

Controlling the oxidation state of arsenic in cyclic arsenic cations

Gregor Reeske and Alan H. Cowley*

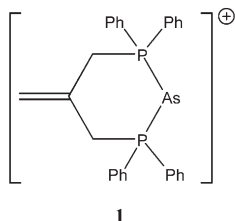
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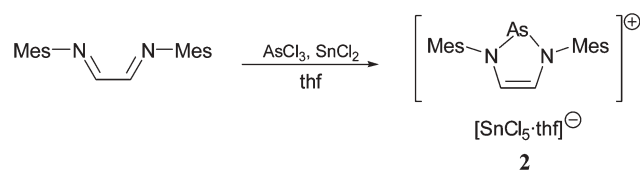
Reduction of AsCl_3 with SnCl_2 , followed by treatment of the “AsCl” with a 1,4-diimine results in electron transfer and formation of an arsenic(III) salt, while treatment of this arsenic(I) reagent or AsI_3 with an α,α' -diiminopyridine forms an arsenic(I) salt.

Cyclic triphosphenium ions have been known for several years.¹ Subsequently, other related ring systems incorporating P–As–P moieties exemplified by **1** have been reported,² as have acyclic systems of the genre $[\text{R}_3\text{PEPR}_3]^+$ (E = P, As).³ In a recent development, it has been demonstrated that the tertiary phosphines in these acyclic cations can be replaced by *N*-heterocyclic carbenes (NHCs).⁴ In general, two strategies have been employed for the synthesis of these interesting species, namely (i) reduction of ECl_3 (E = P, As) by SnCl_2 in the presence of a chelating bis(phosphine),^{1,2} monodentate phosphine³ or NHC,⁴ and (ii) redox reactions of a chelating bis(phosphine) with EI_3 (E = P, As).^{2d,e} A major point of interest in each of the cations produced in these reactions is the deduction that the central phosphorus or arsenic atom is in the +1 oxidation state, a view that is supported by the fact that the ^{31}P NMR chemical shifts for this atom fall in the range δ –210 to –270,^{2b} and the observation that the central phosphorus atom of a triphosphenium ion is sufficiently basic to undergo protonation.⁵ Collectively, these chemical and physical properties are suggestive of the predominance of the canonical form $\text{D} \rightarrow \text{E} \leftarrow \text{D}$ where D represents a phosphorus donor or NHC and E is P or As. In each of the above cases, the P(I) or As(I) moiety is supported by ligands that are not prone to facile reduction. Our attention was therefore drawn to the possibility that, by judicious choice of supporting ligand, it might be possible to control the oxidation state of the pnictogen center, E.



Treatment of an equimolar mixture of AsCl_3 and SnCl_2 with MesDAD (2,4,6-Me₃C₆H₂)NC(H)C(H)N(2,4,6-Me₃C₆H₂)⁶ resulted, after work-up, in an 84% yield of brown, crystalline **2**. The CI mass spectroscopic data for **2**⁷ revealed the presence of $[\text{SnCl}_5]^-$ in the negative mode and $[\text{MesDADAs}]^+$ in the positive

mode. The ^1H NMR chemical shift data indicated that the MesDAD ligand remained intact. Additional insight was gained from a single-crystal X-ray diffraction study of **2**⁸ (Fig. 1) which revealed that the solid-state structure features two independent anion–cation pairs in the asymmetric unit. The closest anion–cation contacts of 2.246(5) and 2.336(5) Å are between the arsenic atom and one of the axial chlorides of the $[\text{SnCl}_5\cdot\text{THF}]^-$ anion. Collectively, the X-ray structural data indicate that the oxidation state of arsenic in **2** is +3. Thus, the C–C (av. 1.363(18) Å), C–N (av. 1.365(17) Å) and N–As (av. 1.820(10) Å) bond distances for **2** are in very good agreement with the range of literature values of 1.338(15)–1.368(15), 1.316(18)–1.404(13) and 1.784(18)–1.8377(14) Å, respectively, reported for the metrical parameters for the C₂N₂As ring of the arsenium cations of the salts $[\text{tBuDADAs}][\text{Cl}]^{9a}$ and $[\text{MesDADAs}][\text{OTf}]^{9b}$. The presence of the counterion $[\text{SnCl}_5\cdot\text{THF}]^-$ in **2** is indicative of the initial formation of “AsCl” as a consequence of the reduction of AsCl_3 by SnCl_2 .¹⁰ Although no mechanistic information is available, a likely scenario is that the “AsCl” fragments are trapped by the bidentate MesDAD ligand prior to or concomitant with abstraction of Cl^- by SnCl_4 to form $[\text{SnCl}_5\cdot\text{THF}]^-$ and two-electron transfer from As to the LUMO of the diimine ligand.¹¹



Attention was turned next to a diimine ligand that would *not* undergo easy reduction. The α,α' -diiminopyridine ligand, $[\alpha,\alpha'$ -{2,6-¹Pr₂PhN=C(Me)}₂(C₅H₃N)] (DppDIMPY) was selected for this purpose.¹² This ligand, well known for its usefulness in

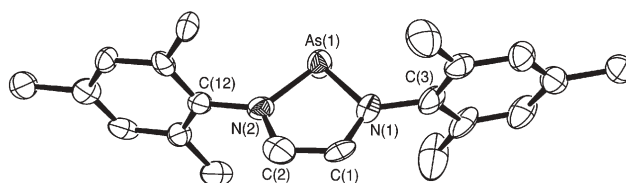


Fig. 1 View of the $[\text{MesDADAs}]^+$ cation of **2** showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°) with the corresponding values for the second molecule in the unit cell shown in brackets. C(1)–N(1) 1.372(16) [1.357(17)], C(1)–C(2) 1.375(18) [1.351(18)], C(2)–N(2) 1.339(16) [1.393(15)], N(1)–As(1) 1.823(10) [1.818(10)], N(2)–As(1) 1.831(11) [1.809(10)], C(1)–N(1)–As(1) 114.2(8) [113.6(9)], C(2)–N(2)–As(1) 113.4(9) [114.1(8)], N(1)–As(1)–N(2) 84.9(5) [85.0(5)].

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, 78712 Austin, Texas, USA.
E-mail: cowley@mail.utexas.edu; Fax: (+1) 512 471 6822;
Tel: (+1) 512 471 7484

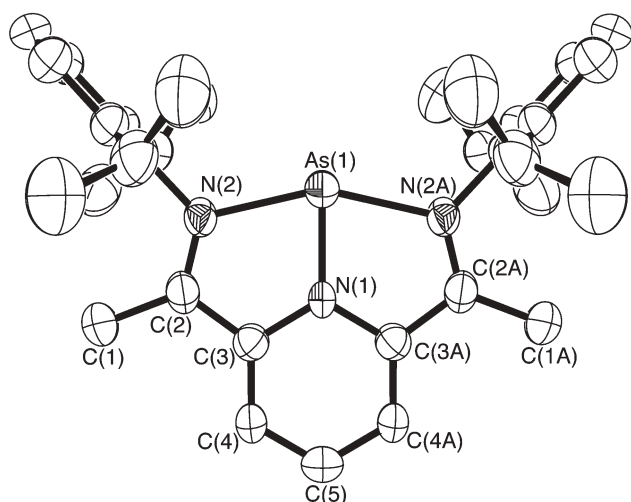
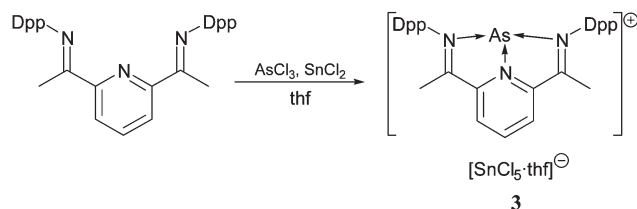


Fig. 2 View of the [DppDIMPYAs]⁺ cation of **3** showing the atom numbering scheme and thermal ellipsoids at 50% probability (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (°) with the corresponding values for the other half cation shown in brackets. C(2)–N(2) 1.302(6) [1.285(6)], C(2)–C(3) 1.424(7) [1.415(7)], C(3)–N(1) 1.395(5) [1.382(5)], N(1)–As(1) 1.862(5) [1.879(5)], N(2)–As(1) 2.095(4) [2.076(4)], C(3)–C(2)–N(2) 113.0(4) [113.0(4)], N(2)–As(1)–N(2A) 154.2(2) [154.2(2)]. Symmetry transformations used to generate equivalent atoms: *x*, *−y* + ½, *z*. The related metrical parameters for the [DppDIMPYAs]⁺ cation of **4** are as follows: C(2)–N(2) 1.310(12), C(2)–C(3) 1.424(15), C(3)–N(1) 1.395(13), N(1)–As(1) 1.877(8), N(2)–As(1) 2.080(9), C(3)–C(2)–N(2) 111.3(10), N(2)–As(1)–N(3) 154.9(3).

polymerization catalysis,¹³ will, in fact, react with Li and Li(naphthalenide) to give trithiated products.¹⁴ However, these reactions do not involve straightforward two-electron reduction processes.

Following the synthetic method described above for **2**, “AsCl” was generated in THF solution prior to the addition of DppDIMPY. After isolation and crystallization, the product (**3**) was characterized on the basis of spectroscopic data⁷ and an X-ray diffraction study.⁸ The asymmetric unit of **3** features two half [DppDIMPYAs]⁺ cations and one [SnCl₅·THF][−] anion (Fig. 2). Within experimental error, the AsN₃C₇ skeleton is planar and the flanking aryl groups are twisted by an average of 89.5° with respect to this plane. The arsenic atom is bonded to the pyridine nitrogen and both imino nitrogen atoms. The bond to pyridine is ~0.2 Å shorter than the other two; however, a survey of the Cambridge Structural Database reveals that all three bonds fall within the range observed for N→As dative bonds. The designation of the latter as dative bonds implies that intramolecular arsenic→ligand electron transfer has not taken place and hence that arsenic is in the +1 oxidation state. Further support for this view stems from examination of the metrical parameters for the remainder of the cationic skeleton. Thus, the average nitrogen–carbon distance of 1.294(6), which is ~0.02 Å larger than that in the free ligand,¹⁵ is consistent with a bond order of 2. Moreover, the average C–C and C–N bond distances for the pyridine ring of **3** are virtually identical to those in the free ligand.¹⁵

A second arsenic(I) salt, [DppDIMPYAs]₂[As₂I₈] (**4**), has been prepared *via* the reaction of the free ligand with AsI₃. In this case, the counterion is [As₂I₈]^{2−} and forms as a consequence of the



redox reaction $4\text{AsI}_3 \rightarrow 2\text{As}^+ + [\text{As}_2\text{I}_8]^{2-} + 2\text{I}_2$. Compound **4** was characterized by single-crystal X-ray diffraction and the metrical parameters for the cation were found to be identical to those found for **3** within experimental error (see Fig. 1 caption).

In summary, it has been found that an *in situ* generated arsenic(I) intermediate reacts with a 1,4-diimine to form an arsenium cation by a redox reaction. On the other hand, the arsenic(I) species retains the +1 oxidation state when coordinated to a diiminopyridine.

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- Spectroscopic data for **2** (84% yield): ¹H NMR (CD₂Cl₂): δ 2.20 (s, 12H, CH₃), 2.40 (s, 6H, CH₃), 7.14 (m, 4H, C_{arom}-Mes), 8.22 (s, 2H, HC=CH). MS (Cl⁺, CH₄): *m/z* 367 (75%, MesDADAs⁺); Cl[−] *m/z* 293 (100%, SnCl₅[−]); HRMS (Cl, CH₄) calcd for C₂₀H₂₅N₂As⁺, 368.1234; found 368.1220. Spectroscopic data for **3** (66% yield): ¹H NMR (CD₂Cl₂): δ 1.09 (d, 12H, ³J_{HH} = 6.9 Hz, ¹Pr-CH₃), 2.29 (sept, 4H, CH), 2.87 (s, 6H, CH₃), 7.38–7.52 (m, 6H, Dpp-H_{arom}), 8.53 (t, 1H, ³J_{HH} = 7.5 Hz, py-H_{arom}), 9.78 (d, 2H, ³J_{HH} = 7.5 Hz, py-H_{arom}). MS (Cl⁺, CH₄): *m/z* 556 (100%, DppDIMPYAs⁺); HRMS (Cl, CH₄) calcd for C₃₃H₄₃N₃As⁺; 556.2673; found 556.2678. Spectroscopic data for **4** (10% yield): ¹H NMR (CD₂Cl₂): δ 1.10 (d, 12H, ³J_{HH} = 6.6 Hz, Dpp-CH₃), 1.18 (d, 12H, ³J_{HH} = 6.6 Hz, Dpp-CH₃), 2.31 (m, 4H, Dpp-CH), 2.87 (s, 6H, CH₃), 7.38–7.49 (m, 6H, Dpp-H_{arom}), 8.43 (t, 1H, ³J_{HH} = 8.1 Hz, py-H_{arom}), 9.04 (d, 2H, ³J_{HH} = 8.1 Hz, py-H_{arom}). MS (Cl⁺, CH₄): *m/z* (100%, DppDIMPYAs⁺); HRMS (Cl⁺, CH₄) calcd for C₃₃H₄₃N₃As⁺, 556.2673; found 556.2678.
- Crystal data* for **2**: C₂₄H₃₂AsCl₅N₂OSn (735.40), monoclinic, space group P2₁/c, *a* = 18.497(4), *b* = 15.947(3), *c* = 20.677(4) Å, β = 91.97(3)°, *V* = 6069(2) Å³, *Z* = 8, *D_c* = 1.603 g cm^{−3}, μ(Mo-Kα) = 2.374 mm^{−1}, *T* = 153(2) K, 13 842 independent reflections (*R*_{int} = 0.1109), final *R* indices (625 parameters) for 13 842 independent reflections [*I* < 2σ(*I*)] are *R*₁ = 0.0852, *wR*₂ = 0.1804, *GOF* = 1.036. For **3**: C₃₇H₅₁AsCl₅N₃OSn (924.69), orthorhombic, space group *Pmma*, *a* = 25.951(5), *b* = 23.306(5), *c* = 17.579(4) Å, *V* = 10 632(4) Å³, *Z* = 8, *D_c* = 1.155 g cm^{−3}, μ(Mo-Kα) = 1.375 mm^{−1}, *T* = 153(2) K, 12 396 independent reflections (*R*_{int} = 0.0567), Final *R* indices (452 parameters) for 12 396 independent reflections [*I* < 2σ(*I*)] are *R*₁ = 0.0593, *wR*₂ = 0.1639, *GOF* = 0.907. For **4**: C₃₃H₄₃As₂I₄N₃ (1139.14), triclinic, space group *P1*, *a* = 10.668(2), *b* = 14.692(3), *c* = 17.074(3) Å, α = 105.32(3)°, β = 98.94(3)°, γ = 107.50(3)°, *V* = 2380(11) Å³, *Z* = 2, *D_c* = 1.590 g cm^{−3},

- $\mu(\text{Mo-K}\alpha) = 4.019 \text{ mm}^{-1}$, $T = 153(2) \text{ K}$, 10 689 independent reflections ($R_{\text{int}} = 0.0762$), final R indices (390 parameters) for 10 689 independent reflections [$I < 2\sigma(I)$] are $R_1 = 0.0588$, $wR_2 = 0.1491$, GOF = 0.812. CCDC: 295979 (2), 295978 (3) and 295977 (4). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602017h.
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