β-Diiminato complexes of arsenic including the formally As^{I} compound [As₃L₃] [L = {N(C₆H₃Prⁱ₂-2,6)C(H)}₂CPh][†]

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The reaction of the potassium β -diiminate KL (L = $[{N(Ar)C(H)}_2CPh]^-$; Ar = $C_6H_3Pr^i_2$ -2,6) with AsI₃ gave [AsI₂L] (1), which upon reduction with KC₈ produced $[(\kappa^1-L)_2As-As=As(\kappa^2-L)]$ (2), having a unique bent chain of the three arsenic atoms in the formal oxidation states +2, 0 and +1.

The chemistry of β-diiminato complexes of Group 15 elements has recently undergone significant development, most of which dealt with phosphorus compounds: C-centred β-diketiminates,¹ N,N'-centred phosphenium salts^{2a-c} and N,C-centred cationic and neutral complexes.^{2d,e} β-Diketiminatoantimony dichloride has been prepared using the mesityl-substituted "nacnac" ligand $(L' = [{N(Ar)C(Me)}_2CH]^-, Ar = C_6H_2Me_3-2,4,6),$ while with $Ar = C_6 H_3 Pr_2^i - 2.6$ the products contained a tautomeric N,C-bonded ligand.³ Attempts to isolate a crystalline arsenic(III) or bismuth(III) β -diketiminate were unsuccessful.^{2e,3} A β-diketiminato ligand was unsuitable for stabilisation of pnictogen(I) compounds.⁴ It is noteworthy that guanidinates or an amidinate $M(L'')Hal_2$ [M = As, Sb, Bi; L'' = ${N(Ar)}_{2}CR$ (Ar = C₆H₃Prⁱ₂-2,6; R = NCy₂, NPrⁱ₂ or Bu^t); Hal = Cl or I] were readily available from $MHal_3$ and the appropriate lithium salt.⁵ Reduction of such an As^{III} dichloride yielded a diarsene; e.g., $[AsCl_2\{(N(Ar))_2C(NCy_2)\}]$ (A) was a precursor to $[As_2\{\mu-(N(Ar))_2C(NCy_2)\}_2]$ (B).

We have recently reported on the application of the β -dialdiminato ligand [{N(Ar)C(H)}₂CPh]⁻ (= [L]⁻; Ar = C₆H₃Prⁱ₂-2,6) in phosphorus^{2c} and Group 13 metal⁶ chemistry; now we describe the successful use of this ligand for stabilisation of both As^{III} and As^I compounds.

Reaction of AsI₃ and KL in thf cleanly produced the arsenic(III) β -dialdiminate [AsI₂L] (1),† Scheme 1. Compound 1 was isolated in good yield as red crystals of a solvate, 1·(Et₂O); it was soluble in thf or benzene and showed the appropriate signals in its ¹H and ¹³C NMR spectra. In contrast, attempted synthesis of a β -diketiminatoarsenic(III) iodide using KL' (Ar = C₆H₃Prⁱ₂-2,6) led to a yellow powder insoluble in common organic solvents preventing its further characterisation. This difference is attributed to the ease of deprotonation of the Me groups of the β -diketiminato ligand backbone and the accessibility of its γ -C, while Me groups are absent in the β -dialdiminato ligand L of 1 and the γ -C is blocked by the bulky Ph substituent.

+ Electronic supplementary information (ESI) available: details of synthetic procedures and crystallographic data for 1 and 2. CCDC 708181 and 708182. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b819723g Crystalline complex **1** is monomeric (Fig. 1),‡ showing a distorted trigonal bipyramidal environment around the As atom with the iodine atoms apical and N1, N2 and a lone pair occupying equatorial positions. The delocalised AsN1C1C2C3N2 six-membered ring has a shallow boat conformation with the As and C2 atoms being out of the N1C1C3N2 plane by 0.661(6) and 0.155(7) Å, respectively. The two As–N bond lengths are nearly identical and are similar to the equatorial As–N distance in the guanidinate **A** at 1.915(2) Å (the axial bond is much longer at 2.076(2) Å).⁵

Reduction of 1 with an excess of KC₈ in diethyl ether gave the trinuclear As compound $[(\kappa^1-L)_2As-As=As(\kappa^2-L)]$ (2) in low yield,[†] Scheme 1. Attempted reduction of 1 with Zn powder or Sn{N(SiMe₃)₂}₂ led to a brown or red-brown precipitate, which was insoluble in common organic solvents. The different outcome of these reductions is attributed to the formation of K₃As (in the case of KC₈ as reducing agent), which may have been the source for the central, naked As atom in **2**.

The structural analysis (Fig. 2)‡ reveals that the molecule **2** has the three As atoms in a bent (*ca.* 90°) chain arrangement with the central As1 atom being two-coordinate and bonded only to the other As atoms. The As2 atom is chelated by a single ligand L with its As–N bonds slightly longer than in **1**, but shorter than even the shortest such contact in the diarsene **B** (2.045(2) Å).⁵ The average As2–N distance (1.977 Å) is close to the value calculated for the optimised neutral molecule [As^I(nacnac)] having C_{2v} (1.955 Å, planar AsNCCCN ring) rather than C_s (1.903 Å, boat-shaped ring, as found in **2**) symmetry.⁴ Each of the two β -dialdiminato ligands, which is κ^1 -bonded to the As3 atom, has localised single and double bonds (in contrast to the π -delocalised ligand arrangement at As2) and thus is better treated as an eneamido ligand.



Scheme 1 Synthesis of compounds 1 and 2.

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Fig. 1 Structure of complex **1** (30% thermal ellipsoids). Selected bond lengths (Å) and angles (°): As–N1 1.922(4), As–N2 1.923(4), As–I1 2.9608(6), As–I2 2.7781(6), N1–C1 1.326(6), N2–C3 1.340(6), C1–C2 1.403(7), C2–C3 1.374(7); N1–As–N2 92.44(17), N1–As–I2 96.66(12), N2–As–I2 96.55(11), N1–As–I1 91.05(12), N2–As–I1 90.08(11), I1–As–I2 169.59(2).



Fig. 2 Structure of complex **2** (30% thermal ellipsoids; atom labels for the ligand substituents are omitted for clarity). Selected bond lengths (Å) and angles (°): As1–As2 2.3328(8), As1–As3 2.4139(9), As2–N1 1.944(5), As2–N2 2.010(5), N1–C1 1.326(7), N2–C3 1.317(8), C1–C2 1.399(8), C2–C3 1.375(9), As3–N3 1.912(5), N3–C34 1.372(7), C34–C35 1.367(8), C35–C36 1.455(8), N4–C36 1.255(8), As3–N5 1.919(4), N5–C67 1.368(7), C67–C68 1.363(8), C68–C69 1.449(8), N6–C69 1.274(7); As2–As1–As3 89.88(3), N1–As2–N2 88.2(2), N3–As3–N5 101.2(2).

Accordingly, the As3–N3 and As3–N5 bonds of **2** are shorter than the chelated As–N bonds in **1** or **2**.

The difference between the As1–As2 and As1–As3 bond lengths suggests a partial double-bond character for the former; however it is longer than in the As^I guanidinate **B** (2.2560(5) Å)⁵ or the bulky aryl derivative [As₂(C₆H₃Trip₂-2,6)₂] (2.285(3) Å, Trip = C₆H₂Prⁱ₃-2,4,6).⁷ This may be attributed to the zero oxidation state for the central As1 atom in **2**, in contrast to the oxidation state +1 for both As atoms in the symmetrically substituted diarsenes.

In conclusion, the crystalline β -dialdiminatoarsenic(III) iodide **1** was readily available *via* a standard metathetical exchange reaction of AsI₃ (*cf.* the more complex reactivity of phosphorus(III) halides). The compound **2**, obtained in a low yield by reduction of **1** with KC₈, represents a rare example⁸ of a trinuclear V-shaped As₃ compound having each As atom in a different formal oxidation state, 0 for the central non-ligated As1 atom, +1 for the chelated As2 atom and +2 for the bis-ligated As3 atom.

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Notes and references

‡ *Crystal data*. For 1·(Et₂O): [C₃₇H₅₁AsI₂N₂O], M = 868.52, monoclinic, space group $P2_1/n$, a = 11.2964(3), b = 24.7180(4), c = 14.2829(4) Å, $\beta = 97.267(1)^\circ$, V = 3956.10(17) Å³, Z = 4, T = 173(2) K, $\mu = 2.45$ mm⁻¹, 7713 independent reflections [$R_{int} = 0.062$], final R1 = 0.047 [for 6182 reflections with $I > 2\sigma(I)$], wR2 = 0.107 (all data). For 2·1.5(C₆H₁₄): [C₉₉H₁₂₃As₃N₆]·1.5(C₆H₁₄), M = 1751.05, triclinic, space group $P\overline{1}$, a = 15.5396(4), b = 18.7915(4), c = 19.6985(5) Å, $\alpha = 101.334(2)$, $\beta = 96.248(1)$, $\gamma = 110.643(2)^\circ$, V = 5177.5(2) Å³, Z = 2, T = 173(2) K, $\mu = 1.01$ mm⁻¹, 20 830 independent reflections [$R_{int} = 0.079$], final R1 = 0.088 [for 13 637 reflections with $I > 2\sigma(I)$], wR2 = 0.226 (all data). CCDC 708181 and 708182. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b819723g

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