A Novel As_4^{2+} Structural Unit with Diphosphinomethanide Bridging Ligands from the Reaction of $AsCl_3$ with $Li[C(PMe_2)_2(SiMe_3)]$

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Two $As_2[C(PMe_2)_2(SiMe_3)]$ five membered ring units are linked *via* an As–As bond and thus form an As_4^{2+} chain in a compound obtained from a redox reaction between $AsCl_3$ and $Li[C(PMe_2)_2(SiMe_3)]$.

Low valent arsenic compounds continue to be of current interest. With more than two arsenic atoms in the molecule, their structures normally represent rings or cages, whereas chains of subvalent arsenic atoms in molecular structures are lacking, if weak van der Waals contacts are ignored.

Lithium phosphinomethanides are oxidatively coupled at transition metal centres as well as with main group elements or compounds.[1] Depending on the substitution pattern of the anionic phosphinomethanides, 1,2-diphosphinoethane (C–C coupling), C-phosphinosubstituted phosphorus ylides (P–C coupling) or P–P coupled bis-ylides are obtained. With transition metal based oxidants, reduced metal complexes are observed as intermediates, but with $BiCl_3$ or $SbCl_3$ as oxidants and $Li[C(PMe_2)_2(SiMe_3)]$ **1**, only the respective elements are isolated [eqn. (1)].[1]

$$MCl_3 + 3\,\underset{\mathbf{1}}{Li[C(PMe_2)_2(SiMe_3)]} \rightarrow M^0 + 1.5\,\underset{\mathbf{2}}{(Me_2P)(Me_3Si)C{=}PMe_2{-}PMe_2{=}C(SiMe_3)(PMe_2)} \qquad (1)$$

(M = Sb, Bi)

$$4\,AsCl_3 + 12\,\mathbf{1} \rightarrow \underset{\mathbf{3}}{\{\mu\text{-}[C(PMe_2)_2(SiMe_3)]\,As_2\}_2} + 5\,\mathbf{2} \qquad (2)$$

In the analogous reaction with the less readily reducible $AsCl_3$ we now also observe a partially reduced intermediate [eqn. (2)]. Besides compounds **3** and **2**, elemental arsenic and other unidentified compounds are formed. The stoichiometry of eqn. (2) is not fully obeyed. The red crystals (pentane) of compound **3** can be easily separated from the oxidation product **2**.†

From the ^{31}P NMR spectrum (AA'BB'spin system), the presence of two diphosphinomethanide ligands, connected *via* arsenic coordination centres, may be deduced. Sharp signals are only obtained at low temperature, the chemical shift values for P_A and P_B are only slightly affected. The structural integrity seems to be maintained in solution over a broad temperature range; line broadening is probably mainly due to conformational non-rigidity. According to X-ray analysis,‡ two diphosphinomethanide ligands each form a bridge between two arsenic atoms of a puckered As_4 chain. Thus two five membered, envelope-shaped As_2P_2C rings are linked *via* arsenic atoms in such a way that there is a centrosymmetric, transoid arrangement along the As(1)–As(1a) bond (Figs. 1, 2).

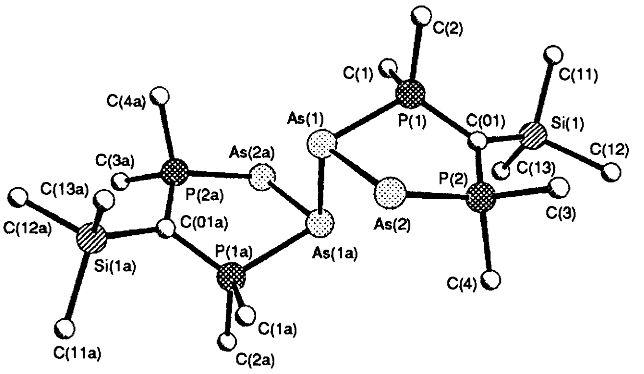

Fig. 1 Molecular structure of **3** (H atoms omitted). Selected bond lengths [Å] and angles [°]: As(1)–As(2): 2.391(1), As(1)–As(1a): 2.492(1), As(1)–P(1): 2.301(1), As(2)–P(2): 2.256(1), P(1)–C(01): 1.718(4), P(2)–C(01): 1.733(4), P(1)–As(1)–As(2): 90.2(1), As(1a)–As(1)–As(2): 104.9(1), As(1a)–As(1)–P(1): 93.3(1), P(2)–As(2)–As(1): 94.5(1), C(01)–P(1)–As(1): 112.0(2), C(01)–P(2)–As(2): 113.6(1), P(2)–C(01)–P(1): 112.4(2).

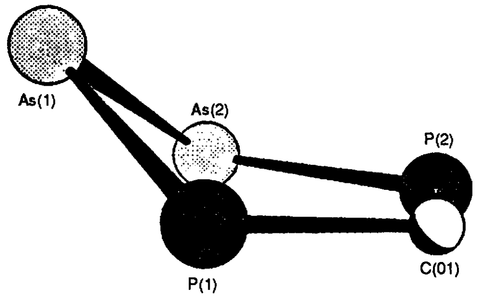

Fig. 2 Five-membered ring substructure of **3** showing the envelope conformation of the five membered rings

This latter As(1) atom deviates by 1.03 Å from a nearly planar As(2)–P(2)–C(01)–P(1) arrangement. Within these rings, As(2) is two-coordinate, whereas As(1) is three-coordinate. A coordination number of two in cyclic arsenic structures is quite common,[2] but in polyarsenic molecules a coordination number of three is found exclusively.[3] As expected, the As(2)–P(2) bond [2.256(1) Å] involving the two-coordinate arsenic atom is significantly shorter than the As(1)–P(1) bond [2.301(1) Å], though the latter is the shortest As–P single bond involving tricoordinate arsenic.[3d,4]

Particularly interesting are the As(2)–As(1) [2.391(1) Å] and the As(1)–As(1a) [2.492(1) Å] bond lengths which reflect the different coordination numbers.[3d] Both phosphorus–carbon distances involving the planar C(01) atom [P(1)–C(01): 1.718(4), P(2)–C(01): 1.733(4) Å] are relatively short and indicate the ylidic character of these bonds, in line with current observations on phosphinomethanide structures.[5] The angles around the arsenic atoms are within the expected range with the exception of As(2)–As(1)–As(1a) [104.9(1)°], which is probably due to repulsive interactions between the arsenic lone pairs.

The average oxidation state of arsenic in **3** is +0.5, which is between the values for the reduction products Bi^0 and Sb^0, eqn. (1), and +1, the latter being found in the phosphorus compounds formed in a related reaction with PCl_3.[6]

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Footnotes

† $\{^1H\}$ ^{31}P NMR (C_6D_6, +20 °C): AA'BB'spin system, not fully resolved, δP_A = +42.2, δP_B = +41.8; ($C_6D_5CD_3$, −90 °C): fully resolved AA'BB'spin system. The spectrum is reproduced computationally with the following parameters: δP_A = +43.29, δP_B = +40.13, $J(AA')$ = 51.31 Hz, $J(BB')$ = −0.80 Hz, $J(AB)$ = $J(A'B')$ = 110.82 Hz, $J(A'B)$ = $J(AB')$ = 2.29 Hz; $\{^1H\}$ ^{13}C(C_6D_6, +20 °C): δ = 21.40 (br, PMe_2), δ = 1.40 (s, $SiMe_3$).

On standing, arsenic is precipitated from the solution as a black powder.

‡ *Crystal data*: for $C_{16}H_{42}As_4P_4Si_2$, M_r = 714.27, monoclinic, a = 14.091(1), b = 8.702(1), c = 13.621(1) Å, β = 111.77(1)°, space group $P2_1/c$, Z = 2, V = 1551.1 Å^3, D_c = 1.529 g cm^{-3}, $F(000)$ = 716; Enraf Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71069 Å), T = +23 °C. Data were corrected for Lorentz and polarisation effects as well as for decay (−11.8%) and absorption [empirical, T_{min} = 0.777, T_{max} = 0.999, μ(Mo-Kα) = 45.5 cm^{-1}]. From 3752 measured [$(\sin\theta/\lambda)_{max}$ = 0.64 Å^{-1}] and 3040 unique reflections (R_{int} = 0.056) 2525 were considered 'observed' [$F_o \geqslant 4\sigma(F_o)$] and used for refinement. All hydrogen atoms were calculated in idealized geometry and included with isotropic contributions [$U_{iso(fix)}$ = 0.08 Å^2]. The non-H atoms were refined with anisotropic displacement parameters. The structure converged for 118 refined parameters to an $R(R_w)$ value of 0.0344 (0.0351). The function minimised was $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. Residual electron densities: +0.52/−0.40 eÅ^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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