

Gas-Phase Synthesis and Characterization of an Azaphosphirenium Ion: The First N,P-Analogue of the Aromatic Cyclopropenyl Cation

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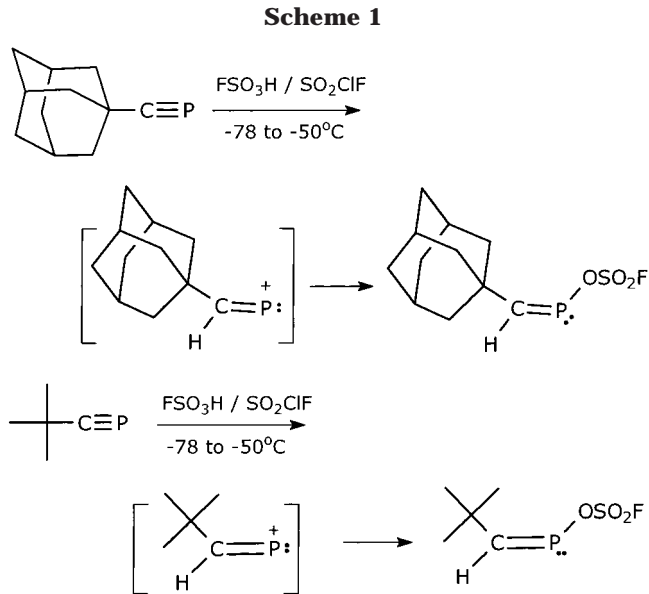
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The 3-(dimethylamino)-1,1-dimethyl-1*H*-azaphosphiren-1-ium ion (**3**), the first member of the hitherto unknown class of azaphosphirenium ions and the first N,P-analogue of the aromatic cyclopropenyl cation, is generated in the gas phase via 70 eV electron ionization and demetalation of a ferriphosphaalkene (**1**) and rapid cyclization of the incipient phosphavinyl cation (**2**). Spontaneous cyclization of **2** to **3** is predicted by Becke3LYP/6-311++G(d,p) calculations, and the structure and reactivity of **3** is probed via collision-induced dissociation and ion–molecule reactions performed via pentaquadrupole mass spectrometry. Gaseous **3** fails to coordinate efficiently with nitrogen and oxygen nucleophiles, but it forms stable adduct ions with phosphorus and sulfur nucleophiles. The adducts of **3** with P and S nucleophiles are likely favored by the incorporation of relatively strong and rare P=S and P=P bonds and through extensive charge delocalization involving dimethylamino substituents. With isoprene, an adduct ion is also readily formed presumably via [4 + 2⁺] cycloaddition (followed by spontaneous ring opening), a reaction which is well documented for phosphenium ions both in solution and in the gas phase.

Introduction

Attempts to observe persistent phosphavinyl cations $R_2C=P^+$ in superacid media by protonation of phosphalkynes under controlled conditions have been unsuccessful, since they led to counterion trapping and formation of phosphalkenes by nucleophilic attack at phosphorus (Scheme 1).^{1,2} In situ generation of $[P=C(TMS)_2]^+$ via ionization of the P–triflate or the P–Cl derivative and its trapping with PPh_3 has also been reported (Scheme 2).³

Normal phosphalkenes are polarized in the sense $P^{\delta+}C^{\delta-}$, and nucleophilic attack is directed to phosphorus.⁴ There has been a recent surge of interest in phosphalkenes with inverse polarity, viz. $P^{\delta-}C^{\delta+}$, whereby electrophilic attack occurs at phosphorus.⁵ Metallophosphaalkenes of type **1** (Scheme 3) with dimethylamino substituents belong to this family. The coordination chemistry of metallophosphaalkenes and their reactivity toward electrophiles and carbenes has received considerable attention during the past decade.^{5,6} Consistent with canonical forms **1** and **1'**, pro-



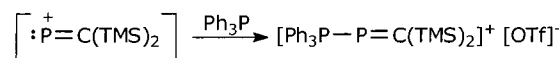
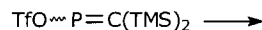
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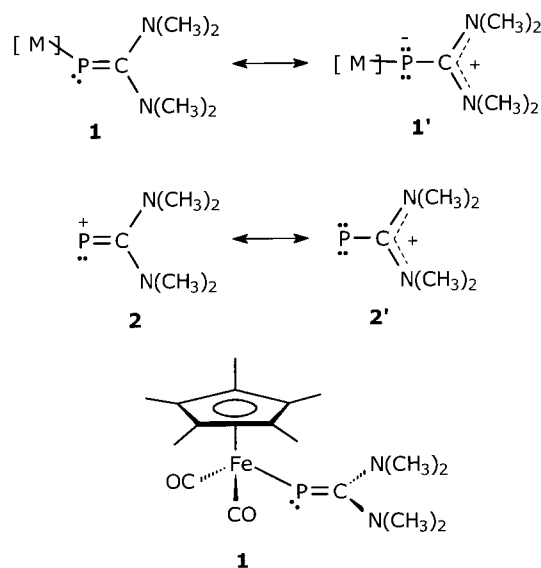
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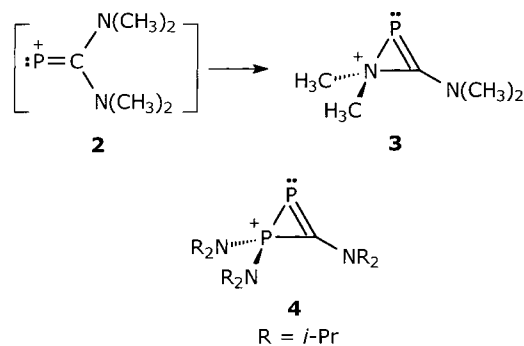
tonation, alkylation, and silylation are directed to phosphorus, yielding metallophosphanyl-functionalized carbocations.⁷ The P-acyl derivatives $RC(CO)P=C(NMe)_2$ are also inversely polarized phosphalkenes.⁸

Scheme 3



Dicoordinated phosphonium ions of the R_2P^+ type have received particular attention because the presence of a vacant p orbital and a lone pair on P confers to these amphoteric cations a high and diverse reactivity toward organic substrates.⁹ The gas phase provides a suitable environment in which to study the intrinsic stability and solvent- and counterion-free reactivity of ions with neutral molecules¹⁰ and to perform fast screening for potential reactants and model reactions.¹¹ Ionic intermediates, which are transient and highly reactive in solution, are often stable and long-lived in the gas phase and, after mass selection, studies of their intrinsic reactivity can be conveniently performed by multiple-stage mass spectrometric (MS) techniques. Several long-lived phosphonium ions R_2P^+ have been successfully formed and isolated in the gas phase and their intrinsic reactivity exploited by several MS techniques.¹² We report here that gas-phase demetalation of **1** upon 70 eV electron ionization (EI) provides facile access to the

unprecedented cyclic azaphosphirenium ion **3** via rapid cyclization of the incipient phosphavinyl cation **2**. Ion



3 is the first N,P-analogue of the aromatic cyclopropenyl cation and the N-analogue of the first diphosphirenium ion, **4**, whose synthesis, structure, and solution reactivity has recently been described.¹³ We used therefore a combination of gas-phase MS experiments and ab initio theory to gain insight into the structure, intrinsic stability and reactivity of **3**.

Experimental Section

The ferrirhosphaphene **1** was available from previous studies.⁷ The neutral substrates used for ion–molecule reactions were high-purity reagents which were used as received. Gaseous **3** was produced, reacted, and its products analyzed via double- (MS^2) and triple-stage (MS^3) pentaquadrupole mass spectrometric experiments¹⁴ performed with an Extrel (Pittsburgh, PA) pentaquadrupole ($Q_1Q_2Q_3Q_4Q_5$) mass spectrometer, which is described in detail elsewhere.¹⁵ Ion **3** was formed by 70 eV EI-induced dissociation of the ferrirhosphaphene **1** (Scheme 3), and high-accuracy mass measurements performed on a EBE Autospec (Micromass U.K.) mass spectrometer confirmed its expected composition: calcd for $C_5H_{12}N_2P$ m/z 131.0738, found 131.0769. For the MS^2 ion–molecule reactions, Q_1 was used to mass-select **3** for further reactions in q_2 with a selected neutral reagent. Ion translational energies were set to near 0 eV as calibrated by the m/z 39:41 ratio in neutral ethylene-ionized ethylene reactions.¹⁶ Product ion mass spectra were acquired by scanning Q_5 , while Q_3 and q_4 were operated in the broad-band rf-only mode. Multiple collision conditions were used in q_2 , as indicated by typical beam attenuations of 50–70%, which increases reaction yields and promotes collisional quenching of both the reactant and product ions.¹⁴

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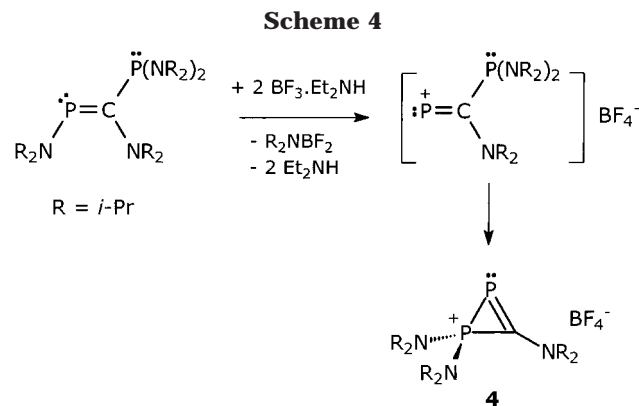
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For the MS³ experiments, a q2-product ion of interest was mass-selected by Q3 for further 15 eV collision-induced dissociation (CID) with argon in q4, while Q5 was scanned to record the mass spectrum. The 15 eV collision energies were taken as the voltage differences between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically 2×10^{-6} (ion source), 8×10^{-6} (q2), and 8×10^{-5} (q4) torr, respectively. The electronic energies of optimized geometries of some ions of interest were obtained by either Becke3LYP/6-31G(d,p) or Becke3LYP/6-311++G(d,p) calculations run on Gaussian98¹⁷ using no symmetry constraints. Details of the optimized structures are available from the authors upon request.

Results and Discussion

Theoretical Studies. To investigate the intrinsic gas-phase stability of **2** (the primary ion of m/z 131 expected from **1**) and the likelihood of its cyclization to **3**,¹³ structure optimization was performed at the Becke3LYP/6-311++G(d,p) level of theory. Ion **2** was found not to be a minimum; it collapses to **3** (Scheme 3) with no energy barrier via intramolecular nucleophilic attack of the dimethylamino nitrogen onto phosphorus. In the gas phase, the nascent phosphavinyl cation **2** is therefore predicted to undergo spontaneous cyclization to the azaphosphirenium ion **3**.

Few heteroatom-containing analogues of the two- π -electron Hückel aromatic cyclopropenyl cation have been isolated.^{13e} Interestingly, **3** is such a rare system—a diheteroatom N,P-containing cyclopropenyl cation analogue! Ion **3** is also the N-analogue of the first diphosphirenium ion, **4** (a diphosphorus analogue of the cyclopropenyl cation), whose synthesis, structure, and reactivity have been recently described.¹³ The analogy between the gas-phase and condensed-phase synthetic routes applied to form **3** (**1** → [**2**] → **3**) and **4** (Scheme 4) via spontaneous cyclization of either a transient 1,3-azaphosphavinyl or 1,3-diphosphavinyl cation intermediate is also noteworthy.

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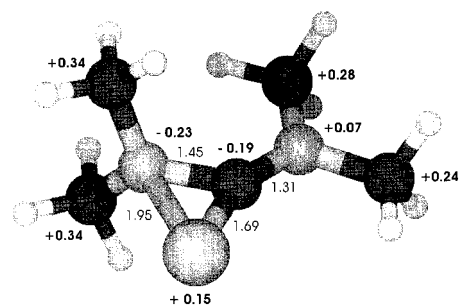
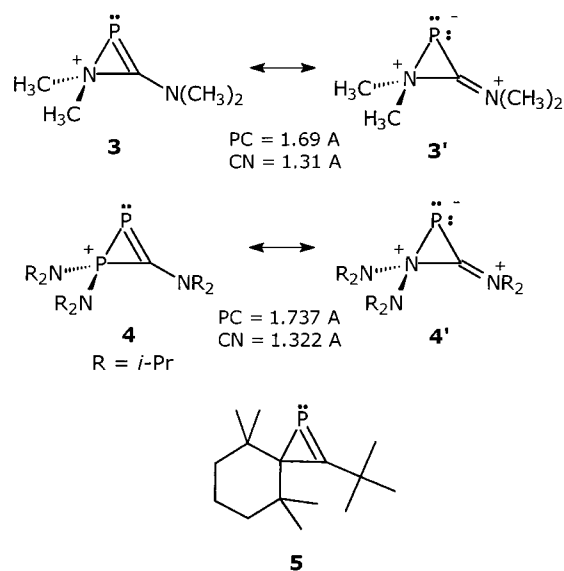


Figure 1. Becke3LYP/6-311++G(d,p) optimized structure with some major bond lengths and main Mulliken charges of the novel cyclic azaphosphirenium ion **3**. For the methyl groups, H charges were summed into C charges.

Figure 1 displays **3** in its optimized structure and summarizes its main bond lengths and charges. No literature precedent exists for a cyclic azaphosphirenium ion such as **3**, but the similarity of the calculated PC and CN bond lengths of **3** with the corresponding X-ray-determined bond lengths of its diphosphorus analogue **4** (see below)^{13e} is remarkable. For **4**, it was concluded that mesomeric **4'** provides the best representation.¹³ It is known that amino substituents considerably increase the stability of the cyclopropenyl cation.¹⁸ The calculated PC (1.69 Å) bond length of **3** is clearly more in the range associated with a PC single bond, and it is considerably longer than that (1.63 Å) of the neutral 2*H*-phosphirene **5**,¹⁹ whereas the CN bond length is clearly in the CN double-bond range. These PC and CN bond lengths (as well as charge distribution with the positive charge mainly shifted outside the ring) suggest therefore, as for **4**,¹³ that **3** is best represented by the canonical form **3'**. However, form **3** will be used, for simplicity.







Dissociation Behavior of 3. Figure 2 illustrates the double-stage CID mass spectrum of **3**. The m/z 91 and 71 fragment ions are formed in greatest abundances, whereas m/z 130, 129, 116, 115, 106, 75, and 72 are also significant. The most abundant fragment of m/z 91 is formed by the loss of a 40 u species which cannot contain

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Table 1. Ionic Products for Reactions of Gaseous **3 with Selected Neutrals**

Entry	Neutral (M)	Products <i>m/z</i> (relative abundance) ^a				
		M + <i>m/z</i> 131	MH ⁺ , M ₂ H ⁺	<i>m/z</i> 91	M + <i>m/z</i> 91	M ⁺
1	CH ₃ -CN	172 (4)	none	(12)	132 (100)	none
2	C ₆ H ₅ N	none	80, 159 (100)	none	none	none
3	NH ₂ N(CH ₃) ₂	none	61 (20)	(100)	151 (2)	60 (21)
4	HN(C ₂ H ₅) ₂	204 (1)	74, 147 (100)	(2)	164 (7)	none
5		202 (1)	72, 43 (100)	(14)	161 (13)	none
6	PhNH ₂	none	94, 187 (58)	(100)	184 (1)	95 (55)
7	CH ₃ OH	163 (1)	33, 65 (8)	none	(100)	none
8		199 (69)	69, 81, 149 ^a (40)	(12)	159 (39)	none
9		219 (61)	89 (90)	(88)	179 (100)	none
10		233 (31)	103 (100)	(7)	193 (17)	none
11	P(OCH ₃) ₃	255 (78)	125 (83)	(38)	215 (100)	none

^a Relative to the product ions excluding the reactant ion. ^b For the products of reactions between protonated and neutral isoprene under the present reaction conditions, see ref 24.

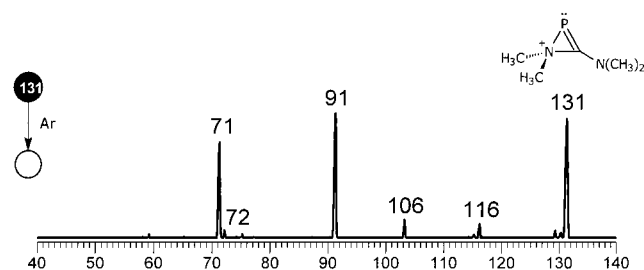
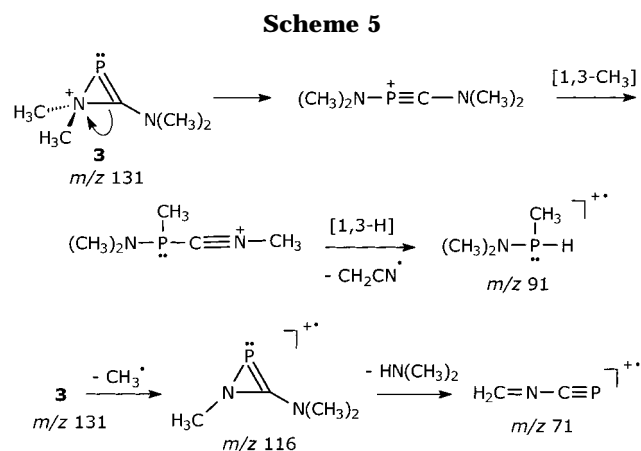


Figure 2. Double-stage (MS²) product ion mass spectrum for collision-induced dissociation of **3** via 15 eV collisions with argon.

phosphorus. Hence, considering also the connectivity of the precursor ion **1**⁺, dissociation of **3** by the loss of a CH₂CN[•] radical is the most likely event, and a possible channel for this dissociation yielding ionized dimethylamine methyl phosphane is rationalized in Scheme 5, together with those for *m/z* 116 and 71.

Ion–Molecule Reactions. Table 1 lists the main products for reactions of **3** (mass-selected by Q1) with neutral nucleophiles (M) in the first collision cell (q2) of the pentaquadrupole mass spectrometer. In reactions with nucleophiles, **3** may produce phosphalkene–onium cations by nucleophilic attack followed by ring opening, in a manner similar to the quenching of phosphavinyl cations in solution (Scheme 2).

O and N Nucleophiles. In the gas phase, two phosphonium ions, PCl₂⁺ and P(OCH₃)₂⁺, have been found to add readily to O and N nucleophiles.¹² Table 1 shows, however, that the cyclic azaphosphirenium ion **3** either fails to produce stable adducts (M + *m/z* 131) with N and O nucleophiles or that such adducts are formed to a limited extent (entries 1–7). Instead, proton



transfer that yields MH⁺ and eventually M₂H⁺ dominates. In fact, the *m/z* 91 fragment (frequently formed from **3** by CID even under the low, near zero energy collision used to perform the reactions) is often more prone to reaction with the O and N nucleophiles (M), forming relatively abundant adducts (M + *m/z* 91, Table 1). Pyridine (entry 2) forms an stable adduct with PCl₂⁺,^{12d} but in reactions with **3** proton transfer dominates and protonated pyridine of *m/z* 80 and the pyridine proton-bonded dimer (M₂H⁺) of *m/z* 159 are readily formed (Figure 3a).

Isoprene. With this conjugated diene (Table 1, entry 8), **3** forms an adduct of *m/z* 199 (Figure 3b). In solution, phosphonium ions are known to react with dienes as carbenoids to form the corresponding unsaturated phosphorus heterocyclic compounds.²⁰ They also react with alkynes in a [2 + 2⁺] fashion to produce phosphirenium salts.²¹ In the gas phase, the phosphonium ion P(OCH₃)₂⁺

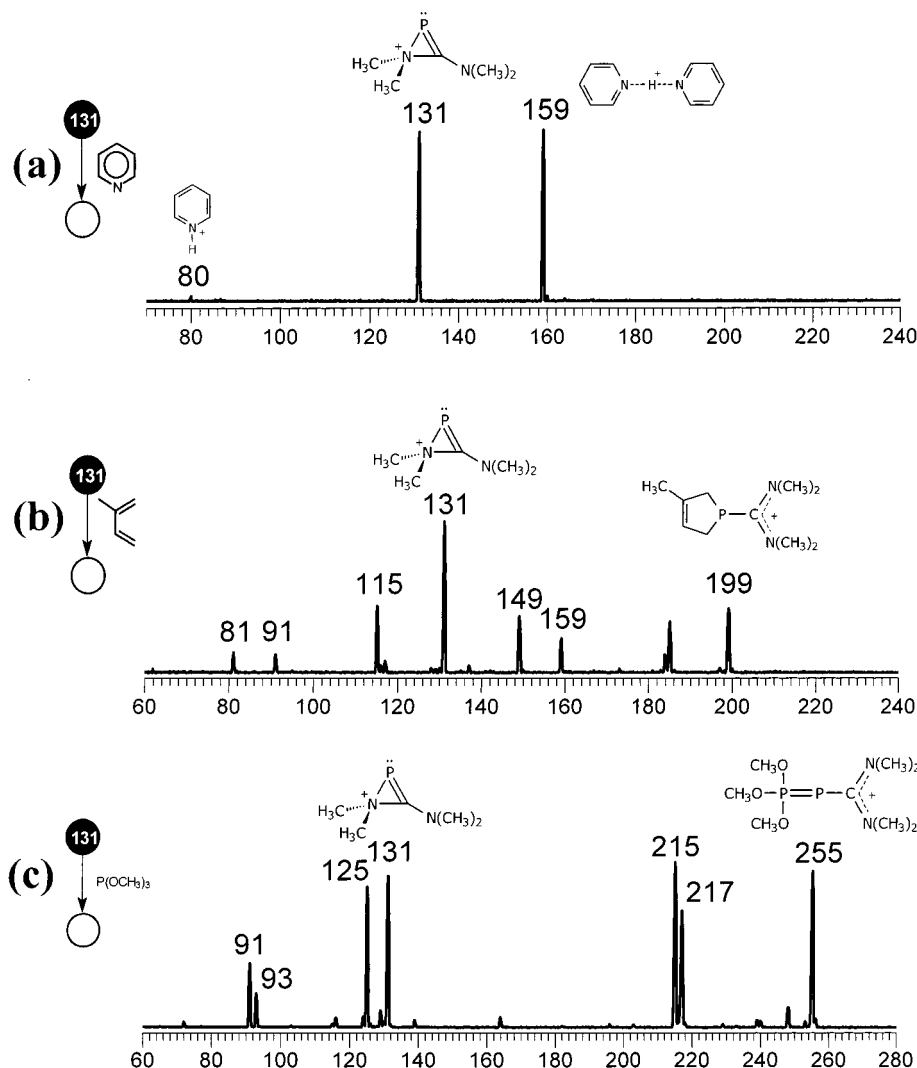
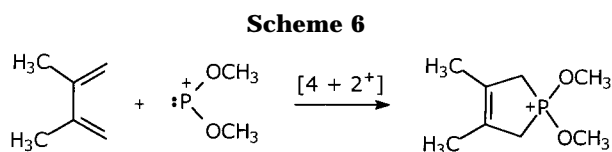


Figure 3. Double-stage (MS^2) product ion mass spectrum for gas-phase reactions of mass-selected **3** with (a) pyridine, (b) isoprene, and (c) trimethyl phosphite.



was recently found to react extensively by [4 + 2⁺] cycloaddition with 2,3-dimethylbutadiene to form the corresponding cyclic phospholenium ion (Scheme 6).²²

It is therefore probable that gaseous **3** reacts with isoprene via [4 + 2⁺] cycloaddition exhibiting a similar phosphonium cation behavior. Becke3LYP/6-31G(d,p) calculations indicate, however, that the nascent adduct is unstable; upon geometry optimization, it undergoes ring opening to form **6** (Scheme 7), a highly resonance-stabilized phosphanyl diaminocarbenium ion. Relief of steric strain in the phosphaspiro[2.4]heptadiene adduct is a logical driving force for ring opening. Because amino

groups are better π donors than phosphanyl groups,²³ the optimized electronic structure of **6** displays its positive charge mainly delocalized on the two dimethylamino groups, whereas the phosphorus remains pyramidal.

After Q3 mass selection and upon 15 eV CID with argon in q4 (spectrum not shown), the putative cycloadduct of m/z 199 dissociates mainly to m/z 131, a pathway assigned to cycloreversion to **3**,²⁴ and to m/z 171 by ethylene loss. A dissociation pathway to m/z 171 that yields an aromatic N-methylated 1,3-azaphospholenium ion is suggested in Scheme 8.

S and P Nucleophiles. With the three third-row P and S nucleophiles tested (Table 1, entries 9–11), **3** readily forms adducts, as exemplified for reactions with trimethyl phosphite in Figure 3c. Binding via relatively favorable and relatively rare²⁵ P=S and P=P bonds²⁶ between two third-row elements and extensive charge delocalization involving the dimethylamino substituents

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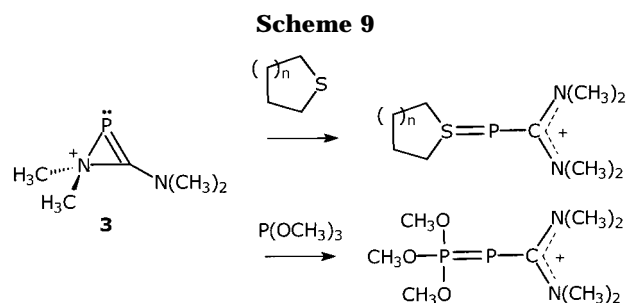
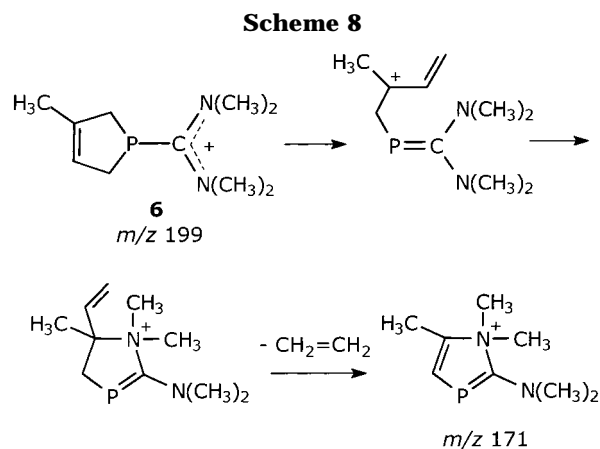
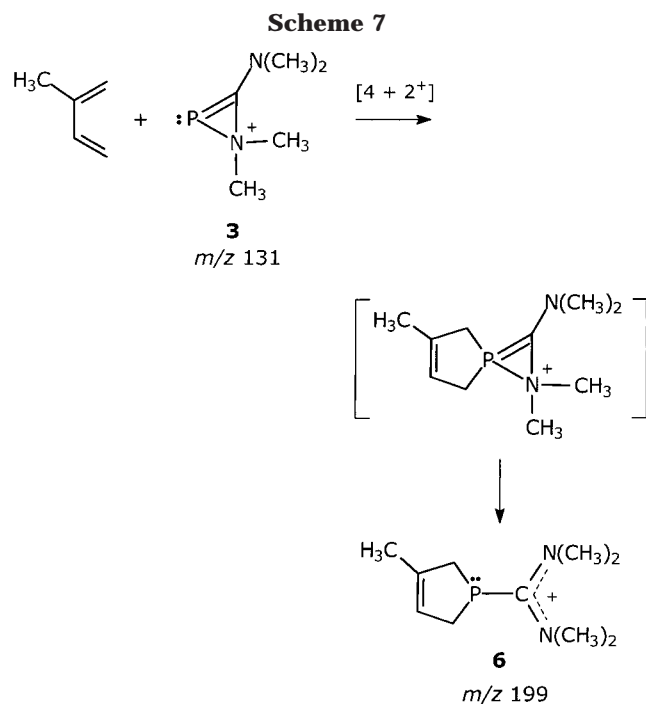
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could explain such a trend (Scheme 9), whereas facile reaction of **3** with $\text{P}(\text{OCH}_3)_3$ has its analogy with the chemistry of phosphonium ions, as outlined in Scheme 2.³ The ring-opening reactions proposed for **3** display analogy with the reactivity observed for **4** with several nucleophiles.^{13c} The adducts of **3** with the P and S nucleophiles dissociate upon collision activation in MS³ experiments (spectra not shown) mainly by cycloreversion to re-form **3** of *m/z* 131.

Conclusion

Cyclic azaphosphirenium ions are as yet unknown in solution. However, as predicted by DFT calculations¹⁷ and shown by pentaquadrupole mass spectrometric experiments, gas-phase demetalation of **1** upon 70 eV EI provides facile access to the first azaphosphirenium ion, **3**, via rapid cyclization of the incipient phosphavinyl cation **2**. The gas-phase experiments aimed at investigating the intrinsic solvent- and counterion-free reactivity of **3** show that it fails to coordinate efficiently with N and O nucleophiles. With the P and S nucleophiles tested, however, **3** forms otherwise stable adducts whose formation likely proceeds by ring opening and are favored by relatively strong and rare P=S and P=P

bonds and extensive charge delocalization on the dimethylamino substituents. With isoprene, **3** also forms an abundant adduct, most likely via [4 + 2⁺] cycloaddition, a process which is well-known for analogous phosphonium ions both in solution and in the gas phase, followed by ring opening of the unstable, sterically constrained phosphaspiro adduct to **6**, a highly resonance-stabilized phosphanyl diaminocarbenium ion. Relief of steric strain in the phosphaspiro[2.4]heptadiene adduct is a logical driving force for ring opening. We hope that our gas-phase and theoretical studies on the formation and characterization of **3**, the first N,P-analogue of the aromatic cyclopropenyl cation, will stimulate studies aimed at its generation and synthetic exploitation in solution.

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