to remember that differences in C-2/C-4, C-3, and C-7 coupling between isomers are present *even though the relative spatial orientation of the coupled atoms remains the same.* It is not a case of dehedral angle dependence, as it is for the α methyls. No satisfactory general model for this has emerged. The utility of the stereospecificities need not be hampered by lack of understanding of their precise mechanisms. Isomer identification is made quite easily, especially for the P(III) compounds, using the α-methyl stereospecificities.

Registry No.—1-Chloro-2,2,3,4,4-pentamethylphosphetane 1-sulfide, 35623-65-5 (isomer A), 35623-66-6 (isomer B).

Acknowledgment.—One of us (S. E. C.) wishes to acknowledge partial support from the National Cancer Institute (Grant CA 11631), the Marquette University Committee on Research, and the Alfred P. Sloan Foundation for a Research Fellowship (1971–1973).

Investigations of Doubly Connected Phosphorus Cations. Diaminophosphenium Ions from 2-R-2-Phospha-1,3-diazacyclohexanes[1]

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Mass spectral analysisof a series of *N,N'*-dimethyl-2-R-2-phospha-1,3-diazacyclohexanes (R = Cl, OCH_3, CH_3, C_2H_5, C_6H_5) reveals a primary fragmentation pathway affording loss of the phosphorus R group and generation of a divalent phosphenium species as the major (base) fragment. Diequatorial orientation of the *N*-alkyl groups is important to stabilization of the cations, as deduced from the failure of certain bicyclic derivatives to provide phosphenium ions when the *N*-alkyl groups are locked in axial positions. Treatment of 2-chloro-2-phospha-1,3-diazacyclohexanes with PCl_5 gave an ionic species which is best interpreted (pmr, ^{31}P nmr, conductance measurements) in terms of a doubly connected phosphorus cation salt.

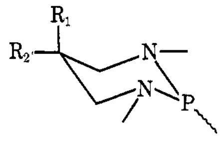
Higher and lower valent cations of many nonmetallic elements (*i.e.*, carbon, halogen, sulfur, nitrogen) have been well recognized and occupy a fundamental place in mechanistic organic chemistry with recent attention being given to pentavalent carbocations (carbonium ions)[2] and divalent nitrenium ions.[3] Somewhat surprisingly, however, very little is known of the behavior, or even existence, of lower valent phosphorus cations (phosphenium ions[4]), although tetracoordinate phosphonium species have played a significant role in phosphorus chemistry for many years.

In the course of conformational analysis studies on 2-R-2-phospha-1,3-diazacyclohexanes,[5] electron impact spectra were recorded as an aid to characterization of these compounds. The observation of a primary fragmentation pathway leading to extremely stable divalent phosphorus cations prompted further exploration in this area, with interest in the factors governing the stability of such cations and possible implications of such species in the mechanisms of trivalent organophosphorus reactions.

Results and Discussion

Diaminophosphenium Ions in the Mass Spectrometer.—The mass spectrum of phosphorus trichloride has been reported to display PCl_2^+ as the most abundant positive ion with a low appearance potential of approximately 12 eV.[6] Other trivalent phosphorus compounds, *e.g.*, $(CH_3)_3P$,[6] Ph_2PCl,[7] and $(Me_2N)_3P$,[7] also give rise to varying populations of divalent positive species by loss of one ligand. However, it is uncommon for the relative abundance of divalent ions derived in this fashion to be very large if further fragmentations are readily achievable;[8] that is, the significance of a high abundance of an individual ion becomes much greater as its opportunity for further decomposition is increased.[9] Along this line, triethylphosphine readily expels ethylene to form $PH(C_2H_5)_2^+$ in abundant amounts, rather than giving up an ethyl group to form the divalent ion, $P(C_2H_5)_2^+$.[10]

On the contrary, electron-impact spectra at 70 eV of various 2-R-2-phospha-1,3-diazacyclohexanes (1) bearing phenyl, ethyl, chloro, methyl, and methoxy substituents on phosphorus have disclosed a primary



1a, $R_1 = R_2 = H$; $R = C_6H_5$
b, $R_1 = R_2 = CH_3$; $R = C_6H_5$
c, $R_1 = H$; $R_2 = CH_3$; $R = C_6H_5$
d, $R_1 = R_2 = H$; $R = C_2H_5$
e, $R_1 = R_2 = CH_3$; $R = C_2H_5$
f, $R_1 = H$; $R_2 = CH_3$; $R = C_2H_5$
g, $R_1 = R_2 = H$; $R = Cl$
h, $R_1 = R_2 = CH_3$; $R = Cl$
i, $R_1 = R_2 = H$; $R = OCH_3$
j, $R_1 = R_2 = R = CH_3$

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(1) Extracted from the Ph.D. Thesis of B. E. M., Drexel University, June 1972.

(2) See G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972), and references cited therein.

(3) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(4) This nomenclature follows the system promoted by Olah (see ref 2) in which higher electron-deficient states of an element are designated "onium" and the lower "enium" ions.

(5) R. O. Hutchins, B. E. Maryanoff, J. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *J. Amer. Chem. Soc.*, in press.

(6) See M. Halman, *Top. Phosphorus Chem.*, **4**, 49 (1967). Herein is contained some general information on the behavior of trivalent phosphorus compounds in the mass spectrometer; see pp 70–77.

(7) R. O. Hutchins and B. E. Maryanoff, unpublished results.

(8) See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 645–653.

(9) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1967.

(10) Y. Wada and R. W. Kiser, *J. Phys. Chem.*, **67**, 2290 (1964).

fragmentation pathway involving loss of the R group and leading to long-lived divalent phosphorus cations (see eq 1). Even phenyl was readily lost before other, usually facile cleavages could occur (*e.g.*, carbon–carbon bond cleavage) to an appreciable extent. Conceivably, the R group may have departed as a negative ion from the un-ionized ground-state parent or as a radical species from the molecular ion. However, the high ionization potential employed coupled with the fact that abundant even-electron ions at high mass are formed by loss of a neutral radical from the molecular ion (or by loss of a neutral molecule from another even-electron ion)[11] point to the latter mechanism (eq 1).[12] It should be noted that in all the compounds studied the divalent ion was the most intense (base) peak in the mass spectrum (see Table I).

TABLE I

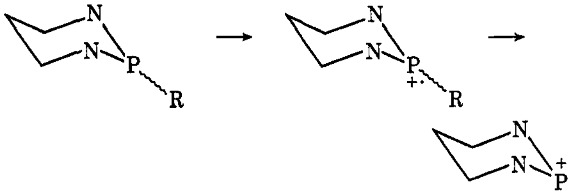
INDICATION OF THE STABILITY OF THE PHOSPHENIUM IONS DERIVED FROM THE 2-R-PHOSPHA-1,3-DIAZACYCLOHEXANES

Compd				Rel intensity, %	
R	R_1	R_2	No.	Molecular ion	Phosphenium ion
C_6H_5	H	H	**1a**	34, 46[a]	100
C_6H_5	CH_3	CH_3	**1b**	23, 90[a]	100
C_6H_5	CH_3	H	**1c**	79	100
Et	H	H	**1d**	17	100
Et	CH_3	CH_3	**1e**	12	100
Et	CH_3	H	**1f**	1	100
Cl	H	H	**1g**	8	100
Cl	CH_3	CH_3	**1h**	9	100
OMe	H	H	**1i**	76	100
Me	CH_3	CH_3	**1j**	12	100

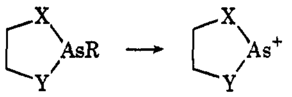
[a] Two different runs.

Surprisingly, representative dioxa and dithia analogs of **1** did not give similar results. For instance, 2-phenyl-2-phospha-1,3-dioxacyclohexane (**2**) did give an analogous divalent ion which, however, was not the base peak and 3-methoxy-3-phospha-2,4-dioxaspiro[5.3]nonane (**3**) gave no peak attributable to a divalent ion. For the dithia system (*i.e.*, **4**), no mass peaks were observed which could have been ascribed to such ions.[13] Evidently, the divalent ions in these cases are not exceptionally stabilized and other pathways compete favorably. This behavior is in contrast to the situation with comparable arsenic heterocycles, which readily lose the arsenic R substituent in the mass spectrometer to give intense cyclic divalent arsenium ions, even though the arsenic atom was flanked by oxygen and sulfur in most of the compounds studied[14] (see eq 2).

Although the results may be rationalized in terms of the weaker nature of the P–O and P–S bonds, it also appears that the nitrogen atoms may exert a stabilizing influence on the electron-deficient phosphorus atom. This latter supposition is based on the fact the delocalization is known to increase when nitrogen is implaced in a system in comparison to, *e.g.*, oxygen[15a] and presumably it is this enhanced delocalization which stabilizes the divalent cation.



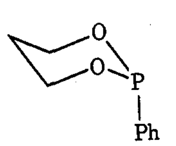
(1)



(2)

X, Y = O, S, or NMe
R = Ph, Et, NR_2

In order to elucidate the factors involved in stabilization, the bicyclic aminophosphines **5–7** were examined. Previous studies[5] have suggested that the nitrogen lone pairs in the phosphadiazacyclohexanes are axial and, under such conditions, should stabilize the vacant orbital of an incipient phosphenium ion with ease. The diaxial situation, however, is not necessary, since an equatorially disposed lone pair on nitrogen would be free to accept an axial position on demand without much difficulty. In **5–7**, the orientation of the nitrogen lone-pair electrons is manipulated by their location at bridgehead positions, which impedes coplanar interaction between the lone pairs and the cationic center.[19] The mass spectra of **5–7** may be compared with that of **1c**, a representative model compound (see Table II).



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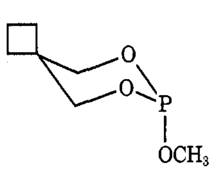

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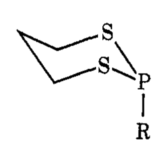

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Constraining one nitrogen lone pair at a bridgehead position, as in **5**, does not grossly alter the mass spectrum with respect to the model compound **1c**. There

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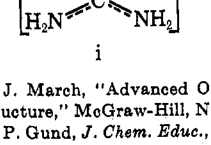
(11) Reference 9, p 68.

(12) It is reasonable to suspect, however, that the *P*-chloro compounds **1g** and **1h** may also undergo fragmentation to produce initially a chloride ion–phosphenium ion pair, which then separates within the mass spectrometer; see M. Halmann and Y. Klein, *J. Chem. Soc.*, 4324 (1964). Negative ion mass spectrometry also has revealed heterolytic decomposition of the halophosphorus compounds in other instances; see T. Kennedy and D. S. Payne, *ibid.*, 1228 (1959); B. L. Donnally and H. E. Carr, *Phys. Rev.*, **93**, 111 (1954).

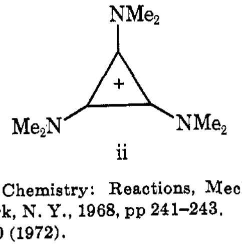
(13) An exception to this was the *P*-chloro derivative of **4** (R = Cl), which did give a minor amount (10%) of the corresponding divalent ion.

(14) R. H. Anderson and R. H. Cragg, *Chem. Commun.*, 1414 (1971).

(15) (a) This is reflected in Hammett σ^+ constants, which are -1.3 and -1.7 for NH_2 and NMe_2 substituents but are only -0.92 and -0.78 for OH and OMe substituents, respectively.[16] Furthermore, an amino moiety exhibits a much greater electron-donating π-conjugative effect (σ_R) than an electron-withdrawing σ-inductive effect (σ_I) in comparison to an oxygen (or any other neutral) moiety.[16] (b) The large resonance stabilization which may be afforded by amino substituents is notably exemplified by the qualification of the guanidinium ion (i) as "the world's most stable carbonium ion"[17] and the remarkable stability of aminocyclopropenium ions (ii).[18]



i



ii

(16) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968, pp 241–243.

(17) P. Gund, *J. Chem. Educ.*, **49**, 100 (1972).

(18) Z. Yoshida and Y. Tawara, *J. Amer. Chem. Soc.*, **93**, 2573 (1971).

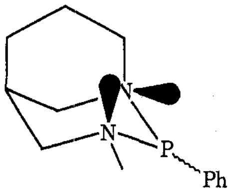
(19) This is a consequence of the near orthogonal orientation of the nitrogen lone pairs with respect to the empty (presumably p) orbital on phosphorus and probably the hampering of planarity in the region of N–P–N overlap; *cf.* Bredt's rule in E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 298–302, 378.

TABLE II

COMPARISON OF THE MASS SPECTRA OF **6–8** WITH THAT OF MODEL PHOSPHADIAZACYCLOHEXANES

	Characteristic peaks, %								
Compd	Parent	P − Ph	109	108	107	78	77	60	39
1c	78	100	37	18	25	0	0	60	10
5	89	100	43	19	21	15	15	64	19
6	60	32	32	20	14	100	85	0	17
7	100	0	37	16	17	16	27	0	16
8	25	100	20	4	8	2	7	5	9

is a change in the *m/e* 77 and 78 peaks, perhaps as a result of the one bridgehead nitrogen, but the significance of this is elusive. When both electron pairs are held fixed at the bridgeheads (**6** and **7**), an entirely new fragmentation pattern is observed. This is exemplified by marked reductions of the P − phenyl peak, the absence of a *m/e* 60 fragment, and the appearance of considerable *m/e* 77 and 78 peaks. It should be noted that *all* the phosphadiazacyclohexane derivatives studied (see Table I) had a P − R base peak and all except **8** had a *m/e* 60 fragment of 40–75% relative abundance. Consideration of the data for **8** (Table II) demonstrates that the absence of the *m/e* 60 peak may be a consequence of having groups other than methyl substituted on the nitrogens (as in **7** and **8**). Nevertheless, the other criteria are valid with respect to **6** and **7** and indicate "abnormal" mass spectral behavior for these compounds. Since **5**, with one bridgehead nitrogen, still followed the general trend observed for the phosphadiazacyclohexanes, it seems that two bridgehead nitrogens are required to heavily disfavor a phosphenium ion. Evidently the stability of the diaminophosphenium ions is dependent on the nitrogen stereochemistry.



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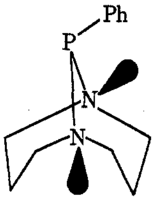

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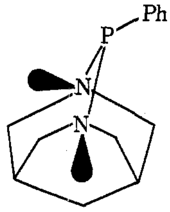

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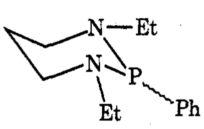


8

In a previous investigation[5] the phosphorus-31 nmr chemical shifts of the cyclic and bicyclic aminophosphines were demonstrated to depend upon the nitrogen stereochemistry. Briefly, compounds **6** and **7** with two bridgehead nitrogen atoms were significantly deshielded (−104 and −109 ppm, respectively) in comparison to compound **5** with a single bridgehead nitrogen (−94 ppm). Furthermore, all these were deshielded with respect to model monocyclic aminophosphines, *i.e.*, **1a**, **1b**, **1c**, and **8**, which ranged from −92 to −81 ppm. This strong deshielding of phosphorus was rationalized in terms of the probable decrease in (p − d) π interaction between the nitrogen lone pairs and the phosphorus and lends some support to a directional influence of the nitrogen lone pairs in the divalent cations, which presumably results in a stable situation when the lone pairs are parallel and coplanar with the unoccupied p orbital on phosphorus.

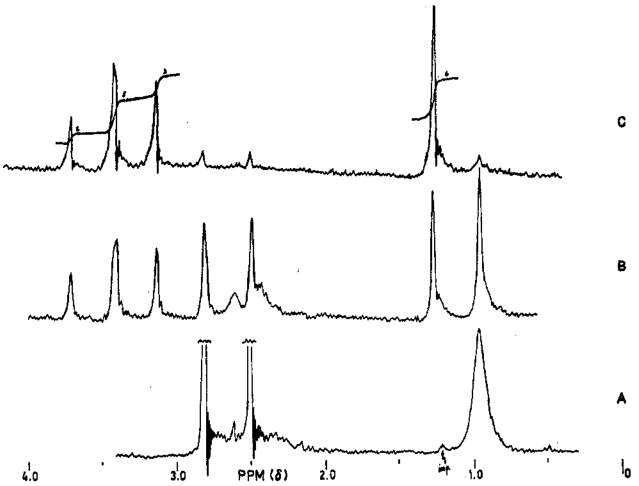
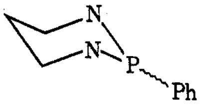
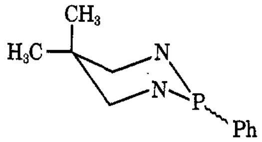


Figure 1.—Reaction of 2-chloro-5,5,*N*,*N'*-tetramethyl-2-phospha-1,3-diazacyclohexane (**1h**) with PCl_5 in nitrobenzene. (A) Pmr spectrum of **1h** in nitrobenzene in the absence of PCl_5; spectrum indicates substantial Cl exchange which averages the signals. (B) Addition of *ca.* 10 mg of PCl_5. (C) Addition of *ca.* 20 mg of PCl_5.

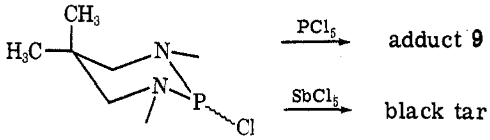


1a



1b

Reaction of 1h with Phosphorus Pentachloride.—In light of the preceding observations, 2-chloro-5,5,*N*,*N'*-tetramethyl-2-phospha-1,3-diazacyclohexane (**1h**) was treated with halide acceptors (Lewis acids) with the aim of chemically producing a stable doubly connected phosphorus cation by removal of chloride anion (see eq 3). Treatment of **1h** in nitrobenzene with phosphorus pentachloride (in an nmr tube) resulted in formation of some sort of adduct (viewed by pmr), whereas treatment with antimony pentachloride afforded a black, metallic mixture (tar) that was not investigated further. The pmr examination of the adduct formation is given in Figure 1.



Treatment of the chloro compound **1h** (spectrum A) with incremental portions of PCl_5 (spectra B and C) caused the original absorptions to gradually disappear, coincident with the appearance of new resonances at lower field. The new resonances were ostensibly derived from a new molecular species and are evidently, from left to right, the methylene (δ 3.55), *N*-methyl (δ 3.35), and *gem*-methyl (δ 1.29) protons of the "adduct;" integration of spectrum C gave the ratio 2:5:3:6.

The pmr spectrum of the pure chloro compound **1h** in dilute solution is presented in Figure 2 and reveals

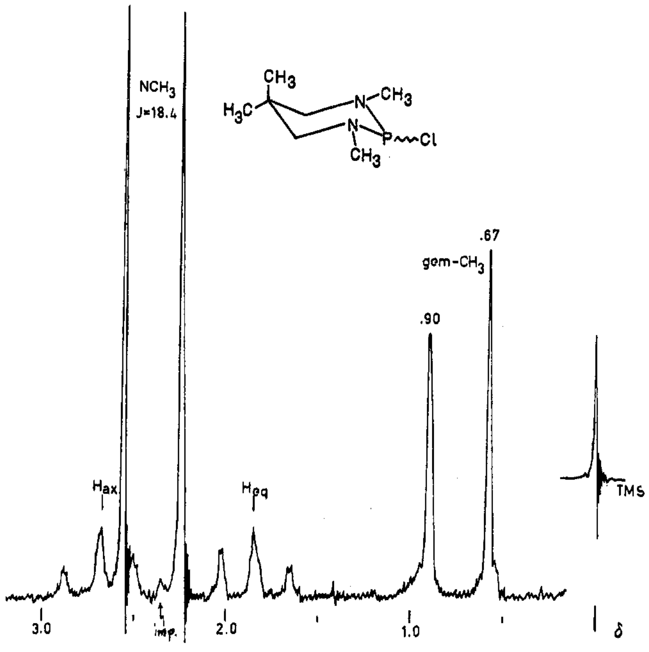
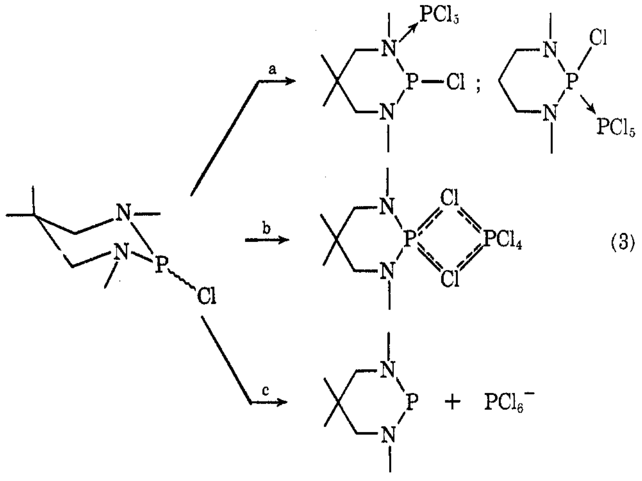


Figure 2.—Pmr spectrum of 2-chloro-5,5,*N*,*N*′-tetramethyl-2-phospha-1,3-diazacyclohexane dilute solution in benzene solvent. The low-field methyl signal δ(0.90) is assigned to the axial methyl group.

the geometry of the ring (unexchanged) to be virtually a single chair conformation with three-bond coupling of phosphorus to the methylene protons of approximately 10 Hz and to the methyl groups of 18.6 Hz. An increase in concentration brings about halogen exchange[20] with attendant degeneration of substituent stereochemistry. This is evident to some degree in spectrum A (Figure 1), and even more so in spectrum B. In the latter, unreacted **1h** is apparently undergoing more rapid exchange in response to acid or chloride-ion catalysis.[5] It is important to note that the adduct formed (spectrum C) also exhibits no substituent stereoisomerism but rather appears as some type of averaged spectrum, as in the case of **1h**, which is rapidly exchange inverting.

In consideration of the nature of the "adduct" three likely possibilities emerge: (a) a complex in which a nonbonded pair of electrons on phosphorus or nitrogen is donated to the PCl_5; (b) a complex in which chlorine supplies the electron pair and which is probably chlorine-bridged; and (c) a diaminophosphenium ion, a consequence of complete abstraction of chloride to form it and PCl_6^- (see eq 3). The first possibility is the least likely, as such a complex would have to be exceptionally labile to account for the conformational mobility evident in the nmr. The second and third species would lack substituent stereoisomerism in agreement with the observations. Furthermore, the strong deshielding of the protons is suggestive of cation formation, since the electron density about nitrogen would be expected to decrease in a mesomeric diaminophosphenium ion. This latter interpretation is further supported by the enhanced three-bond phosphorus–methylene coupling of 17.5 Hz (10 Hz in **1h**), demonstrating an increased P–N bond order. In addition,

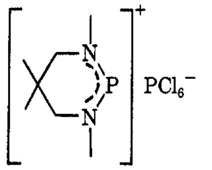


(3)

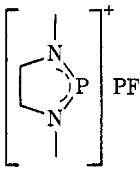
the adduct showed a highly deshielded phosphorus-31 nmr absorption at −222 ppm (*vs.* −150 ppm for **1h**), thus connoting a very electron-deficient phosphorus atom.

The adduct **9** was generated on a larger scale and was isolated as a hygroscopic, crystalline substance. Protected in a sealed capillary, the substance was viewed under a microscope and appeared as minute, irregular prisms. The adduct **9** was both air and water sensitive; however, **9** could be preserved indefinitely *in vacuo* or under an atmosphere of dry nitrogen. The adduct **9** was apparently inert to benzene, chlorobenzene, nitrobenzene, and nitromethane, but it reacted quickly with dimethyl sulfoxide, liberating dimethyl sulfide (deoxygenation) and, with acetonitrile, forming a white, unidentified precipitate (complex?). Elemental analysis confirmed a 1:1 adduct and conductance measurements in nitromethane (see Experimental Section) were in agreement with an ionic material. The pmr spectrum of the pure salt **9** shows the doublet due to the phosphorus-coupled methylene protons, which was difficult to see in the previous spectrum of the *in situ* generated adduct. Again, the coupling is an unusually large 17.5 Hz and the integration gives the expected intensity ratio of 2:5:3:6. Taken together, the data seem best explained by a relatively stable phosphenium ion salt.

Our interpretation in terms of the formation of a stable phosphenium ion is in accordance with the recent work of Fleming and coworkers,[21] in which the five-membered ring diaminophosphenium ion (**10**) was



9



10

produced and described. These authors recorded a ^{31}P chemical shift of −264 ppm for this species. Interestingly, Fleming, *et al.*,[21] found that when BF_3 was used as a fluoride acceptor an equilibrium between a 1:1 complex (at nitrogen) and the cation–anion system $[CH_3NCH_2CH_2(CH_3)NP]^+$ $(B_2F_7)^-$ occurred, the concentration of the salt increasing with an increasing

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[20] The diamino *P*-Cl derivatives are capable of bimolecular chlorine exchange, which inverts the configuration at phosphorus. Coupled with consequent ring inversion, this results in the averaging of the nmr parameters; see ref 5.

[21] S. Fleming, M. K. Upton, and K. Jekot, private communication; *Inorg. Chem.*, in press. We thank Dr. Fleming for communicating their results prior to publication. The compound investigated was 2-fluoro-*N*,*N*′-dimethyl-2-phospha-1,3-diazacyclopentane (**11**).

excess of BF_3. Figure 1 illustrates that the final adduct in our case is formed directly; there is no evidence for any intervening species. This contrast reflects a decreased ability for BF_3 to act as a halide acceptor in relation to PCl_5 and probably PF_5, although the intervention of a complex in this latter case was not mentioned.[21]

To furnish a comparison between **9** and **10** the nmr spectral data for the unreacted ligands (**1h** and **11**, respectively) and the derived cations, **9** and **10**, are given in Table III.

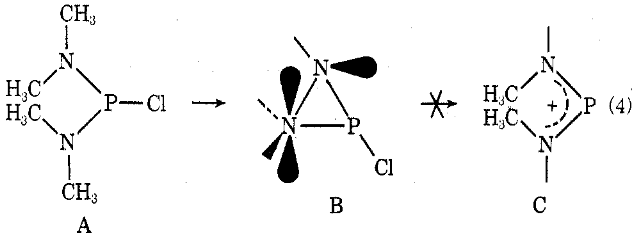
Table III

Nmr Spectral Data for **1h** and **9** and the Corresponding Unreacted Ligands[a]

Compd	δ_{NCH_3}	δ_{NCH_2}	$^3J_{PNCH_3}$	$^3J_{PNCH_2}$	δ (^{31}P)
1h (exch)[b,c,d]	2.66	2.82	~19	~10	−150 ± 1
11[e,f]	2.72	3.15	13	d	−138
9[b,g]	3.28	3.59	16.5	17.5	−222
10[f,h]	3.10	3.83	11	5	−264[i]

[a] Chemical shifts are in parts per million downfield from TMS or 85% H_3PO_4; coupling constants are in hertz. [b] In nitrobenzene. [c] Geminal methyl groups at δ 1.02. Complex multiplet reported (ref 21); however, the spectral parameters reported by Albrand, *et al.*, would afford an averaged coupling of *ca.* 5–6 Hz: J. P. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *Tetrahedron*, **78**, 819 (1971); J. P. Albrand, A. Cogne, D. Gagnaire, J. Martin, J. B. Robert, and J. Verrier, *Org. Magn. Resonance*, **3**, 75 (1971). [d] Reference 7. [e] No solvent. [f] Reference 21. [g] Geminal methyl groups at δ 1.28. [h] In acetonitrile-d_3. [i] In 1,2-dichloroethane.

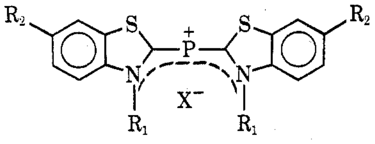
Curiously, treatment of bis(dimethylamino)chlorophosphine did not produce similar proton or ^{31}P nmr results as for **1h**. At best, the substrate merely partially complexed with the PCl_5 in a similar manner as may be observed for aminophosphines which cannot lose a ligand (*e.g.*, complexation occurred between PCl_5 and **1b**). There was no evidence for cation formation using pmr (*N*-methyl doublet shifted from 2.68 to 2.83, ^3J was virtually unchanged) or ^{31}P nmr [δ (^{31}P) merely shifted from −163.6 to −167.5 ppm]. It might be speculated that the attainment of coplanarity is impossible in the diaminophosphenium ion of this molecule because of severe steric interactions. This is illustrated in eq 4, where the planar situation A would be very sterically unfavored, thus favoring situation B. Consequently, the necessary planarity in the mesomeric ion C would also be disfavored by steric interactions. Of course, this type of steric interplay would be eschewed in the cyclic systems, which do give phosphenium ions.



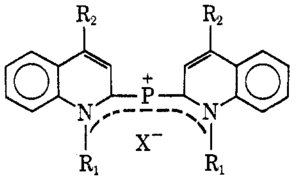
It should also be mentioned that diphenylchlorophosphine did not appear to form a divalent cation, Ph_2P^+, with PCl_5, although the ion is abundant in the mass spectrometer. This is presumably because phenyl cannot sufficiently stabilize the positive charge under normal conditions.

Another type of dicoordinate phosphorus cation has been reported by Dimroth and Hoffman.[22] These "phosphacyanines," **12** and **13**, were stable salts (much more stable than **9** and **10**) and possessed a large amount of resonance stabilization, attested to by their uv-visible spectra [ν_{max} 472–605 nm (ϵ 3.35–5.15 × 10^4)] and ^{31}P chemical shifts (*ca.* −24.9 ppm for type **12** and *ca.* −48.8 ppm for type **13**).[23] The molecular structure of **12** (R_1 = C_2H_5; R_2 = H) was determined by X-ray crystallography.[24] The compound was found to exist in the cis form (as depicted) with each group mutually twisted 6° out of the molecular plane; the C–P–C angle was 104.6° and the pertinent bond lengths were in support of a mesomeric structure.

Thus, it appears that doubly connected phosphorus cations can be stable molecular species under ambient conditions but only when a delocalized bonding system is available. This work suggests that a favorable disposition of the lone pairs on nitrogen and the ability to approach planarity is necessary for the formation of stable diaminophosphenium ions. The implication of such species in reactions of tervalent phosphorus derivatives is currently under investigation.



12



13

X = BF_4^-, ClO_4^-

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Pmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane (TMS) as an internal reference. Phosphorus-31 nmr spectra were recorded at 40.5 MHz on a Varian HA-100 spectrometer using 85% phosphoric acid as an external reference. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU-6 mass spectrometer operating at 70 eV. Microanalyses was performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. All reactions involving trivalent phosphorus were carried out under an atmosphere of dry nitrogen.

Materials.—All the cyclic diaminophosphines employed in this study were synthesized and characterized as previously described.[5] Tris(dimethylamino)phosphine was purchased from Aldrich Chemical Co., Milwaukee, Wis., and was purified by distillation. Diphenylchlorophosphine was kindly supplied by Stauffer Chemical Co., New York, N. Y., as a free sample; it was distilled prior to use. Phosphorus pentachloride was reagent grade and was used from a freshly opened bottle without further purification. Antimony pentachloride and nitrobenzene were purified by distillation. Nitromethane, which was employed as a solvent for conductance measurements, was reagent grade; it was deoxygenated by bubbling dry nitrogen through it and then

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[22] (a) K. Dimroth and P. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **3**, 384 (1964); (b) *Chem. Ber.*, **99**, 1325 (1966).

[23] In fact, Dimroth and Hoffman were astounded at the "unexpectedly large" (*i.e.* highly shielded) ^{31}P chemical shifts for such an expectedly electron-deficient phosphorus atom; ref 22a.

[24] R. Allmann, *Chem. Ber.*, **99**, 1332 (1966).

stored over molecular sieves (3A) under an atmosphere of dry nitrogen.

Bis(dimethylamino)chlorophosphine.—According to the report of Van Wazer and Maier,[25] phosphorus trichloride (0.682 g, 5 mol) was cooled to −78° in Dry Ice–acetone and, with stirring, treated with tris(dimethylamino)phosphine (1.63 g, 10 mol), bp 70–71° (30 mm), which was added all at once. The mixture was allowed to warm to ambient temperature, stirred for 15 min, and then distilled at reduced pressure. After a forerun was collected [up to 82° (25 mm)], the product came over, bp 83–84° (25 mm) [lit. bp 64° (10 mm),[26a] 93–97° (47–49 mm)];[26b] the yield was 1.05 g (45%).

Nmr Study of Reaction of 1h with Phosphorus Pentachloride.—A pmr sample of **1h** in nitrobenzene was prepared (0.3 ml of *ca.* 10% solution) with the intention of examining the reaction of **1h** with phosphorus pentachloride. Nitrobenzene was selected because of its high polarity and anticipated inertness. The pmr spectrum was recorded (Figure 1). Subsequently, small portions (*ca.* 10 mg) of PCl_5 were added incrementally and a spectrum was recorded after each treatment (see Figure 1). A colorless solid was observed to precipitate from the solution, contrasting with some pale yellow PCl_5 which remained undissolved and deposited in the bottom of the nmr tube. For the ^{31}P nmr study a similar mode of operation was taken. In this case the peak assigned to **1h** at −150 ppm gradually diminished upon addition of small portions of PCl_5, while a peak at −222 ppm gradually increased in intensity.

Reaction of 1h with Phosphorus Pentachloride.—In line with the positive results obtained in the nmr study of this reaction, a scaled-up reaction was performed in order to isolate the adduct which had been formed. About 5 drops (*ca.* 50 mg) of the *P*-chloro compound **1h** were placed in a 5-ml flask which had been meticulously cleaned and flushed with dry nitrogen. The flask had one neck which was equipped with a stopcock. During the course of the reaction nitrogen was continuously admitted through the stopcock to prevent air from entering the reaction flask during manipulations. A saturated solution of PCl_5 in nitrobenzene (3 ml) (an excess of theory) was added in a stream of nitrogen *via* a syringe. An immediate and slightly exothermic reaction took place and a colorless, apparently crystalline solid precipitated. The flask was swirled gently. After 30 min, the supernatant solution was extracted by means of a long-stemmed pipet and discarded. The precipitate was then rinsed with two portions of chlorobenzene followed by two portions of *n*-hexane or benzene. The rinses were conducted by a pipet which was inserted through the open stopcock, under a steam of nitrogen. Drying was initially effected by the passage of a stream of nitrogen into the vessel, after which the white solid was further dried and preserved under high vacuum (*ca.* 0.008 mm). Because of its hygroscopic nature and decomposition under normal conditions, the material was always handled under a stream of nitrogen, or better, in a glove bag. The solid in a sealed capillary melted at 213–215° with decomposition and evolution of a gas: ir (KBr) 3000–2800 (m), 1470 (m), 1375 (w–m), 1252 (m–s), 1195 (m), 1180 (m), 1095 (s), 1037 (s), 1003 (m–s), 780 (m–s, shoulder 790), 725 (w), 600 (vs), 552 (m–s), 508 (m–s), 440–430 (vs), 340 cm^{-1} (vw). *Anal.* Calcd for $C_7H_{16}Cl_6N_2P_2$: C, 20.86; 4.00. Found: C, 21.09; H, 4.17.

2,5,5,*N*,*N*′-Pentamethyl-2-phenyl-2-phospha-1,3-diazacyclohexane Iodide.—The phosphine **1b** (4 drops) was dissolved in *ca.* 5 ml of dry ether. An excess of methyl iodide was added and the solution was stoppered and allowed to stand. After just 5 min, a white precipitate was deposited. An hour elapsed and the mixture was filtered. The solid was rinsed with some dry ether and dried. Pale yellow needles (slight iodine discoloration) were obtained from 2-propanol, mp 188–189°. *Anal.* Calcd for $C_{14}H_{24}IN_2P$: C, 44.48; H, 6.40; I, 33.52. Found: C, 44.42; H, 6.27; I, 33.74.

Conductance Measurements.—Conductivities were measured on approximately 0.0008–0.005 *M* solutions at 25° with an A. H. Thomas Model RCM 15 Bl conductance bridge at 1000 Hz; the bridge was connected to a Yellow Springs Instrument Co. Model 3403 conductivity cell ($K = 1.0$). The solvent employed in all instances was deoxygenated, anhydrous nitromethane. In Table IV the molar conductances for the adduct **9** and for some compounds offered for comparison are presented. The weighing and other handling of **9** was done in a glove bag containing a nitrogen atmosphere and its conductance was measured under nitrogen. The data indicate beyond a doubt that **9** is an ionic material; however, the conductance value for **9** is somewhat lower than would be expected by comparison with the ammonium salt or the phosphonium salt. A partial explanation may reside in the fact that the measurement of **9**, which was plagued by its sensitivity to both air and moisture, may have reflected some impurities created during handling. On the other hand, that **9** in solution may be a mixture of an ionic species (1:1 electrolyte) and a nonionic species (*e.g.*, a chlorine-bridged complex) in rapid equilibrium cannot be excluded.

TABLE IV

MOLAR CONDUCTANCES FOR 9 AND SOME COMPOUNDS OFFERED FOR COMPARISON[a]

Compd	Concn, *M*[b]	λ, mho/cm²-mol[c]
9	0.000819	44.4
$(n\text{-}C_4H_9)_4N^+ClO_4^-$	0.000849	95.6
2,5,5,*N*,*N*′-Pentamethyl-2-phenyl-2-phospha-1,3-diazacyclohexane iodide	0.00102	82.6
PCl ($PCl_4^+PCl_6^-$)	0.00225	10.2
Pyridine–borane	0.0046	0

[a] The cell was calibrated to a 0.01 *N* KCl solution. The "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Co., Cleveland, Ohio, p D-121, gives the value of 141.27 for the equivalent conductance of a 0.01 *N* KCl solution at 25°. [b] Error is *ca.* ±1%. [c] Error is *ca.* ±2%.

Nmr Study of the Reaction of Bis(dimethylamino)chlorophosphine with Phosphorus Pentachloride.—Addition of PCl_5 to a nitrobenzene solution of $(Me_2N)_2PCl$ (0.3 ml of *ca.* 15% solution) gave a slow reaction and no heat was evolved. The pmr spectrum showed the slow appearance of a new doublet centered at δ 2.83 and the decrease in intensity of the original doublet at δ 2.68. Decomposition, which resulted in a number of unassignable peaks, quickly ensued, at which point about 20% of the "complex" was present. ^{31}P nmr gave a similar result as pmr. A new peak accounting for 20–25% material balance arose at a slightly downfield position (−167.5 ppm compared to −163.6 ppm for starting material) upon treatment with PCl_5, but would not increase in intensity in response to subsequent doses. Decomposition products were not observed.

Pmr Study of the Reaction of Diphenylchlorophosphine with Phosphorus Pentachloride.—This study was performed in the above-described manner. Very little change in the pmr spectrum was observed on treatment of a nitrobenzene-d_5 solution of Ph_2PCl with PCl_5. Some complexation may have occurred but was not well defined (the evidence was very slight shifts of some resonance lines).

Registry No.—**1c**, 35661-63-3; **1h**, 35661-64-4; **5**, 35661-65-5; **6**, 35661-66-6; **7**, 35820-68-9; **8**, 35661-67-7; **9**, 35665-40-8; 2,5,5,*N*,*N*′-pentamethyl-2-phenyl-2-phospha-1,3-diazacyclohexane iodide, 35737-17-8; phosphorus pentachloride, 10026-13-8.

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(25) J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, **86**, 811 (1964).

(26) (a) G. Ewart, D. Payne, A. Porte, and A. Lane, *J. Chem. Soc.*, 3984 (1962); (b) H. Noeth and H. Vetter, *Chem. Ber.*, **96**, 1109 (1963).