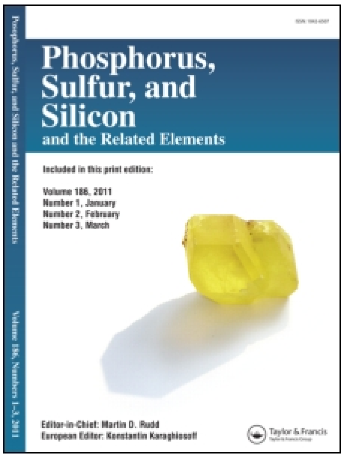

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Novel Cyclisations of the Chalcogeno-Phosphoryl Unit and the Formation of Genuine Heterocycles

Neil Burford[a]; Rupert E. V. H. Spence[a]; J. Marc Whalen[a]; John F. Richardson[b]; Robin D. Rogers[c]
[a] Department of Chemistry, Dalhousie University, hali, 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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NOVEL CYCLISATIONS OF THE CHALCOGENO-PHOSPHORYL UNIT AND THE FORMATION OF GENUINE HETEROCYCLES

NEIL BURFORD*, RUPERT E. v. H. SPENCE and J. MARC WHALEN,
Department of Chemistry, Dalhousie University, Halifax,
Nova Scotia, CANADA.

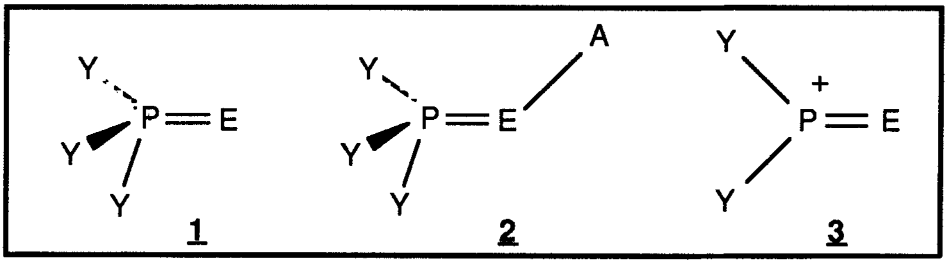
JOHN F. RICHARDSON,
Department of Chemistry, University of Louisville, Louisville,
Kentucky, USA.

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

Abstract A study of the interaction of imino-, oxo-, thio- and seleno- phosphorylic systems with Lewis acids has produced a number of interesting results, which represent a significant experimental contribution towards our understanding of the phosphorylic system. The most novel observations involve the heavier chalcogenophosphoryl systems, which produce new heterocyclic structures.

INTRODUCTION

The chemistry of the chalcogenophosphorylic unit 1 (E = O, S, Se) has been extensively investigated, and the most common mode of reactivity involves the Lewis base behavior of the electron-rich centre (E) 2.[1] However, phosphorylic systems which possess a labile group in one of the Y positions offer an alternative and potentially competitive means of reactivity. Maier[2], Paine[3], Sanchez[4] and others have recognised the significance of such activity in the development of phosphorus chemistry in terms of the possible identification of an *alkenic* phosphonium cation 3. However, evidence for systems resulting from



1 2 3

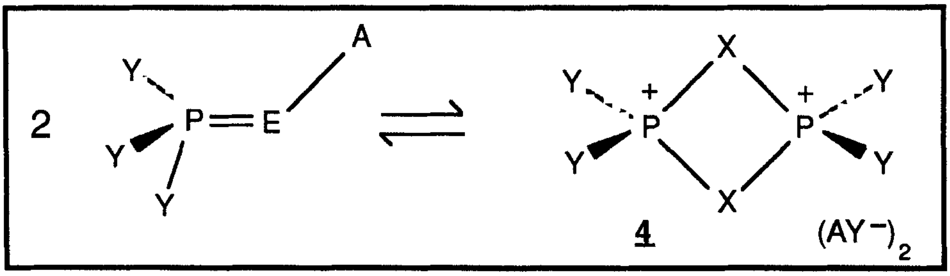
heterolytic activity of the P-Y bond is inconclusive, and the only example of a tricoordinate phosphonium centre has been obtained from a phosphinocarbene.[5]

Our studies collectively illustrate the thermodynamic instability of the tricoordinate phosphonium bonding arrangement 3.[6] Nevertheless, consequences include the discovery of a variety of novel heterocyclic systems and a realisation of the synthetic potential of the chalcogenophosphorylic unit as a diverse heterocyclic source.

ALKYLAMINOCHALCOGENOPHOSPHONIUM CATIONS

We have examined the reactions of a number of phosphorylic chloride systems with Lewis acids. While there are exceptions, the reactions are generally quantitative, and most commonly provide a simple Lewis acid-base complex 2 in solution. Such systems are readily identified by the NMR spectroscopic features, especially in the case of aluminate complexes, which exhibit distinctive ^{27}Al signal patterns.[1] Many of the systems retain their coordinate complex arrangement in the solid state as illustrated for $(^{i}Pr_2N)_2P(Cl)S\text{-}AlCl_3$[7] and $(^{i}Pr_2N)_2P(Cl)N(Ph)\text{-}AlCl_3$[6] in FIGURE 1. Such behaviour might be considered typical for any phosphorylic unit, but should not be considered general for the phosphorylic halides. While spectroscopic data show the ethyl derivative $(Et_2N)_2P(Cl)S\text{-}AlCl_3$ to be a typical covalent complex in solution, an ionic structure is observed in the solid state.[7] As illustrated in FIGURE 2, the salt consists of a novel dimeric dicationic diphosphonium heterocycle 4 each of which is associated with two tetrachloraluminate anions by means of weak interionic contacts. Interestingly, a similar dimeric ionic structure has been observed for the ethyl and methyl derivatised iminophosphorylic halides $(R_2N)_2P(X)NR$ (X = Cl, Br)[8] by means of an autoionisation of the P-X bond, while the more sterically protected isopropyl derivative is a covalent system.[9]

2



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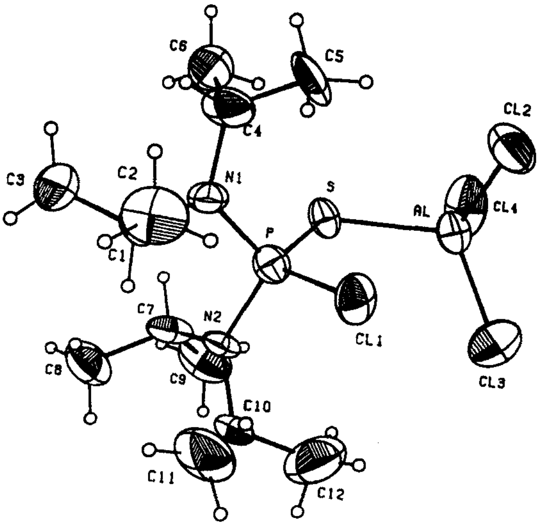

Crystallographic view of $({}^{i}Pr_2N)_2P(Cl)S\text{-}AlCl_3$

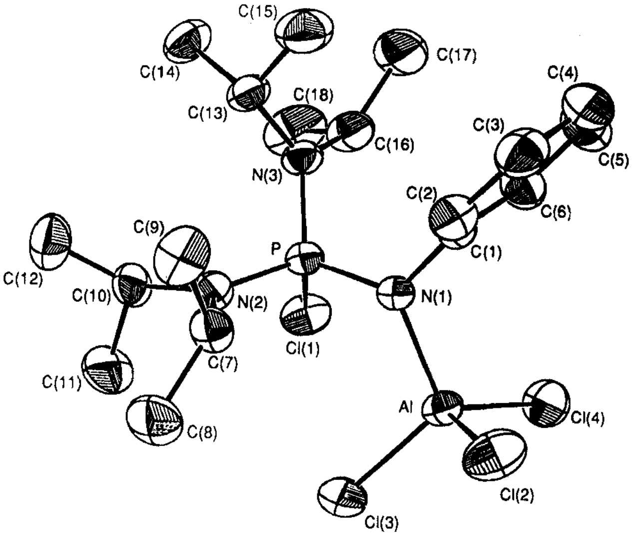

FIGURE 1 Crystallographic view of $({}^{i}Pr_2N)_2P(Cl)N(Ph)\text{-}AlCl_3$

Solvation of the ethylaminothiophosphonium dications effects a quantitative regeneration of the covalent complex **2** $(Et_2N)_2P(Cl)S$-$AlCl_3$, implying the existence of a well defined equilibrium process involving, dissociation (association) of the complex, heterolytic cleavage (formation) of the P-Cl bond, Al-Cl bond formation (dissociation), and dimerisation (monomerisation) of the chalcogenophosphonium cation. It would seem that the energetic differences between covalent and ionic arrangements are small, and are affected by steric constraints, such as the distinction between ethyl and isopropyl substituents. The dimeric structure **4** is observed for the seleno- derivative $[(Et_2N)_2PSe]_2\ [AlCl_4]_2$, however, the solution contains only ionic species.[7]

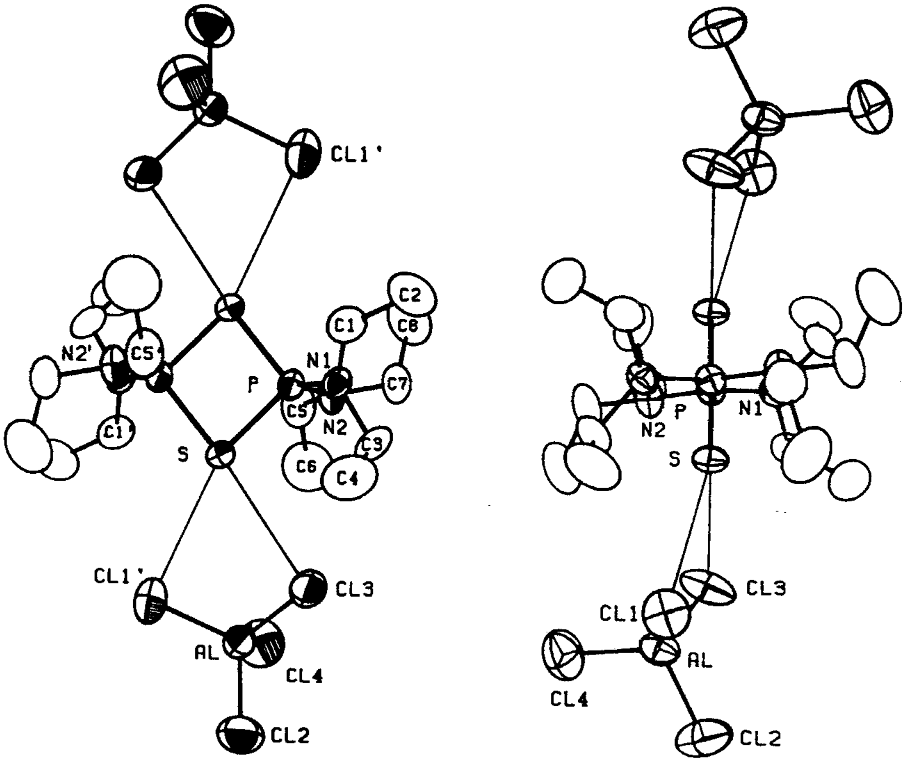

FIGURE 2 Crystallographic views of $[(Et_2N)_2PS]_2\ [AlCl_4]_2$

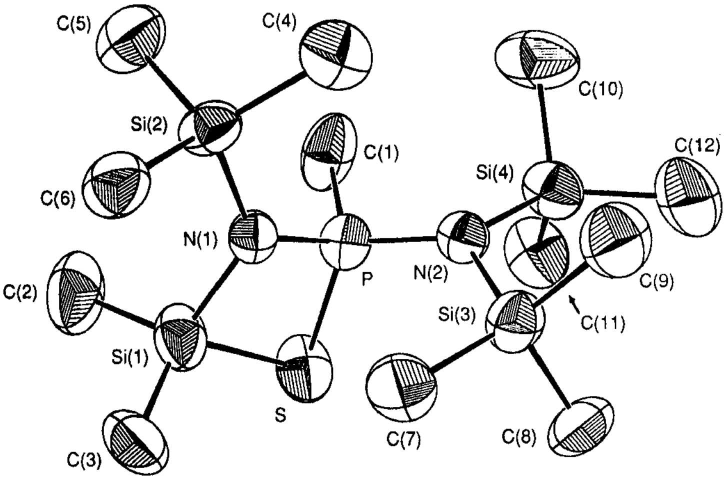

FIGURE 3 Crystallographic view of the cation of $[(Me_3SiN)-(Me_2Si)-S-P(Me)(Me_3Si)_2N]$ <u>6</u> $[GaCl_4]$

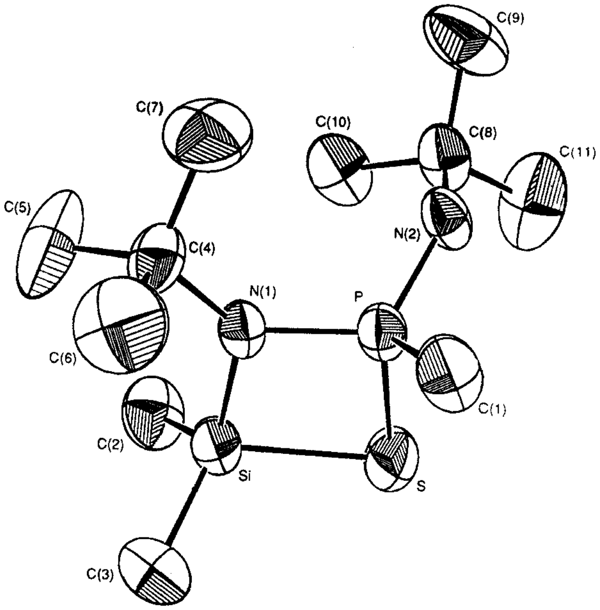

FIGURE 4 Crystallographic view of the cation of $[(^tBuN)-(Me_2Si)-S-P(Me)(^tBuNH)]$ <u>8</u> $[SO_3CF_3]$

SILYLAMINOCHALCOGENOPHOSPHONIUM CATIONS

The steric features of the trimethylsilyl- substituent clearly exceed those of the isopropyl moiety, and on this basis we had expected that reactions of $[(Me_3Si)_2N]_2P(S)Cl$ 5 with Lewis acids would produce similar complexes to the isopropyl derivatives. However, NMR studies of the reaction indicated a variety of intermediates with the ultimate formation of a novel heterocyclic cationic system 6 in 80% yield[10] (SCHEME). A view of the cation is shown in FIGURE 3.

The same NSiSP heterocyclic framework has been formed from the tricoordinate phosphorane $[(Me_3Si)^tBu](^tBuN)PS$ 7 upon reaction with a variety of acids, including a proton.[10,11] A crystallographic view of the protonated system 8 is shown in FIGURE 4. In common with the reaction of the phosphorylic chloride analog 5, the cyclisation of 7 incorporates a 1,3-methyl migration from silicon to phosphorus and Si-S bond formation. On this basis, we envisage a similar tricoordinate phosphonium intermediate for both reactions, one formed as the result of chloride ion abstraction from 5 and the other the result of coordination of the imino- nitrogen centre of 7 to the acid to create an amino- substituent (SCHEME).

The new heterocycles 6 and 8 represent the first examples of compounds containing the NSiSP framework. Perhaps more interesting is their novelty as rare examples of cyclic systems containing only one atom of each element in the cyclic assembly. We define such systems as "Genuine Heterocycles", and recognise them as the ultimate limit in the diversification of non-metal chemistry.

ACKNOWLEDGEMENTS

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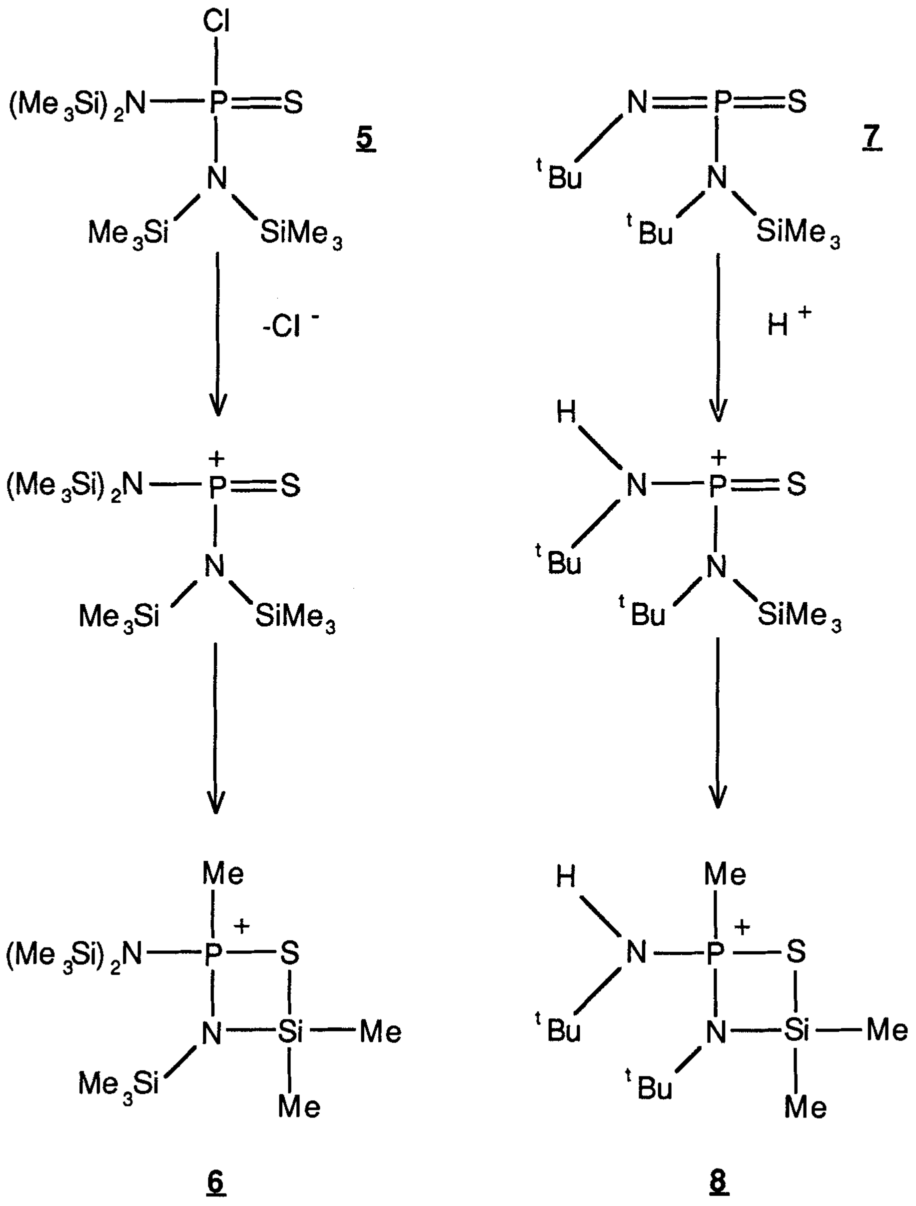
SCHEME Representation of the reactions of $[(Me_3Si)_2N]_2P(S)Cl$ and $[(Me_3Si)^tBu](^tBuN)PS$ with Lewis acids.



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