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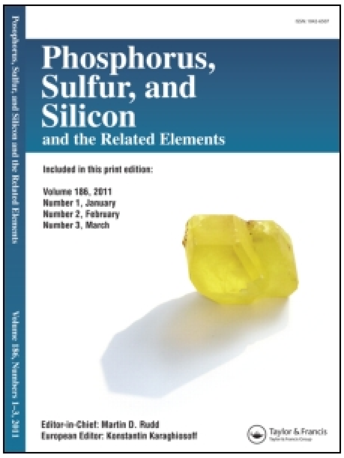

Phosphorus, Sulfur, and Silicon and the Related Elements

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Coordination Chemistry of Phosphenium and Arsenium Cations

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To cite this Article Burford, Neil , Clyburne, Jason A. C. , Losier, Pierre , Parks, Trenton M. , Cameron, T. Stanley and Richardson, John F.(1994) 'Coordination Chemistry of Phosphenium and Arsenium Cations', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 301 — 304

To link to this Article: DOI: 10.1080/10426509408021840

URL: http://dx.doi.org/10.1080/10426509408021840

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Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 301–304
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COORDINATION CHEMISTRY OF PHOSPHENIUM AND ARSENIUM CATIONS

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Abstract The Lewis acidic phosphenium and arsenium cations are employed as coordination sites and exhibit diverse and novel structural features.

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Phosphenium cations contain a dicoordinate phosphorus centre with formally six valence electrons, two bonds and a lone pair, and are frequently referred by analogy with carbenes. Many derivatives have been reported and the chemistry of phosphenium cations is extensive.[1] The anticipated Lewis acidic behaviour of phosphenium cations has been demonstrated, but the diversity of such interactions is underestimated. They are obvious candidates for a rich coordination chemistry and we have examined some

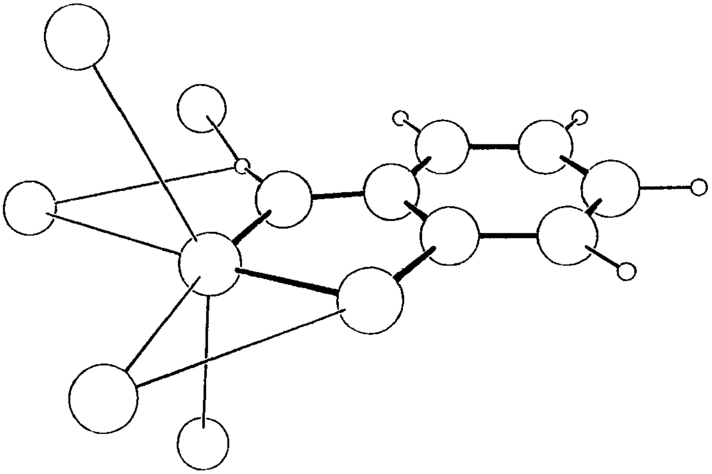


FIGURE 1 View of 1,3,2-benzothiazarsolium cation showing contacts between arsenic and the chlorine centres of the anions.

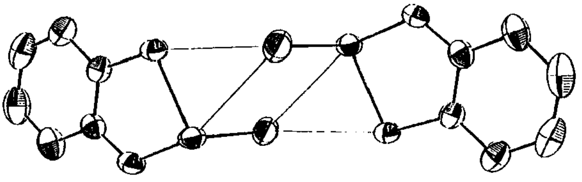


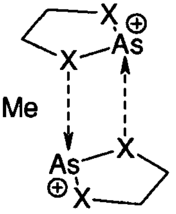
FIGURE 2 View of the 2-chloro-1,3,2-benzothiazarsole showing the dimer linkage involving the donation from chlorine to arsenic.

possibilities for a series of phosphenium cations and the first examples of arsenium cations.

Cations of *p*-block elements generally form weak interactions with their anions, which are viewed as donations from the anion to the cation,[2] or weak coordinative interactions. Consistent contact arrays are observed around the pnicogenium sites and are evident in both sterically hindered[3] and highly π-delocalized systems,[4] as illustrated in Figure 1. Such interactions are also responsible for the dimer linkages between some halopnicogines (eg. Figure 2).[4] Although long and weak, these interactions represent examples of coordination chemistry for pnicogenium centres and we have discovered new examples of such complexes which offer new directions in the systematic development of pnicogenium chemistry.

Phosphenium cations are monomeric in the solid state[3] and likely in solution, however the analogous arsenium cations form novel dimeric arrangements **1** which are fluctional in solution.[5] The dimer linkage involves two mutual donations from the electron-rich neighbour of the arsenic centre in one monomer to the arsenic centre of the other monomer, and each represents a coordinative bond. We view such interactions as a means of satisfying the coordinative unsaturation of the arsenic centre in the monomer, and they are precluded in phosphenium systems by the more favourable π-interaction with the neighbouring electron-rich centres **2**. Consequently, phosphenium cations are best viewed as three centre, four π-electron systems.

X = S, NMe



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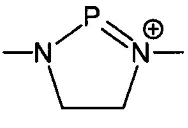

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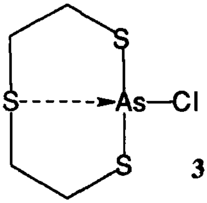
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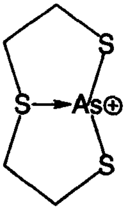
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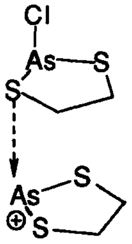
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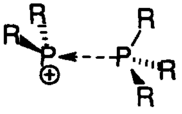
A weak intramolecular cross-ring S→As donor interaction is observed in the arsocane 3.[6] This is significantly shortened on removal of a chloride ion to give 4,[7] illustrating the enhanced Lewis acidity or intramolecular coordinative potential of the arsenium centre.

A coordination complex is observed between the dithiaarsenium cation and its chloroarsine precursor 5, with the sulfur centre of the latter providing the most basic site.[5] As is the case for the dimers presented earlier, 5 is fluctional in solution, rendering all methylenes equivalent at room temperature.

Similar complexes might be envisaged for phosphenium cations, but the first structural confirmation of a phosphenium complex was only recently reported.[8] Phosphino-phosphenium complexes 6 have been identified in solution by NMR spectroscopy,[9] and it is clear that aminophosphines coordinate to phosphenium centres via the phosphorus centre, however these compounds are labile and have not been structurally characterized. Our studies of the prototypical phosphenium cation Me_2P^+ have shown that it can exhibit both Lewis acidic and basic behaviour simultaneously in the complex cation 7, which has been structurally characterized as the $GaCl_4^-$ salt.[10] The coordinate P-Ga bond in the cation dissociates in solution. In contrast, amino substituted phosphino-phosphenium cations react with excess Lewis acid to generate two equivalents of the aminophosphenium salt.[9] The basicity of the phosphenium site in the alkylated systems is induced by the presence of the phosphine, and we describe such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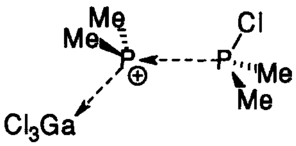
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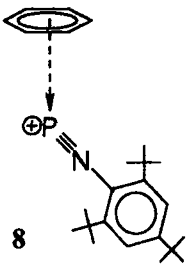
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interactions as ***Base-induced Coordination.***[10] One can view the phosphenium centre as an intermediary linkage between the Lewis basic phosphine and the Lewis acidic $GaCl_3$.

The potential diversity for the coordination chemistry of pnicogenium cations is illustrated by the first arene π-coordination to a phosphorus centre.[11] We have discovered that Niecke's iminophosphenium cation[12] forms complexes with a variety of arenes in which the aromatic carbon centres are equidistant from phosphorus **8**. The complexes retain their structure in methylene chloride solution as shown by NMR spectroscopy.

The presently limited but diverse coordination chemistry of the pnicogenium cations represents an exciting direction in the systematic development of group 15 chemistry, and there are many possibilities for analogies between the coordinative behaviour of the *p*-block elements and metals.

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