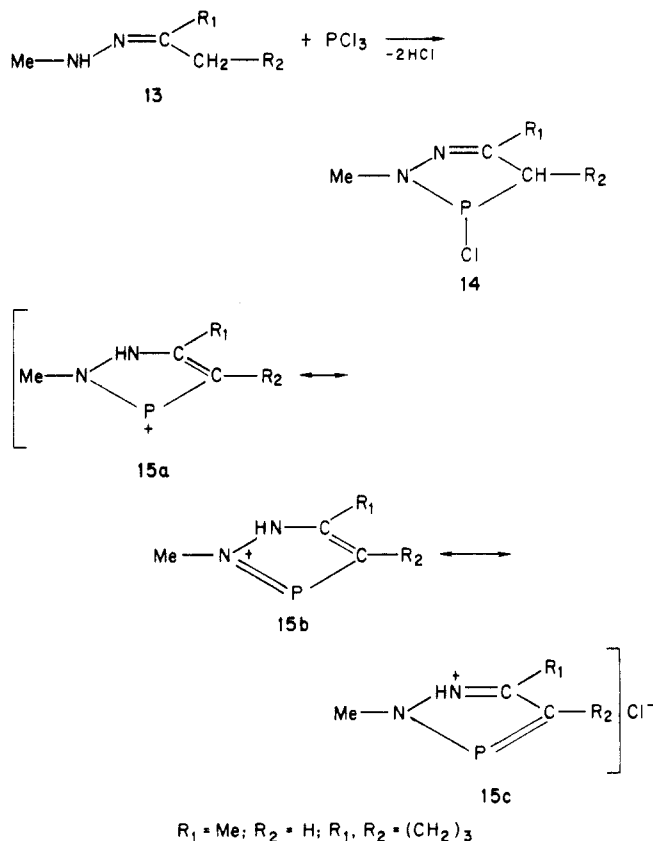


Figure 1. Structure of $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ showing the atom numbering scheme. Important parameters: $\text{P-N}(1) = 1.611(4) \text{ \AA}$; $\text{P-N}(2) = 1.615(4) \text{ \AA}$; $\text{N}(1)\text{-P-N}(2) = 114.8(2)^\circ$.

D. Miscellaneous Methods

Schmidpeter et al.^{27,29,30} have reported a novel situation in which a halide anion is apparently extruded in a spontaneous fashion from a cyclic halophosphine derivative. For example, reaction of the hydrazone **13** with PCl_3 afforded the interesting cyclic cation **14**. Inferentially, **14** is the precursor of **15**, and the stability



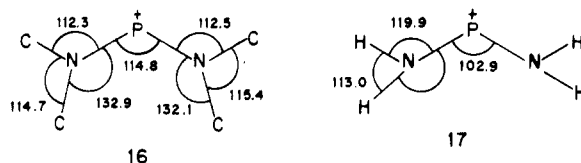
of the latter evidently stems from the fact that it is a 6π -electron system. A subsequent study has shown that the equilibrium $12 \rightleftharpoons 13$ is substituent dependent.²⁸

Finally, novel bis(cations) of the type $\text{R}_2\text{NP}^+\text{-N}=\text{P}^+(\text{NR}_2)(\text{X})$ ($\text{X} = \text{Cl}, \text{N}_3$) have been observed in the reaction of phosphonium ions with azides (vide infra).³²

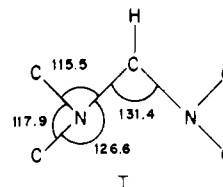
III. Structures of Phosphenium Ions

So far, three phosphenium ions have been characterized by X-ray crystallography. The skeletal geometry of $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ (Figure 1) is consistent with the view

that the phosphorus atom is approximately sp^2 hybridized.¹⁶ Diminution of the $\text{N}(1)\text{-P-N}(2)$ angle from the ideal value to $114.8(2)^\circ$ can be understood on the basis of repulsions between the phosphorus lone pair and the P-N bonds. The subunit $\text{C}(1)\text{C}(2)\text{N}(1)\text{PN}(2)\text{C}(3)\text{C}(4)$ is approximately planar, a conformation which maximizes dative π bonding between the nitrogen lone pairs and the formally vacant $\text{P}(3p)$ orbital. Conjugation of this type is supported by the fact that, within experimental error, the endo C-N-P angle is considerably wider than the other two (**16**). However,

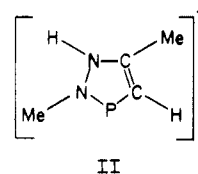


ab initio calculations on the virtually strain-free model cation $[(\text{H}_2\text{N})_2\text{P}]^+$ revealed a similar trend of bond angles (**17**).^{5b} Moreover, it is interesting to note that a similar pattern of bond angles is evident in the iso-valent N,N,N',N' -tetramethylformadimium cation **I**.³⁷



The structure of the zwitterionic phosphonium ion **9** has been determined by Pohl.³⁸ Both nitrogen atoms adopt a trigonal-planar geometry, and, within experimental error, the P-N bond length ($1.614(6) \text{ \AA}$) is the same as that in $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$. The relatively small N-P-N bond angle in **9** ($97.4(4)^\circ$) is obviously a consequence of the cyclic structure.

In the diazaphospholium cation **II**, the bond angle at phosphorus is even smaller ($90.4(1)^\circ$) and the P-N bond length is somewhat longer ($1.674(2) \text{ \AA}$) than in $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ or **9**.^{29b} The planarity of the ring and the pattern of the bond length in **II** are consistent with 6π -delocalization.



IV. NMR Data for Phosphenium Ions

A. ^{31}P NMR Data

^{31}P NMR spectroscopy is an ideal tool both for the identification of phosphenium ions and for the elucidation of subsequent reactions. As might be anticipated from the low coordination number and the presence of a formal positive charge at phosphorus, the ^{31}P chemical shifts of phosphenium ions are rather deshielded and fall in the range $+111.0$ to $+513.2$ ppm (Table I). With the exception of $[(\text{Me}_5\text{C}_5)(\text{Me}_2\text{N})\text{P}]^+$, the ^{31}P chemical shifts of phosphenium ions are ~ 100 ppm downfield of those of the precursor halophosphines. In the case of $[(\text{Me}_5\text{C}_5)(\text{Me}_2\text{N})\text{P}]^+$, the 33.8 ppm upfield shift ac-

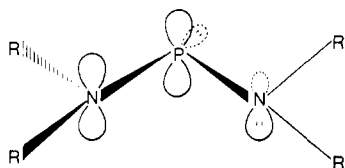


Figure 2. Transition state for P-N rotation of $[(R_2N)_2P]^+$ cations.

companying chloride ion abstraction was attributed to multihapto bonding between P^+ and the Me_5C_5 ring.²¹ Other trends can also be interpreted on the basis of conjugative effects. For example, the downfield shifts which are observed when an R_2N group is replaced by Cl can be explained by the inferior conjugating ability of the latter. Moreover, the observation that $[(Me_2N)(t-Bu)P]^+$ possesses the most deshielded ^{31}P chemical shift can be ascribed to the inability of the $t-Bu$ to π -donate.

Another conspicuous feature of the ^{31}P NMR data is the fact that ferrocenyl-substituted phosphenium ions are relatively shielded. This observation has been attributed¹⁹ to the well-known ability of the ferrocenyl moiety to disperse positive charge.³⁹

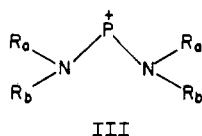
Steric effects also play a role in determining the ^{31}P chemical shifts. Note, for example, that the ^{31}P chemical shifts of the bis(amido)-substituted cations increase with increasing ligand size. This trend has been interpreted on the basis of progressive twisting of the R_2N groups with respect to the P^+ center, thereby reducing the $N(2p)$ - $P(3p)$ overlap with increasing ligand bulk.¹⁷

B. ^{27}Al NMR Data

^{27}Al NMR spectroscopy can play a highly useful role when phosphenium ions are prepared by Al_2Cl_6 -promoted chloride ion abstraction techniques. In these cases, phosphenium ion formation is accompanied by the production of the highly symmetrical $AlCl_4^-$ anion which is manifested as a sharp singlet at δ 102.2 ($w_h \approx 0$ Hz) in the $^{27}Al\{^1H\}$ spectrum.⁴⁰

C. Variable-Temperature NMR Studies

Variable-temperature 1H and $^{13}C\{^1H\}$ NMR studies have provided information pertinent to the static and dynamic stereochemistry of acyclic bis(amido)phosphenium ions (III). Typically, anisochronous R groups



are detectable at lower temperatures.^{13,16,17,41} The averaging of the R_a and R_b environments, which occurs at higher temperatures, could arise from N-P bond rotation and/or inversion at the P^+ center becoming rapid on the NMR time scale. This question was probed¹⁶ by investigating the variable-temperature 1H NMR spectra of $[(Me_2N)(i-Pr_2N)P]^+$. Interestingly, separate coalescence phenomena were detected for the Me_2N and $i-Pr_2N$ groups (Table II), thus indicating that P-N bond rotation is the rate-determining process. Furthermore, it appears that as rotation around a given P-N bond occurs, the rest of the cation remains fixed in order to minimize the loss of $p\pi-p\pi$ conjugation. The implied rotational transition state is depicted in Figure

2. The foregoing conclusions are in accord with theoretical studies on $[(H_2N)_2P]^+$ and $[(H_2N)(H)P]^+$ which indicate that the barrier to inversion at phosphorus is significantly higher than that due to P-N bond rotation.^{5b,42} Interestingly, the variable-temperature 1H and ^{13}C NMR spectra of $[(Me_2N)((Me_3Si)_2N)P]^+$ indicated that, while the Me_2N was fluxional, the Me_3Si groups of the $(Me_3Si)_2N$ moiety remained equivalent throughout the temperature range studied.¹⁷ These observations were explained by the postulate that the Me_3Si groups are rotated out of the N-P-N plane to a sufficient degree that anisochrony is not detectable. A similar explanation has been advanced by Nielson and Wells⁴³ to explain the equivalence of Me_3Si groups in $(Me_3Si)_2N$ -substituted boranes. The diminution of the P-N rotational (Table II) barrier in proceeding from $[(Me_2N)_2P]^+$ to $[(Me_2N)_2PFe(CO)_4]^+$ (Table II) is consistent with competitive π -donation for the formally vacant $P(3p)$ orbital by filled $N(2p)$ and $Fe(3d)$ orbitals.

V. Theoretical Aspects of Phosphenium Ions

Harrison et al.⁴⁴ have investigated the electronic structures of the model phosphenium ions $[H_2P]^+$, $[(H)(F)P]^+$, and $[F_2P]^+$ using generalized valence bond (GVB) wave functions. These GVB calculations predict that each cation possesses a singlet ground state. Moreover, as expected, the singlet-triplet separations increase with increasing ligand electronegativity: $[H_2P]^+$ (20.4 kcal/mol), $[(H)(F)P]^+$ (42.6 kcal/mol), and $[F_2P]^+$ (84.0 kcal/mol). These results are in accord with the available structural data and the fact that NMR spectra can be recorded for all isolable phosphenium ions.

First principles calculations^{5b,42} on the model systems $[(H_2N)_2P]^+$ and $[(H_2N)(H)P]^+$ produce satisfactory agreement both with the observed ground-state geometry of $[(i-Pr_2N)_2P]^+$ and with earlier extended Hückel calculations¹³ on $[(Me_2N)_2P]^+$. Furthermore, all the calculations support the view that dative π -bonding takes place between the nitrogen lone pair(s) and the formally vacant $P(3p)$ orbital. Ab initio^{5b} and Fenske-Hall calculations^{45,46} on $[(H_2N)_2P]^+$ and $[PN(R)CH_2CH_2NR]^+$ ($R = H, Me$), respectively, produced the orbital sequence shown in Figure 3. The HOMO, which is nonbonding, possesses a_2 symmetry and comprises an out-of-phase combination of $N(2p)$ AO's. The LUMO, which possesses b_1 symmetry, is π -antibonding in character. The a_1 MO is essentially phosphorus lone pair in character and is directed perpendicular to the $N(2p)$ AO's. At lowest energy, the $4b_1$ level is best described as a three-center π -bonding MO.

VI. Comments on the Stabilities of Phosphenium Ions

With the exception of $[(Fc)_2P]^+$ and $[(Me_5C_5)(t-Bu)P]^+$, all isolable phosphenium ions feature at least one amido substituent. In conjunction with the above discussion of structural, theoretical, and spectroscopic data, this observation highlights the necessity for the thermodynamic stabilization of phosphenium ions by means of ligand $\rightarrow P^+$ π -bonding. In the case of diazaphospholium cations, this π -bonding constitutes part of a more extensive 6π -delocalization. As with the corresponding carbocations, the ferrocenyl substituent

Table I. Synthetic Methods and ^{31}P Chemical Shifts for Phosphine Ions^a

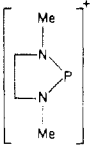
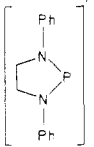
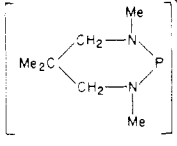
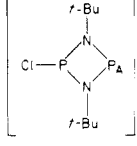
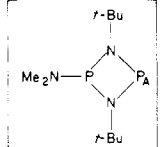
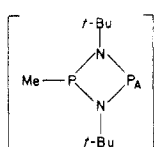
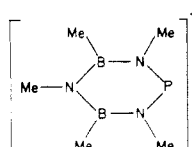
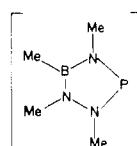
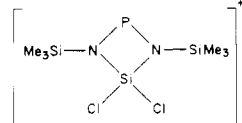
cation	synth method ^b	^{31}P chem shifts	ref
$[(\text{Me}_2\text{N})_2\text{P}]^+$	A, B	264	12, 13
$[(\text{Et}_2\text{N})_2\text{P}]^+$	A	263	14, 15
$[(i\text{-Pr}_2\text{N})_2\text{P}]^+$	A	313	16
$[(\text{Me}_3\text{Si})_2\text{N})_2\text{P}]^+$	A	450.3	17
$[(\text{Me}_2\text{N})(i\text{-Pr}_2\text{N})\text{P}]^+$	A	290	16
$[(\text{Me}_2\text{N})(\text{Me}_3\text{Si})_2\text{N})\text{P}]^+$	A	354.3	17
$[(\text{Me}_2\text{N})(t\text{-BuMe}_2\text{Si})_2\text{N})\text{P}]^+$	A	370.1	17
$[(\text{Me}_2\text{N})(\text{Cl})\text{P}]^+$	A	325	12, 13
$[(i\text{-Pr}_2\text{N})(\text{Cl})\text{P}]^+$	A	334	18
$[(\text{Fc})_2\text{P}]^+{}^c$	A	183.7	19
$[(\text{Me}_2\text{N})(\text{Fc})\text{P}]^+{}^c$	A	258.5	19
$[(\text{Me}_5\text{C}_5)(\text{Me}_2\text{N})\text{P}]^+$	A	111.0	21
$[(\text{Me}_2\text{N})(t\text{-Bu})\text{P}]^+$	A	513.2	17
$[(\text{Me}_5\text{C}_5)(t\text{-Bu})\text{P}]^+$	A	168	20
$[(\text{Me}_5\text{C}_5)(\text{Me}_3\text{Si})_2\text{CHP}]^+$	A	265.9	20
	A	264	10
	A	254	22
	A	222	11
	A	$P_A, 365.7$	17
	A	$P_A, 334.5$	23
	A	$P_A, 252$	24
	A	302	25
	A	228.0	25
	C	343	26

Table I (Continued)

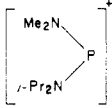
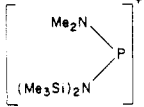
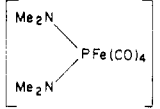
cation	synth method ^b	³¹ P chem shifts	ref
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	C	379	26
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	D	P _A , 293.5	22, 32
	D	P _A , 301.4	22, 32
	D	230.7 (Cl ⁻ salt) 232.0 (Br ⁻ salt)	27 28
	D	209.3	27
	D	237.7 (Cl ⁻ salt) 228.5 (Br ⁻ salt)	29 28
	D	211.0	30
	D	195.2	30
	D	230.3	31
	D	220.0	28
	D	231.1 (Cl ⁻ salt) 229.9 (Br ⁻ salt)	28 28

^a ³¹P chemical shifts referenced to 85% H₃PO₄ (external), positive values to high frequency. ^b Method A: phosphorus-halogen bond heterolysis. Method B: protic attack of phosphorus-nitrogen bonds. Method C: electrophilic attack of element-phosphorus double bonds. Method D: miscellaneous methods. ^c Fc = ferrocenyl.

effects stabilization via the dispersion of positive charge.³⁹ The (marginal) stability of [(Me₅C₅)(*t*-Bu)P]⁺ is attributable to multihapto bonding between the Me₅C₅ ligand and P⁺ and the concomitant delocalization of positive charge.²⁰

In principle, other substituents such as halogens and RO should be capable of conjugatively stabilizing phosphonium ions. However, unless the phosphonium ions are coordinated to a transition metal moiety (vide infra), these groups have insufficient π-donor character

TABLE II. P-N Rotational Barriers for Acyclic Phosphenium Ions^a

cation	barrier, kcal/mol	ref
$[(\text{Me}_2\text{N})_2\text{P}]^+$	14.6 ^a	13
	13.6 ^a	41
$[(i\text{-Pr}_2\text{N})_2\text{P}]^+$	11.1	16
	11.9 (<i>i</i> -Pr)	16
	14.1 (Me)	
	16.4 (Me)	17
	11.5	41

^aThere is evidence for the dependence of the magnitude of the rotational barrier in the nature of the counterion. See ref 13.

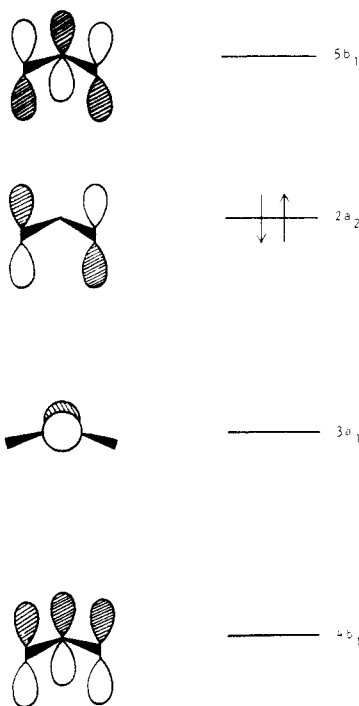
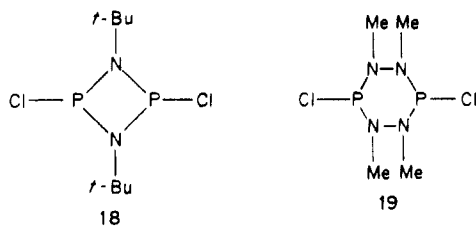


Figure 3. Some molecular orbitals for the model cation $[(\text{H}_2\text{N})_2\text{P}]^+$.

to impart the necessary thermodynamic stabilization. Thus, the reactions of PX_3 ($\text{X} = \text{Cl}, \text{F}$) with Al_2Cl_6 resulted in donor-acceptor complexes of the type X_3PAlCl_3 rather than phosphenium ions.⁴⁷

The necessity for adequate retro-bonding is also evident from attempts to prepare polyphosphenium cations. Thus, treatment of 18 with an excess of Al_2Cl_6



results in the abstraction of only one chloride ion and

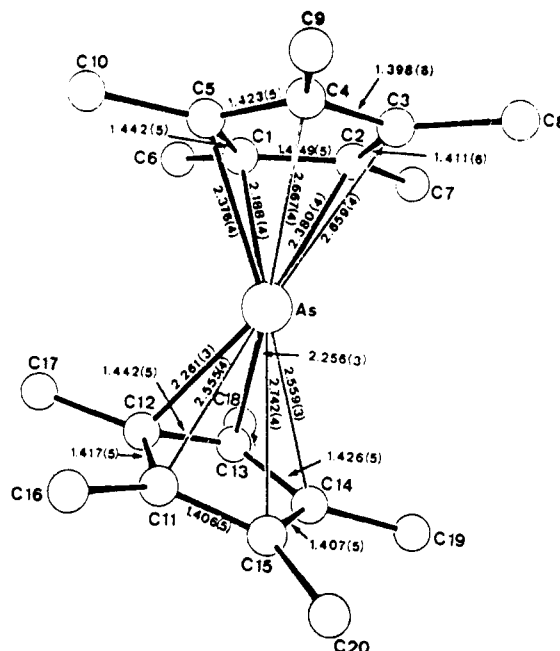


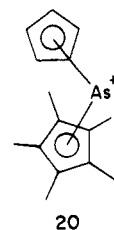
Figure 4. View of $[(\text{Me}_5\text{C}_5)_2\text{As}]^+$ showing the atomic number scheme and important bond lengths (\AA).

formation of the monocation (Table I). Interestingly, however, Nöth and Ullmann⁴⁸ have discovered that 19 forms a bis AlCl_3 adduct which can be regarded as the AlCl_4^- salt of the corresponding bis(phosphenium) ion. Evidently, at least four nitrogen atoms are necessary to satisfy the conjugative requirements of two phosphenium ion centers in the same molecule.

VII. Heavier Congeners of Phosphenium Ions—Arsenium and Stibonium Ions

There is X-ray crystallographic evidence⁴⁹ for contributions from the ionic form $[\text{F}_2\text{As}]^+[\text{SbF}_6]^-$ in the solid state of the adduct of AsF_3 and SbF_5 . However, the environment around arsenic is somewhat complex, there being two nearest-neighbor fluorine atoms at 1.64 \AA , two intermediate neighbors at 2.01 and 2.39 \AA , and two long contacts at 2.73 \AA . Moreover, the octahedral array around antimony is significantly distorted, with one Sb-F distance being appreciably longer than the other five.

The first clear-cut examples of arsenium ions were produced by chloride ion abstraction reactions from $(\text{Me}_5\text{C}_5)(\text{Me}_2\text{N})\text{AsCl}$ and $(\text{Me}_5\text{C}_5)(\text{C}_5\text{H}_5)\text{AsCl}$.^{21a} A bis η^5 geometry, 20, was proposed for $[(\text{Me}_5\text{C}_5)_2(\text{C}_5\text{H}_5)\text{As}]^+$



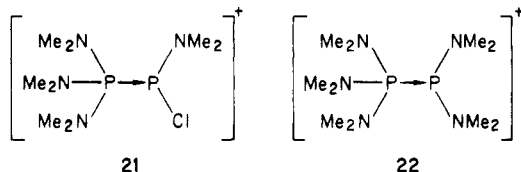
on the basis of theoretical calculations and NMR spectroscopic evidence. In a highly significant publication, Jutzi et al.⁵⁰ have described the isolation of $[(\text{Me}_5\text{C}_5)_2\text{E}]^+$ ($\text{E} = \text{As}, \text{Sb}$) cations as their BF_4^- salts. An X-ray crystal structure of the arsenium cation (Figure 4) revealed that, like the isovalent neutral group 14¹⁰⁰ compounds $(\text{Me}_5\text{C}_5)_2\text{E}$ ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$),⁵¹ it

possesses a bent-sandwich structure⁵² with a somewhat distorted bis η^5 attachment of Me_5C_5 rings.

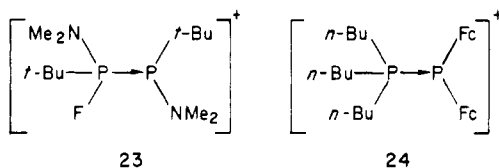
VIII. Reactions of Phosphenium Ions

A. Reactions with Lewis Bases

Given that phosphenium ions possess a formal positive charge and a sextet of electrons at phosphorus, they are expected to function as Lewis acids. This expectation was verified by Parry et al.^{12b} several years ago when they formulated materials of composition $[2(\text{Me}_2\text{N})_2\text{P}]\cdot\text{AlCl}_3$ and $(\text{Me}_2\text{N})_3\text{P}\cdot(\text{Me}_2\text{N})_2\text{P}\cdot\text{AlCl}_3$ as phosphine adducts of the phosphenium ion $[(\text{Me}_2\text{N})_2\text{P}]^+$, **21** and **22**. Since that time, other



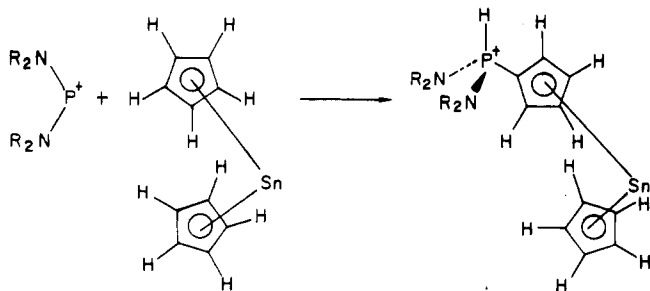
phosphine adducts **23**¹⁷ and **24**^{19b} have been prepared.



An interesting facet of the ³¹P NMR spectra of these diphosphorus cations is that *both* phosphorus nuclei are more shielded than those of the individual components. This observation has been attributed by Parry et al.^{12b} to the fact that coordination numbers at both phosphorus centers increase upon formation of the P→P dative bond. The one-bond ³¹P–³¹P coupling constants for **21**–**24** fall in the range 336–506 Hz.

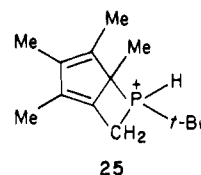
B. C–H Insertion Reactions

As noted above, phosphenium ions possess (i) an electropositive center, (ii) a formally vacant (P(3p)) orbital at phosphorus, and (iii) they are coordinatively unsaturated. As such they might be expected to cause C–H bond activation. Interestingly, the first example of C–H activation occurred somewhat by accident. Our original intent in exploring the reactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}$ or $(\eta^5\text{-C}_5\text{H}_5)_2\text{Pb}$ with $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ was to prepare compounds with formed double bonding between Sn or Pb and P⁺. However, the reaction of stannocene or plumbocene with $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ results in phosphenium salt formation via oxidative addition of a cyclopentadienyl C–H bond to the P⁺ center (or, alternatively, via electrophilic aromatic substitution),⁵³ viz.

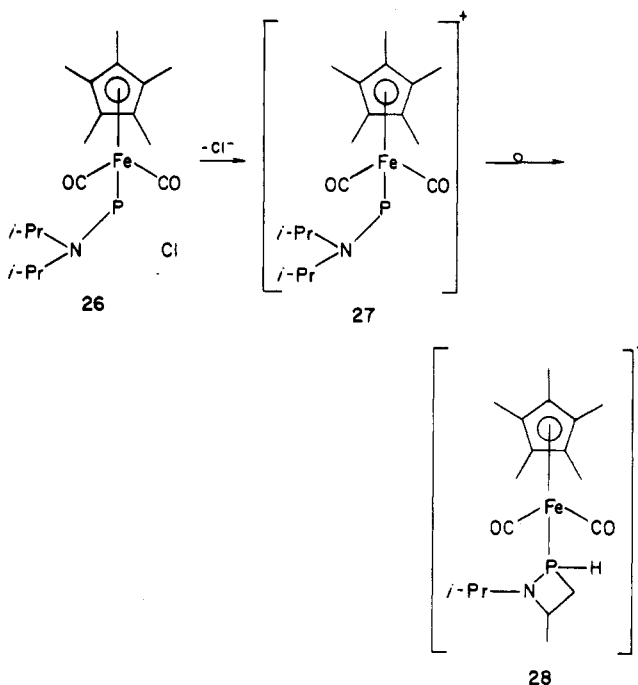


Subsequently, other examples of C–H activation by

phosphenium ions have materialized. Thus, aluminum chloride promoted chloride ion abstraction from $(\eta^1\text{-Me}_5\text{C}_5)(t\text{-Bu})\text{PCl}$ affords initially the phosphenium ion $[(\text{Me}_5\text{C}_5)(t\text{-Bu})\text{P}]^+$. On standing for ~5 days at ambient temperature in CH_2Cl_2 solution $[(\text{Me}_5\text{C}_5)(t\text{-Bu})\text{P}]^+$ rearranged to the cyclic phosphonium salt **25**.²⁰ The intramolecular nature of this rearrangement was established by the observation that no P–D bond formation took place when the reactions were conducted in CD_2Cl_2 .



Another example of C–H activation is provided by halide ion abstraction from $(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{PClN}(i\text{-C}_3\text{H}_7)_2)$ (**26**). Thus, treatment of **26** with Al_2Cl_6 or



$\text{Ph}_3\text{C}^+\text{BF}_4^-$ is believed (on ³¹P spectroscopic evidence) to produce **27**, which can be regarded as a cationic phosphinidene complex or a metallaphosphenium ion.^{54,55} Although the final product **28** could conceivably arise from radical byproducts and/or precursors to **27**, it is reasonable to suggest that it arises from insertion of P⁺ into a C–H bond of an *i*-Pr₂N group as suggested above.

Finally, and to set the foregoing in a broader context, we note that several other ring closures of 2,4,6-*(t*-Bu)₃C₆H₂ moieties have been observed.^{36,56}

C. Reactions of Phosphenium Ions with Unsaturated Organic Molecules

Over 3 decades ago, McCormack⁵⁷ recognized that dihalophosphines react with 1,3-dienes and upon hydrolysis produce phospholene oxides. While representing a useful synthesis of phosphorus heterocycles, the McCormack reaction is somewhat sluggish and reaction times can be as long as days or weeks for the less reactive dienes. SooHoo and Baxter⁵⁸ and our group⁵⁹

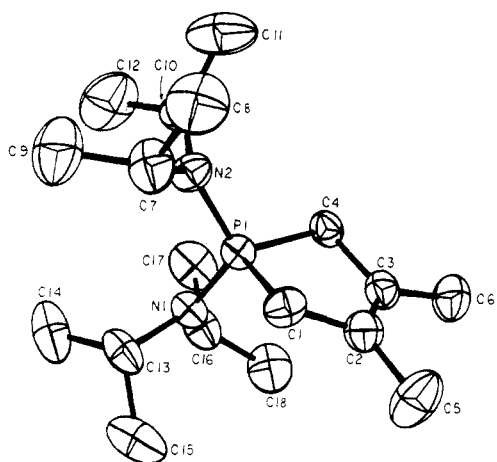
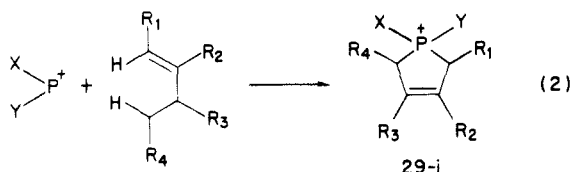


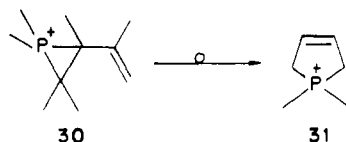
Figure 5. View of the 3-phospholenium cation **29h** showing the atom numbering scheme.

recognized that, being electrophilic carbenoids,⁶⁰ phosphonium ions might react much more rapidly with 1,3-dienes. This is indeed the case and reaction times are reduced dramatically. The actual reaction times are dependent on steric and electronic factors. For example, $[(\text{Me}_2\text{N})_2\text{P}]^+$ reacts completely with 2,3-dimethyl-1,3-butadiene and isoprene in ~ 1 h upon warming from -78 to $+25$ °C. On the other hand, the more sterically encumbered dienes *trans*-1,3-pentadiene and *trans*-2-*trans*-4-hexadiene react with the bulkier phosphonium ion $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ in 3 and 9 days, respectively. Reactivity can be increased by (a) decreasing the bulk of the phosphonium ion substituents and (b) increasing the electrophilicity at phosphorus. Thus, $[(i\text{-Pr}_2\text{N})(\text{Cl})\text{P}]^+$ reacts with 2,3-dimethyl-1,3-butadiene in ~ 30 min at ambient temperature. The overall reaction of phosphonium ions with 1,3-dienes is summarized in (2).



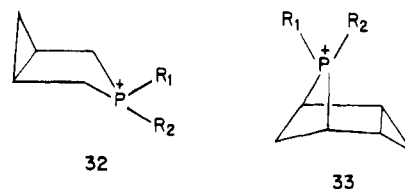
- 29 a. X = Y = Me₂N; R₂ = Me; R₁ = R₃ = R₄ = H
 b. X = Y = Et₂N; R₂ = Me; R₁ = R₃ = R₄ = H
 c. X = Y = Et₂N; R₁ = R₄ = H; R₂ = R₃ = Me
 d. X = Y = *i*-Pr₂N; R₁ = R₂ = R₃ = R₄ = H
 e. X = Y = *i*-Pr₂N; R₁ = Me; R₂ = R₃ = R₄ = H
 f. X = Y = *i*-Pr₂N; R₁ = R₄ = Me; R₂ = R₃ = H
 g. X = Y = *i*-Pr₂N; R₂ = Me; R₁ = R₃ = R₄ = H
 h. X = Y = *i*-Pr₂N; R₁ = R₄ = H; R₂ = R₃ = Me
 i. X = *i*-Pr₂N; Y = Cl; R₁ = R₄; R₂ = R₃ = Me

Note that in each case, 1,4 addition is observed. This assignment was confirmed by an X-ray crystal structure determination⁵⁹ on a representative phospholenium ion (Figure 5). This study showed that the double bond is located between C(2) and C(3). Interestingly, the $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$ unit changes only modestly upon coordination; e.g., the P–N bond lengths increase by 0.013 (4) Å and the N–P–N angle widens by 1.3 (2)°. As pointed out by SooHoo and Baxter,⁵⁸ there are several possible mechanisms for the reaction of phosphonium ions with 1,3-dienes. As demonstrated for transient phosphinidene complexes of the type $\text{PhP}=\text{M}(\text{CO})_5$ (M = Cr, Mo, W),⁶¹ the reaction could proceed via a two-step process, the first of which would be the 1,2 adduct **30** which could then rearrange to the 1,4 product **31**. Alternatively, reaction could proceed in one step by a



concerted [2 + 4] cheletropic addition. Of these two mechanisms, we prefer the [2 + 4] cheletropic process because the reaction of phosphonium ions with *trans*-2-*trans*-4-hexadiene is highly stereospecific and results in only one product. In principle, one should also consider the possibility of biradical intermediates emanating from triplet phosphonium ion. However, MO calculations⁴⁴ indicate that phosphonium ions are ground-state singlets hence this mechanism is unlikely.

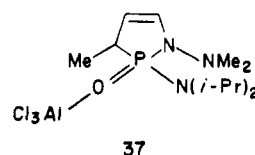
Phosphonium ions are also reactive toward 1,4-dienes. In fact, several years previously, Kashman and co-workers⁶² reported that complexes of the type RPX_2 , AlX_3 (R = Me, Ph; X = Cl, Br) react with, e.g., 1,4-dienes to afford phosphorus-containing heterocycles. It was quite conceivable that phosphonium ions are involved in these reactions; however, we were unable to detect $[\text{MePX}]^+$ or $[\text{PhPX}]^+$ by ³¹P NMR spectroscopy when PRCl_2 was treated with Al_2Cl_6 . We were therefore curious regarding the reactivity of stabilized phosphonium ions toward 1,4-dienes. Indeed, $[(i\text{-Pr}_2\text{N})\text{P}(\text{Cl})]^+$ reacts readily with 1,4-pentadiene or 1,4-hexadiene to afford two configurational isomers in each case (**32** and **33**).¹⁸ An X-ray crystallographic study of the predom-



32 **33**
R₁ or R₂ = Cl or *i*-Pr₂N

inant isomer from the 1,4-pentadiene reaction demonstrated a proximal relationship between the *i*-Pr₂N and cyclopropane moieties.¹⁸

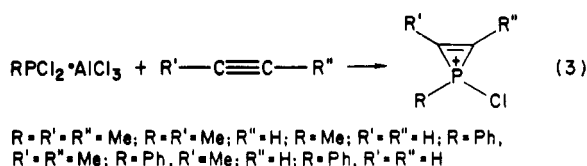
More recently, the phosphonium ion reactions have been extended to the heteroatom systems $\text{MeCH}=\text{CHCH}=\text{NNMe}_2$ (**34**), $\text{Me}_2\text{C}=\text{NN}=\text{CMe}_2$ (**35**), and $\text{Me}_2\text{NN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NNMe}_2$ (**36**). Compound **34** reacts readily with $[(i\text{-Pr}_2\text{N})\text{P}(\text{Cl})]^+$ to afford the heterocycle **37**.⁶³ Presumably, **37** is formed as a result of



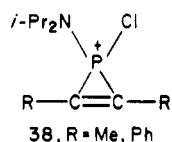
partial hydrolysis of the initial product. For the reactions of **35** or **36** with $[(i\text{-Pr}_2\text{N})\text{P}(\text{Cl})]^+$, large quantities of *i*-Pr₂NPCL₂ were detected by ³¹P NMR spectroscopy in each case. These reactions are presumably caused by the attachment of AlCl_3 units to imino or amino nitrogen lone pairs, i.e., $\text{AlCl}_4^- \rightarrow \text{AlCl}_3 + \text{Cl}^-$. In turn, Cl^- attack of the phosphonium ion affords the neutral dihalophosphine. A similar reaction was observed⁶⁴ in attempting to prepare amido-substituted silicenium ions.

Fongers, Hogveen and Kingma⁶⁵ were the first to demonstrate that alkynes will react with phosphonous dichlorides in the presence of aluminum chloride to

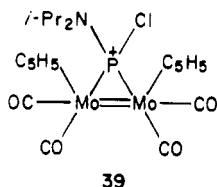
afford phosphirenium cations as indicated in (3).



Subsequently, this methodology was extended to the reactions of $\text{R}_2\text{P}^+\text{Cl}$ (R = Ph, Et) with $\text{EtC}\equiv\text{CEt}$ and $\text{PhC}\equiv\text{CPh}$ by Breslow and Deuring.⁶⁶ These authors noted that phosphirenium cations are of considerable theoretical interest because P(3d) orbital participation permits three-orbital, two-electron delocalization characteristic of cyclopropenyl cations. Given that transient phosphirenium ions such $[\text{MePCl}]^+$ and $[\text{Ph}_2\text{P}]^+$ can be implied in the foregoing reactions, it was of interest to determine whether stabilized phosphirenium ions would react with alkynes. Indeed, preliminary work⁶⁷ indicates that $[\textit{i}\text{-Pr}_2\text{NCl}]^+$ reacts with $\text{MeC}\equiv\text{CMe}$ and $\text{PhC}\equiv\text{CPh}$ to afford phosphirenium cation 38. Moreover, recognizing the isolobal rela-

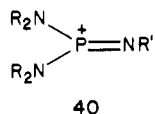


tionship of alkynes to compounds with metal-metal triple bonds,⁶⁸ we have also explored the reactivity of $[\textit{i}\text{-Pr}_2\text{NPCl}]^+$ toward $\text{C}_5\text{H}_5(\text{CO})_2\text{Mo}\equiv\text{Mo}(\text{CO})_2(\text{C}_5\text{H}_5)$. Spectroscopic evidence has led us to the preliminary conclusion that the product is the dimetal-phosphirenium cation 39.



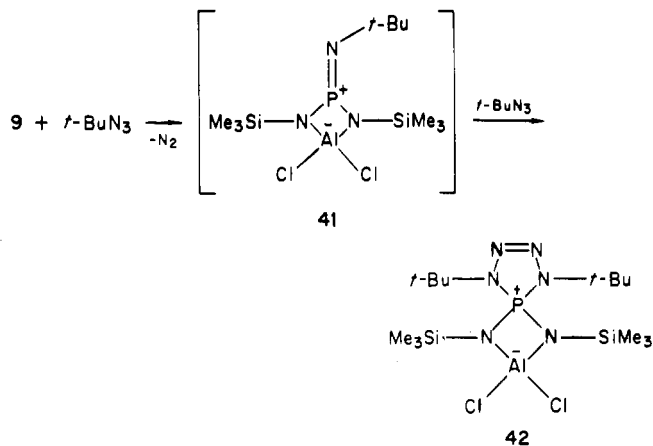
D. Reactions of Phosphenium Ions with Azides

In an interesting extension of the Staudinger reaction, it has been found that bis(dialkylamino)phosphenium ions react with azides to afford the corresponding bis(dialkylamino)iminophosphenium ions 40.^{22,32,69} Con-

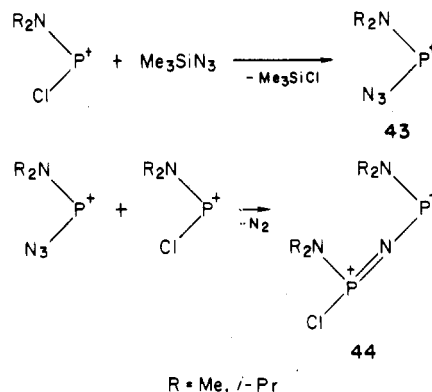


trasting with this observation is the report that in the reaction of the zwitterionic phosphirenium ion 9, with $t\text{-BuN}_3$ it is impossible to isolate the iminophosphenium cation 41 because of subsequent reaction with azide to produce the spiroheterocycle 42.²⁶

Yet another reaction pathway has been observed when chloro(amido)phosphenium ions are treated with Me_3SiN_3 . The first step of the reaction is believed to be a metathesis reaction resulting in the azido-phosphenium ion 43.³² In turn, 43, being itself an azide, reacts with the halophosphenium ion to produce novel phosphenium-iminophosphenium dication 44. In independent experiments it was established that azido-



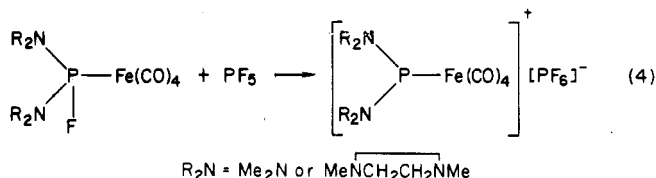
phosphenium ions 43 will self-condense to afford polymers and bis(cations) analogous to 44.³²



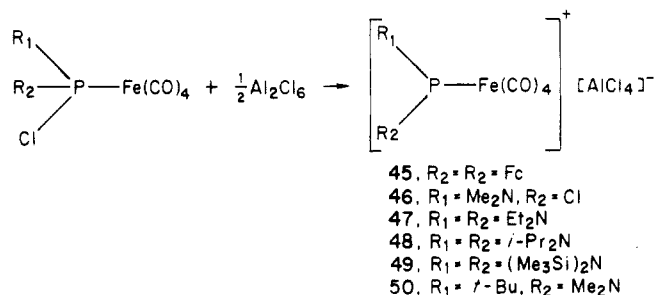
E. Coordination Chemistry of Phosphenium Ions

The presence of a lone pair and a vacant π -orbital renders phosphenium ions excellent ligands. In the case of amido-substituted cations, MO calculations on the model systems^{5b,46} suggest that σ -donor behavior stems from utilization of the second MO (3a₁) and that π -acceptance results from interaction of occupied nd orbitals with the 5b₁ LUMO (Figure 3). As noted by Paine⁴⁶ and Parry¹³ et al., intriguing parallels exist between phosphenium ions, carbenes, SO_2 , NO, and other small molecules.

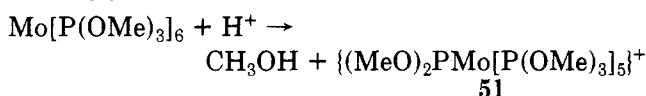
It is convenient to divide the discussion into cationic and neutral phosphenium ion complexes. The first examples of the former were reported by Parry et al.,⁷⁰ who abstracted fluoride ions from precursor fluoro-phosphine complexes as represented in (4). Interest-



ingly, the same complexes can be formed by direct reactions of the phosphenium ions with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$.⁷⁰ Chloride ion abstraction also represents a viable approach to cationic phosphenium ion complexes 45–50.¹⁵ Note, however, that only one halophosphenium ion complex has been prepared by this route. Other attempts to generate such ions were unsuccessful.¹⁵ For example, $\text{Me}_2\text{NP}(\text{F})_2\text{Fe}(\text{CO})_4$ failed to react with PF_5 and the reaction of $\text{Cl}_3\text{PFe}(\text{CO})_4$ or $\text{F}_2\text{P}(\text{Cl})\text{Fe}(\text{CO})_4$ with Al_2Cl_6 resulted in the production



of $\text{P}(\text{Cl})_3$. Inferentially, retro-bonding from the halogen substituents is insufficient to impart thermodynamic stability to the complexed PX_2^+ entity. It is interesting to note, however, that a complex of $[(\text{MeO})_2\text{P}]^+$ (51) has, in fact, been prepared⁷¹ by protic attack of $\text{Mo}[\text{P}(\text{OMe})_3]_6$.



X-ray crystal structure data have been reported for two cationic phosphonium complexes. Within 0.036 Å, the MPO_2 framework for the phosphonium ion ligand of 51 is planar, suggesting multiple order for this Mo–P bond.⁷¹ Supportive of this idea is the fact that the Mo–P bond length for the cation (2.229 (4) Å) is significantly shorter than the average of those for the neutral $(\text{MeO})_3\text{P}$ ligands (2.428 Å).

The solid state of 47 is fairly complex and involves four crystallographically unrelated cations.⁷² However, the geometries of all four cations are similar. In contrast to axially substituted (halophosphine) $\text{Fe}(\text{CO})_4$ complexes such as $[\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PF}(\text{CO})_4]^+$,⁷³ the phosphonium moiety adopts an equatorial site of a local trigonal-bipyramidal geometry at iron. The phosphorus geometry is planar and the average Fe–P bond length (2.10 (5) Å) is quite short. The metric parameters for the coordinated $[(\text{Et}_2\text{N})_2\text{P}]^+$ ligand are quite similar to those of unligated $[(i\text{-Pr}_2\text{N})_2\text{P}]^+$, the only major change accompanying coordination being diminution of the N–P–N angle by $\sim 10^\circ$. Equatorially substituted $\text{Fe}(\text{CO})_4$ complexes are, in fact, quite rare, the only examples of which we are aware being $(\text{Ph}_2\text{P})_2(\text{Ph})\text{PFe}(\text{CO})_4$,⁷⁴ $[\text{trans}\{-[\text{Fe}(\text{CO})_4]_3[\text{PCH}(\text{SiMe}_3)_2]\}]$,⁷⁵ and $(2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)_2\text{P}_2\text{Fe}(\text{CO})_4$.⁷⁶ Clearly, it is a subtle interplay of steric and electronic factors that is responsible for the observed site preferences. In the case of the phosphonium complex, the equatorial preference probably stems from the π -acceptor nature of the phosphonium ligand since theoretical studies by Rossi and Hoffmann⁷⁷ have demonstrated that for $d^8\text{-}d^{10}$ trigonal bipyramidal systems π -acceptor ligands prefer an equatorial location. Interestingly, Sosinsky et al.⁷⁸ have interpreted Mössbauer data for $[(\text{Fc}_2\text{PFe}(\text{CO})_4)]^+$ in terms of axial substitution of the phosphonium ion ligand. This observation would suggest that σ -donation is more important than π -acceptance for $[\text{Fc}_2\text{P}]^+$, while for the amido-substituted ligands, the reverse is true.

The π -acceptor nature of cationic phosphonium ion ligands can also be inferred from other lines of evidence. For example, the CO stretching frequencies of coordinated phosphonium ions are $\sim 80\text{--}100\text{ cm}^{-1}$ greater than those of the precursor halophosphine complexes.^{15,70} Another manifestation of the π -acceptor character of

TABLE III. Comparison of ^{31}P NMR Data of Uncoordinated Phosphonium Ions, Cationic Phosphonium Ion Complexes, and Precursor Chloride Complexes

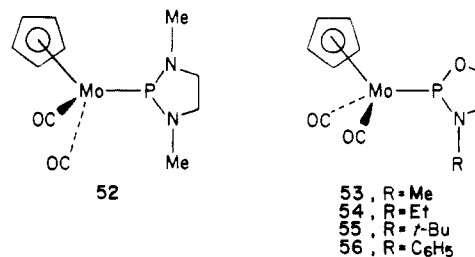
phosphonium ion ^a	$\text{Fe}(\text{CO})_4$ complex	coordination chem shift ^b	$(\text{R}_2\text{P}(\text{Cl})\text{-Fe}(\text{CO})_4)$	
$[\text{Me}_2\text{N}(\text{Cl})\text{P}]^+$	325	286.8 ^c	-38.2	192.2 ^c
$[(\text{Me}_2\text{N})_2\text{P}]^+$	264	311 ^d	+47	194 ^c
$[(\text{Et}_2\text{N})_2\text{P}]^+$	263	307.6 ^c	+44.6	183.8 ^c
$[(i\text{-Pr}_2\text{N})_2\text{P}]^+$	313	311.3 ^c	-1.7	182.5 ^c
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{P}]^+$	450.3	349.7 ^c	-100.6	268.0 ^c
$[(t\text{-Bu})(\text{Me}_2\text{N})\text{P}]^+$	513.2	441.5 ^c	-71.7	219.3 ^c
$[\text{Fc}_2\text{P}]^+$	264	300 ^d	+36	
$[\text{Fc}_2\text{P}]^+$	183	280 ^e	+97	161 ^c

^a Data from Table I. ^b $\delta_{\text{complex}} - \delta_{\text{ligand}}$. ^c Data from ref 15. ^d Data from ref 70. ^e Data from ref 19.

phosphonium ion ligands is provided by the fact that, at ambient temperature, it is not possible to record ^{13}C NMR resonances for the CO ligands of $\text{R}_2\text{PFe}(\text{CO})_4^+$ complexes. This interesting observation was made first by Bennett and Parry⁷⁹ and attributed to rapid intermolecular CO exchange in complexes of this type. This conclusion was confirmed qualitatively by ^{13}C studies which showed that for phosphonium ion complexes, statistical exchange was complete in $<0.5\text{ h}$ at 25°C .⁷⁹

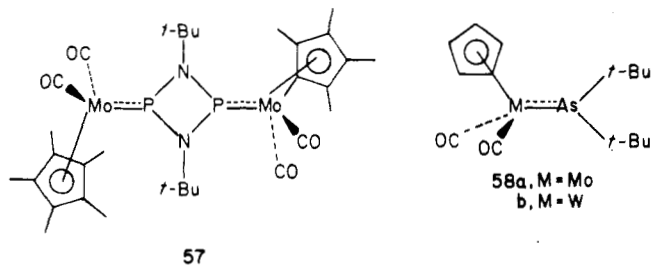
The ^{31}P NMR chemical shifts of cationic phosphonium ion complexes have been assembled in Table III along with the available data for uncoordinated phosphonium ions and precursor chlorophosphine complexes. As in the case of unligated phosphonium ions, a substantial deshielding ($\sim 80\text{--}230\text{ ppm}$) accompanies halide ion abstraction. However, the coordination chemical shifts (i.e., the differences in chemical shifts of the coordinated and free phosphonium ions) can be either positive or negative. Such a pattern is difficult to understand by considering only the diamagnetic contributions to the ^{31}P chemical shift. It is therefore possible that anisotropic contributions are important in these $\text{Fe}(\text{CO})_4$ complexes.

Complexes of the type represented by 52 were first isolated by Paine et al.^{45,80} from the reaction of $[(\text{C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3]^-$ with the corresponding cyclic diamino-halophosphine. Complexes 53–56 have been prepared⁸¹

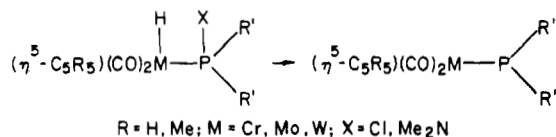


by similar reactions with the analogous aminohalophosphites $\text{RNCH}_2\text{CH}_2\text{OPCl}$ (R = Me, Et, *t*-Bu, C₆H₅). X-ray crystallographic studies have been performed on 52 and 55. The structure of 52 is illustrated in Figure 6. For both complexes the sums of angles at the phosphorus and nitrogen atoms are $\sim 360^\circ$ and the Mo–P distances (2.13 (1) Å) in 52 and 2.207 (1) Å in 55 are significantly shorter than normal P–Mo single bond

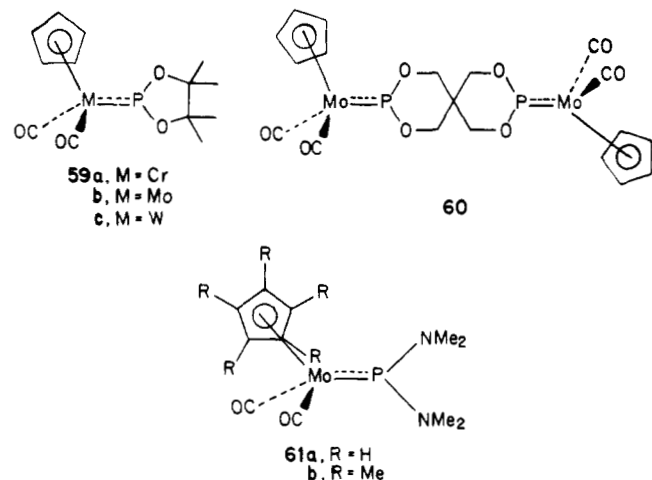
lengths which fall in the range 2.40–2.57 Å.⁸² The Mo geometry in each complex is pseudooctahedral and the PN₂ and PNO rings are perpendicular to the plane of the (η⁵-C₅H₅)Mo(CO)₂ group. More recently, Paine et al.⁸³ have extended their approach to the synthesis of the bimetallic derivative 57, which also features planar phosphorus atoms and relative short P–Mo bond lengths (2.245 (1) Å). Related complexes of the type



58 have been prepared by Malisch et al.⁸⁴ via thermolysis or irradiation of the precursor tricarbonyl complexes (η⁵-C₅H₅)(CO)₃MAs(*t*-Bu)₂. It should be noted, however, that when the arsenic substituents are less bulky than *t*-Bu, it is necessary to resort to matrix isolation techniques to detect the desired compounds.⁸⁵ Very recently, the range of these complexes has been increased significantly by the development of a novel 1,2 elimination methodology summarized in (5).



Complexes 59–61 have been prepared by using this technique.⁸⁶ An X-ray crystal structure analysis of 59c revealed that the structure was very similar to those of 52 and 55 but with an even shorter metal–phosphorus bond length (2.181 (1) Å).⁸⁶



From an electron counting standpoint all the complexes 52–61 require three-electron donation on the part of the planar phosphorus ligand. Conceptually they may be regarded as [R₂P]⁺ complexes of 16-electron anions [(η⁵-C₅H₅)(CO)₂M]⁻; i.e., the phosphenium ion functions as a two-electron donor.⁸⁷ Alternatively, these species can be regarded as featuring metal–phosphorus or metal–arsenic double bonds, i.e., L_nM=ER₂. The question as to whether they be regarded as phosphenium ion or phosphido complexes will obviously depend

Table IV. ³¹P Chemical Shifts for Terminal Phosphido (Neutral Phosphenium) Complexes

compd	³¹ P chem shift	ref
	+ 271	45, 80
	+ 266	81
	+ 266	81
	+ 258	81
	+ 260	81
	+ 226.8	86
	+ 358.0	86
	+ 298	86
	+ 283	86
	P _A , 270 P _B , -15.3	88 88
	977	89
	404.1	90
	307	91
	P _A , 33.5 P _B , 334.9	93
	233	95

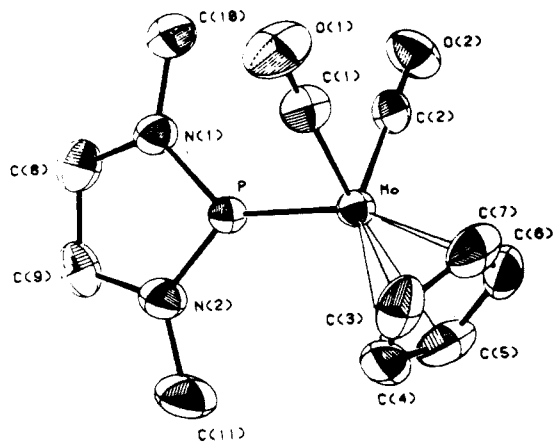
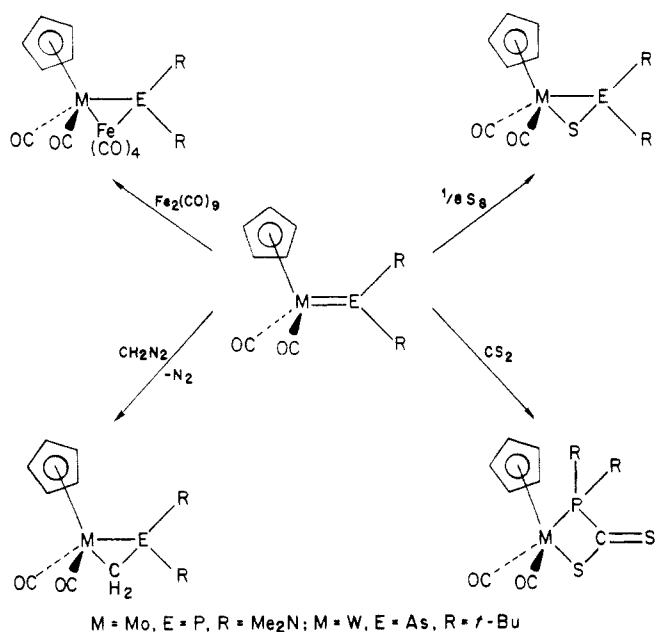


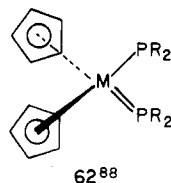
Figure 6. View of $\text{MeNCH}_2\text{CH}_2\text{N}(\text{Me})\text{PMo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ showing the atom numbering scheme. Important parameters: $\text{Mo-P} = 2.213$ (1), $\text{P-N}(1) = 1.641$ (5), $\text{P-N}(2) = 1.650$ (5) Å; $\text{N}(1)\text{-P-Mo} = 132.4$ (2), $\text{N}(2)\text{-P-Mo} = 135.5$ (2), $\text{N}(1)\text{-P-N}(2) = 92.1$ (3)°.

SCHEME II^{84,86}

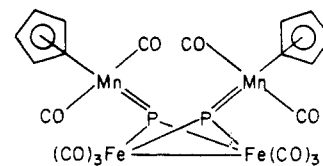
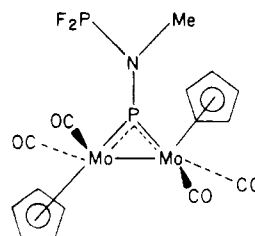
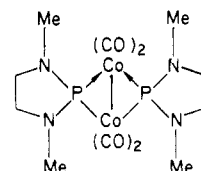
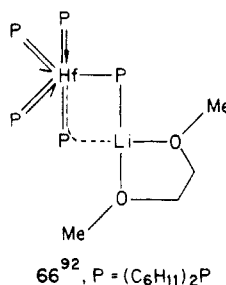
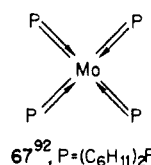
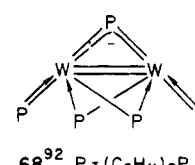
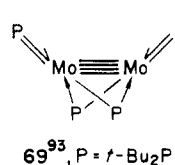
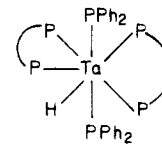
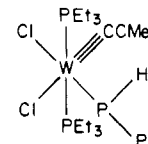
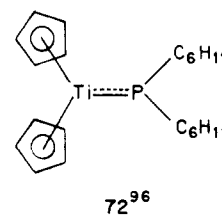


on the nature of the ligands L and R and the transition metal M. Fenske-Hall type calculations on **52**⁴⁵ indicate that the charge on phosphorus is +0.73. Qualitatively, a positive charge of this magnitude is in accord with the observation that the ³¹P chemical shifts of the trigonal-planar phosphorus complexes (Table IV) are similar to those of the cationic complexes (Table III). On the other hand, the reactivity patterns^{84,86} of these complexes (Scheme II) are best understood in terms of metal-phosphorus or metal-arsenic double bonding.

Finally, to set the foregoing results in a somewhat broader context, we note that other compounds **62-72** have been prepared with trigonal-planar phosphorus. The extreme deshielding of the ³¹P chemical shift of **63** (Table IV) is particularly noteworthy. Finally, we draw attention to the similarity in the structure of **67** and analogous amido and sulfido complexes such as $\text{Mo}(\text{NMe}_2)_4$ ⁹⁷ and $\text{Mo}(t\text{-BuS})_4$.⁹⁸ Like an R_2N group⁹⁹ the R_2P can function as a three-electron donor by using a $\text{P}(3p)$ lone pair to supplement the $\text{P-metal } \sigma$ -bond.

62⁸⁸

$\text{M} = \text{Zr}, \text{R} = \text{Et}; \text{M} = \text{Zr}, \text{R} = \text{C}_6\text{H}_{11};$
 $\text{M} = \text{Zr}, \text{R} = \text{Ph}; \text{M} = \text{Hf}, \text{R} = \text{Et};$
 $\text{M} = \text{Hf}, \text{R} = \text{C}_6\text{H}_{11}; \text{M} = \text{Hf}, \text{R} = \text{Ph}$

63⁸⁹64⁹⁰65⁹¹66⁹², $\text{P} = (\text{C}_6\text{H}_{11})_2\text{P}$ 67⁹², $\text{P} = (\text{C}_6\text{H}_{11})_2\text{P}$ 68⁹², $\text{P} = (\text{C}_6\text{H}_{11})_2\text{P}$ 69⁹³, $\text{P} = t\text{-Bu}_2\text{P}$ 70⁹⁴, $\text{P} = \text{Me}_2\text{P} \text{---} \text{PMe}_2$ 71⁹⁵72⁹⁶

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- (100) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)