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

A. H. COWLEY*† and R. A. KEMP‡

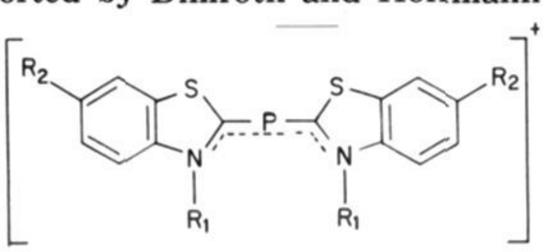
Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, and Shell Development Company, Westhollow Research Center, Houston, Texas 77001

Contents

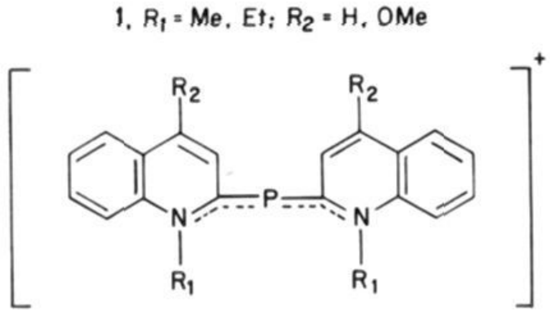
I.	Introduction and Scope of the Review	367
II.	Preparation of Phosphenium Ions	368
	A. Phosphorus–Halogen Bond Heterolysis	368
	B. Protic Attack of Phosphorus–Nitrogen Bonds	369
	C. Electrophilic Attack of Element–Phosphorus Double Bonds	369
	D. Miscellaneous Methods	370
III.	Structures of Phosphenium Ions	370
IV.	NMR Data for Phosphenium Ions	370
	A. ^{31}P NMR Data	370
	B. ^{27}Al NMR Data	371
	C. Variable-Temperature NMR Studies	371
V.	Theoretical Aspects of Phosphenium Ions	371
VI.	Comments on the Stabilities of Phosphenium Ions	371
VII.	Heavier Congeners of Phosphenium Ions—Arsenium and Stibenium Ions	374
VIII.	Reactions of Phosphenium Ions	375
	A. Reactions with Lewis Bases	375
	B. C–H Insertion Reactions	375
	C. Reactions of Phosphenium Ions with Unsaturated Organic Molecules	375
	D. Reactions of Phosphenium Ions with Azides	377
	E. Coordination Chemistry of Phosphenium Ions	377

I. Introduction and Scope of the Review

The first dicoordinate phosphorus cations 1 and 2 were reported by Dimroth and Hoffmann[1] in 1964.



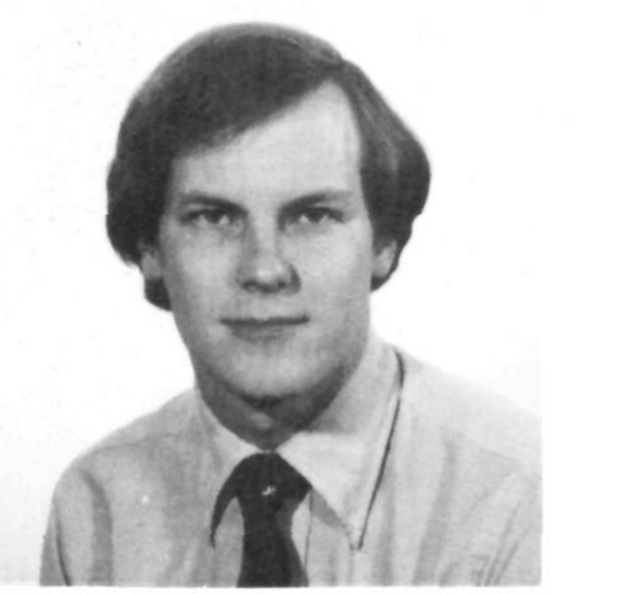
1, R_1 = Me, Et; R_2 = H, OMe



2, R_1 = Et; R_2 = H, Me

Since that time, many other so-called phosphamethine cyanines have been prepared and this exciting field has been reviewed.[2] However, the ^{31}P NMR chemical shifts and patterns of reactivity of these cations suggest extensive charge delocalization as exemplified by canonical forms **3a,b**. Since the positive charge is not located

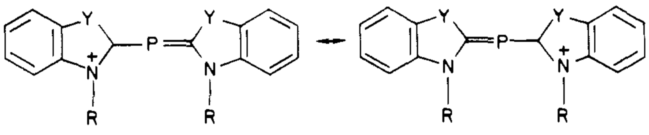
Alan H. Cowley was born in Manchester, England. He received B.Sc., M.Sc., and Ph.D. degrees from the Victoria University of Manchester. Graduate study was conducted under the supervision of the late Professor F. Fairbrother. After postdoctoral study with Professor H. H. Sisler at the University of Florida 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.



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.

† University of Texas at Austin.
‡ Shell Development Co.

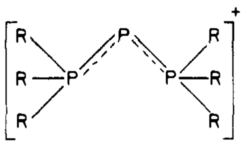
0009-2665/85/0785-0367$06.50/0



3a 3b

Y = S, NR, CH=CH

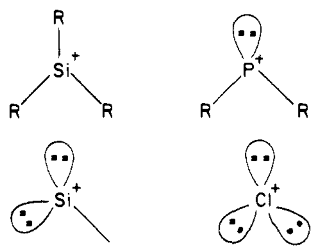
primarily at phosphorus, the phosphamethine cyanines are considered to fall outside the scope of the present review. Similar reasoning has been used to exclude a novel series of triphosphorus cations represented by 4 which have been reported recently by Schmidpeter et al.[3]



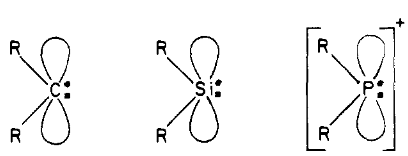
4, R = alkyl, aryl, R_2N, RO

We use the term phosphenium ion[4,5] to imply a high degree of positive charge accumulation at the two-coordinate phosphorus center. From the standpoint of ^{31}P NMR spectroscopy, the localization of charge at phosphorus is evident from a chemical shift in the range +200 to +500 ppm (vide infra).

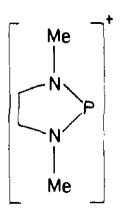
Phosphenium ions can be considered to constitute one member of an isoelectronic series that extends from silicenium[6] to chloronium[7] ions.



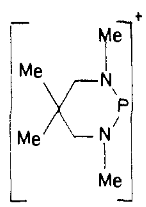
An alternative view recognizes the parallel between the singlet states of phosphenium ions, carbenes, and silylenes and focuses attention on the lone pair of electrons and the formally vacant 3p orbital at phosphorus.



Phosphenium ions have been invoked as reactive intermediates for several years.[8] Moreover, these species are responsible for the presence of prominent peaks in the mass spectra of, e.g., phosphinous halides and diphosphines.[9] The first example of a stabilized phosphenium ion, 5, was reported by Fleming, Jekot, and Lupton.[10] This development was followed closely by



5



6

a paper by Maryanoff and Hutchins[11] in which a second stabilized cation, 6, was described. Both cyclic phosphenium ions 5 and 6 were prepared by halide ion abstraction from precursor diaminohalophosphines. The scope of this approach was broadened significantly by Parry and co-workers[12] who were able to prepare $[(Me_2N)_2P]^+$ and $[(Me_2N)(Cl)P]^+$, the first examples of acyclic phosphenium ions.

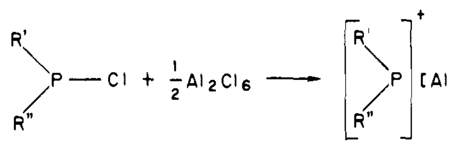
Interest in phosphenium ion chemistry has grown steadily since the mid1970s, and it is already clear that these cations are useful reagents. Versatility is a key feature in the reactivity patterns of phosphenium ions. As anticipated, many reactions can be attributed to the electrophilic character of these cations. On the other hand, dative action by the phosphorus lone pair is evident inter alia from their reactivity toward azides and from the fact that phosphenium ions exhibit a rich coordination chemistry.

II. Preparation of Phosphenium Ions

Reference to Table I indicates that the list of phosphenium ions is quite extensive. Various synthetic approaches to phosphenium ions have now evolved, and these are discussed under separate sub-headings.

A. Phosphorus–Halogen Bond Heterolysis

So far, the most widely used method of phosphenium ion synthesis involves chloride ion abstraction from precursor chlorophosphines. As shown in eq 1, Cl^- ab-



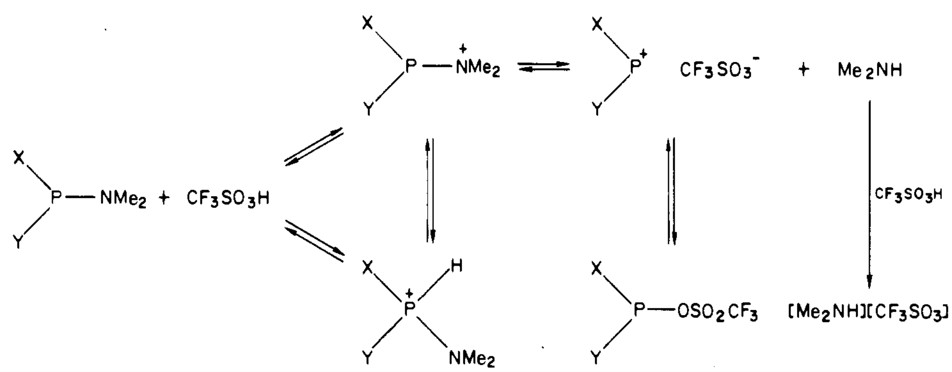
(1)

R' = R_2N, $(Me_3Si)_2N$, R" = R_2N, $(Me_3Si)_2N$, Cl, *t*-Bu, Me_5C_5, Fc; R' = R" = Fc

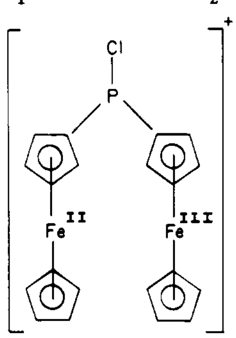
straction by Al_2Cl_6 has proved to be the most versatile approach. However, there are instances when chloride ion acceptors such as $GaCl_3$,[12] $FeCl_3$,[13] and PCl_5[11] have been employed. In general, the preparation of phosphenium ions is effected by allowing a mixture of the appropriate phosphorus chloride and a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution to warm slowly from −78 °C to room temperature. In many instances the reactions are complete at −78 °C. The progress of the reaction can be monitored conveniently by ^{31}P NMR spectroscopy (vide infra). Methylene chloride is the solvent of choice for these reactions because it is noncoordinating yet possesses a sufficiently high dielectric constant to permit solubilization of the phosphenium salts. In this context, caution should be exercised when SO_2 is used as a solvent because, in the absence of Al_2Cl_6, it causes oxidation of $(R_2N)_2PCl$ to $(R_2N)_2P(O)Cl$.[16]

In the case of the reaction of Fc_2PCl with Al_2Cl_6, it was not clear what the product would be because elegant work by Bock and co-workers[33] has demonstrated that Al_2Cl_6 in CH_2Cl_2 can function as an oxidizing agent if the binding energy of the valence electrons is 7.9 eV or less. Since the first ionization potential of ferrocene is ~6.9 eV,[34] the possibility of oxidation of Fc_2PCl to the mixed-valence bridged ferrocene 5 had to be considered. However, an ^{57}Fe Mössbauer study[19] of the

SCHEME I



product of the reaction of Fc_2PCl with Al_2Cl_6 revealed that it is the phosphenium ion Fc_2P^+, and not **5**.



7

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 $(Me_2N)(R)PF$ (R = Me_2N, *t*-Bu) with AsF_5 results in the formation of four-coordinate difluorophosphonium cations rather than a phosphenium ion.[5b]

R = Me_2N, *t*-Bu

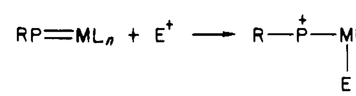
While the mechanism of this net F^+ transfer is not known, it is speculated that at least two steps are involved, viz., oxidative fluorination of the fluorophosphine forming a trifluorophosphorane, followed by fluoride ion abstraction by AsF_3 or (AsF_5).

B. Protic Attack of Phosphorus–Nitrogen Bonds

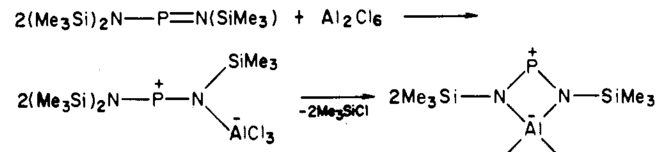
Cleavage of P–N bonds with strong acids represents a promising new approach to phosphenium ion synthesis.[35] Trifluoromethanesulfonic acid was selected as the proton source because of the low nucleophilicity of the $[CF_3SO_3]^-$ anion. However, even with this anion, covalent products are formed unless the phosphenium ion is stabilized extensively by delocalization, e.g., X = Y = Me_2N. 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.



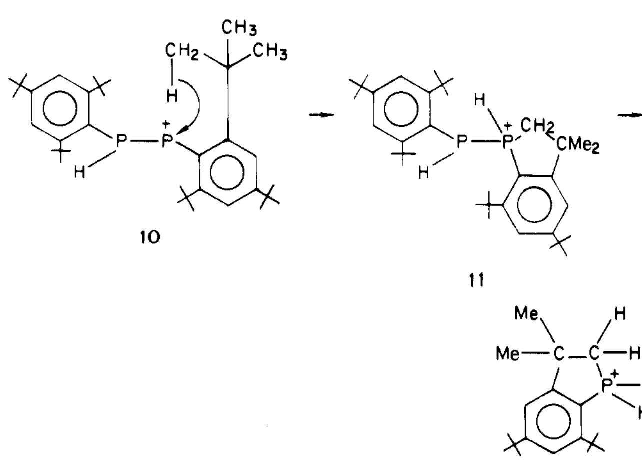
However, at the present time there are only two examples of this approach. Thus, Niecke and Kröher[26] prepared the acyclic zwitterion **8** by Al_2Cl_6 attack of a phosphorus–nitrogen double bond as shown. In turn,



8 9

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-$(t\text{-Bu})_3C_6H_2P{=}P$(2,4,6-$(t\text{-Bu})_3C_6H_2$ 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 monophosphonium salt **12**·BF_4.



10 11 12

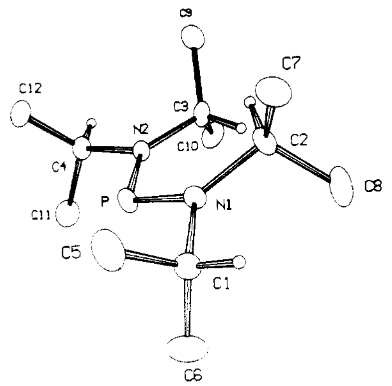
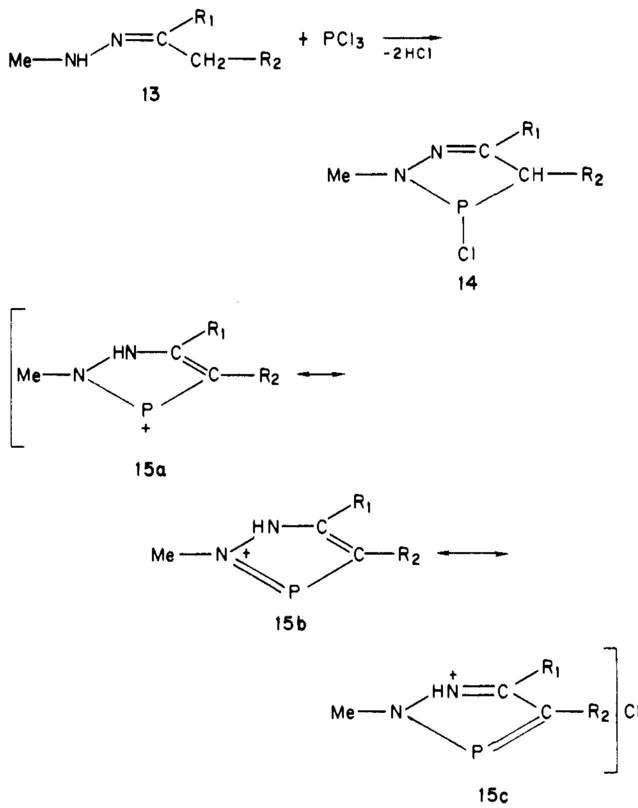


Figure 1. Structure of $[(i\text{-}Pr_2N)_2P]^+$ showing the atom numbering scheme. Important parameters: P–N(1) = 1.611 (4) Å; P–N(2) = 1.615 (4) Å; N(1)–P–N(2) = 114.8 (2)°.

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



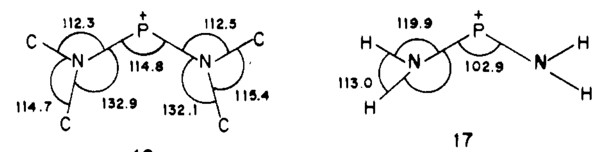
R_1 = Me; R_2 = H; R_1, R_2 = $(CH_2)_3$

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

Finally, novel bis(cations) of the type $R_2NP^+{-}N{=}P^+(NR_2)(X)$ (X = Cl, N_3) have been observed in the reaction of phosphenium ions with azides (vide infra).[32]

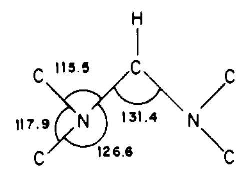
III. Structures of Phosphenium Ions

So far, three phosphenium ions have been characterized by X-ray crystallography. The skeletal geometry of $[(i\text{-}Pr_2N)_2P]^+$ (Figure 1) is consistent with the view that the phosphorus atom is approximately sp^2 hybridized.[16] Diminution of the N(1)–P–N(2) angle from the ideal value to 114.8 (2)° can be understood on the basis of repulsions between the phosphorus lone pair and the P–N bonds. The subunit C(1)C(2)N(1)PN(2)C(3)C(4) is approximately planar, a conformation which maximizes dative π bonding between the nitrogen lone pairs and the formally vacant 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,



16 **17**

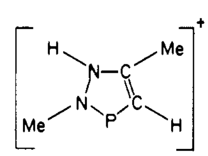
ab initio calculations on the virtually strain-free model cation $[(H_2N)_2P]^+$ revealed a similar trend of bond angles (**17**).[5b] Moreover, it is interesting to note that a similar pattern of bond angles is evident in the isovalent *N,N,N′,N′*-tetramethylformadinium cation I.[37]



I

The structure of the zwitterionic phosphenium 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) Å) is the same as that in $[(i\text{-}Pr_2N)_2P]^+$. The relatively small N–P–N bond angle in **9** (97.4 (4)°) is obviously a consequence of the cyclic structure.

In the diazaphospholium cation II, the bond angle at phosphorus is even smaller (90.4 (1)°) and the P–N bond length is somewhat longer (1.674 (2) Å) than in $[(i\text{-}Pr_2N)_2P]^+$ or **9**.[29b] The planarity of the ring and the pattern of the bond length in II are consistent with 6π-delocalization.



II

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 $[(Me_5C_5)(Me_2N)P]^+$, the ^{31}P chemical shifts of phosphenium ions are ~100 ppm downfield of those of the precursor halophosphines. In the case of $[(Me_5C_5)(Me_2N)P]^+$, the 33.8 ppm upfield shift ac-

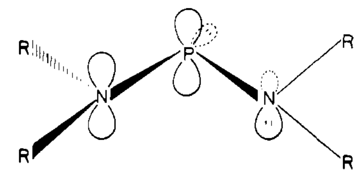


Figure 2. Transition state for P–N rotation of $[(R_2N)_2P]^+$ cations.

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 $[(Me_2N)(t\text{-Bu})P]^+$ 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 attributed[19] to the well-known ability of the ferrocenyl moiety to disperse positive charge.[39]

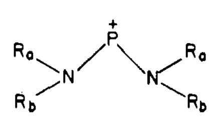
Steric effects also play a role in determining the ^{31}P chemical shifts. Note, for example, that the ^{31}P chemical shifts of the bis(amido)-substituted cations increase with increasing ligand size. This trend has been interpreted on the basis of progressive twisting of the R_2N groups with respect 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



III

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 probed[16] by investigating the variable-temperature ^1H NMR spectra of $[(Me_2N)(i\text{-}Pr_2N)P]^+$. 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 pπ–pπ 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 Wells[43] 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 $[(i\text{-}Pr_2N)_2P]^+$ and with earlier extended Hückel calculations[13] 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 $[\overline{PN(R)CH_2CH_2NR}]^+$ (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 $[(Me_5C_5)(t\text{-Bu})P]^+$, 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→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]

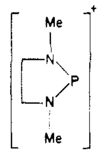
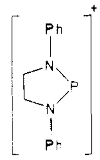
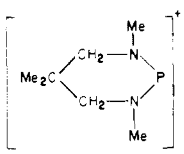
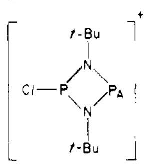
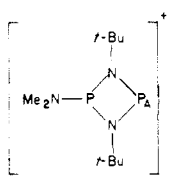
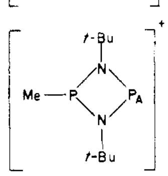
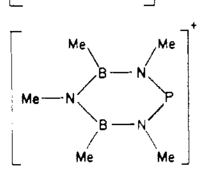
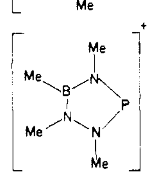
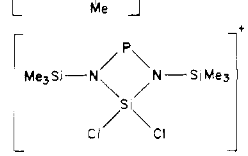
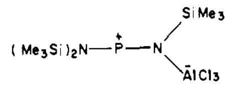
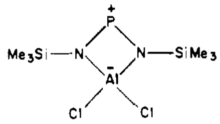
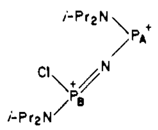
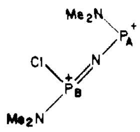
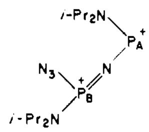
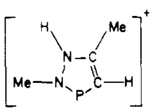
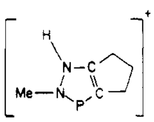
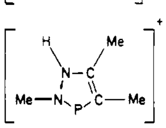
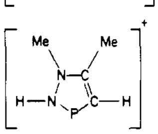
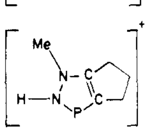
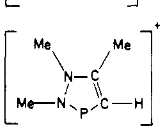
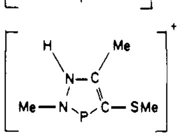
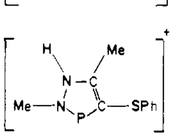
cation	synth method[b]	^{31}P chem shifts	ref
$[(Me_2N)_2P]^+$	A, B	264	12, 13
$[(Et_2N)_2P]^+$	A	263	14, 15
$[(i\text{-}Pr_2N)_2P]^+$	A	313	16
$[((Me_3Si)_2N)_2P]^+$	A	450.3	17
$[(Me_2N)(i\text{-}Pr_2N)P]^+$	A	290	16
$[(Me_2N)((Me_3Si)_2N)P]^+$	A	354.3	17
$[(Me_2N)((t\text{-}BuMe_2Si)_2N)P]^+$	A	370.1	17
$[(Me_2N)(Cl)P]^+$	A	325	12, 13
$[(i\text{-}Pr_2N)(Cl)P]^+$	A	334	18
$[(Fc)_2P]^+$ [c]	A	183.7	19
$[(Me_2N)(Fc)P]^+$ [c]	A	258.5	19
$[(Me_5C_5)(Me_2N)P]^+$	A	111.0	21
$[(Me_2N)(t\text{-}Bu)P]^+$	A	513.2	17
$[(Me_5C_5)(t\text{-}Bu)]^+$	A	168	20
$[(Me_5C_5)(Me_3Si)_2CHP]^+$	A	265.9	20
	A		
	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*)

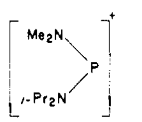
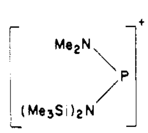
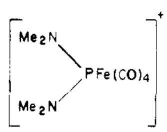
cation	synth method[b]	^{31}P chem shifts	ref
	C	450	26
	C	379	26
	D	P_A, 311.3	22, 32
	D	P_A, 293.5	22, 32
	D	P_A, 301.4	22, 32
	D	230.7 (Cl^- salt) 232.0 (Br^- salt)	27 28
	D	209.3	27
	D	237.7 (Cl^- salt) 228.5 (Br^- salt)	29 28
	D	211.0	30
	D	195.2	30
	D	230.3	31
	D	220.0	28
	D	231.1 (Cl^- salt) 229.9 (Br^- salt)	28 28

[a] ^{31}P chemical shifts referenced to 85% H_3PO_4 (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 $[(Me_5C_5)(t\text{-Bu})P]^+$ is attributable to multihapto bonding between the Me_5C_5 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 phosphenium ions. However, unless the phosphenium 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
$[(Me_2N)_2P]^+$	14.6[a]	13
	13.6[a]	41
$[(i\text{-}Pr_2N)_2P]^+$	11.1	16
	11.9 (i-Pr) 14.1 (Me)	16
	16.4 (Me)	17
	11.5	41

[a] There is evidence for the dependence of the magnitude of the rotational barrier in the nature of the counterion. See ref 13.

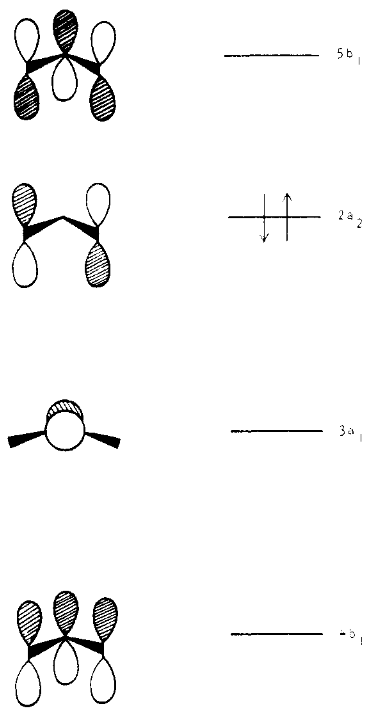
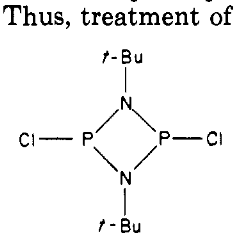


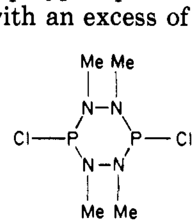
Figure 3. Some molecular orbitals for the model cation $[(H_2N)_2P]^+$.

to impart the necessary thermodynamic stabilization. Thus, the reactions of PX_3 (X = Cl, 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



18



19

results in the abstraction of only one chloride ion and

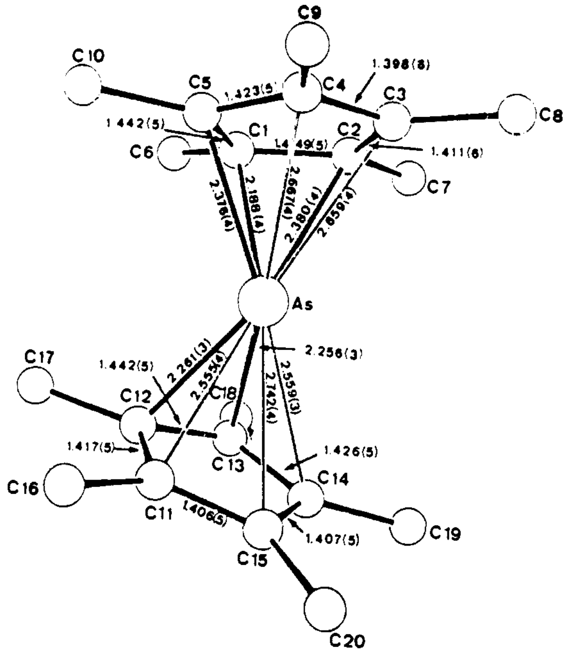


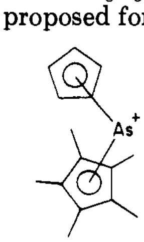
Figure 4. View of $[(Me_5C_5)_2As]^+$ showing the atomic number scheme and important bond lengths (Å).

formation of the monocation (Table I). Interestingly, however, Nöth and Ullmann[48] 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 Stibenium Ions

There is X-ray crystallographic evidence[49] for contributions from the ionic form $[F_2As]^+[SbF_6]^-$ 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 Å, two intermediate neighbors at 2.01 and 2.39 Å, and two long contacts at 2.73 Å. 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 $(Me_5C_5)(Me_2N)AsCl$ and $(Me_5C_5)(C_5H_5)AsCl$.[21a] A bis η^5 geometry, **20**, was proposed for $[(Me_5C_5)(C_5H_5)As]^+$



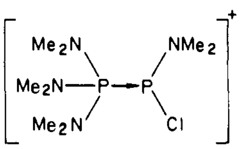
20

on the basis of theoretical calculations and NMR spectroscopic evidence. In a highly significant publication, Jutzi et al.[50] have described the isolation of $[(Me_5C_5)_2E]^+$ (E = As, 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 14[100] compounds $(Me_5C_5)_2E$ (E = Ge, Sn, Pb),[51] it possesses a bent-sandwich structure[52] with a somewhat distorted bis η^5 attachment of Me_5C_5 rings.

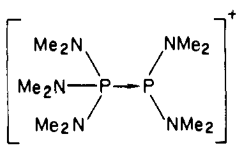
VIII. Reactions of Phosphenium Ions

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 $[2(Me_2N)_2PCl]\cdot AlCl_3$ and $(Me_2N)_3P\cdot(Me_2N)_2PCl\cdot AlCl_3$ as phosphine adducts of the phosphenium ion $[(Me_2N)_2P]^+$, **21** and **22**. Since that time, other

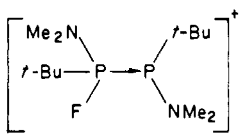


21

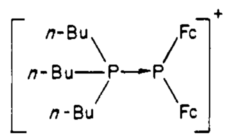


22

phosphine adducts **23**[17] and **24**[19b] have been prepared.



23

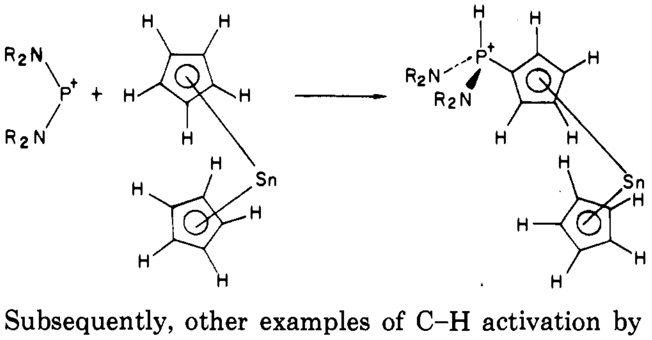


24

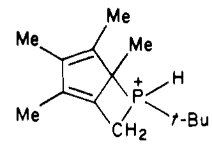
An interesting facet of the ^{31}P NMR spectra of these diphosphorus cations is that *both* phosphorus nuclei are more shielded than those of the individual components. This observation has been attributed by Parry et al.[12b] to the fact that coordination numbers at both phosphorus centers increase upon formation of the P→P dative bond. The one-bond ^{31}P–^{31}P 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 $(\eta^5\text{-}C_5H_5)_2Sn$ or $(\eta^5\text{-}C_5H_5)_2Pb$ with $[(i\text{-}Pr_2N)_2P]^+$ was to prepare compounds with formed double bonding between Sn or Pb and P$^+$. However, the reaction of stannocene or plumbocene with $[(i\text{-}Pr_2N)_2P]^+$ results in phosphonium salt formation via oxidative addition of a cyclopentadienyl C–H bond to the P$^+$ center (or, alternatively, via electrophilic aromatic substitution),[53] viz.

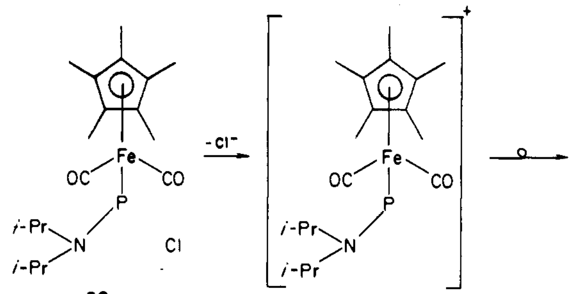


Subsequently, other examples of C–H activation by phosphenium ions have materialized. Thus, aluminum chloride promoted chloride ion abstraction from $(\eta^1\text{-}Me_5C_5)(t\text{-}Bu)PCl$ affords initially the phosphenium ion $[(Me_5C_5)(t\text{-}Bu)P]^+$. On standing for ~5 days at ambient temperature in CH_2Cl_2 solution $[(Me_5C_5)(t\text{-}Bu)P]^+$ 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.

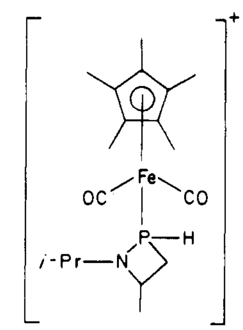


25

Another example of C–H activation is provided by halide ion abstraction from $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(PClN(i\text{-}C_3H_7)_2)$ (**26**). Thus, treatment of **26** with Al_2Cl_6 or



26 **27**



28

$Ph_3C^+BF_4^-$ is believed (on ^{31}P 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 $i\text{-}Pr_2N$ 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-$(t\text{-}Bu)_3C_6H_2$ moieties have been observed.[36,56]

C. Reactions of Phosphenium Ions with Unsaturated Organic Molecules

Over 3 decades ago, McCormack[57] 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 Baxter[58] and our group[59]

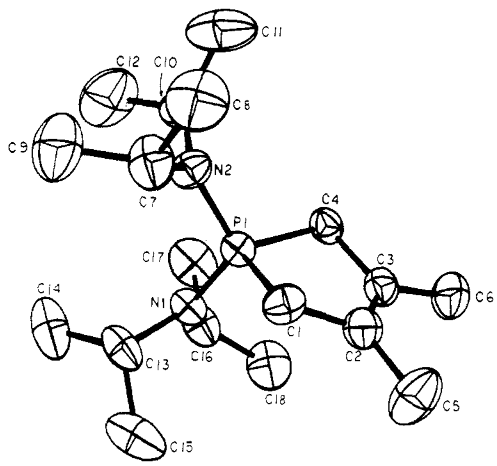
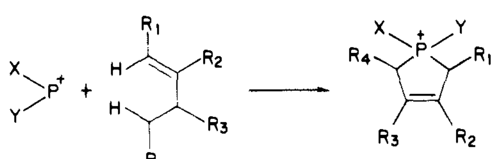


Figure 5. View of the 3-phospholenium cation **29h** showing the atom numbering scheme.

recognized that, being electrophilic carbenoids,[60] phosphenium 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, $[(Me_2N)_2P]^+$ 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 phosphenium ion $[(i\text{-}Pr_2N)_2P]^+$ in 3 and 9 days, respectively. Reactivity can be increased by (a) decreasing the bulk of the phosphenium ion substituents and (b) increasing the electrophilicity at phosphorus. Thus, $[(i\text{-}Pr_2N)(Cl)P]^+$ reacts with 2,3-dimethyl-1,3-butadiene in ~30 min at ambient temperature. The overall reaction of phosphenium ions with 1,3-dienes is summarized in (2).

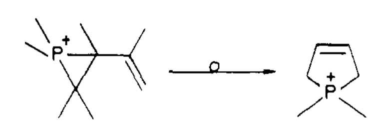


(2)

29-i

29a. X = Y = Me$_2$N; R$_2$ = Me; R$_1$ = R$_3$ = R$_4$ = H
b. X = Y = Et$_2$N; R$_2$ = Me; R$_1$ = R$_3$ = R$_4$ = H
c. X = Y = Et$_2$N; R$_1$ = R$_4$ = H; R$_2$ = R$_3$ = Me
d. X = Y = *i*-Pr$_2$N; R$_1$ = R$_2$ = R$_3$ = R$_4$ = H
e. X = Y = *i*-Pr$_2$N; R$_1$ = Me; R$_2$ = R$_3$ = R$_4$ = H
f. X = Y = *i*-Pr$_2$N; R$_1$ = R$_4$ = Me; R$_2$ = R$_3$ = H
g. X = Y = *i*-Pr$_2$N; R$_2$ = Me; R$_1$ = R$_3$ = R$_4$ = H
h. X = Y = *i*-Pr$_2$N; R$_1$ = R$_4$ = H; R$_2$ = R$_3$ = Me
i. X = *i*-Pr$_2$N; Y = Cl, R$_1$ = R$_4$; R$_2$ = R$_3$ = Me

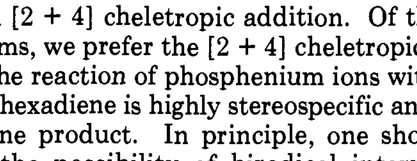
Note that in each case, 1,4 addition is observed. This assignment was confirmed by an X-ray crystal structure determination[59] on a representative phospholenium ion (Figure 5). This study showed that the double bond is located between C(2) and C(3). Interestingly, the $[(i\text{-}Pr_2N)_2P]^+$ unit 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 phosphenium ions with 1,3-dienes. As demonstrated for transient phosphinidene complexes of the type $PhP{=}M(CO)_5$ (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



30 31

concerted [2 + 4] cheletropic addition. Of these two mechanisms, we prefer the [2 + 4] cheletropic process because the reaction of phosphenium 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 phosphenium ion. However, MO calculations[44] indicate that phosphenium ions are ground-state singlets hence this mechanism is unlikely.

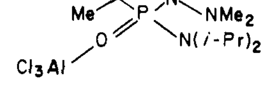
Phosphenium ions are also reactive toward 1,4-dienes. In fact, several years previously, Kashman and coworkers[62] reported that complexes of the type $RPX_2 \cdot AlX_3$ (R = Me, Ph; X = Cl, Br) react with, e.g., 1,4-dienes to afford phosphorus-containing heterocycles. It was quite conceivable that phosphenium ions are involved in these reactions; however, we were unable to detect $[MePX]^+$ or $[PhPX]^+$ by ^{31}P NMR spectroscopy when $PRCl_2$ was treated with Al_2Cl_6. We were therefore curious regarding the reactivity of stabilized phosphenium ions toward 1,4-dienes. Indeed, $[i\text{-}Pr_2NPCl]^+$ 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 predominant isomer from the 1,4-pentadiene reaction demonstrated a proximal relationship between the *i*-Pr$_2$N and cyclopropane moieties.[18]



32 33

R$_1$ or R$_2$ = Cl or *i*-Pr$_2$N

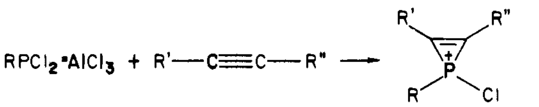
More recently, the phosphenium ion reactions have been extended to the heteroatom systems MeCH=CHCH=NNMe$_2$ (**34**), Me$_2$C=NN=CMe$_2$ (**35**), and Me$_2$NN=C(Me)C(Me)=NNMe$_2$ (**36**). Compound **34** reacts readily with $[i\text{-}Pr_2NPCl]^+$ to afford the heterocycle **37**.[63] Presumably, **37** is formed as a result of



37

partial hydrolysis of the initial product. For the reactions of **35** or **36** with $[i\text{-}Pr_2NPCl]^+$, large quantities of *i*-Pr$_2$NPCl$_2$ were detected by ^{31}P 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., $AlCl_4^- \rightarrow AlCl_3 + Cl^-$. In turn, Cl^- attack of the phosphenium ion affords the neutral dihalophosphine. A similar reaction was observed[64] in attempting to prepare amido-substituted silicenium ions.

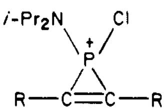
Fongers, Hogveen and Kingma[65] were the first to demonstrate that alkynes will react with phosphonous dichlorides in the presence of aluminum chloride to afford phosphirenium cations as indicated in (3).



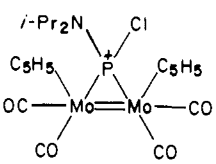
(3)

R = R' = R" = Me; R = R' = Me; R" = H; R = Me; R' = R" = H; R = Ph, R' = R" = Me; R = Ph, R' = Me; R" = H; R = Ph, R' = R" = H

Subsequently, this methodology was extended to the reactions of R_2PCl (R = Ph, Et) with EtC≡CEt and PhC≡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 phosphenium ions such $[MePCl]^+$ and $[Ph_2P]^+$ can be implied in the foregoing reactions, it was of interest to determine whether stabilized phosphenium ions would react with alkynes. Indeed, preliminary work[67] indicates that $[i\text{-}Pr_2NCl]^+$ reacts with MeC≡CMe and PhC≡CPh to afford phosphirenium cation **38**. Moreover, recognizing the isolobal relationship of alkynes to compounds with metal–metal triple bonds,[68] we have also explored the reactivity of $[i\text{-}Pr_2NPCl]^+$ toward $C_5H_5(CO)_2Mo{\equiv}Mo(CO)_2(C_5H_5)$. Spectroscopic evidence has led us to the preliminary conclusion that the product is the dimetallaphosphirenium cation **39**.



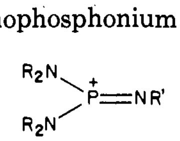
38, R = Me, Ph



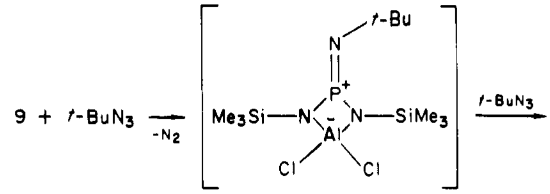
39

D. Reactions of Phosphenium Ions with Azides

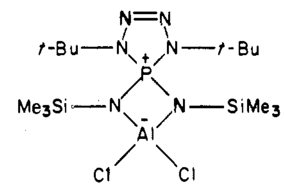
In an interesting extension of the Staudinger reaction, it has been found that bis(dialkylamino)phosphenium ions react with azides to afford the corresponding bis(dialkylamino)iminophosphonium ions **40**.[22,32,69] Contrasting with this observation is the report that in the reaction of the zwitterionic phosphenium ion **9**, with $t\text{-}BuN_3$ it is impossible to isolate the iminophosphonium cation 41 because of subsequent reaction with azide to produce the spiroheterocycle 42.[26]



40

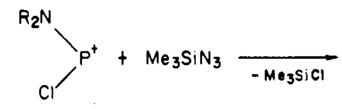


41

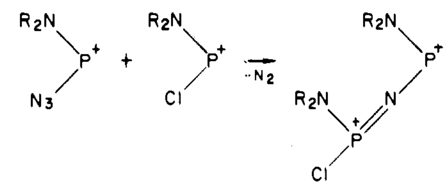


42

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 azidophosphenium ion **43**.[32] In turn, **43**, being itself an azide, reacts with the halophosphenium ion to produce novel phosphenium–iminophosphonium dications **44**. In independent experiments it was established that azidophosphenium ions **43** will self-condense to afford polymers and bis(cations) analogous to **44**.[32]



43



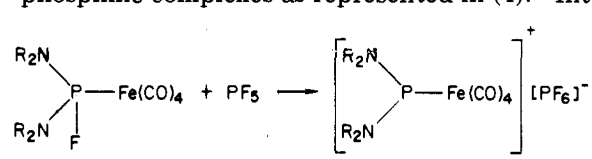
44

R = Me, *i*-Pr

E. Coordination Chemistry of Phosphenium Ions

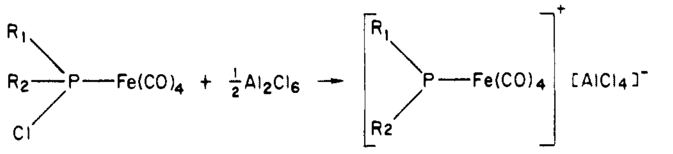
The presence of a lone pair and a vacant π-orbital renders phosphenium ions excellent ligands. In the case of amido-substituted cations, MO calculations on the model systems[5b,46] suggest that σ-donor behavior stems from utilization of the second MO ($3a_1$) and that π-acceptance results from interaction of occupied nd orbitals with the $5b_1$ LUMO (Figure 3). As noted by Paine[46] and Parry[13] 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 fluorophosphine complexes as represented in (4). Interestingly, the same complexes can be formed by direct reactions of the phosphenium ions with $Fe(CO)_5$ or $Fe_2(CO)_9$.[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, $Me_2NP(F)_2Fe(CO)_4$ failed to react with PF_5 and the reaction of $Cl_3PFe(CO)_4$ or $F_2P(Cl)Fe(CO)_4$ with Al_2Cl_6 resulted in the production



(4)

R_2N = Me_2N or $\overline{MeNCH_2CH_2NMe}$



45, R_2 = R_2 = Fc
46, R_1 = Me_2N, R_2 = Cl
47, R_1 = R_2 = Et_2N
48, R_1 = R_2 = i-Pr_2N
49, R_1 = R_2 = $(Me_3Si)_2N$
50, R_1 = t-Bu, R_2 = Me_2N

of PCl_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 $[(MeO)_2P]^+$ (**51**) has, in fact, been prepared[71] by protic attack of $Mo[P(OMe)_3]_6$.

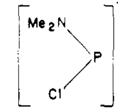
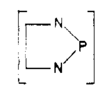
$$Mo[P(OMe)_3]_6 + H^+ \rightarrow CH_3OH + \{(MeO)_2PMo[P(OMe)_3]_5\}^+ \quad \mathbf{51}$$

X-ray crystal structure data have been reported for two cationic phosphenium complexes. Within 0.036 Å, the MPO_2 framework for the phosphenium 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 $(MeO)_3P$ 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) $Fe(CO)_4$ complexes such as $[CH_3NCH_2CH_2N(CH_3)PF]Fe(CO)_4$,[73] the phosphenium 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 $[(Et_2N)_2P]^+$ ligand are quite similar to those of unligated $[(i\text{-}Pr_2N)_2P]^+$, the only major change accompanying coordination being diminution of the N–P–N angle by ~10°. Equatorially substituted $Fe(CO)_4$ complexes are, in fact, quite rare, the only examples of which we are aware being $(Ph_2P)_2(Ph)PFe(CO)_4$,[74] $[trans\text{-}\{[Fe(CO)_4]_3[PCH(SiMe_3)_2]\}$,[75] and $(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2P_2Fe(CO)_4$.[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 phosphenium complex, the equatorial preference probably stems from the π-acceptor nature of the phosphenium ligand since theoretical studies by Rossi and Hoffmann[77] have demonstrated that for d^8–d^{10} trigonal bipyramidal systems π-acceptor ligands prefer an equatorial location. Interestingly, Sosinsky et al.[78] have interpreted Mössbauer data for $[(Fc_2PFe(CO)_4]^+$ in terms of axial substitution of the phosphenium ion ligand. This observation would suggest that σ-donation is more important than π-acceptance for $[Fc_2P]^+$, while for the amido-substituted ligands, the reverse is true.

The π-acceptor nature of cationic phosphenium ion ligands can also be inferred from other lines of evidence. For example, the CO stretching frequencies of coordinated phosphenium ions are ~80–100 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 Phosphenium Ions, Cationic Phosphenium Ion Complexes, and Precursor Chloride Complexes

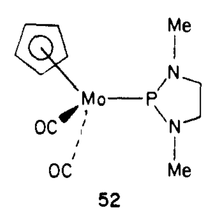
phosphenium ion[a]		$Fe(CO)_4$ complex	coordinatn chem shift[b]	(R_2PCl)-$Fe(CO)_4$
	325	286.8[c]	−38.2	192.2[c]
$[(Me_2N)_2P]^+$	264	311[d]	+47	194[c]
$[(Et_2N)_2P]^+$	263	307.6[c]	+44.6	183.8[c]
$[(i\text{-}Pr_2N)_2P]^+$	313	311.3[c]	−1.7	182.5[c]
$[\{(Me_3Si)_2N\}_2P]^+$	450.3	349.7[c]	−100.6	268.0[c]
$[(t\text{-}Bu)(Me_2N)P]^+$	513.2	441.5[c]	−71.7	219.3[c]
	264	300[d]	+36	
$[Fc_2P]^+$	183	280[e]	+97	161[c]

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

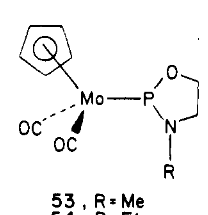
phosphenium ion ligands is provided by the fact that, at ambient temperature, it is not possible to record ^{13}C NMR resonances for the CO ligands of $R_2PFe(CO)_4^+$ complexes. This interesting observation was made first by Bennett and Parry[79] and attributed to rapid intermolecular CO exchange in complexes of this type. This conclusion was confirmed qualitatively by ^{13}CO studies which showed that for phosphenium ion complexes, statistical exchange was complete in <0.5 h at 25 °C.[79]

The ^{31}P NMR chemical shifts of cationic phosphenium ion complexes have been assembled in Table III along with the available data for uncoordinated phosphenium ions and precursor chlorophosphine complexes. As in the case of unligated phosphenium ions, a substantial deshielding (~80–230 ppm) accompanies halide ion abstraction. However, the coordination chemical shifts (i.e., the differences in chemical shifts of the coordinated and free phosphenium 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 $Fe(CO)_4$ complexes.

Complexes of the type represented by **52** were first isolated by Paine et al.[45,80] from the reaction of $[(C_5H_5)Mo(CO)_3]^-$ with the corresponding cyclic diaminohalophosphine. Complexes **53**–**56** have been prepared[81]

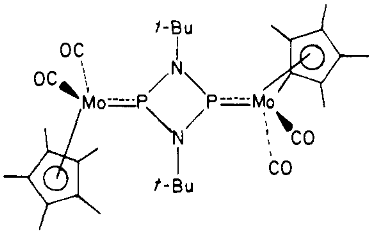


52

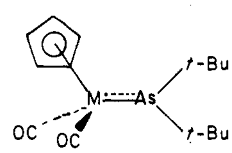


53, R = Me
54, R = Et
55, R = t-Bu
56, R = C_6H_5

by similar reactions with the analogous aminohalophosphites $RNCH_2CH_2OPCl$ (R = Me, Et, t-Bu, C_6H_5). 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 ~360° 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 PN_2 and PNO rings are perpendicular to the plane of the $(\eta^5\text{-}C_5H_5)Mo(CO)_2$ 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

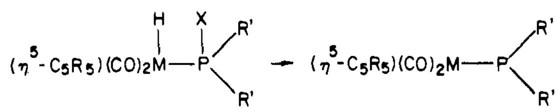


57



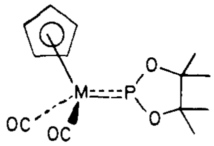
58a, M = Mo
b, M = W

58 have been prepared by Malisch et al.[84] via thermolysis or irradiation of the precursor tricarbonyl complexes $(\eta^5\text{-}C_5H_5)(CO)_3MAs(t\text{-}Bu)_2$. 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).

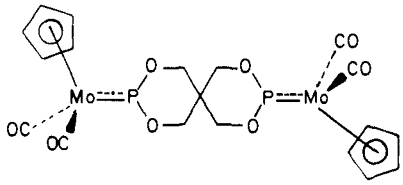


R = H, Me; M = Cr, Mo, W; X = Cl, Me₂N

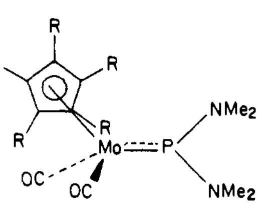
Complexes **59**–**61** have been prepared by using this technique.[86] An X-ray crystal structure analysis of **59c** revealed that the structure was very similar to those of **52** and **55** but with an even shorter metal–phosphorus bond length (2.181 (1) Å).[86]



59a, M = Cr
b, M = Mo
c, M = W



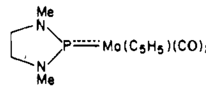
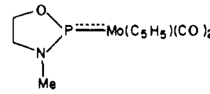
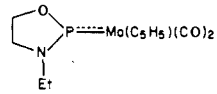
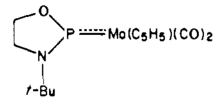
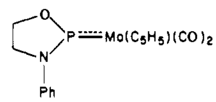
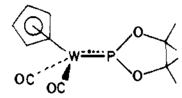
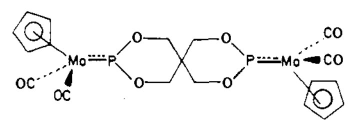
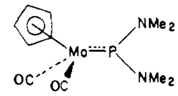
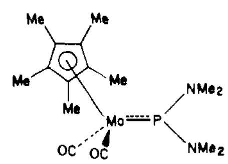
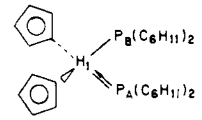
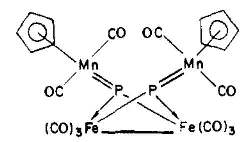
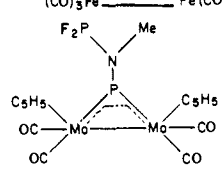
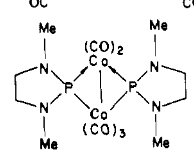
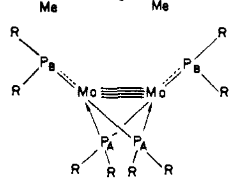
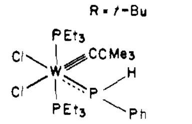
60



61a, R = H
b, R = Me

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 $[R_2P]^+$ complexes of 16-electron anions $[(\eta^5\text{-}C_5H_5)(CO)_2M]^-$; 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., $L_nM{=}ER_2$. The question as to whether they be regarded as phosphenium ion or phosphido complexes will obviously depend

Table IV. ^{31}P 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

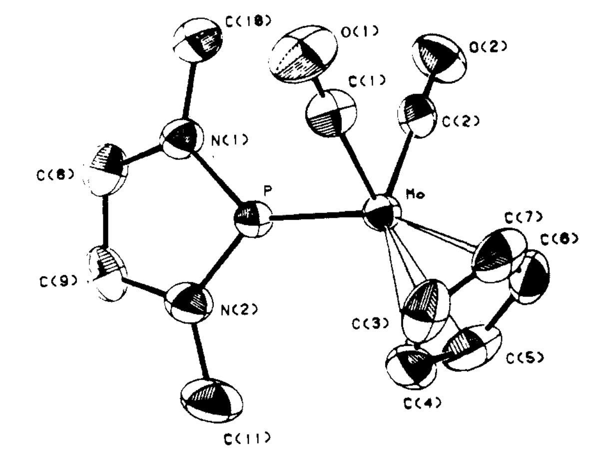
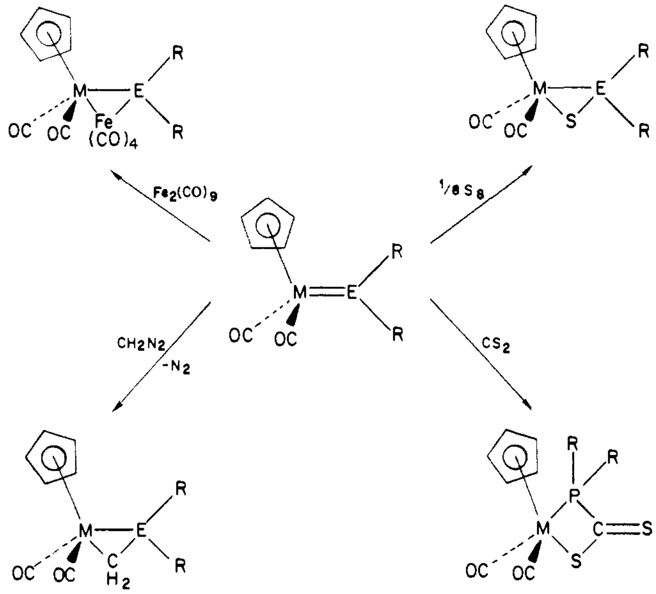
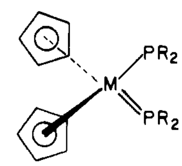


Figure 6. View of MeNCH$_2$CH$_2$N(Me)PMo(η^5-C$_5$H$_5$)(CO)$_2$ showing the atom numbering scheme. Important parameters: Mo-P = 2.213 (1), P-N(1) = 1.641 (5), P-N(2) = 1.650 (5) Å; N(1)-P-Mo = 132.4 (2), N(2)-P-Mo = 135.5 (2), N(1)-P-N(2) = 92.1 (3)°.

SCHEME II[84,86]

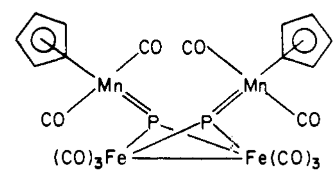


M = Mo, E = P, R = Me$_2$N; M = W, E = As, R = *t*-Bu

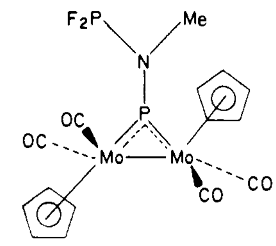


62[88]

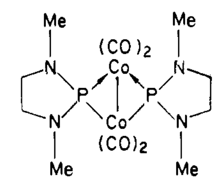
M = Zr, R = Et; M = Zr, R = C$_6$H$_{11}$; M = Zr, R = Ph; M = Hf, R = Et; M = Hf, R = C$_6$H$_{11}$; M = Hf, R = Ph



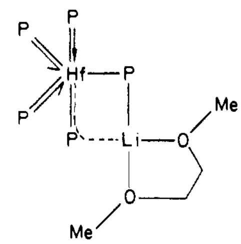
63[89]



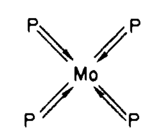
64[90]



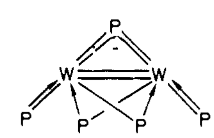
65[91]



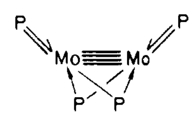
66[92], P = (C$_6$H$_{11}$)$_2$P



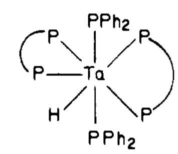
67[92], P = (C$_6$H$_{11}$)$_2$P



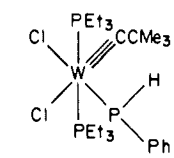
68[92], P = (C$_6$H$_{11}$)$_2$P



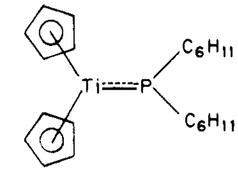
69[93], P = *t*-Bu$_2$P



70[94], P⌒P = Me$_2$P⌒PMe$_2$



71[95]



72[96]

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 in accord with the observation that the ^{31}P 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 ^{31}P 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 Mo(NMe$_2$)$_4$[97] and Mo(*t*-BuS)$_4$.[98] Like an R$_2$N group[99] the R$_2$P can function as a three-electron donor by using a P(3p) lone pair to supplement the P–metal σ-bond.

Acknowledgments. Gratitude is expressed to the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation for financial support.

References

(1) (a) Dimroth, K.; Hoffmann, P., *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 384. See also: (b) Dimroth, K.; Hoffmann, P. *Chem. Ber.* **1966**, *99*, 1325.
(2) Dimroth, K. *Top. Curr. Chem.* **1973**, *38*, 1. Somewhat similar compounds have been reported by Gamon and Reichardt. See, e.g.: Gamon, N.; Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 404; *Leibigs Ann. Chem.* **1980**, 2072.
(3) (a) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 63. (b) Schmidpeter, A.; Lochschmidt, S.; Burget, G. *Phosphorus Sulfur* **1983**, *18*, 23. (c) Schmidpeter, A.; Lochschmidt, S.; Willhalm, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *23*, 903. (d) Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226.
(4) (a) This system of nomenclature follows the organic chemistry convention suggested by Olah[4b] in which the cations with lower coordination number are given the suffix "enium", while those of higher coordination number are given the suffix "onium". (b) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.
(5) For brief reviews of phosphenium ion chemistry, see: (a) Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193. (b) Cowley,

A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789.
(6) For recent evidence for a silicenium ion in solution, see: Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671.
(7) For a thorough discussion of halonium ions, see: Olah, G. A. "Halonium Ions"; Wiley: New York, 1975.
(8) See, for example: Jungermann, E.; McBride, J. J., Jr.; Clutter, R.; Mais, A. *J. Org. Chem.* **1962**, *27*, 606.
(9) Halmann, M. *J. Chem. Soc.* **1962**, 3270. See also the review by: Granoth, I. *Top. Phosphorus Chem.* **1976**, *8*, 41.
(10) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534.
(11) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475.
(12) (a) Kopp, R. W.; Bond, A. C.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3042. (b) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046.
(13) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.
(14) Kemp, R. A. Ph.D. Dissertation, The University of Texas at Austin, 1982.
(15) Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289.
(16) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.
(17) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916.
(18) Cowley, A. H.; Stewart, C. A.; Whittlesey, B. R.; Wright, T. C. *Tetrahedron Lett.* **1984**, *25*, 815.
(19) (a) Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 714. (b) Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Inorg. Chem.* **1983**, *22*, 3475. (c) Sena, S. F. Ph.D. Dissertation, The University of Texas at Austin, 1981.
(20) Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1983**, *105*, 2074.
(21) (a) Baxter, S. G.; Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1981**, *103*, 5572. See also: (b) Baxter, S. G.; Cowley, A. H.; Kemp, R. A.; Mehrotra, S. K. *ACS Symp.* **1981**, *No. 171*.
(22) Marre, M.-R.; Sanchez, M.; Wolf, R. *Phosphorus Sulfur* **1982**, *13*, 27.
(23) Keat, R.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1978**, 634.
(24) Scherer, O. J.; Schnabl, G. *Chem. Ber.* **1976**, *109*, 2996.
(25) (a) Barlos, K.; Nöth, H.; Wrackmeyer, B.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1979**, 801. (b) See also: Barlos, K.; Nöth, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 415.
(26) Niecke, E.; Kröher, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 692.
(27) Luber, J.; Schmidpeter, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 111.
(28) Högel, J.; Schmidpeter, A. *Chem. Ber.* **1985**, *118*, 1621.
(29) (a) Luber, J.; Schmidpeter, A. *J. Chem. Soc., Chem. Commun.* **1976**, 886. (b) Friedrich, P.; Huttner, G.; Luber, J.; Schmidpeter, A. *Chem. Ber.* **1978**, *111*, 1558.
(30) Weinmaier, J. H.; Luber, J.; Schmidpeter, A. *Angew. Chem.* **1979**, *91*, 442.
(31) Weinmaier, J. H.; Brunnhuber, G.; Schmidpeter, A. *Chem. Ber.* **1980**, *113*, 2278.
(32) Marre, M.-R.; Sanchez, M.; Wolf, R. *J. Chem. Soc., Chem. Commun.* **1984**, 566.
(33) (a) Bock, H.; Brähler, G.; Fritz, G.; Matern, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 699. (b) Bock, H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 4429. (c) Bock, H.; Kaim, W.; Connolly, J. W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 700. (d) Bock, H.; Kaim, W.; Nöth, H.; Semkow, A. *J. Am. Chem. Soc.* **1980**, *102*, 4421. (e) Bock, H.; Kaim, W. *Chem. Ber.* **1978**, *111*, 3552.
(34) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 45 and references therein.
(35) Dahl, O. *Tetrahedron Lett.* **1982**, *23*, 1493.
(36) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845.
(37) Prick, P. A. J.; Beurskens, P. T. *Cryst. Struct. Commun.* **1979**, *8*, 293.
(38) (a) Pohl, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1342. (b) Pohl, S. *Chem. Ber.* **1979**, *112*, 3159.
(39) At least three models have been proposed to explain the charge delocalization in ferrocenyl-substituted carbocations: (i) interaction of the central metal with a "fulvene" π system with concomitant shift of the metal toward the exocyclic carbon, (ii) conjugation between the 2p orbital of the exocyclic carbon with the π system of the substituted ring, and (iii) distortion and bending of bonds in the substituted ring, thus bringing the exocyclic carbon closer to the metal atom. See: (a) Hill, E. A.; Richards, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3480. (b) Cais, M.; Dannenburg, J. J.; Eisenstadt, A.; Levenburg, M. I.; Richards, J. H. *Tetrahedron Lett.* **1966**, 1694. (c) Traylor, T. G.; Ware, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2304. (d) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *Ibid.* **1971**, *93*, 5715. (e) Fitzpatrick, J. D.; Watts, L. Pettit, R. *Tetrahedron Lett.* **1966**, 1299. (f) Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688. (g) Corriu, M. *Organomet. Chem. Rev.* **1966**, *1*, 435.
(40) Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5*, 465.
(41) Bennett, D. W. Ph.D. Thesis, University of Utah, 1978, p 77.
(42) Trinquier, G.; Marre, M.-R. *J. Phys. Chem.* **1983**, *87*, 1903.
(43) Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.
(44) (a) Harrison, J. F.; Liedtke, R. C.; Liebmann, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 7162. (b) Harrison, J. F. *Ibid.* **1981**, *103*, 7406.
(45) Hutchins, L. D.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 4521.
(46) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics*, **1982**, *1*, 1254.
(47) Alton, E. R.; Montemayer, R. G.; Parry, R. W. *Inorg. Chem.* **1974**, *13*, 2267.
(48) Nöth, H.; Ullmann, R. *Chem. Ber.* **1976**, *109*, 1942.
(49) Edwards, A. J.; Sills, R. J. C. *J. Chem. Soc. A* **1971**, 942.
(50) Jutzi, P.; Wippermann, T.; Krüger, C.; Kraus, H.-J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 250.
(51) (a) Jutzi, P.; Kohl, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757. (b) Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 924.
(52) For a theoretical model for bent-sandwich compounds of the main-group elements see: Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064.
(53) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239.
(54) Nakazawa, H.; Buhro, W. E.; Bertrand, G.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 3433.
(55) This view is in accord with the very deshielded ^{31}P NMR chemical shift ascribed to **27** (+954 ppm).
(56) (a) Baceiredo, A.; Bertrand, G.; Mazerolles, P.; Majoral, J.-P. *J. Chem. Soc., Chem. Commun.* **1981**, 1197. (b) Yoshifuji, M.; Shima, I.; Ando, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, *24*, 933. (c) Cadogan, J. I. G.; Cowley, A. H.; Gosney, I.; Pakulski, M.; Yaslak, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1408. (d) Cowley, A. H.; Pakulski, M. *Tetrahedron Lett.* **1984**, *25*, 2125.
(57) McCormack, W. B. U.S. Patents 2663736, 2663737, 1953; *Chem. Abstr.* **1955**, *49*, 7601. For reviews of this reaction, see: Quin, L. D. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; pp 47–96. Quin, L. D. In "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981; Chapter 2.
(58) SooHoo, C. K.; Baxter, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 7443.
(59) Cowley, A. H.; Kemp, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 7444.
(60) For an earlier discussion of the similarities between carbenes and phosphenium ions see ref 13.
(61) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456 and references therein.
(62) (a) Kashman, Y.; Menachem, Y.; Benary E. *Tetrahedron* **1973**, *29*, 4279. (b) Kashman, Y.; Rudi, A. *Tetrahedron Lett.* **1976**, 2810. (c) Rudi, A.; Kashman, Y. *Ibid.* **1978**, 2209.
(63) Cowley, A. H.; Kren, R. W.; Westmoreland, D., to be submitted for publication.
(64) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624.
(65) Fongers, K. A.; Hogveen, H.; Kingma, R. F. *Tetrahedron Lett.* **1983**, *24*, 643.
(66) Breslow, R.; Duering, L. A. *Tetrahedron Lett.* **1984**, *25*, 1345.
(67) Cowley, A. H.; Westmoreland, D., to be submitted for publication.
(68) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.
(69) Iminophosphonium salts can also be prepared by photolysis of azidophosphonium salts. See: Majoral, J.-P.; Bertrand, G.; Baceiredo, A.; Mulliez, M.; Schmutzler, R. *Phosphorus Sulfur* **1983**, *18*, 221. Mulliez, M.; Majoral, J.-P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284.
(70) Montemayer, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2231.
(71) (a) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S. S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056. (b) Choi, H. W.; Gavin, R. M.; Muetterties, E. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1085. (c) Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657.

(72) Cowley, A. H.; Kemp, R. A.; Ebsworth, E. A. V.; Rankin, D. W. H.; Walkinshaw, M. D. *J. Organomet. Chem.* **1984**, *265*, C19.
(73) Bennett, D. W.; Neustadt, R. J.; Parry, R. W.; Cagle, F. W., Jr. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 3362.
(74) Sheldrick, W. S.; Morton, S.; Stelzer, O. *Z. Anorg. Allg. Chem.* **1981**, *475*, 232.
(75) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085.
(76) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Organometallics* **1984**, *3*, 1044.
(77) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(78) Sosinsky, B. A.; Norem, N.; Shong, R. G. *Inorg. Chem.* **1982**, *21*, 4229.
(79) Bennett, D. W.; Parry, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 755.
(80) Light, R. W.; Paine, R. T. *J. Am. Chem. Soc.* **1978**, *100*, 2230.
(81) Hutchins, L. D.; Duesler, E. N.; Paine, R. T. *Organometallics* **1984**, *3*, 399.
(82) Corbridge, D. E. C. "The Structural Chemistry of Phosphorus"; Elsevier: Amsterdam, 1974. Brown, I. D.; Brown, M. D.; Hawthorne, F. C. "Bond Index to the Determination of Inorganic Crystal Structures"; Institute for Materials Research, McMaster University: Canada, 1969–1977.
(83) Dubois, D. A.; Duesler, E. N.; Paine, R. T. *Organometallics* **1983**, *2*, 1903.
(84) Luksza, M.; Himmel, S.; Malisch, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 416.
(85) Mahmoud, K. A.; Rest, A. J.; Luksza, M.; Jörg, K.; Malisch, W. *Organometallics* **1984**, *3*, 501. Gross, E.; Burschka, C.; Malisch, W. *Chem. Ber.*, in press.
(86) Bross, E.; Jörg, K.; Fiederling, K.; Göttlein, A.; Malisch, W.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 738.
(87) For a summary of this view, see: Paine, R. T.; Hutchins, L. D.; Dubois, D. A.; Duesler, E. N. *Phosphorus Sulfur* **1983**, *18*, 263.
(88) Baker, B. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049.
(89) Lang, H.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 976.
(90) Light, R. W.; Paine, R. T.; Maier, D. E. *Inorg. Chem.* **1979**, *18*, 2345. The structure of **64** is based on spectroscopic and analytical data.
(91) Hutchins, L. D.; Light, R. W.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 266.
(92) Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 6763.
(93) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184.
(94) Domaille, P. J.; Foxman, B. M.; McNeese, T. J.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4114.
(95) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.
(96) Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Inorg. Chem.*, submitted for publication.
(97) Chisholm, M. H.; Cotton, F. A.; Extine, M. W. *Inorg. Chem.* **1978**, *17*, 1329.
(98) Otsuka, S.; Kamata, M.; Kirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011.
(99) For a review, see: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Horwood Ltd.: New York, 1980.
(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.)