

# Synthesis, structure and reactivity of a cyapho-cyanamide salt

Doruk Ergöçmen<sup>[a]</sup> and Jose M. Goicoechea<sup>\*[a]</sup>

[a] Mr. D. Ergöçmen, Prof. Dr. Jose M. Goicoechea  
Department of Chemistry  
University of Oxford  
Chemistry Research Laboratory, 12 Mansfield Road, Oxford, OX1 3TA, U.K.  
E-mail: jose.goicoechea@chem.ox.ac.uk

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**Abstract:** We describe a facile synthesis of the cyapho-cyanamide salt  $[\text{Na}(18\text{-crown-6})][\text{N}(\text{CN})(\text{CP})]$  from reaction of  $[\text{Na}(18\text{-crown-6})][\text{PH}_2]$  (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) with dimethyl *N*-cyanocarbonimidate,  $(\text{MeO})_2\text{C}=\text{N}(\text{CN})$ . The reaction proceeds with elimination of two equivalents of methanol. Careful tuning of the reaction conditions allowed for the isolation and characterization of the *N*-cyano(carboximidate)phosphide intermediate  $[\text{HP}\{\text{C}(\text{OMe})\text{N}(\text{CN})\}]^-$ . Due to the adverse effects of methanol in these reaction mixtures, a bulk scale synthesis of  $[\text{Na}(18\text{-crown-6})][\text{N}(\text{CN})(\text{CP})]$  could be achieved by addition of a base (LiHMDS) to neutralize the resulting alcohol. Further reactivity studies of this anion reveal that functionalization at the phosphorus atom is viable to yield a new family of cyanide-functionalised phosphorus heterocycles.

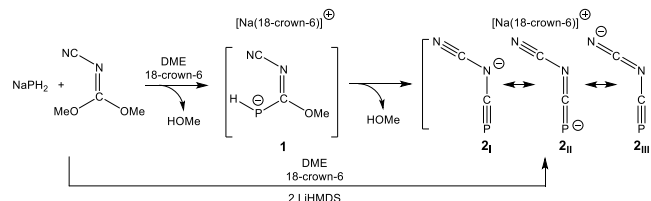
Sodium dicyanamide ( $\text{Na}[\text{N}(\text{CN})_2]$ ) was first synthesised by Madelung and Kern from the reaction of disodium cyanamide ( $\text{Na}_2[\text{NCN}]$ ) with cyanogen bromide ( $\text{BrCN}$ ).<sup>[1]</sup> Due to its inherent stability, high degree of conjugation, and wealth of coordination modes, it has been widely employed in a number of technologically relevant areas. For example, ionic liquids of the dicyanamide ion have received significant attention on account of their low viscosity and high conductivity.<sup>[2–7]</sup> Similarly, in coordination chemistry, metal-dicyanamide coordination polymers have been shown to exhibit interesting luminescent and magnetic properties.<sup>[8–16]</sup>

Analogues of the dicyanamide ion in which one (or several) of the nitrogen atoms are replaced by a heavier group 15 element are rare. The dicyanophosphide ion ( $[\text{P}(\text{CN})_2]^-$ ) was first synthesised by Schmidpeter in 1977 and structurally authenticated two years later,<sup>[17,18]</sup> however the reported syntheses for this anion were low yielding and atom inefficient.<sup>[17–20]</sup> As a result, the chemistry of this ion has remained unexplored for the last forty years. Recently, Macdonald and co-workers reported a convenient synthesis of this species (and its heavier arsenic-containing analogue,  $[\text{As}(\text{CN})_2]^-$ ) by reaction of a cyclic 2-phosphido-1,3-diphosphonium salt (or its 2-arsido- congener) with tetraphenylphosphonium cyanide.<sup>[21]</sup> This discovery will no doubt stimulate further research on the chemistry of  $[\text{E}(\text{CN})_2]^-$  ions ( $\text{E} = \text{P}, \text{As}$ ).

In principle, a number of other ions are available by exploiting the valence isoelectronic relationship of the group 15 elements. Anions such as  $[\text{Pn}(\text{CP})_2]^-$  ( $\text{Pn} = \text{N–Bi}$ ) may become available with the advent of a suitable cyaphide ( $\text{CP}^-$ ) precursor.<sup>[22]</sup> Similarly, constitutional isomers of  $[\text{P}(\text{CN})_2]^-$ , such as  $[\text{N}(\text{CN})(\text{CP})]^-$  may also be invoked, however to the best of our knowledge, no such

isomers of dicyanophosphide are known. A related phosphanyl cyanophosphide  $[(\text{NHP})\text{PCN}]^-$  ( $\text{NHP} = \text{N-heterocyclic phosphonium}$ ) was recently reported by Borger, Grützmacher and co-workers, and shown to act as a source of the formally dianionic  $[\text{PCN}]^{2-}$  ion.<sup>[23]</sup> While this dianion has the same core atoms of the targeted  $[\text{N}(\text{CN})(\text{CP})]^-$  ion, functionalization at the nitrogen atom has yet to be realized. Compounds with the same  $\text{P}=\text{C}=\text{N}$  core such as phosphacumulenes,  $\text{RP}=\text{C}=\text{NR}'$ ,<sup>[24–27]</sup> aminophosphaalkynes,  $\text{R}_2\text{NCP}$ ,<sup>[28–30]</sup> and their anionic counterparts,  $[\text{RNCP}]^-$ ,<sup>[31–32]</sup> have been previously reported via a number of synthetic routes. Herein we explore the synthesis of the cyapho-cyanamide ion,  $[\text{N}(\text{CN})(\text{CP})]^-$  by making use of a synthetic strategy that has previously proven successful for the synthesis of the 2-phosphaethynolate anion ( $\text{PCO}^-$ ),<sup>[33]</sup> and of its heavier congeners  $\text{AsCO}^-$  and  $\text{PnCC}^-$  ( $\text{Pn} = \text{P}, \text{As}; \text{Ch} = \text{S}, \text{Se}$ ).<sup>[34,35]</sup>

In the first instance we attempted the reaction of a dimethoxyethane (DME) solution of sodium phosphanide ( $\text{NaPH}_2$ ) with dimethyl *N*-cyanocarbonimidate (also referred to as *N*-cyano-isocyanate-dimethylacetal),  $(\text{CN})\text{N}=\text{C}(\text{OMe})_2$ , in the presence of 18-crown-6.<sup>[36]</sup> This reaction affords dark orange solutions over the course of 24 hours (Scheme 1). *In situ*  $^{31}\text{P}$  NMR spectroscopy reveals the presence of three compounds, two of which occur as doublets at  $-82.1$  and  $-85.7$  ppm [corresponding to two isomers of *N*-cyano(carboximidate)phosphide,  $[\text{HP}\{\text{C}(\text{OMe})\text{N}(\text{CN})\}]^-$  (**1**)], and a singlet resonance at  $-234.5$  ppm arising from the target anion,  $[\text{N}(\text{CN})(\text{CP})]^-$  (**2**). Over time (or on heating), the two doublets decrease in intensity and the singlet becomes the predominant product. However, it was found that the methanol generated as a side product of this reaction had a deleterious effect on the synthesis of the target compound, and consequently the procedure was optimised to ensure that  $[\text{Na}(18\text{-crown-6})][\text{2}]$  could be prepared as a compositionally pure product.

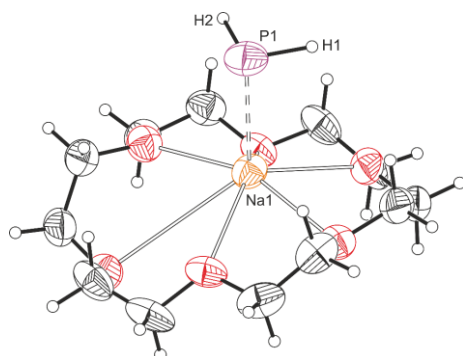


**Scheme 1.** Formation of ions **1** and **2** from reaction of  $\text{NaPH}_2$  with dimethyl cyanocarbonimidate.

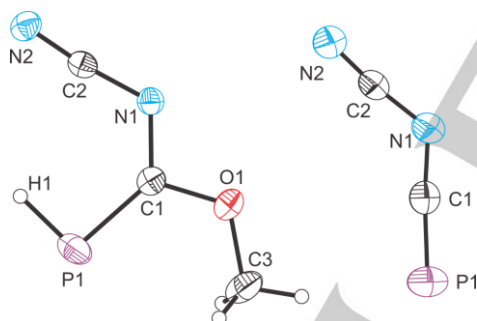
In an effort to obtain cleaner reaction mixtures,  $[\text{Na}(18\text{-crown-6})][\text{PH}_2]$  was synthesised and isolated as a compositionally pure

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compound on a multi-gram scale.<sup>[37]</sup> This compound exhibits a triplet resonance in its  $^{31}\text{P}$  NMR spectrum at  $-283.5$  ppm ( $^1J_{\text{P-H}} = 138.9$  Hz) which collapses to a singlet on proton decoupling. Further characterization of this species by single crystal X-ray diffraction (Figure 1) and combustion analysis confirmed its identity and compositional purity. With  $[\text{Na}(18\text{-crown-6})][\text{PH}_2]$  in hand, we turned to reactions with *N*-cyano(carboximidate)phosphide. It was found that low temperatures ( $-78$  °C) favoured the formation of **1**, whereas upon warming to room temperature, this species eliminated methanol to afford **2**. In order to avoid the deleterious effects of methanol in the reaction mixture, Li(HMDS) was added to neutralise the alcohol.



**Figure 1.** Molecular structure of  $[\text{Na}(18\text{-crown-6})][\text{PH}_2]$ . Anisotropic displacement ellipsoids pictured at 50% probability. There are two crystallographically independent  $[\text{Na}(18\text{-crown-6})][\text{PH}_2]$  units in the asymmetric unit, for clarity bond metric data for only one of them is provided. Selected bond lengths (Å) and angles (°):  $\text{Na1}\cdots\text{P1}$ , 2.8922(14);  $\text{P1-H1}$ , 1.36(2);  $\text{P1-H2}$ , 1.37(2);  $\text{H1-P1-H2}$ , 98(5).



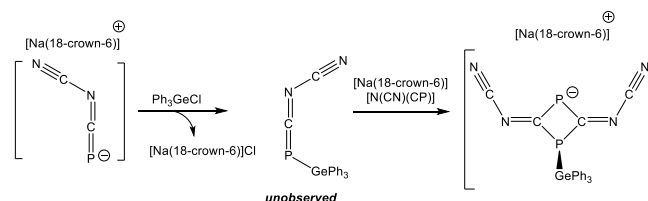
**Figure 2.** Molecular structure of the anionic components of  $\text{Na}[\text{Na}(18\text{-crown-6})][\mathbf{1}]_2$  (left) and  $[\text{Na}(18\text{-crown-6})][\mathbf{2}]$  (right). Anisotropic displacement ellipsoids pictured at 50% probability. There are two crystallographically independent anions in  $\text{Na}[\text{Na}(18\text{-crown-6})][\mathbf{1}]_2$ , for clarity bond metric data for only one of them is provided. Selected bond lengths (Å) and angles (°) **1**:  $\text{P1-C1}$ , 1.7377(11);  $\text{C1-N1}$ , 1.3525(14);  $\text{N1-C2}$ , 1.3067(14);  $\text{C2-N2}$ , 1.1617(15);  $\text{C1-O1}$ , 1.3593(13);  $\text{O1-C3}$ , 1.4294(15);  $\text{P1-C1-N1}$ , 131.40(8);  $\text{P1-C1-O1}$ , 121.06(8);  $\text{N1-C1-O1}$ , 107.52(9). **2**:  $\text{P1-C1}$ , 1.5525(18);  $\text{C1-N1}$ , 1.286(2);  $\text{N1-C2}$ , 1.303(2);  $\text{C2-N2}$ , 1.152(2);  $\text{P1-C1-N1}$ , 175.07(15);  $\text{C1-N1-C2}$ , 124.64(16);  $\text{N1-C2-N2}$ , 174.17(18).

Anions **1** and **2** were structurally characterised as  $\text{Na}[\text{Na}(18\text{-crown-6})][\mathbf{1}]_2$  and  $[\text{Na}(18\text{-crown-6})][\mathbf{2}]$ , respectively (Figure 2). As anticipated, both ions are planar due to conjugation throughout the PCNCN backbone. The structure of **1** represents an intermediate in the formation of **2** whereby the nucleophilic attack of  $\text{PH}_2^-$  at the carbon atom of dimethyl cyanocarbonimidate gives rise to the loss of one molecule of methanol. Subsequent elimination of a further molecule of methanol affords **2**. This sequential loss of LiOMe was postulated by Becker in his original

publication on the synthesis of  $\text{PCO}^-$  from  $\text{LiP}(\text{SiMe}_3)_2$  and dimethyl carbonate,<sup>[38]</sup> however, to the best of our knowledge, this is the first time an intermediate species has been isolated from such reaction mixtures. Notably on going from **1** to **2** there is a shortening of the P–C bonds in these compounds, which are 1.738(1) and 1.553(2) Å, respectively. The C1–N1 bond length also decreases, although to a lesser degree, going from 1.353(2) Å in **1** to 1.286(2) Å in **2**.

Calculations at the density functional level of theory (DFT) were carried out on **1** and **2** and reveal optimised geometries that are in good agreement with the crystallographic structures. Extensive  $\pi$ -orbital delocalisation in **1** allows for the depiction of three main resonance structures for the ion. A cyapho-cyanamide ion  $[\text{N}(\text{CP})(\text{CN})]^-$  with a formal negative charge on the central nitrogen ion (**2<sub>i</sub>**), and two heteroallene-like structures in which the formal negative charge accumulates on the terminal phosphorus (**2<sub>ii</sub>**) or nitrogen atoms (**2<sub>iii</sub>**), as depicted in Scheme 1. When compared to dicyanamide  $[\text{N}(\text{CN})_2]^-$  the replacement of one of the terminal nitrogen atoms for a heavier, less electronegative, phosphorus atom affects the overall distribution of electron density in the ion. A natural resonance theory analysis of **2** (see SI) reveals that the weighting of the resonance structures favours **2<sub>i</sub>** (30.15%), with **2<sub>ii</sub>** being the second most significant depiction of the ion (21.48%). Wiberg bond indices support the important contribution of a  $\text{N}\equiv\text{C}-\text{N}=\text{C}=\text{P}^-$  resonance structure, as the bond index for the terminal C–E bond (E = N, P) is found to decrease to 2.41 from 2.64 for dicyanamide. The highest occupied molecular orbital (HOMO) for **2** also reveals significant phosphorus atom  $p_\pi$  orbital character. Overall, this picture suggests that functionalization at the terminal phosphorus atom may be favoured over the central nitrogen atom.

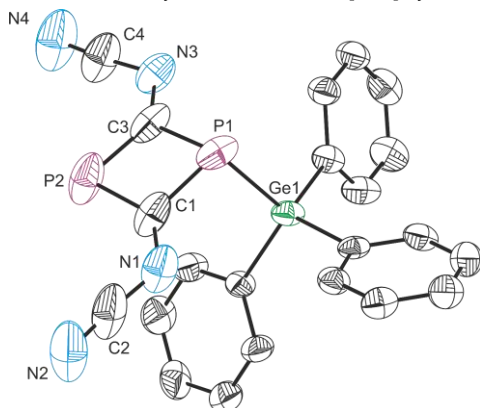
Having synthesised  $[\text{Na}(18\text{-crown-6})][\mathbf{2}]$  on a reasonable scale we were prompted to explore its reactivity towards electrophiles. Our preliminary findings thus far, show that the cyapho-cyanamide ion, is quite unreactive on account of the extensive delocalisation of negative charge throughout the anion. For example, solution of  $[\text{Na}(18\text{-crown-6})][\mathbf{2}]$  were found to be stable in the presence of water, and our attempts to protonate this species and isolate the parent acid have thus far been unfruitful. One reaction that has shown to work is the reaction of  $[\text{Na}(18\text{-crown-6})][\mathbf{2}]$  towards  $\text{Ph}_3\text{GeCl}$ . When conducted in a 1:1 ratio, this reaction give rise to a new product, and unreacted  $\text{Ph}_3\text{GeCl}$  (as evidenced in the  $^1\text{H}$  NMR spectrum). Optimisation of the reaction conditions using a 2:1 ratio gives rise to a single product exhibiting two resonances in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 50.9 ppm ( $\text{PGePh}_3$ ), 252.6 ppm ( $\text{P}\{\text{C}(\text{NCN})\}_2$ ) (Scheme 2).



**Scheme 2.** Reaction of  $[\text{Na}(18\text{-crown-6})][\mathbf{2}]$  with 0.5 equivalents of  $\text{Ph}_3\text{GeCl}$  to afford  $[\text{Na}(18\text{-crown-6})][\mathbf{3}]$ .

The structure of the resulting product was determined by single crystal X-ray diffraction (Figure 3). We postulate that formation of this compounds takes through initial functionalisation of the  $[\text{N}(\text{CN})(\text{CP})]^-$  ion at the terminal phosphorus centre to afford

a neutral intermediate which rapidly dimerises with a further equivalent of  $[\text{Na}(18\text{-crown-6})][2]$  to give the product  $[\text{Na}(18\text{-crown-6})][3]$ . Such four-member anionic heterocycles are well-established in the chemistry of the related 2-phosphaethynolate ion,  $\text{PCO}^-$ , which is known to react with heterocumulenes such as carbodiimides and isocyanates in related [2+2] cyclisations.<sup>[39,40]</sup>



**Figure 3.** Molecular structure of the anionic component of  $[\text{Na}(18\text{-crown-6})][3]$ . Anisotropic displacement ellipsoids pictured at 50% probability. Selected bond lengths (Å) and angles (°): P1–Ge1, 2.3401(16); P1–C1, 1.836(8); C1–P2 1.779(6); P2–C3, 1.779(8); C3–P1, 1.851(5); C1–N1, 1.312(8); N1–C2, 1.342(11); C2–N2, 1.157(12); C3–N3, 1.296(8); N3–C4, 1.340(8); C4–N4, 1.160(9); C1–P1–C2, 77.7(3); P1–C3–P2, 100.0(3); C3–P2–C1, 81.1(3); P2–C1–P1, 100.5(3); C1–N1–C2, 117.9(6); N1–C2–N2, 174.9(7); C3–N3–C4, 115.8(6); N3–C4–N4, 174.7(8).

To conclude, we have shown that the cyapho-cyanamide ion can be accessed by reaction of sodium phosphanide,  $\text{NaPH}_2$ , with dimethyl *N*-cyanocarbonimidate, and that an intermediate in the formation of this novel anion can be isolated and characterised. This study helps address a question first raised by Pyykkö and Zhao in 1990 as to whether ionic phosphacyanides were isolable.<sup>[41]</sup> In their article, the authors argued that the heats of formation the  $\text{PCN}^{2-}$  dianion are significantly higher than those of  $\text{N}_3^-$ ,  $\text{NCN}^{2-}$  and  $\text{PCO}^-$ . Here we demonstrate that, by use of an electron withdrawing cyanide group, the PCN moiety can be stabilized through functionalisation at the nitrogen atom in the form of  $\text{PCNCN}^-$ , and that this species can be used as a building block to novel phosphorus-containing heterocycles by functionalization with electrophiles.

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**Keywords:** multiple bonds • phosphorus • phosphanides • cyaphide • heteroallenes

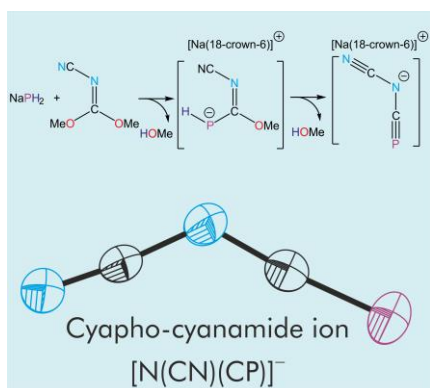
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- [36] See SI for all experimental details. CCDC 2105692–2105695 contain the supplementary crystallographic data for all of the structures reported in this paper. These can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [37] The structure of NaPH<sub>2</sub> has in [Na(DME)<sub>3</sub>][Na<sub>12</sub>(PH<sub>2</sub>)(O<sup>t</sup>Bu)<sub>12</sub>] Na<sub>13</sub>(PH<sub>2</sub>)(O<sup>t</sup>Bu)<sub>12</sub> has previously been reported here: M. Podewitz, J. D. van Beek, M. Wörle, T. Ott, D. Stein, H. Rüegger, B. H. Meier, M. Reiher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2010**, *49*, 7465–7469.
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## Entry for the Table of Contents



We describe the step-wise synthesis of the novel cyapho-cyanamide ion,  $[\text{N}(\text{CN})(\text{CP})]^-$ , obtained by the reaction of sodium phosphanide,  $\text{Na}(\text{PH}_2)$ , with *N*-cyanocarbonimidate,  $(\text{MeO})_2\text{C}=\text{N}(\text{CN})$ . Preliminary reactions of the ion with electrophiles reveal the cyclisation reactions are available on functionalisation.

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