

Direct synthesis of the 1,2,3-[C₆H₄P≡P≡P][−] anion, isoelectronic with the indenyl anion [C₆H₄CH≡CH≡CH]^{−†}

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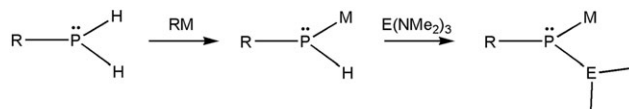
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The two products obtained from the reaction of 1,2-(PH₂)₂C₆H₄ with the mixed-metal base ⁿBuLi–Sb(NMe₂)₃ in the presence of 12-crown-4, [Li(12-crown-4)₂]⁺[C₆H₄P₃][−] (**1**) and {[Li(12-crown-4)₂]⁺}₃[Sb₁₁]^{3−} (**2**), represent thermodynamic sinks in which P–P and Sb–Sb bonding are maximized at the expense of P–Sb bonding, providing access to the 1,2,3-[C₆H₄P₃][−] phospholide anion.

A major area of research for us in the past ten years has been the investigation of the synthesis and properties of heterometallic *p*-block element–alkali metal cages, containing bridging phosphanediide ligands (RP^{2−}).¹ General access to these species is provided by the stepwise deprotonation of primary phosphines with alkali metal reagents [RM], followed by reaction with the potent bases E(NMe₂)_n (E = *p*-block element; M = alkali metal) (Scheme 1). A particular interest in this area stems from the realization that such heterometallic *p*-block metal phosphanediides are thermodynamically destabilized with respect to P–P and metal–metal bond formation.² The primary driving force for the decomposition of these complexes is the exceptionally high value of the homoatomic P–P bond energy, which at 201 kJ mol^{−1} is the highest of all of the group 15 elements. This gives a type of cage-to-alloy reaction which provides the means to deposit photoactive alkali metal alloys from solution at low temperature, as seen in the Sb^{III}–Li complex {[Sb(PCy)₃]₂Li₆·6Me₂NH} (Cy = cyclohexyl) which decomposes at 30–40 °C to give the Zintl compound [Sb₇{Li·2Me₂NH}₃]₂,² effectively a molecular alloy containing the nortricyclic Sb₇^{3−} anion. The byproduct of this reaction, the cyclic phosphane [CyP]₄, represents the other side of the thermodynamics and provides the principal driving force for the overall reaction.

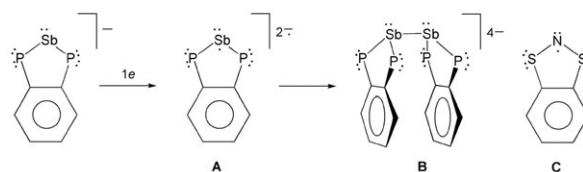
More recently, we have explored the use of mixed-base systems of the type RM–E(NMe₂)_n in the multiple deprotonation of multifunctional organic acids.^{3–5} Pertinent to the current study, the reaction of ⁿBuLi–Sb(NMe₂)₃ with 1,2-(PH₂)₂C₆H₄ in neat TMEDA (= Me₂NCH₂CH₂NMe₂) gives [C₆H₄P₂Sb][−][Li(TMEDA)₂]⁺, containing the 6π aromatic anion [C₆H₄P₂Sb][−].⁵ However, if the same reaction is under-



Scheme 1 Stepwise deprotonation of a primary phosphine to a phosphanediide (RP^{2−}).

taken in the presence of a stoichiometric amount of TMEDA in thf then one-electron reduction of this anion occurs, resulting in the ion-paired complex [C₆H₄P₂Sb]₂(Li·TMEDA)₄ containing the Sb–Sb bonded distibane anion [C₆H₄P₂Sb]₂^{4−} (**B**) (Scheme 2).⁵ DFT calculations of the latter tetraanion show that dissociation into the radical dianion constituents [1,2-C₆H₄P₂Sb]^{2•−} (**A**) should occur in the absence of Li⁺ coordination. The latter would be isoelectronic with the well known dithiazolyl radicals (**C**), which have extensive potential applications in magnetic storage devices.

In order to test this hypothesis, the reaction of 1,2-(PH₂)₂C₆H₄ with ⁿBuLi–Sb(NMe₂)₃ was repeated now in thf in the presence of 12-crown-4. The stability of the sandwich cation [Li(12-crown-4)₂]⁺ and its ability to promote charge separation have long been established,⁶ and its formation, we reasoned, might favour the ion-separated complex {[Li(12-crown-4)₂]⁺}₂[1,2-C₆H₄P₂Sb]^{2•−}. However, remarkably, the major product of this reaction is [Li(12-crown-4)₂]⁺[1,2-C₆H₄P₃][−] (**1**) (47% isolated yield) (see ESI[†]), as shown by *in situ* ³¹P NMR spectroscopy of the reaction solution.⁷ This reaction occurs using a variety of conditions, more slowly in thf–12-crown-4 at room temperature but more rapidly in thf alone or thf–12-crown-4 at reflux. In contrast, **A** and **B** (Scheme 2) were obtained at room temperature in our previous study² and represent potential intermediates in this reaction. Prolonged storage of the reaction also gives the Zintl compound {[Li(12-crown-4)₂]⁺}₃[Sb₁₁]^{3−} (**2**). Although the mechanism of this intriguing reaction is currently unknown, this route provides a route to the 1,2,3-benzo-triphospholide anion [1,2-C₆H₄P₃][−]. It can be noted that *in situ* ³¹P NMR studies show that the reactions of 1,2-(PH₂)₂C₆H₄ with ⁿBuLi



Scheme 2

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[†] Electronic supplementary information (ESI) available: Synthesis of **1** and **2**, X-ray data for **1** and **2**, NBO calculations and NMR data for the anion of **1**. See DOI: 10.1039/b718425e

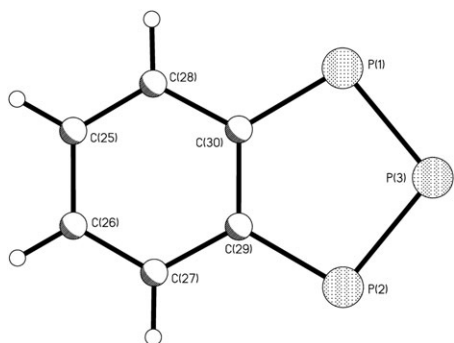


Fig. 1 The $[\text{C}_6\text{H}_4\text{P}_3]^-$ anion found in **1**. Selected bond lengths (Å) and angles ($^\circ$); P(1)–P(3) 2.0923(5), P(2)–P(3) 2.0881(5), P(2)–C(29) 1.7760(11), P(1)–C(30) 1.774(1), C(25)–C(28) 1.369(2), C(25)–C(26) 1.409(2), C(26)–C(27) 1.375(2), C(27)–C(29) 1.418(2), C(29)–C(30) 1.434(2), C(28)–C(30) 1.426(2), P(2)–P(3)–P(1) 101.08(2), C(29)–P(2)–P(3) 99.19(4), C(30)–P(1)–P(3) 99.00(4), C(29)–C(30)–P(1) 120.51(9), C(28)–C(30)–P(1) 121.28(9).

(4 equiv.) or $\text{Sb}(\text{NMe}_2)_3$ alone (1 equiv.) in the presence of 12-crown-4 under the same conditions as before do not generate **1**. Evidence of the formation of **1** is seen in the ^{31}P NMR spectrum, showing the presence of an $\text{AA}'\text{B}$ system composed of two doublet of doublets due to the coupling of the nearly-equivalent 1- and 3-P atoms ($\delta = 260.7$) with the central 2-P atom ($\delta = 335.2$) [$^1J_{\text{P}(1,3)\text{-P}(2)} = \text{ca. } 500 \text{ Hz}$, $^2J_{\text{P}(1)\text{-P}(3)} = \text{ca. } 10 \text{ Hz}$] (see ESI †). Although the spectrum of **1** is similar to that of the parent ion $[(\text{CH})_2\text{P}_3]^-$ [ABB' system with $\delta(1,3) = 262.9$, $\delta(2) = 273.1$, $^1J_{\text{P}(1,3)\text{-P}(2)} = 485 \text{ Hz}$, $^2J_{\text{P}(1)\text{-P}(3)} = 8.6 \text{ Hz}$],⁸ the particularly high chemical shift observed for P(2) compared to other 1,2,3-phospholide anions is worthy of note.^{8,9} This chemical shift is similar to that found in $[(\text{RN})_2\text{P}]^-$ ligands, which also contain two-coordinate P^{III} .¹⁰ Surprisingly, bearing in mind the greater electronegativity of N compared to P, the ^{13}C chemical shift of the quaternary carbon atoms in the anion of **1** ($\delta = 173.1$) is significantly higher than that found in the benzo-triazolyl anion of $[\text{C}_6\text{H}_4\text{N}_3\text{Li}\cdot 2\text{DMSO}]_\infty$ ($\delta = 145.3^{11}$).¹²

6 π -Phosphorus heterocycles $[(\text{CH})_n\text{P}_{5-n}]^-$ ($n = 0\text{--}4$) form an important link between organic and inorganic chemistry.¹³ However, although the chemistry of 1,3,4-triphospholide ions is well developed, far less is known about the chemistry of 1,2,3-triphospholides and there is no simple route to the 1,2,3-phospholide framework.¹⁴ For example, the parent ion 1,2,3- $[(\text{CH})_2\text{P}_3]^-$ can only be obtained as a mixture with $[(\text{CH})\text{P}_4]^-$ from the thermolysis of P_4 and Na in diglyme,⁸ and the 1,2,3- $[(\text{PhC})_2\text{P}_3]^-$ ligand can only be obtained either from a multi-step synthesis⁹ or *via* reaction at a transition metal centre.¹⁵ The importance of obtaining **1** is that it provides a very ready crystalline source of the 1,2,3-benzo-phospholide anion, which is the first phospholide analogue of the indenyl anion $[\text{C}_6\text{H}_4(\text{CH})_3]^-$. It can be noted, of course, that this is also a homologue of the triazolyl anion $[\text{C}_6\text{H}_4\text{N}_3]^-$, which has been used extensively in coordination chemistry.^{11,16}

The low-temperature X-ray structure of **1** (Fig. 1) confirms the identity of the product which consists of separate $[\text{Li}(12\text{-crown-4})_2]^+$ and $[\text{C}_6\text{H}_4\text{P}_3]^-$ ions. \ddagger This is only the second structurally-characterised 1,2,3-triphospholide complex to be reported, the only other example being the organo-

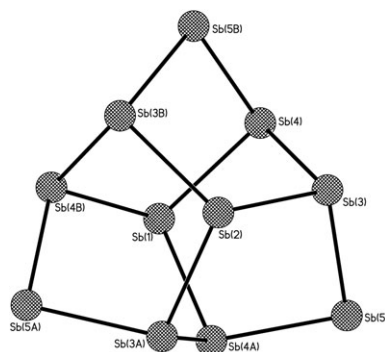


Fig. 2 One of two independent C_3 -symmetric Sb_{11}^{3-} anions of **2**.

metallic complex $[(\eta^5\text{-}1,2,4\text{-tBu}_3\text{C}_5\text{H}_2)\text{Fe}\{\eta^5\text{-(CPh)}_2\text{P}_3\}]^{15}$. The P=P bonds within the C_2P_3 heterocyclic ring of the anion of **1** are typical of P=P single bonds [2.0881(5)–2.0923(5) Å].¹⁷ In addition, the C=P bond lengths [mean 1.775 Å] are only slightly shorter than expected for single C–P bonds [ca. 1.80–1.83 Å; *cf.* C=P bonded ylides (1.63–1.71 Å)].¹⁷ Interestingly, within the C_6H_4 unit the C=C bond lengths within the 1,4-butadiene fragment $\text{C}(27)=\text{C}(26)=\text{C}(25)=\text{C}(28)$ [range 1.369(2)–1.409(2) Å] are significantly shorter than the C=C bonds within the $\text{C}(28)=\text{C}(30)=\text{C}(29)=\text{C}(27)$ fragment [range 1.418(2)–1.434(2) Å]. The pattern of bond lengths within the anion of **1** appears to suggest a significant degree of charge transfer is occurring from the P=P=P unit to the C_6H_4 ring unit.

The Zintl compound $\{[\text{Li}(12\text{-crown-4})_2]^+\}_3[\text{Sb}_{11}^{3-}]$ (**2**), the minor isolated product of the reaction, could only be characterized by low-temperature X-ray crystallography \ddagger since removal from the reaction solution or drying of crystals led to decomposition.¹⁸ Although the X-ray data are of poor quality, owing to rapid decomposition of crystals in the X-ray beam, nonetheless the identity of the anion was shown to be Sb_{11}^{3-} (Fig. 2).

Other, isostructural E_{11}^{3-} anions ($\text{E} = \text{P}, \text{As}, \text{Sb}$) have been structurally characterized previously,¹⁹ obtained in the conventional way by addition of group 15-alkali metal alloys to $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{NH}_3(\text{l})$ followed by stabilization with crown ethers or 2,2,2-crypt.¹⁸ While we have observed formation of Zintl ions during cage-to-alloy reactions involving heterometallic single-source precursors in earlier studies,² we have not previously identified examples of these larger Zintl ions. The reason for the formation of the Sb_{11}^{3-} anion (as opposed to the Sb_7^{3-} observed in all cases previously) appears to be largely thermodynamic, as is indicated by the fact that decomposition of our original precursor $\{[\text{Sb}(\text{PCy})_3]_2\text{Li}\cdot 6\text{Me}_2\text{NH}\}^3$ now in the presence of excess 12-crown-4 also gives **2**.²⁰ Thus, it appears that the thermochemical radius of the cation and its associated effect on the lattice energy are the primary influences on the Zintl ion formed.

Overall, the formation of **1** and **2** provides perhaps the most dramatic illustration of the thermodynamic driving force associated with P–P bond formation in this type of reaction. Although the detailed mechanism is unknown at this stage, we have noted previously in regard to related alkali metal–Sn^{II} phosphanediides that a stepwise dehydrocoupling pathway is the most likely course in the initial steps in this type of

reaction.²¹ Stephan and coworkers have described related chemistry involving the reactions of $[\text{Cp}_2^*\text{ZrH}_3]^-$ with primary phosphines.²² Interestingly, the reaction involving 1,2-(PH_2)₂ C_6H_4 follows a different course to the current study, giving the dimeric tetraphosphane $[(\text{C}_6\text{H}_4\text{P})\text{PH}]_2$ as an intermediate,^{22a,22b} which then couples into the cyclic octamer $[\text{C}_6\text{H}_4\text{P}_2]_8$. The formation of **1** in our case is particularly surprising since, although it is uncertain whether it actually involves the anions **A** and **B** as intermediates (Scheme 2), it must involve a C–P bond cleavage step.

DFT calculations at the B3LYP/6-311G* level combined with NBO analysis²³ allow a comparison to be made between the isoelectronic phospholide $[\text{C}_6\text{H}_4\text{P}_3]^-$ (**D**), indenyl $[\text{C}_6\text{H}_4(\text{CH})_3]^-$ (**E**) and triazolyl $[\text{C}_6\text{H}_4\text{N}_3]^-$ (**F**) anions (ESI†). The $\text{P}=\text{P}=\text{P}$ unit of **D** only carries *ca.* $-0.10e$ of the overall charge of the anion, with significant charge transfer occurring to the C_6H_4 ring (total charge *ca.* $-0.90e$). In the case of **E** the charge is split almost equally between the $\text{CH}=\text{CH}=\text{CH}$ ($-0.47e$) and C_6H_4 ($-0.52e$) groups. However, in **F** the division of charge is almost the inverse of that found in **D**, with the $\text{N}=\text{N}=\text{N}$ unit carrying $-0.85e$ and the C_6H_4 ring *ca.* $-0.15e$ of the overall negative charge. The increase in the negative charge found within the allylic fragments moving from **D**, **E** and **F** is clearly the result of the increase in electronegativity moving from P ($\chi_{\text{Pauling}} = 2.19$), to C (2.54), to N (3.05).²⁴ It should be noted also that whereas all of the N and C atoms in the indenyl (**E**) and triazolyl (**F**) anions are negatively charged, only the central P atom of the triphospholide is negatively charged, with the other two being almost neutral. Despite these differences in charges and charge distribution, all three anions have a similar amount of π -bonding between the P, N and C atoms of their allylic fragments (*i.e.*, *ca.* $1\sigma + 1/3\pi$). From these calculations, it is easy to see why the triazolyl anion (**F**) commonly behaves as an N_3 -donor set to metal ions.¹³ On the other hand, the indenyl anion (**E**) is known to adopt a range of π -(η^5 - or η^3 -) or σ -(η^1 -) bonding modes.¹⁵ The extent of charge transfer to the C_6H_4 ring unit and the relatively small fraction of the negative charge carried by the $\text{P}=\text{P}=\text{P}$ in **D** are suggestive of a generally greater tendency to π -bond than the nitrogen counterpart (**F**), and a closer similarity to the behaviour of the indenyl anion.

In summary, we have reported a very simple synthesis of a 1,2,3-triphospholide anion promoted *via* a surprising P–P bond formation reaction. This route to this anion now offers the potential for the systematic exploration of the coordination and organometallic chemistry of this ligand in relation to its indenyl and triazolyl analogues.

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† CCDC 668765–668766. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718425e

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