

# 1,2-Diphosphenobenzene as a synthon for the 1,2,3-triphospha- and 2-arsa-1,3-diphosphaindenyl anions and a stable organo derivative of the P<sub>8</sub> unit of Hittorf's phosphorus†

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The electronic structure of the 1,2,3-triphosphaindenyl ligand suggests that it should exhibit enhanced  $\pi$ -acceptor properties when compared to the  $\eta^5$ -indenyl system; this insight encouraged us to develop a simple synthetic pathway from 1,2-diphosphenobenzene to the 1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub> and 2-As-1,3-C<sub>6</sub>H<sub>4</sub>P<sub>2</sub> anions, both of which have been structurally characterised by X-ray crystallography; as a bonus from these studies we also obtained the first structurally characterised organo derivative of the P<sub>8</sub> unit present in Hittorf's phosphorus.

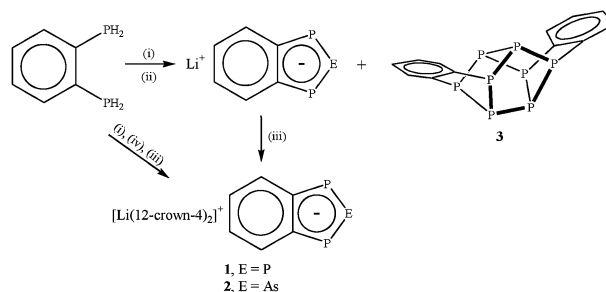
The cyclopentadienyl ligand and several of its complexes have an iconic status in the development of organometallic chemistry, and it is interesting that recently experimental and theoretical studies<sup>1,2</sup> with complexes derived from the 1,2,4-triphospholide anion, [C<sub>2</sub>Bu'<sub>2</sub>P<sub>3</sub>]<sup>−</sup>, have shown that replacement of the CH groups in the C<sub>5</sub>H<sub>5</sub> ring system by isolobal phosphorus atoms can lead to ligands with enhanced  $\pi$ -acceptor properties. This led us to consider the possibility of accessing the 1,2,3-triphosphaindenyl anion in the expectation that the 1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub> ligand present in complexes derived from this anion would show enhanced  $\pi$ -acceptor properties and that perhaps these complexes would show enhanced reactivity in ligand substitution reactions analogous to that observed with  $\eta^5$ -indenyl substituted complexes.<sup>3–5</sup> We succeeded in this goal, and as a bonus obtained crystals of a minor product whose  $\alpha$ -P<sub>8</sub>(4) skeleton<sup>6</sup> is one of the principal structural features of the pentagonal tubes that comprise Hittorf's phosphorus.<sup>7</sup>

As a first step, we probed the electronic structure of the target anion, [C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>]<sup>−</sup>, using density functional theory and following the approach recently applied to the 1,2,4-triphosphorus-substituted analogues of cyclopentadienyl.<sup>1,2</sup> The findings, which are discussed in detail in ESI†, showed three main distinctions between the [1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>]<sup>−</sup> anion relative to its all-carbon counterpart, [C<sub>9</sub>H<sub>7</sub>]<sup>−</sup>: (i) the presence of three phosphorus atoms substantially stabilises the  $\pi$  manifold; (ii)

both the five- and six-membered rings of [1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>]<sup>−</sup> are less aromatic compared to [C<sub>9</sub>H<sub>7</sub>]<sup>−</sup>; (iii) the stabilisation of the  $\pi^*$  LUMO of [1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>]<sup>−</sup> results in enhanced backbonding when coordinated to a transition metal centre.

With this encouraging background we then set out to explore the use of commercially available 1,2-diphosphenobenzene as a building block for both the [1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>]<sup>−</sup> and [2-As-1,3-C<sub>6</sub>H<sub>4</sub>P<sub>2</sub>]<sup>−</sup> anions.<sup>8a</sup> Reaction of a THF solution of 1,2-diphosphenobenzene with 4 equiv. of Bu<sup>n</sup>Li at −78 °C gives an orange coloured solution.† Subsequent reaction with 1 equiv. of PCl<sub>3</sub> gives a dark red coloured solution from which may be crystallised a minor product, **3**, the identity of which is discussed later in this report. The major product, **1**, may be isolated by addition of 12-crown-4 (8 equiv.); this leads to an orange–yellow precipitate which may be removed by filtration (Scheme 1), and storage of the resulting solution for 16 h at 5 °C results in a reasonable yield (49%) of yellow plate-like crystals of **1**. The analogous procedure with AsCl<sub>3</sub> in place of PCl<sub>3</sub> yields green plate-like crystals of **2**. Single crystal X-ray crystallography (see ESI†) showed **1** and **2** to be ion-separated, consisting of [Li(12-crown-4)<sub>2</sub>]<sup>+</sup> cations and anions which are triphospha- and arsa-diphospha- analogues of the indenyl anion (Fig. 1).§

The <sup>31</sup>P NMR spectrum of a D<sub>8</sub>-THF solution of **1** is fully consistent with this structure, showing two resonances at  $\delta$  = 335 and 260 ppm resulting from an AA'B spectrum.<sup>9</sup> The analogous spectrum for **2** showed a singlet at  $\delta$  = 303 ppm. The P–C bond lengths in **1** (av. 1.778 Å) are intermediate between typical P–C single and double bonds (1.83 Å, 1.60–1.70 Å, respectively).<sup>10</sup> Similarly, the P–P bond lengths (av. 2.093 Å) are intermediate between typical P–P single and P=P double bonds (2.22 Å<sup>11</sup> and 2.00–2.05 Å,<sup>11</sup> respectively).

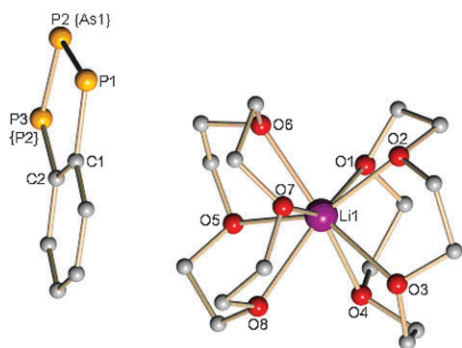


Scheme 1 (i) 4 Bu<sup>n</sup>Li, (ii) PCl<sub>3</sub>, (iii) 8 equiv. 12-crown-4, (iv) AsCl<sub>3</sub>.

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† Electronic supplementary information (ESI) available: Syntheses and experimental data for **1** and **2**; Crystal data for **1–3**; DFT studies on **1**. Synthesis of **3** and a comparison of the molecular dimensions of polymorphs *a* and *b*. See DOI: 10.1039/b717204d

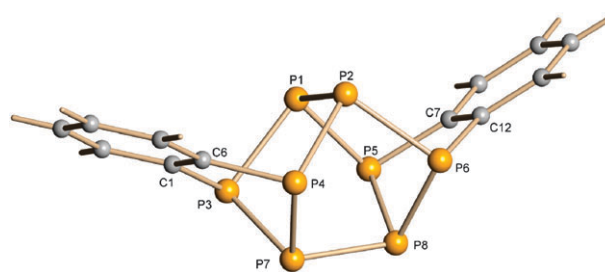


**Fig. 1** Molecular structure of **1**; if different, the corresponding numbering scheme for **2** is in parentheses. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: P(1)–C(1) 1.780(2), P(1)–P(2) 2.094(1), P(2)–P(3) 2.094(1), P(3)–C(2) 1.784(2), C(1)–C(6) 1.419(3), C(1)–C(2) 1.426(3), C(2)–C(3) 1.414(3), C(3)–C(4) 1.373(3), C(4)–C(5) 1.407(3), C(5)–C(6) 1.375(3); C(1)–P(1)–P(2) 98.93(7), P(1)–P(2)–P(3) 101.04(3), C(2)–P(3)–P(2) 99.12(7), C(2)–C(1)–P(1) 120.8(2), C(1)–C(2)–P(3) 120.1(2). Selected bond lengths (Å) and angles (°) for **2**: As(1)–P(1) 2.202(1), As(1)–P(2) 2.202(1), P(1)–C(1) 1.773(4), P(2)–C(2) 1.771(4), C(1)–C(6) 1.423(6), C(1)–C(2) 1.437(5), C(2)–C(3) 1.425(5), C(3)–C(4) 1.367(6), C(4)–C(5) 1.413(6), C(5)–C(6) 1.371(6); P(1)–As(1)–P(2) 97.69(4), C(1)–P(1)–As(1) 99.1(1), C(2)–P(2)–As(1) 99.2(1), C(6)–C(1)–P(1) 119.8(3), C(3)–C(2)–P(2) 120.1(3).

Similar features are apparent in the structure of **2** (av. P–C 1.772 Å, av. P–As 2.202 Å, *cf.* P–As single and P=As double bond lengths of 2.32–2.36 Å<sup>12</sup> and 2.13 Å,<sup>13</sup> respectively). These parameters, along with the fact that the anions of **1** and **2** are planar, is consistent with significant aromaticity in the five-membered ring. The angles in the five-membered rings vary widely, with the carbon atoms showing almost ideal sp<sup>2</sup> hybridisation, but the angles at the pnictogen centres are significantly compressed. The C–C bond distances in the six-membered rings alternate in a way that is commonly observed for the all-carbon indenyl anion.<sup>3</sup> The structure of the cation of both **1** and **2** is unremarkable.

Although preparations of 1,2,3-triphospholide anions, [R<sub>2</sub>C<sub>2</sub>P<sub>3</sub>]<sup>−</sup>, have been previously reported,<sup>14–16</sup> the synthetic protocols all have their limitations, either being complicated multistep procedures or not giving access to the anionic reagent; moreover, they cannot be extended to provide access to the [1,2,3-C<sub>6</sub>H<sub>4</sub>P<sub>3</sub>]<sup>−</sup> anion of **1**. The synthetic protocol described in this paper has the advantages of being rapid (preparation time of *ca.* 1 h) and using commercially available starting materials.

As mentioned above, a second product was identified from the 1,2-diphosphenobenzene–4 Bu<sup>n</sup>Li–PCl<sub>3</sub> reaction mixture. In addition to signals from the anion of **1**, low intensity resonances from a minor product were observed in the <sup>31</sup>P NMR spectrum of the reaction mixture as three intricate multiplets<sup>¶</sup> at δ = 122.7, 104.2 and 31.9 ppm, but the origin of these signals only became clear when a THF solution of the products was layered with *n*-hexane, yielding a small crop of yellow prismatic crystals that were suitable for X-ray crystallography (see ESI<sup>†</sup>).<sup>§</sup> This showed the species to be a cage structure (Fig. 2), whose α-P<sub>8</sub>(4) skeleton is one of the principal structural features of the pentagonal tubes that comprise



**Fig. 2** The molecular structure of **3**. Selected bond lengths (Å) and angles (°): P(1)–P(3) 2.222(1), P(1)–P(5) 2.224(1), P(1)–P(2) 2.243(1), P(2)–P(6) 2.231(1), P(2)–P(4) 2.234(1), P(3)–P(7) 2.218(1), P(4)–P(7) 2.220(1), P(5)–P(8) 2.216(1), P(6)–P(8) 2.218(1), P(7)–P(8) 2.220(1), P(3)–C(1) 1.832(3), P(4)–C(6) 1.842(3), P(5)–C(7) 1.832(3), P(6)–C(12) 1.843(3); P(3)–P(1)–P(5) 86.36(3), P(3)–P(1)–P(2) 102.36(3), P(5)–P(1)–P(2) 102.24(3), P(6)–P(2)–P(4) 88.13(3), P(6)–P(2)–P(1) 103.14(3), P(4)–P(2)–P(1) 102.69(3), C(1)–P(3)–P(7) 92.65(9), C(1)–P(3)–P(1) 100.66(8), P(7)–P(3)–P(1) 100.17(3), C(6)–P(4)–P(7) 92.30(8), C(6)–P(4)–P(2) 100.50(8), P(7)–P(4)–P(2) 99.09(3), C(7)–P(5)–P(8) 92.93(9), C(7)–P(5)–P(1) 98.99(8), P(8)–P(5)–P(1) 99.93(3), C(12)–P(6)–P(8) 92.63(8), C(12)–P(6)–P(2) 99.04(8), P(8)–P(6)–P(2) 98.90(3), P(3)–P(7)–P(8) 100.56(3), P(3)–P(7)–P(4) 92.64(3), P(8)–P(7)–P(4) 101.43(3), P(5)–P(8)–P(6) 93.20(3), P(5)–P(8)–P(7) 100.82(3), P(6)–P(8)–P(7) 101.58(3).

Hittorf's phosphorus.<sup>7</sup> Subsequent experiments yielded further crystals of this material as a polymorph (both crystallise in the triclinic space group *P* $\bar{1}$ ); the legend for Fig. 2 contains structural parameters for polymorph *a*; molecular dimensions for polymorph *b* are ostensibly the same and are compared to the equivalent dimensions of polymorph *a* in ESI.<sup>†</sup>

The molecular structure of **3** shows two benzenoid fragments flanking a P<sub>8</sub> core which consists of four envelope-shaped P<sub>5</sub> rings sharing common edges. The P–P bond lengths fall within a narrow range {2.216(1)–2.242(1) Å, av. 2.225 Å} which is typical of P–P single bonds;<sup>17</sup> bond angles at the phosphorus centres are distributed into two distinct sets, with each P atom having one relatively acute angle (~90°) and two more obtuse angles (~100°), which is presumably a reflection of the known ability of phosphorus to adopt flexible bond angles in order to maintain strong bonding. This is, to our knowledge, the first structural characterisation of a stable organo derivative of the P<sub>8</sub> core of Hittorf's phosphorus compound, although we note that the same P<sub>8</sub> core topology is present in the transition metal clusters [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>4</sub>Fe<sub>4</sub>(CO)<sub>6</sub>P<sub>8</sub>],<sup>18</sup> [(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>Me)<sub>6</sub>Fe<sub>6</sub>(CO)<sub>13</sub>P<sub>8</sub>]<sup>18</sup> and [{Ir(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(CO)}<sub>2</sub>{Cr(CO)<sub>5</sub>}<sub>3</sub>P<sub>8</sub>]<sup>19</sup> and as part of the central framework of the larger organophosphanes P<sub>10</sub>Pr<sub>4</sub><sup>20</sup> and P<sub>12</sub>Pr<sub>4</sub>.<sup>21</sup> The dimensions of the P<sub>8</sub> core of **3** are consistent with these previously characterised examples of the P<sub>8</sub> framework in molecular species,<sup>18,19,21</sup> but contain a narrower range of P–P distances than is observed in the P<sub>8</sub> units in Hittorf's violet and related phosphorus allotropes, which show two relatively elongated bonds in each P<sub>8</sub> unit.<sup>22–24</sup>

Given the stoichiometry of the reaction, the origin of the P<sub>8</sub> cage is unclear. Rather curiously, we note that mass spectrometry (EI) on a pure crystalline sample of **1** gives rise to a signal characteristic of **3**, suggesting that it may arise through decomposition of the 1,2,3-triphosphaindenyl anion.

Attempts to mimic this in the laboratory have so far proved fruitless.

Related polycyclic phosphanes have a rich history which has been extensively probed by the group of Baudler. In a series of seminal papers, she reported syntheses of many large and elaborate phosphanes from reduction of dihalophosphanes under a variety of conditions. Of particular relevance to the current account is the report of synthesis of  $P_8Pr^i_4$ ,<sup>25</sup> for which the  $\alpha$ - $P_8(4)$  isomer undergoes facile irreversible isomerisation under thermal conditions to form a  $\beta$ - $P_8(4)$  skeleton<sup>6</sup> with a tricyclo[3.2.1.0<sup>2,4</sup>]octaphosphane core. The apparent instability of the  $\alpha$ - $P_8(4)$  species was identified to be a result of the eclipsed nature of the organic groups which destabilise the structure. This is supported by MNDO calculations (using  $P_8Me_4$  as a model) which revealed that the tricyclo[3.2.1.0<sup>2,4</sup>]octaphosphane isomer is more stable than the tricyclo[3.3.0.0<sup>3,7</sup>]octaphosphane isomer built from four pentagonal units by 4.3 kcal mol<sup>-1</sup>, leading the authors to suggest that the  $\alpha$ - $P_8(4)$  configuration would only be stabilised by incorporation into a larger  $P_n$  framework. We attribute the stability of the  $\alpha$ - $P_8(4)$  core of **3** to the fact that the bidentate 1,2- $P_2C_6H_4$  template (rather than the monodentate RP units in previous studies) affords kinetic stabilisation of the cluster by blocking isomerisation to a tricyclo[3.2.1.0<sup>2,4</sup>]octaphosphane isomer.

In summary, the preparation of **1–3** has shown the synthetic utility of commercially available 1,2-diphosphenobenzene in the synthesis of both pnictogen containing analogues of the indenyl anion and kinetically stabilised cage polyphosphorus molecules. A detailed exploration of the coordination chemistry of the anionic ligands is currently underway in our laboratory, and we are seeking to optimise the conditions for the synthesis of **3** in order to explore the reaction chemistry of the  $P_8R_4$  ( $R = C_6H_4$ ) system.

During the course of the preparation of this manuscript, it was reported that the highly sensitive 2-stiba-1,3-diphosphenindenyl anion can be prepared by metallation of the dilithium salt of 1,2-diphosphenobenzene with  $Sb(NMe_2)_3$ .<sup>26</sup>

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## Notes and references

‡ The reaction of 1,2-diphosphenobenzene with 4 equivalents of  $Bu^tLi$  requires comment. The procedure used is simply a diphosphine variant of the dilithiation procedure reported previously for a range of primary phosphines (see ref. 8b). Stepwise addition of each equivalent of  $Bu^tLi$  results in a distinct colour change of the solution, but the <sup>31</sup>P NMR spectrum following addition of all four equivalents of  $Bu^tLi$  defies simple explanation, with no signal being identifiable even though the product(s) is soluble in THF solution. Nevertheless, in common with many related multi-lithiated systems, the species behaves as a tetraanionic reagent; indeed with respect to formation of dianions, the acronym QUADAC (Quasi Dianion Complexes) has been coined in relation to species that may not be formally dianions but simulate the reactivity of one.

§ CCDC 655738–655739, 666609–666610. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717204d

¶ The <sup>31</sup>P NMR spectrum of an  $\alpha$ - $P_8$  core would be expected to give an AA'MM'XX'X''X''' spectrum. We calculated the spectrum for **3** which gave broad multiplets at  $\delta = 130.8$ , 101.5 and 37.6 ppm; although the chemical shifts and appearance of computed and experimental resonances are similar, we have never been able to satisfactorily model the spectrum to extract the coupling constants. This may be a result of dynamic effects similar to those observed for other cyclic oligophosphanes, but our attempts to probe this by low-temperature NMR have been thwarted by the poor solubility of **3** at low temperatures.

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