Co-ordinatively Unsaturated Group 15 Elements: The Isolation and Crystal Structure of a Novel Dimeric Dithiarsolidinium Cation

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The first example of a dithiarsolidinium cation has a novel dimeric structure, while the spirocyclic bis(ethanediyldithio)phosphonium cation has been isolated from attempts to obtain the corresponding dithiaphospholidinium cation, both observations illustrating the importance of supplemental stabilisation for low-co-ordinate group 15 elements.

Stable low-co-ordinate environments for the heavier elements of group 15 generally involve pπ-bonding to the neighbouring atoms, and are stabilised by steric shielding or electronic factors.[1] For example, the co-ordinative unsaturation at the phosphorus centre in the diazaphosphenium cation (**1**)[2] is satisfied by means of π-donation from the nitrogen centres.[1a] This electronic stabilisation can be enhanced if the hetero-moiety is a component of a Hückel system.[3] In an attempt to establish the limits of low-co-ordinate stability for the group 15 elements, we have examined the chemistry of the 2-chloro-1,3-dithia-phospha- and -arsa-cyclopentanes (**2Cl**)[4] and (**3Cl**)[5] with $AlCl_3$ and/or $GaCl_3$ as potential routes to the corresponding 1,3,2-dithiaphospholidinium (**2**) and 1,3,2-dithiarsolidinium (**3**) cations, respectively. Here we report a novel structural alternative to co-ordinative unsaturation at arsenic and the unexpected spirocyclisation of the corresponding phosphorus system.

The reaction of (**2Cl**) (11 mmol) with $GaCl_3$ (11 mmol) has been monitored by ^{31}P NMR spectroscopy and shows a complex solution behaviour, which includes the formation of PCl_3 and several as yet unidentified phosphorus-containing species. Over a period of minutes bis(ethanediyldithio)phosphonium (**4**) tetrachlorogallate (1.4 mmol, 25%) precipitates from the reaction mixture. The salt has been characterised spectroscopically and by *X*-ray crystallography† and is iso-

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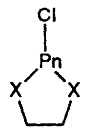
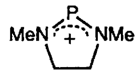
† Elemental analyses were satisfactory; NMR, δ (^{31}P), 154 ppm; (δ (^{1}H) 3.94 ($^{3}J_{PH}$ 22.9 Hz); δ (^{13}C) 44.3; decomp. 120 °C. *Crystal data* for $C_4H_8Cl_8Ga_2PS_4$: orthorhombic, space group *Pbcn*, $a = 15.549(3)$, $b = 15.287(2)$, $c = 12.942(2)$ Å, $V = 3058.5$ Å^3, $Z = 8$; *cf.* ref. 6.



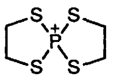
(1Cl) Pn = P, X = NMe
(2Cl) Pn = P, X = S
(3Cl) Pn = As, X = S



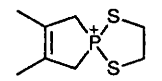
(1)

(2)

(3)



(4)



(5)

structural with the previously reported **(4)** BCl_4^-, which was prepared directly from $PCl_4^+BCl_4^-$.[6] An NMR study of the reaction of **(2Cl)** (6.4 mmol) with $AlCl_3$ (6.4 mmol) in the presence of an equimolar quantity of 2,3-dimethylbutadiene shows the high-yield formation of a bicyclic phospholenium cation **(5)**,‡ indicating the intermediate formation of the phospholidinium cation **(2)**.[7]

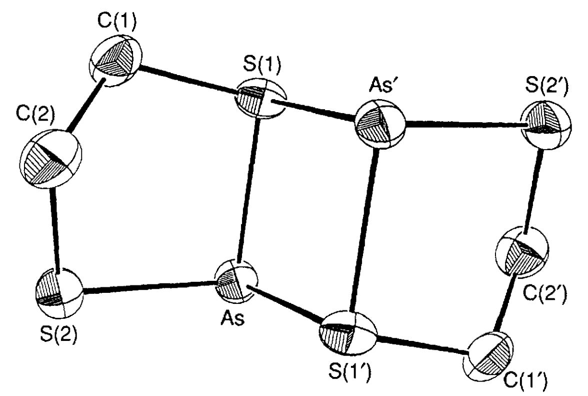
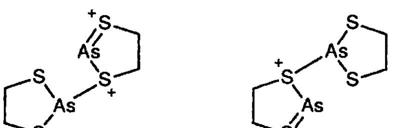


Figure 1. View of dication **(3)**$_2$ $(GaCl_4)_2$. Selected bond lengths (Å) and angles (°): As–S(1), 2.326(2); As–S(2), 2.181(1); As–S(1′), 2.423(2); S(1)–C(1), 1.826(6); S(2)–C(2), 1.826(7); C(1)–C(2), 1.493(9); S(1)–As–S(2), 93.14(6); S(1)–As–S(1′), 86.87(6); S(1)–As–S(2′), 96.96(6); As–S(1)–As′, 93.13(6); As–S(1)–C(1), 98.7(2); As–S(2)–C(2), 100.6(2); S(1)–C(1)–C(2), 112.7(5); S(2)–C(2)–C(1), 111.7(4).



(6)

Addition of a solution of $GaCl_3$ (4.3 mmol) in CH_2Cl_2 (*ca.* 2 ml) to a solution–suspension of **(3Cl)** (4.3 mmol) in CH_2Cl_2 (*ca.* 8 ml) gave a yellow solution over a pale yellow precipitate. Removal of solvent from the filtered solution gave a crystalline solid§ (non-optimised yield 0.8 mmol, 35%), which has been shown by *X*-ray crystallography§ to be the tetrachlorogallate salt of the dication shown in Figure 1. The cationic unit is a dimer of the five-membered arsolidinium heterocycle **(3)**, bound together by means of a four-membered As_2S_2 ring, and related by a crystallographic inversion centre. The three As–S bonds vary in length. The As–S(2) bond [2.181(1) Å] is among the shortest reported to date,[3a,8] and indicates some degree of localised π-bonding. The other two bonds are substantially longer [As–S(1), 2.326(2) Å; As–S(2′) 2.423(2) Å] than appropriate for an As–S single bond [*cf.* As_4S_4, 2.23(2) Å],[8] as if to satisfy the trivalency at As, in spite of the multiple character evident in As–S(2). Resonance structures **(6)** represent a simple bonding model, and imply that cation **(3)** adopts an intermediate between a fully σ-bonded As environment and As–S π-bonding. Dimer formation offers a co-ordinatively saturated σ-bonded alternative to ineffective π-bonding over the S–As–S moiety.¶

The contrasting modes of accommodating co-ordinative unsaturation in the dithiaphospholidinium and dithiarsolidinium systems is possibly a function of the stronger P–S σ-bond and less thermodynamically favourable arsonium environment. The results emphasise the requirement of supplemental stabilising influences, such as Hückel electron count, for the low-co-ordinate environments of the heavier non-metals.

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‡ NMR, δ (^{31}P; 85% H_3PO_4 reference) 111 ppm; δ {^{27}Al; $[Al(H_2O)_6]^{3+}$ reference} 102 ppm ($AlCl_4^-$); δ (^1H) ($CDCl_3$): 3.95 (SCH_2, d, $^3J_{PH}$ 15.8 Hz), 3.58 (PCH_2, d, $^2J_{PH}$ 9.7 Hz), and 1.88 (CH_3); δ (^{13}C) 129 (alkene, d, $^2J_{CP}$ 9.7 Hz), 43.4 (SCH_2), 41.2 (PCH_2, d, $^1J_{CP}$ 42.6 Hz), and 16.0 (CH_3, d, $^3J_{CP}$ 14.6 Hz). Assignments made by comparison with those in ref. 7.

§ Elemental analyses were satisfactory; very air-sensitive, m.p. 88—91 °C, δ (^1H) 4.1; δ (^{13}C) 45.4.

Crystal data for $C_4H_8As_2Cl_8Ga_2S_4$: $M = 378.64$, monoclinic, $P2_1/c$, $a = 6.454(20)$, $b = 14.360(3)$, $c = 11.536(2)$ Å, $\beta = 104.62(2)°$, $V = 1034.5$ Å^3, $Z = 4$, $D_c = 2.43$ Mg m^{-3}, $\mu = 71.9$ cm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.70930$ Å) using the ω–2θ scan technique ($2\theta_{max.} = 55°$). The structure was solved by direct methods and refined by full-matrix least-squares to $R = 0.030$, $R_W = 0.037$ for 1796 reflections with $F_o > 3\sigma(F_o)$ and with 104 parameters. All calculations were performed on a VAX computer using the SDP/VAX packages, B. A. Frenz, 'The Enraf-Nonius CAD-4 SDP—A Realtime System for Concurrent X-Ray Data Collection and Crystal Structure Determination,' in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. van Konigsveld, and G. C. Bassi, Delft University Press, Delft, Holland, 1978, p. 64. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ The crystal structure of the analogous 1,3-dimethyldiazarsolidinium (Pn = As, X = NMe) tetrachlorogallate shows similar structural features, N. Burford, B. W. Royan, E. J. Gabe, and R. Hynes, unpublished results. Note that the spectroscopic data for cation **(3)** are indicative of monomeric species in solution, consistent with studies on $(Et_2N)_2As^+$ $AlCl_4^-$ (and $CF_3SO_3^-$): C. Payrastre, Y. Madaule, and J. G. Wolf, *Tetrahedron Lett.*, 1990, **31**, 1145.

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