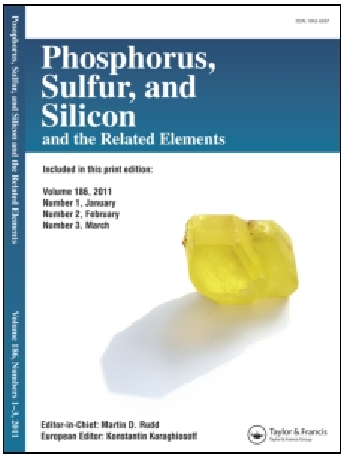

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Neil Burford[a]; Pierre Losier[a]; Simon Mason[a]; Bruce W. Royan[a]; Rupert E. V. H. Spence[a]; Pradip K. Bakshi[a]; Bozena Borecka[a]; T. Stanley Cameron[a]; John F. Richardson[b]; Robin D. Rogers[c]
[a] Department of Chemistry, Dalhousie University, Nova Scotia, CANADA [b] Department of Chemistry, University of Louisville, Louisville, Kentucky, USA [c] Department of Chemistry, Northern Illinois University, DeKalb, Illinois, USA

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THE STABILITY OF *CARBENIC* AND *ALKENIC* PHOSPHORUS ENVIRONMENTS

NEIL BURFORD*, PIERRE LOSIER, SIMON MASON, BRUCE W. ROYAN,
RUPERT E. v. H. SPENCE, PRADIP K. BAKSHI, BOZENA BORECKA
and T. STANLEY CAMERON,
Department of Chemistry, Dalhousie University, Halifax,
Nova Scotia, CANADA.

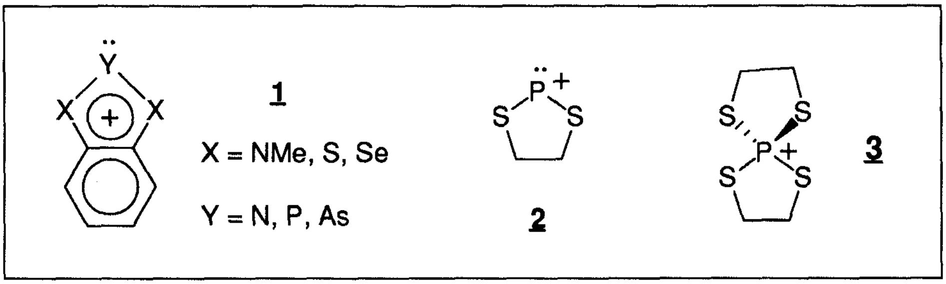
JOHN F. RICHARDSON,
Department of Chemistry, University of Louisville, Louisville,
Kentucky, USA.

ROBIN D. ROGERS,
Department of Chemistry, Northern Illinois University, DeKalb,
Illinois, USA.

Abstract The factors responsible for the isolation or identification of (*carbenic*) phosphenium and (*alkenic*) tricoordinate phosphonium salts are discussed. Structural features, reactivity and observations of intramolecular rearrangement are presented, which illustrate some of the requirements for stability in each case.

Bonding environments for phosphorus that are electronically analogous to those of carbon are an important key to the systematic development of phosphorus chemistry and pnicogen chemistry, in general. *Alkanic* environments are most typical for heavier non-metal elements, and the unsaturated *alkenic*, *alkynic*, *allenic*, and *carbenic* environments are rare if not unknown. Nevertheless, examples of *carbenic* phosphenium cations have been known since the 1970s,[1,2] and the first confirmed example of *alkenic* phosphonium salts were recently reported.[3,4] The highly electrophilic nature of these cations renders them susceptible to hydrolysis and reactions which generally lead to expansion of the coordination number at phosphorus. Here we present some observations regarding the specific structural or electronic features that are responsible for stability or reaction inhibition of *carbenic* and *alkenic* phosphorus.

The chemistry of phosphenium cations is already extensive, however, their format is essentially restricted to having a tetrachloroaluminate anion and either a nitrogen centre or Cp* (Me_5C_5) substituent directly attached to phosphorus. We have diversified the nature of the cation by introducing sulfur centres in place of the amines,[5] but such systems are only isolable when the phosphenium unit is incorporated into a heteronaphthalenic system 1 (10π-electrons), which benefits from the consequences of a Huckel π-electron count.



1

X = NMe, S, Se

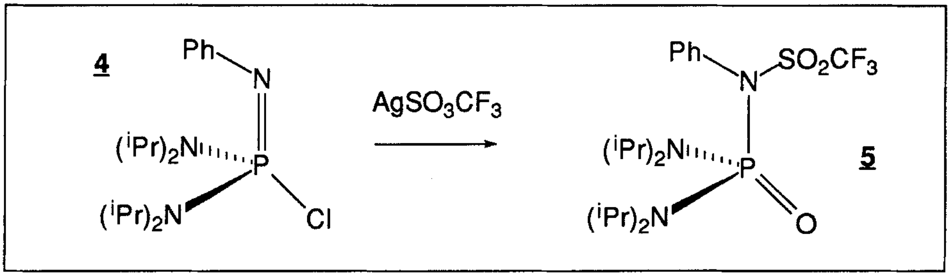
Y = N, P, As

2

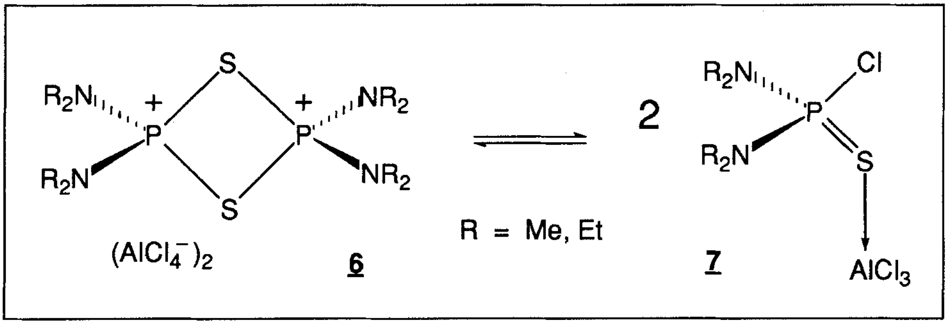
3

Consequently, the non-Huckel dithiaphospholidinium cation 2 undergoes an oxidative disproportionation at low temperature to give the spirocyclic tetrathiaphosphonium cation 3 and PCl_3.[6] Indeed, the phosphenium centre is most susceptible to oxidation, and reactions involving cycloadditions to cyclopropanes, alkynes, 1,3-dienes and 1,4-dienes, insertion into C-H, N-H and C-C bonds, coordination to metal centres and oxidation with azides, all result in phosphonium products.[1] Recently, we have observed the oxidative addition of CH_2Cl_2 to the phosphenium centre of the first phosphenium tetraphenylborate salt. This result is significant as much of phosphenium chemistry has been performed in CH_2Cl_2. We conclude that the chemistry of phosphenium tetrachloroaluminate salts is mediated by electrostatic interactions between the anions and the cationic phosphorus centre, preventing reaction with the solvent, yet allowing reaction with the more reactive substrate. In the presence of the more (than $AlCl_4^-$) weakly nucleophilic BPh_4^- anion, the phosphenium cation exhibits a more potent reactivity than anticipated, and we are currently investigating the potential activity for other non-metal cations in the presence of weakly basic anions.

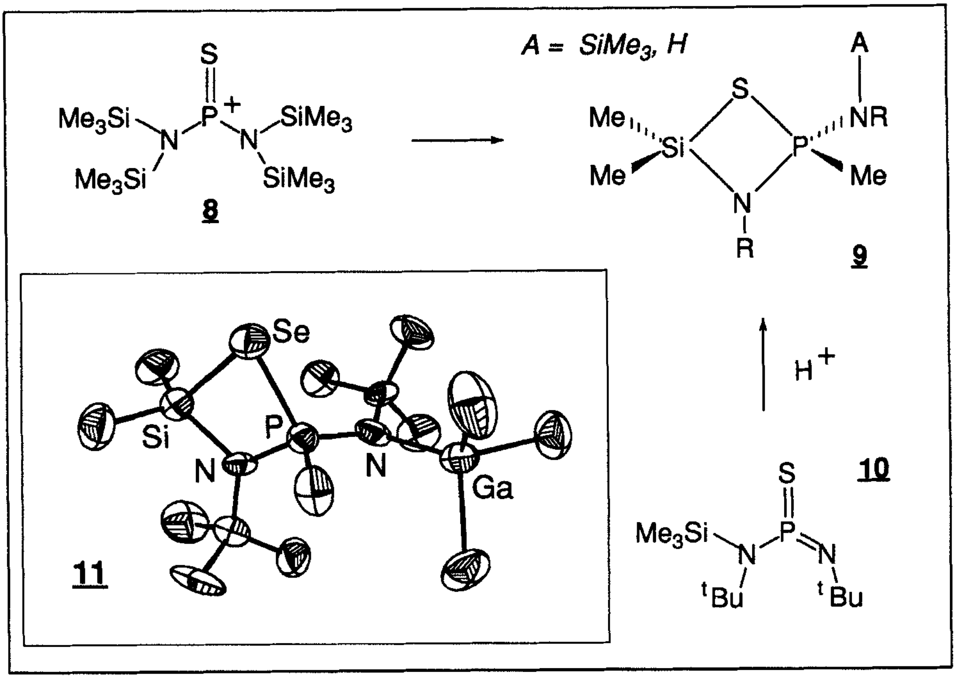
Halide ion abstraction from a phosphoryl chloride system has proven to be a useful approach towards tricoordinate phosphonium cations. However, in the absence of sufficient steric shielding, the cations are observed to undergo a variety of interesting structural adjustments, which culminate in the achievement of a tetracoordinate phosphorus centre. The phenyliminophosphonium triflate 4 rearranges to a covalent trisaminophosphine oxide 5, by means of oxygen transfer from sulfur to phosphorus, with the remainder of the triflate anion attached to the imino- nitrogen centre.[7] This result is in contrast to the stability observed for the analogous (same substitution and anion) disilylmethylenephosphonium triflate salt,[3] implying that the methylene phosphonium salts rely on steric shielding at both the phosphorus and carbon centres.



Thio- and selenophosphonium tetrachloroaluminates are observed as dicationic phosphetane dimers 6 in the solid state, but in solution achieve an interesting equilibrium with a covalent alternative monomeric coordination complex 7.[8] While it is tempting to assign a monomeric cation as an intermediate in this equilibrium, there is no evidence for such a species and the process appears to be complex.



The more sterically hindered bis[bis(trimethylsilyl)amino]thiophosphonium cation 8 is observed at low temperature in the reaction of the thiophosphoryl chloride with Lewis acids, however, on warming to room temperature an interesting intramolecular cyclisation occurs involving a 1,3-methyl shift from silicon to phosphorus. The resulting system 9 is an example of a "Genuine Heterocycle"[9] (a ring system containing only one atom of each element in the heterocyclic framework). Consistently, the ultimate result is identical when an imino(silylamino)thio-phosphorane 10 is converted to a diaminothiophosphonium cation by reaction with a proton or a Lewis acid. A variety of intermediates are apparent in this process prior to the genuine heterocyclisation, nevertheless, methyl migration is one of the initial steps in the rearrangement, demonstrating the vunerability of the tricoordinate *alkenic* environment at the phosphorus centre. The genuine heterocyclisation has some generality in that the constituent components of the heterocycle can be changed by substituion at the iminoaminochalcogenophosphorane, and the seleno-derivative provides the first example of a PNSiSe heterocycle **11**.[9]



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