Cyclic phosphenium and arsenium cations with 6π electrons and related systems

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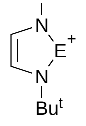
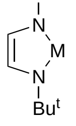
Cyclic phosphenium (1a) and arsenium (1b) cations are formed either by treatment of germylene 2b with ECl_3 (E = P, As) or *via* the metathetical reaction of LiN(Bu^t)C=CN(Bu^t)Li with ECl_3 and the structures of 1a and 1b are compared with those of pertinent saturated analogues.

Cyclic phosphenium (**1a**) and arsenium (**1b**) cations are isoelectronic with the corresponding silylenes **2a**[1] and germylenes **2b**.[2] As such, they raise interesting questions concerning circumannular delocalisation since, in principle, **1a**,**b** and **2a**,**b** possess six π electrons. Given that the group 15 systems bear a formal positive charge at the phosphorus or arsenic centre, it might be expected that these species would exhibit more extensive delocalisation than their neutral group 14 counterparts. (For a similar argument for nitrenium ions *vis-à-vis* carbenes, see ref. 3). A cyclic phosphenium ion with the same skeleton as **1a** was structurally characterised several years ago;[4] however, this cation features a 2-chloro substituent thus potentially complicating interpretations of bonding. More recently, **1a** has been synthesised and identified spectroscopically.[5] We report the following new developments in this field: (*i*) a novel synthetic route to **1a** and **1b** based on the redox reactions of **2b** with ECl_3 (E = P, As); (*ii*) X-ray crystallographic data for **1a** and **1b** and (*iii*) syntheses and X-ray crystallographic data for pertinent saturated analogues of **1a** and **1b**.

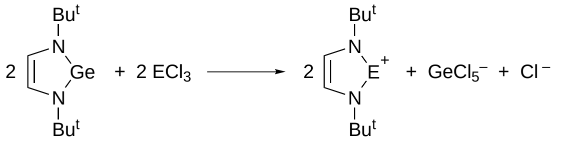


1a (E = P), **1b** (E = As)



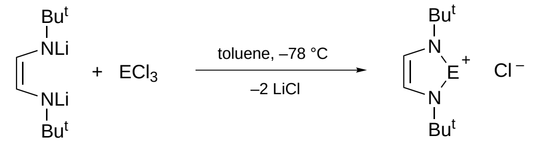
2a (M = Si), **2b** (M = Ge)

The reaction of **2b** with PCl_3 or $AsCl_3$ takes place under mild conditions and affords moderate yields of the corresponding phosphenium or arsenium ions [eqn. (1)].† The reaction mechanism has not been elucidated; however, it is clear that germanium is oxidised from the +2 to the +4 state and that **1a** and **1b** crystallise with equimolar quantities of $GeCl_5^-$ and Cl^- anions. A noteworthy feature of **1b** is that it is monomeric in contrast to the previously reported cyclic arsenium cation, $MeNCH_2CH_2N(Me)As^+$, which is dimeric.[6,7] Since it was not obvious from the foregoing whether autoionisation of the E–Cl bonds of the products would occur, we sought a system free of chloride ion acceptors. It was found that the metathetical reactions summarised in eqn. (2) proceed in good yields.†



(1)

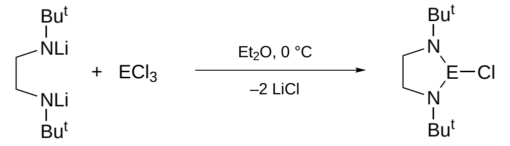
2b **1a** (E = P), **1b** (E = As)



(2)

1a (E = P), **1b** (E = As)

Analogous metathetical reactions were employed for the synthesis of the related saturated systems [eqn. (3)].



(3)

3a (E = P), **3b** (E = As)

The structures of **1a**,**b** (Fig. 1) and **3a**,**b** (Fig. 2) have been determined by X-ray crystallography.‡ Autoionisation is observed in the case of **1a**. While shorter than the van der Waals radii, the P···Cl separation in **1a** [2.715(2) Å] is nevertheless considerably longer than those of typical covalent P–Cl bonds *e.g.* PCl_3 2.043 Å, mes*NPCl 2.142(4) Å.[9] Anion–cation interactions which are less than the sum of the van der Waals radii are common for non-metals and certain phosphenium salts.[10] It has been observed previously that such anion–cation interactions have little or no effect on the structural features within the cation or anion.[11] Indeed, the structural features of **1a** derived from either the germanium exchange or metathetical route are identical within experimental error. Interestingly, the P–Cl distance in the corresponding C–C saturated analogue, **3a** [2.425(4) Å] is also longer than that of typical P–Cl bonds but shorter than that in **1a** thus implying that this compound is partway along the P–Cl heterolysis pathway. There is therefore an interesting parallel with carbene chemistry in the sense that the unsaturated imidazol-2-ylidenes (Arduengo type)[12] are more stable than the C–C saturated imidazol-2-ylidenes (Wanzlick type).[13] The case of the analogous arsenic system is not as clear because we have only been successful in isolating X-ray quality crystals of the mixed anion species, $[\mathbf{1b}]_2[GeCl_5]Cl$.

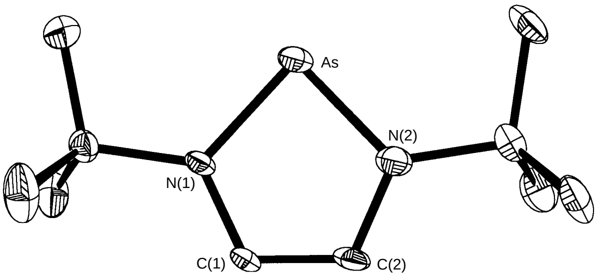


Fig. 1 Molecular structure of **1b** showing the atom numbering scheme. Selected distances (Å) and angles (°) for **1b** (corresponding values for **1a** shown in parentheses): As–N(1) 1.810(9) [P–N(1) 1.650(4)], As–N(2) 1.812(9) [P–N(2) 1.651(4)], N(1)–C(1) 1.38(1) [1.370(6)], N(2)–C(2) 1.38(2) [1.383(6)], C(1)–C(2) 1.36(2) [1.330(6)], N(1)–As–N(2) 86.2(4) [N(1)–P–N(2) 90.4(2)].

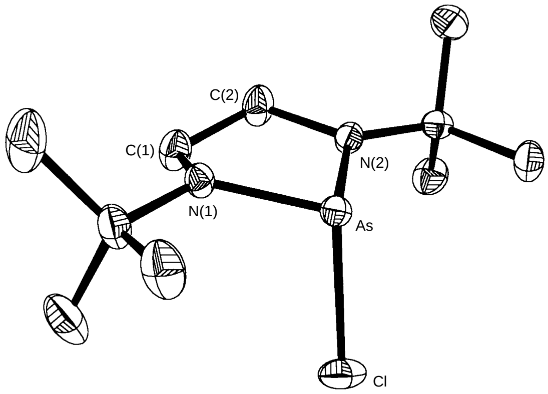
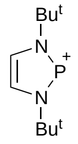
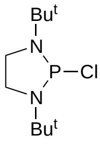
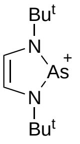
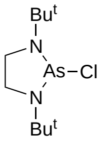


Fig. 2 Molecular structure of **3b** showing the atom numbering scheme. Selected distances (Å) and angles (°) for **3b** (corresponding values for **3a** shown in parentheses): As–N(1) 1.773(6) [P–N(1) 1.629(9)], As–N(2) 1.789(6) [P–N(2) 1.645(9)], As–Cl 2.375(2) [P–Cl 1.425(4)], N(1)–C(1) 1.468(9) [1.41(1)], N(2)–C(2) 1.464(9) [1.43(1)], C(1)–C(2) 1.44(1) [1.43(1)], N(1)–As–N(2) 88.7(3) [N(1)–P–N(2) 90.6(5)], N(1)–As–Cl 103.7(2) [N(1)–P–Cl 103.1(4)], N(2)–As–Cl 101.8(2) [N(1)–P–Cl 101.9(3)].

However, it is interesting to note that the C–C saturated chloride, **3b**, also possesses an elongated As–Cl bond with a bond length of 2.375(2) Å, a feature which is also observed in the related compounds, $\mathrm{Me\overline{NCH_2CH_2N(Me)As}Cl}$ [2.390(5) Å] and $\mathrm{Me\overline{N(CH_2)_3N(Me)As}Cl}$ [2.357(2) Å].[8]

The metrical parameters for **1a**,**b** and the C–C saturated analogues **3a**,**b** (Table 1) are pertinent to the question of electron delocalisation in these systems. One of the first points to note is that the P–N bond distance in **1a** is longer than that in the acyclic phosphenium cation, $[\mathrm{P(NPr^i{}_2)_2}]^+$ [av. 1.613(4) Å].[14] Moreover, the P–N and As–N bond lengths in **1a,b** are longer than those in the corresponding saturated derivatives **3a,b,** and the C–C bond lengths in **1a** and **1b** correspond to localised double bonds. The $\mathrm{EN_2C_2}$ rings of **1a** and **1b** are planar within experimental error, as are the geometries at the nitrogen centres. However, it is interesting that the $\mathrm{PN_2C_2}$ ring of **3a** is planar whilst the $\mathrm{AsN_2C_2}$ ring of **3b** is not. Thus, in contrast to the view[5] that **1a** 'possesses aromatic 6π-stabilisation,' the foregoing metrical parameters indicate that the cyclic phosphenium and arsenium cations **1a** and **1b** possess relatively localised electronic structures.

Table 1 Metrical parameters for compounds **1a**,**b** and **3a**,**b**

	 **1a**	 **3a**	 **1b**	 **3b**
E–N(av.)/Å	1.651(4)	1.637(9)	1.812(9)	1.781(6)
N–CH(av.)/Å	1.376(6)	1.42(1)	1.38(2)	1.466(9)
C–C/Å	1.330(6)	1.43(1)	1.36(2)	1.44(1)
N–E–N/°	90.4(2)	90.6(5)	86.2(4)	88.7(3)

Footnotes and References

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† *Experimental procedures*: the experimental procedures outlined below relate to the preparations of **1a** and **3a**; however, similar methods were employed for the preparations of **1b** and **3b**.

$[\mathbf{1a}]_2[\mathrm{GeCl_5}]\mathrm{Cl}$: a solution of $\mathrm{PCl_3}$ (0.433 g, 3.16 mmol) in thf (20 $\mathrm{cm^3}$) was added dropwise to a stirred solution of **2b** (0.76 g, 3.16 mmol) in thf (30 $\mathrm{cm^3}$) resulting in the formation of an orange coloured solution and precipitate. The reaction mixture was stirred overnight and then filtered through Celite resulting in a dark orange solution which was reduced *in vacuo* to a volume of approximately 20 $\mathrm{cm^3}$. Cooling of this solution to −20 °C overnight afforded a 40% yield of orange, crystalline $[\mathbf{1b}]_2[\mathrm{GeCl_5}]\mathrm{Cl}$.

$[\mathbf{1a}]\mathrm{Cl}$: a toluene solution (40 $\mathrm{cm^3}$) of $\mathrm{LiN(Bu^t)C{=}CN(Bu^t)Li}$ (2.09 g, 11.47 mmol) was added dropwise to a solution of $\mathrm{PCl_3}$ (1 $\mathrm{cm^3}$, 11.47 mmol) in toluene (20 $\mathrm{cm^3}$) at −78 °C. The reaction mixture was stirred overnight with slow warming to room temp. After filtering through Celite, the volume of the filtrate was reduced to 20 $\mathrm{cm^3}$ and cooling of the solution to −20 °C afforded a 55% yield of orange crystalline $[\mathbf{1a}]\mathrm{Cl}$.

Further experimental details can be obtained as supplementary material upon request from the authors.

‡ *Crystal data*: $[\mathbf{1a}]_2[\mathrm{GeCl_5}]\mathrm{Cl}$: $\mathrm{C_{20}H_{40}Cl_6GeN_4P_2}$, M = 683.79, monoclinic, space group $P2_1/c$, a = 10.445(2), b = 17.059(2), c = 19.846(3) Å, β = 93.35(2)°, U = 3530(1) $\mathrm{Å^3}$, Z = 4, D_c = 1.287 g $\mathrm{cm^{-3}}$, T = 298(2) K, μ = 1.428 $\mathrm{mm^{-1}}$. wR_2 = 0.2347 (6187 independent reflections), R = 0.0995 [$I > 2\sigma(I)$].

$[\mathbf{1b}]_2[\mathrm{GeCl_5}]\mathrm{Cl}$: $\mathrm{C_{20}H_{40}As_2Cl_6GeN_4}$, M = 771.69, monoclinic, space group $P2_1/c$, a = 10.567(4), b = 16.954(5), c = 19.675(7) Å, β = 93.02(2)°, U = 3520(2) $\mathrm{Å^3}$, Z = 4, D_c = 1.456 g $\mathrm{cm^{-3}}$, T = 183(2) K, μ = 3.207 $\mathrm{mm^{-1}}$. wR_2 = 0.2433 (4364 independent reflections), R = 0.0765 [$I > 2\sigma(I)$].

$[\mathbf{1a}]\mathrm{Cl}\cdot0.5\mathrm{C_7H_8}$: $\mathrm{C_{13.5}H_{24}ClN_2P}$, M = 280.77, monoclinic, space group $C2/c$, a = 20.535(4), b = 11.356(4), c = 13.939(4) Å, β = 97.30(2)°, U = 3224(2) $\mathrm{Å^3}$, Z = 8, D_c = 1.157 g $\mathrm{cm^{-3}}$, T = 298(2) K, μ = 0.322 $\mathrm{mm^{-1}}$. wR_2 = 0.2320 (2835 independent reflections), R = 0.0686 [$I > 2\sigma(I)$].

3a: $\mathrm{C_{10}H_{22}ClN_2P}$, M = 236.72, orthorhombic, space group $Pbca$, a = 11.978(2), b = 11.439(3), c = 19.533(3) Å, U = 2676.4(8) $\mathrm{Å^3}$, Z = 8, D_c = 1.175 g $\mathrm{cm^{-3}}$, T = 298(2) K, μ = 0.375 $\mathrm{mm^{-1}}$. wR_2 = 0.1603 (2348 independent reflections), R = 0.0883 [$I > 2\sigma(I)$].

3b: $\mathrm{C_{10}H_{22}AsClN_2}$, M = 280.67, orthorhombic, space group $Pbca$, a = 12.140(1), b = 11.405(1), c = 19.907(3) Å, U = 2756.3(6) $\mathrm{Å^3}$, Z = 8, D_c = 1.353 g $\mathrm{cm^{-3}}$, T = 298(2) K, μ = 2.631 $\mathrm{mm^{-1}}$. wR_2 = 0.1275 (2419 independent reflections), R = 0.0529 [$I > 2\sigma(I)$]. CCDC 182/645.

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