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Stabilised phosphorus(I) and arsenic(I) iodide: readily-synthesised reagents for low oxidation state main group chemistry†

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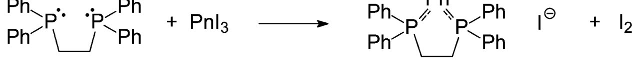
Herein we report a surprisingly facile and clean synthesis of base-stabilised phosphorus(I) and arsenic(I) iodide salts, which are reagents that provide convenient access to new low oxidation state main group compounds.

The study of low coordinate compounds of phosphorus has been a focus of main group chemistry for more than two decades. The fascinating results of such research have provided for an incredible development in the understanding of structure, bonding and reactivity of phosphorus and the main group elements in general. Investigations of phosphorus compounds have primarily dealt with the element in either of its common oxidation states (+3 or +5). The chemistry of compounds containing phosphorus in lower oxidation states has been limited to investigations of transient phosphinidenes, their cyclic polyphosphine oligomers, other catenated polyphosphines and elemental phosphorus.[1,2] The chemistry of analogous arsenic derivatives has been almost completely ignored.[3,4] As a preliminary aspect of our investigation of low oxidation state p-block chemistry, we required readily accessible and functionalisable low oxidation state group 15 reagents; "triphosphenium" compounds similar to those of Schmidpeter presented an ideal starting point.[5,6] In the course of our studies, we have discovered a convenient synthesis for stable and "bottleable" phosphorus(I) and arsenic(I) iodide reagents. Herein we detail the synthesis of these reagents, explain their stability and demonstrate their utility for the generation of air-stable low oxidation state compounds.

The room temperature reaction of equimolar amounts of PnI_3 and bis(diphenylphosphino)ethane (dppe) in dichloromethane affords burgundy (Pn = P) or orange (Pn = As) solutions (Scheme 1). After 2 hours of stirring, the volatile components were removed *in vacuo* and the solid was washed with THF or ether to remove the resultant I_2, then pentane to remove residual dppe. Redissolution in dichloromethane and filtration affords colourless (Pn = P) or yellow (Pn = As) solutions that yield solid upon concentration.‡§ Multinuclear NMR spectra of the resultant solids exhibit signals that are attributable to the cations $[(dppe)P]^+$ **1** or $[(dppe)As]^+$ **2**, respectively. Negative-ion electrospray mass spectrometry experiments confirm the presence of the iodide anion and do not show any indication of the triiodide anion; analytical data are consistent with the proposed compositions.

While the unnecessary nature of an additional reducing agent was recently reported for similar reactions, the explanation proposed, at least in the case of the pnictogen triiodides, is not entirely consistent with our experimental observations.[7] The suggestion has been that a phosphine ligand acts as the redox couple for the reduction of the P(III) to P(I) in that it is oxidized to the iodo-phosphonium iodide (P(III) to P(V)). Although such a redox couple is possible, ^{31}P NMR spectra of the reaction mixtures do not show formation of the iodo-phophonium salts (which are soluble in dichloromethane, ^{31}P δ = 33 ppm) during the reaction as shown in Figure 1. In fact, significant amounts of the phosphonium iodide are only observed if the initial reaction mixtures are allowed to stir for extended periods in THF. We believe that the experimental observations suggest that the reaction producing the previously observed phosphonium iodide is actually that of two equivalents of I_2 and dppe.[8] We have confirmed that the latter reaction proceeds efficiently with colour changes that are consistent with those observed after the formation of the low oxidation state salts.



Scheme 1

Furthermore, ^{31}P NMR experiments reveal that, in solution, PI_3 is in equilibrium with P_2I_4 and I_2. We suggest that a further disproportionation to oligomeric $(PI)_n$ is occurring to provide "PI" fragments that are complexed by the dppe chelate. This additional disproportionation is likely facilitated by the presence of the dppe.[9] While proof of the suggested mechanism requires further investigation, we have confirmed that the reaction of two equivalents of dppe with P_2I_4 also produces **1**[I] in 48% yield. The potential synthetic utility of mild *in situ* generation and complexation of "PnI" for the formation of new classes of low oxidation state reagents has not escaped our attention.

While the "as prepared" salts of both **1**[I] and **2**[I] are microcrystalline materials that are unsuitable for single crystal diffraction studies, crystals of **1**[I] were obtained by recrystallisation from THF. The salt crystallises in the space group $P1$ with two independent cations and anions in the asymmetric unit, as shown in Figure 2. The most important feature of the structure is the lack of any close interactions between the cations and the anions. The closest P-I contact is 4.702 Å and the closest contacts to the iodide anions are, in fact, from various H atoms on the dppe ligands; these contacts are all

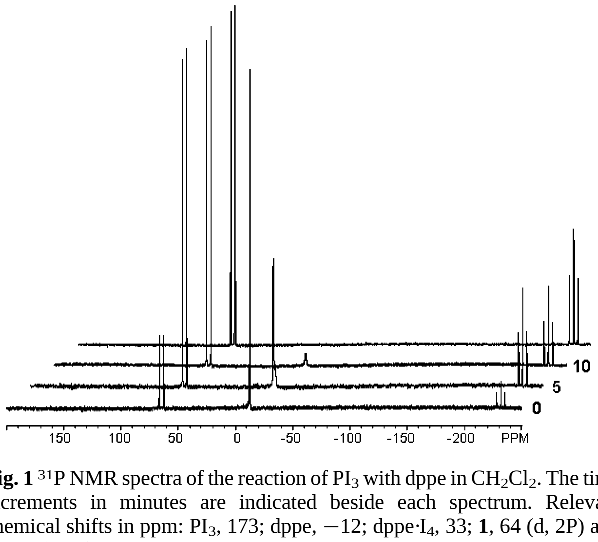


Fig. 1 ^{31}P NMR spectra of the reaction of PI_3 with dppe in CH_2Cl_2. The time increments in minutes are indicated beside each spectrum. Relevant chemical shifts in ppm: PI_3, 173; dppe, −12; dppe·I_4, 33; **1**, 64 (d, 2P) and −231 (t, 1P).

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† Electronic supplementary information (ESI) available: summary of DFT calculation and crystallographic data. See http://www.rsc.org/suppdata/cc/b3/b302292g/

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in excess of 3.056 Å. The metrical parameters of the cation are similar to those that have been observed in the salt $\mathbf{1}_2[SnCl_6]$[10] and do not require significant comment.

The iodide salts of **1** and **2** are valuable reagents for the metathetical synthesis of salts containing more robust or less reactive anions. The desired reactivity is illustrated by the reaction of **1**[I] with $Na[BPh_4]$ in THF or CH_2Cl_2.‡ Multinuclear NMR spectra of the reaction mixture and isolated product exhibit signals attributable only to **1**$[BPh_4]$. In addition, the similarity of the ^{31}P chemical shift of the central P atom ($\delta = -231$ ppm in **1**[I], $\delta = -236$ ppm in **1**$[BPh_4]$) in both the iodide and tetraphenylborate salts suggests that there is no significant interaction between the iodide anion and the cation in solutiont.

Crystals of **1**$[BPh_4]$ suitable for crystallographic structure determination were obtained by recrystallisation from THF and, although of poor quality, illustrate the components of the salt. The salt crystallises in the space group $P2_1/c$ and there are no unusually short contacts between the cations and the anions. The asymmetric unit, depicted in Figure 3, consists of cations and anions with metrical parameters that are consistent with those reported previously for such ions.

In contrast to most of the previously reported examples of univalent phosphorus or arsenic species, salts of **1** and **2** with appropriate counter anions are surprisingly stable in air. For example, both solid samples and aliquots of solutions of **1**$[BPh_4]$ show no signs of decomposition by ^{31}P NMR after 3 hours of exposure to the atmosphere. The apparent stability of the low oxidation state cations in air prompted us to re-examine their electronic structure to ascertain the reason for their non-reactivity.

The results of density functional theory calculations (see ESI† for details) reveal that the relative stability of **1** and **2** is attributable to back-bonding of π-electrons from the central atom to anti-bonding orbitals on the P atoms of the dppe ligand. By removing some of the electron density, such back-bonding effectively increases the oxidation state of the pnictogen atom. In this light, the electronic structure suggests that it should be possible to activate the univalent reactivity through the replacement of the phosphine ligands by donors that are less π-acidic.

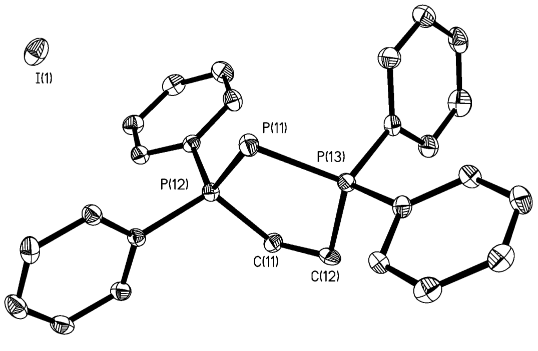

Fig. 2 Thermal ellipsoid (30%) plot of **1**[I]. Selected metrical parameters, bond lengths in angstroms and angles in degrees [parameters for the second cation are listed in brackets]: P(11)–P(12) 2.131(2) [2.133(2)]; P(11)–P(13) 2.126(2) [2.129(2)]; P(12)–P(11)–P(13) 89.35(6) [88.45(6)].

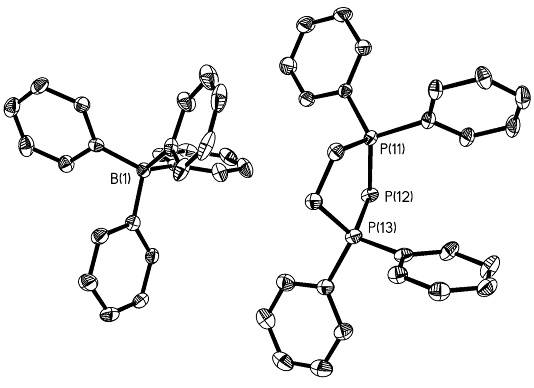

Fig. 3 Thermal ellipsoid (30%) plot of **1**$[BPh_4]$. Selected metrical parameters, bond lengths in angstroms and angles in degrees: P(11)–P(12) 2.135(2); P(11)–P(13) 2.122(2); P(12)–P(11)–P(13) 86.44(7).

In conclusion, we have found a practical synthesis for “bottleable” group 15 reagents that allow for the convenient preparation and investigation of low oxidation state main group compounds. In this context, we are currently exploring the coordination, redox and Wittig chemistry of these and related species. A detailed description of our experimental and computational investigations will be reported in a forthcoming full paper.

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Notes and references

‡ Selected characterisation data for **1**[I], **2**[I] and **1**$[BPh_4]$.

1[I]: White powder, yield 51%, d.p. 149–150 °C. $^{31}P\{^1H\}$ NMR δ: A_2B $\delta_A = 63.8$, $\delta_B = -231.0$, $J_{AB} = 451$. ^1H NMR δ: 3.62 (d, br, 4 H), 7.85 (m, 10 H), 7.61 (m 10 H). ^{13}C NMR δ: 30.1, 30.6, 125.8, 126.7, 130.1, 130.2, 130.3, 133.0, 134.1. Elemental Analysis ($C_{26}H_{24}IP_3$, 600.25) Calcd: C 56.14; H 4.35. Found: C 54.92; H 4.32%.

2[I]: Tan powder, yield 53%, dp 142–143 °C. $^{31}P\{^1H\}$ NMR δ: 60.8. ^1H NMR δ: 3.04 (s, br, 4 H), 7.54 (m, 20 H). ^{13}C NMR δ: 53.6, 129.9, 132.9, 133.0, 133.1. Elemental Analysis ($C_{26}H_{24}IP_3$, 556.30) Calcd: C 52.03; H 4.03. Found: C 53.98; H 4.46%.

1$[BPh_4]$: White powder, yield 47%, mp 174–175 °C. $^{31}P\{^1H\}$ NMR δ: A_2B $\delta_A = 64.4$, $\delta_B = -235.7$, $J_{AB} = 456$. $^{13}C\{^1H\}$ NMR δ: 122.3, 126.1, 129.4, 130.0, 130.1, 130.2, 131.0, 132.6, 134.1, 136.2. $^{11}B\{^1H\}$ NMR δ: −6.9. Elemental Analysis ($C_{50}H_{44}BP_3$, 748.62) Calcd: C 80.22; H 5.92. Found: C 77.83; H 6.68%.

§ Suitable single crystals of **1**[I] and **1**$[BPh_4]$ were covered with mineral oil and mounted in the 174 K N_2 stream of a Bruker Apex CCD diffractometer equipped with a Mo Kα radiation ($\lambda = 0.71073$ Å) source. Both structures were solved by direct methods and refined using full matrix, least squares on F^2.

Crystal data for **1**[I]: $C_{26}H_{24}IP_3$, triclinic, $P\bar{1}$, $a = 10.1340(5)$, $b = 13.5928(7)$, $c = 19.726(1)$ Å, $\alpha = 71.990(1)°$ $\beta = 81.307(1)°$, $\gamma = 68.853(1)°$,$V = 2407.6(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.535$ g cm^{-3}, μ (Mo Kα) = 1.541 mm^{-1}. A total of 23,284 reflections was collected in the range $2.18 < 2\theta < 55.08$. Of these, 10,966 were considered observed ($I > 2.0\sigma(I)$); $wR2 = 0.1151$, $R = 0.0584$.

Crystal data for **1**$[BPh_4]$: $C_{50}H_{44}BP_3$, monoclinic, $P2_1/c$, $a = 11.9875(6)$, $b = 17.5408(6)$, $c = 20.9570(9)$ Å, $\beta = 113.18(2)°$, $V = 4050.9(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.227$ g cm^{-3}, μ (Mo Kα) = 0.182 mm^{-1}. A total of 29,472 reflections was collected in the range $3.14 < 2\theta < 55.02$. Of these, 9,065 were considered observed ($I > 2.0\sigma(I)$); $wR2 = 0.2134$, $R = 0.1190$. CCDC 212868 and 212869. See http://www.rsc.org/suppdata/cc/b3/b302292g/ for crystallographic data in .cif or other electronic format.

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