

Main-Group Chemistry

Cyano(triphenylsilyl)phosphanide as a Building Block for P,C,N Conjugated Molecules

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Dedicated to Herbert W. Roesky on the occasion of his birthday

Abstract: The cyano(triphenylsilyl)phosphanide anion was prepared as a sodium salt from 2-phosphaethynolate. The electronic structure of this new cyano(silyl)phosphanide was studied via computational methods and its reactivity investigated using various electrophiles and Lewis acids, demonstrating its P- and N-nucleophilicity. The ambident reactivity is in agreement with computations. The silyl group also shows lability and therefore the cyano(silyl)phosphanide can be considered as a phosphacyanamide synthon, $[\text{PCN}]^{2-}$, and serves as building block for the transfer of a PCN moiety.

Phosphorus analogues of common nitrogen anions are of interest as building blocks. Examples are the development of $[\text{PCO}]^-$ chemistry in the last few decades^[1] and the recent report of a $[\text{CP}]^-$ transfer reagent.^[2] The chemistry of compounds with an $\text{NCN}^{[3]}$ unit such as in cyanamides like $\text{Ca}[\text{N}=\text{C}=\text{N}]$ produced on large scale, or carbodiimides,^[4] or species containing an NCC group^[5] is well-established. In contrast, compounds with a PCN sequence are comparatively little investigated.

Bulky substituents R and R' are required to allow isolation of 1-phospha-3-azaallenes, $\text{R}-\text{P}=\text{C}=\text{N}-\text{R}'^{[6]}$ which include functionalised derivatives with a sterically demanding disilyl,^[7] phosphanyl,^[8] or boryl^[9] substituent at phosphorus. Related phosphallenenes, $\text{R}-\text{P}=\text{C}=\text{CR}'_2$, with bulky substituents were likewise characterised.^[6a,10] Anionic P,C,N derivatives or compounds, which can at least be regarded as

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synthons for these, are especially rare. The best-known examples are salts of the dicyanophosphide anion, $[\text{P}(\text{CN})_2]^-$ **A** (Scheme 1), the phosphorus analogue of dicyanamide, first reported in 1977 by Schmidpeter et al.^[11] This anion is stable in combination with 18-crown-6 (18-C-6) coordinated sodium or potassium cations and can be obtained either by CN abstraction from $\text{P}(\text{CN})_3$ or in a disproportionation reaction of tetraphosphorus, P_4 , using potassium cyanide as a reagent.^[12]

The synthesis of stable tetraphenylphosphonium salts $[\text{Ph}_4\text{P}][\text{P}(\text{CN})_2]$ and $[\text{Ph}_4\text{P}][\text{As}(\text{CN})_2]$ is also possible while ammonium salts of $[\text{P}(\text{CN})_2]^-$ are unstable.^[13]

Various adducts of the type $(\text{NHC})-\text{PCN}$ ($\text{NHC} = \text{N}$ -heterocyclic carbene) (see **B** in Scheme 1) demonstrate the use of $[\text{P}(\text{CN})_2]^-$ as PCN transfer reagent.^[14] Remarkably, $[\text{P}(\text{CN})_2]^-$ is a weak nucleophile but reacts as an electrophile with reagents such as phenyllithium to give $[\text{P}(\text{Ph})\text{CN}]^-$.^[15] Alkynyl phosphanide **C**, a related PCC anion (Scheme 1), was prepared by deprotonation of the corresponding alkynyl-substituted secondary phosphine.^[16] 1-Aza-3-phosphaallene anions like $[\text{PCN}^i\text{Pr}]^-$ **D** (Scheme 1) behave as ambident nucleophiles and react via the nucleophilic nitrogen or phosphorus center.^[17] Deprotonation of aryl cyanophosphines gives cyanophosphides but only sterically protected species such as **I** (Scheme 1) are stable while smaller derivatives eliminate cyanide salts.^[18]

The phosphorus analogue of the cyanamide dianion, $[\text{PCN}]^{2-}$, was studied theoretically.^[19] Recently, compounds were discovered which can be viewed as synthons for $[\text{PCN}]^{2-}$. These are the phosphanyl phosphacyanide salt **E** and the bis(triphenylstannyl)phosphanyl cyanide **F** which can be used to synthesize phosphallenenes such as $\text{R}-\text{P}=\text{C}=\text{N}=\text{BR}'_2$, metal complexes such as $[(\text{LAu})_3\text{PCN}]^+$, or solutions of the parent phosphacyanamide H_2PCN .^[8] Other functionalised PCN and AsCN derivatives such as **H**,^[20] **G**^[9] and **J**,^[21] were likewise reported lately.

Here we report the synthesis of the salt $[\text{Na}(18\text{-C-6})][\text{P}(\text{SiPh}_3)(\text{CN})]$, $[\text{Na}(18\text{-C-6})][\mathbf{1}]$, and show that this push-pull-substituted phosphide $[\mathbf{1}]^-$ is a precursor to a number of compounds which contain a 1-phospha-3-aza-allene unit.

The best results were achieved by adding a freshly prepared mixture of $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ and Ph_3SiCl dissolved in toluene/DME to a concentrated solution of $\text{Na}(\text{OCP})$ in toluene/DME at -20°C , followed by warming to room temperature and stirring the reaction mixture for two days (Scheme 2, see Supporting Information for details). Then 18-C-6 is added, which allows to isolate the salt $[\text{Na}(18\text{-C-6})][\text{P}(\text{SiPh}_3)\text{CN}]$, $[\text{Na}(18\text{-C-6})][\mathbf{1}]$, as crystalline powder

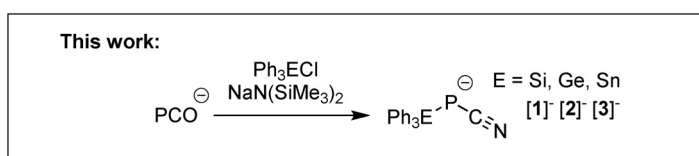
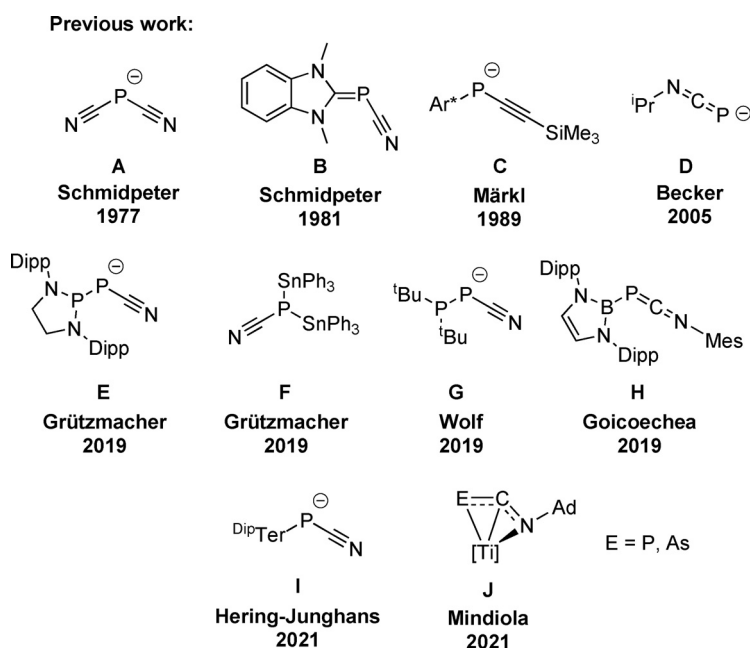
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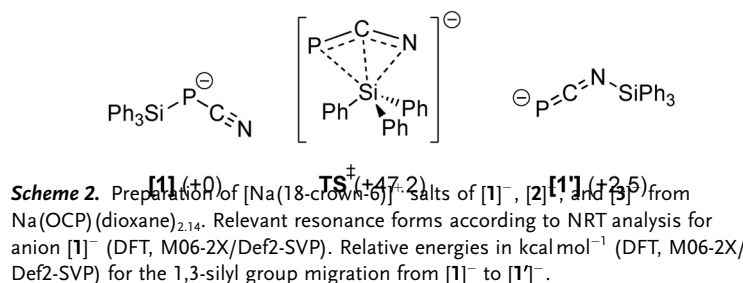
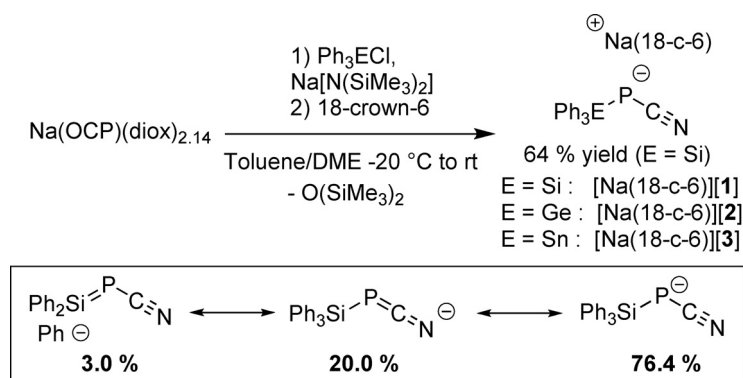
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Scheme 1. Relevant anions **A**, **C**, **D**, **F**, **I** with a central PCN or PCC unit or equivalents (**E**, **G**, **J**) thereof (Dipp = 2,6-ⁱPr₂-C₆H₃, ^{Dipp}Ter = 2,6-Dipp-C₆H₃, [Ti] = (hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate)titanium. Generic formula of silyl, germyl, and stannyl cyano phosphides [P(EPh₃)(CN)]⁻ [1]⁻, [2]⁻, [3]⁻ reported in this work (counter cation [Na(18-C-6)]⁺).



(64% yield). The ³¹P{¹H}-NMR spectrum ([D₈]THF) shows a signal at δ(³¹P) = -283 ppm (¹J_{P,Si} = 68 Hz) for the anion [P(SiPh₃)(CN)]⁻, [1]⁻.

During the synthesis, another species, **4** is detected by ³¹P{¹H}-NMR at δ(³¹P) = -295 ppm after a few hours but this signal disappears during the progress of the reaction (see below).

The germyl and stannyl phosphaketene derivatives Ph₃E-P=C=O (E = Ge, Sn) were likewise reacted with Na[N(SiMe₃)₂] to give solutions of the corresponding anions [Na(18-C-6)][P(EPh₃)CN], E = Ge: [Na(18-C-6)][2] [δ(³¹P) = -278 ppm], and E = Sn: [Na(18-C-6)][3] [δ(³¹P) = -315 ppm],^[8] respectively. But these salts are unstable and decompose forming insoluble precipitates, which in the case of [3]⁻ contained NaCN. Similar observations have been reported with anions of the type [Ar-PCN]⁻.^[18] Nevertheless single crystals of [Na(18-C-6)][2] and [Na(18-C-6)][3] were grown at low temperatures by layering a solution of [Na(18-C-6)][N(SiMe₃)₂] with a solution of Ph₃E-PCO. The structures of all compounds [Na(18-C-6)][1-3] were determined by X-ray diffraction (XRD) experiments (see the SI for details).^[27] Selected bond lengths and angles are given in Table 1. Exemplary, the structure of [Na(18-C-6)][1] in a single crystal grown from 1,2-difluorobenzene (DFB) is shown in Figure 1 showing a dimeric aggregate in which one oxygen center in each 18-C-6 acts as a bridge between two sodium cations.

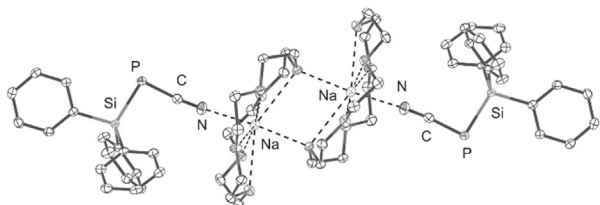
The P-C (1.760 ± 0.003 Å) and C-N (1.162 ± 0.003 Å) bond lengths in all compounds lie within a narrow range and are very similar to those observed in **D** and **F**. In contrast to [PrN=C=P]⁻ **D** (P-C 1.603(3) Å; C-N 1.248(5) Å], in which the substituent is bound to the nitrogen center, the P-C bonds in the [Ph₃E-P-CN]⁻ anions are significantly longer while the CN bond is significantly shorter. This indicates that of the two resonance structures [Ph₃E-P-C≡N] (**I**) ↔ [Ph₃E-P=C=N⁻] (**II**), the first is the main contributor to the electronic ground state. This is confirmed by DFT calculations (M06-2X/Def2-SVP, Scheme 2) and natural resonance theory (NRT), which show that the phosphide resonance structure has a weight of 76% while the 1-aza-3-phosphaallene structure has a weight of 20%.

The calculation also indicates that the P-silylated isomer [Ph₃Si-P-C≡N]⁻ [1]⁻ is slightly more stable than the N-silylated isomer [P=C=N-SiPh₃]⁻ [1']⁻ (+2.5 kcal mol⁻¹). A large energy barrier of 47.2 kcal mol⁻¹ would prevent an equilibrium via a 1,3-silyl shift (see the Supporting information for details). The transition state (**TS**) for this process shows a bent η³-bound PCN unit attached to the SiPh₃ group. Related structures have been observed in a lanthanide complex of the [SCP]⁻ anion^[22] and in a titanium complex of [Ad-NCP]⁻.^[21]

The reaction of Na(18-crown-6)[1] with one equivalent of chlorotriphenylsilane in toluene or C₆D₆ produced instant precipitation of colorless NaCl and gave a single product **4**

Table 1: Crystallographic and spectroscopic data for anions [1][−]–[3][−].

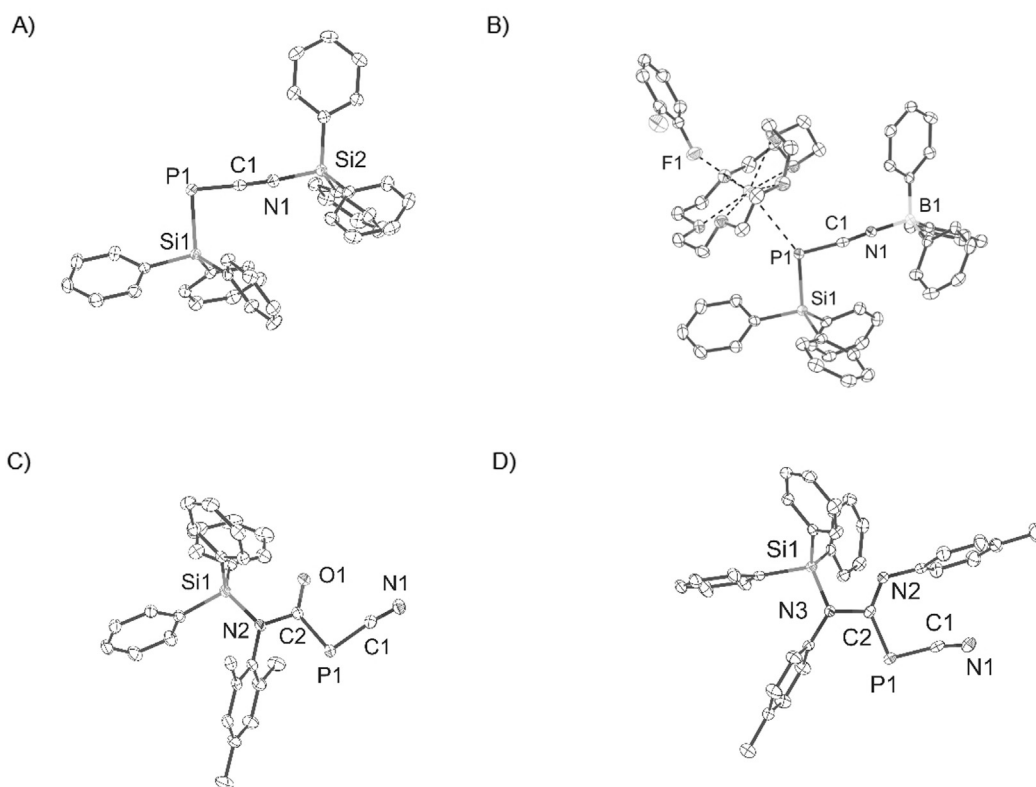
	[1] [−]	[2] [−]	[3] [−]
$\delta(^{31}\text{P})$ in ppm	−283	−278	−315
$\delta(^{13}\text{C})$ in ppm	139.5	n.d.	n.d.
P–E in Å	2.2059(4)	2.2784(5)	2.4428(6)
P–C in Å	1.761(1)	1.763(2)	1.758(2)
C–N in Å	1.161(1)	1.160(3)	1.165(3)
E–P–C [°]	95.50(4)	92.29(6)	93.15(8)

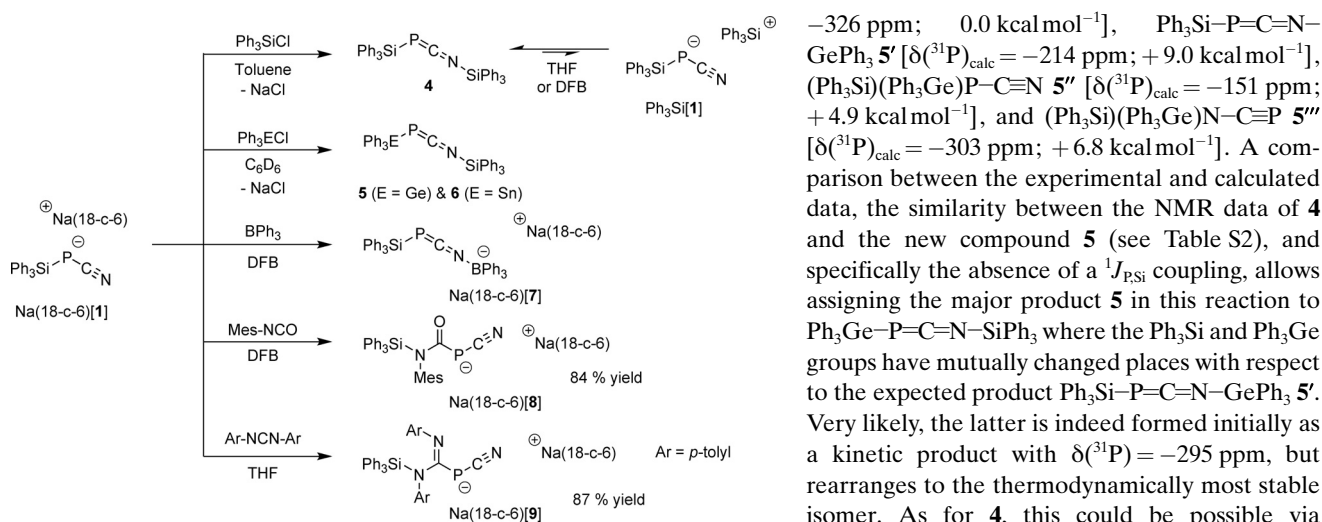
**Figure 1.** Structure of [Na(18-c-6)][1] (hydrogens omitted for clarity) showing the formation of dimers via sodium cation bridging $\mu^2\text{-O}$ oxygen centers in the 18-crown-6 units.

($\delta(^{31}\text{P}) = -295$ ppm; Table 2). ^{29}Si satellites ($^1J_{\text{P,Si}} = 47$ Hz) indicate a P–Si bond. This species is identical to the one observed as intermediate in the preparation of [1][−] (see above) and suggests that the formation of $\text{Ph}_3\text{Si-P}=\text{C}=\text{O}$ from $\text{Na}(\text{OCP})$ and Ph_3SiCl is slower than the formation of **4** from $[\text{Ph}_3\text{Si-P-CN}]^-$ and Ph_3SiCl .

Single crystals containing **4** and one 18-crown-6 molecule could be obtained at low temperature (-30°C). An XRD experiment allowed us to assign the structure of **4** unambiguously as a 1-phospha-3-azaallene $\text{Ph}_3\text{Si-P}=\text{C}=\text{N-SiPh}_3$. The structure is shown in Figure 2 A.^[27] Compound **4** decomposes in solution into an insoluble dark material over a few days (likely due to an auto-redox process).^[23]

The P–C bond distance in **4** (1.68 Å) is in the typical range of P=C double bonds^[24] and significantly shorter than the one in [1][−] (1.76 Å). On the other hand, the C–N bond distance is only slightly longer in the neutral allene **4** (1.18 Å vs. 1.16 Å in [1][−]) and still close to a C=N triple bond distance. Both, the C–N–Si angle (166°) and P–C–N angle (177°) are close to linearity while the Si–P–C angle remains small (92°). When the reaction is performed in a solvent with a polarity higher than toluene such as tetrahydrofuran (THF) or DFB, a broad resonance at $\delta(^{31}\text{P}) \approx -293$ ppm indicates a dynamic process. Upon cooling a DFB solution to 243 K, the $^{31}\text{P}\{^1\text{H}\}$ -NMR signal of **4**,

**Figure 2.** Structures of **4** (A), Na(18-crown-6)(DFB)[7] (B), Na(18-crown-6)[8] (C), and Na(18-crown-6)(THF)[9] (D) (hydrogens, THF (D), Na (C & D) and 18-crown-6 (A, C, D) omitted for clarity). Selected bond distances [Å] and angles [°]. A) **4**: P1–Si1 2.2572(5), P1–C1 1.6843(15), N1–C1 1.182(2), Si2–N1 1.7456(13); C1–P1–Si1 91.87(5), N1–C1–P1 176.57(13), C1–N1–Si2 165.74(13). B) Na(18-crown-6)(DFB)[7]: P1–Si1 2.2224(8), P1–C1 1.734(2), N1–C1 1.162(3), N1–B1 1.573(3); Si1–P1–C1 100.19(7), P1–C1–N1 174.22(18), C1–N1–B1 173.0(2). C) Na(18-crown-6)[8]: P1–C1 1.7722(14), N1–C1 1.1550(18), Si1–N2 1.7622(11), N2–C2 1.4016(15), O1–C2 1.2380(16), P1–C2 1.8243(13); N1–C1–P1 172.80(13), C1–P1–C2 94.70(6), O1–C2–P1 127.86(10), O1–C2–N2 117.48(11). D) Na(18-crown-6)(THF)[9] P1–C2 1.809(2), P1–C1 1.770(3), C1–N1 1.146(3), C2–N3 1.411(3); C2–N2 1.295(3), C1–P1–C2 99.51(10), N1–C1–P1 168.6(2).



Scheme 3. Reactions of Na(18-crown-6)[1] with various main-group element electrophiles and Lewis acids at room temperature.

including the ²⁹Si satellites, as well as a broad resonance at $\delta(^{31}\text{P}) \approx -281$ ppm typical for [1]⁻ is observed, indicating an equilibrium $[\text{Ph}_3\text{Si}-\text{P}=\text{C}=\text{N}-\text{SiPh}_3] \text{ (4)} \rightleftharpoons [\text{Ph}_3\text{Si}-\text{P}=\text{C}=\text{N}]^- [\text{Ph}_3\text{Si}(\text{solv})]^+$ (see $[\text{Ph}_3\text{Si}][1]$, Scheme 3). This prompted us to inspect the relative energies of 4 and its constitutional isomers (Ph₃Si)₂N-C≡P 4' and (Ph₃Si)₂P-C≡N 4'' by DFT. With respect to the phospho-aza-allene 4 (0.0 kcal mol⁻¹), the amino phosphoalkyne 4' is 3.0 kcal mol⁻¹, and the bis(silyl) cyano phosphane 4'' 5.1 kcal mol⁻¹ less stable. Calculations of the ³¹P-NMR chemical shifts give a very good agreement for 4 [$\delta(^{31}\text{P})_{\text{exp}} = -300$ ppm; $\delta(^{31}\text{P})_{\text{calc}} = -305$ ppm] while the calculated shifts for 4' [$\delta(^{31}\text{P})_{\text{calc}} = -98$ ppm] and 4'' [$\delta(^{31}\text{P})_{\text{calc}} = -216$ ppm] do not correspond to any experimentally observed resonances, and hence, make the presence of these species unlikely.

Upon mixing Na(18-crown-6)[1] with Ph₃GeCl in C₆D₆, three species were initially detected by ³¹P{¹H}-NMR. One major signal at $\delta(^{31}\text{P}) = -292$ ppm and two signals of low intensity at $\delta(^{31}\text{P}) = -195$ ppm and $\delta(^{31}\text{P}) = -295$ ppm. The latter disappears overnight. The ²⁹Si{¹H}-NMR spectrum shows one singlet at $\delta(^{29}\text{Si}) = -23$ ppm and one doublet of low intensity at 1 ppm ($J_{\text{P,Si}} = 48$ Hz). After 16 hours at room temperature, the resonance at $\delta(^{31}\text{P}) = -292$ ppm is the most intense one and the ¹³C{¹H}-NMR spectrum of the reaction mixture exhibits a doublet at $\delta(^{13}\text{C}) = 172$ ppm ($J_{\text{P,C}} = 95$ Hz; Table 2), which is very similar to the ¹³C-NMR resonance observed in 4 ($\delta(^{13}\text{C}) = 170$ ppm, $J_{\text{P,C}} = 89$ Hz). DFT was used to calculate the ³¹P-NMR chemical shifts and relative energies of possible isomers Ph₃Ge-P=C=N-SiPh₃ 5 [$\delta(^{31}\text{P})_{\text{calc}} =$

-326 ppm; 0.0 kcal mol⁻¹], Ph₃Si-P=C=N-GePh₃ 5' [$\delta(^{31}\text{P})_{\text{calc}} = -214$ ppm; $+9.0$ kcal mol⁻¹], (Ph₃Si)(Ph₃Ge)-P-C≡N 5'' [$\delta(^{31}\text{P})_{\text{calc}} = -151$ ppm; $+4.9$ kcal mol⁻¹], and (Ph₃Si)(Ph₃Ge)-N-C≡P 5''' [$\delta(^{31}\text{P})_{\text{calc}} = -303$ ppm; $+6.8$ kcal mol⁻¹]. A comparison between the experimental and calculated data, the similarity between the NMR data of 4 and the new compound 5 (see Table S2), and specifically the absence of a $J_{\text{P,Si}}$ coupling, allows assigning the major product 5 in this reaction to Ph₃Ge-P=C=N-SiPh₃, where the Ph₃Si and Ph₃Ge groups have mutually changed places with respect to the expected product Ph₃Si-P=C=N-GePh₃ 5'. Very likely, the latter is indeed formed initially as a kinetic product with $\delta(^{31}\text{P}) = -295$ ppm, but rearranges to the thermodynamically most stable isomer. As for 4, this could be possible via a dissociative pathway as outlined on top of Scheme 3, which is moreover supported by the fact that solutions of 5 in THF or DFB again show broad ³¹P-NMR resonances. The minor compound with $\delta(^{31}\text{P}) = -195$ ppm does not find any fit among the calculated structures, but its chemical shift agrees with the reported one of $[\text{P}(\text{CN})_2]^-$ [$\delta(^{31}\text{P}) = -193$ ppm^[11]].

The reaction of [Na(18-C-6)][1] with one equivalent Ph₃SnCl in C₆D₆ gives a very similar result. One product 6 is observed and the NMR data ($\delta(^{31}\text{P}) = -328$ ppm ($J_{\text{P,Sn}} = 795$ Hz and 833 Hz); $\delta(^{29}\text{Si}) = -28$ ppm; $\delta(^{13}\text{C}) = 169$ ppm ($J_{\text{P,C}} = 101$ Hz); Table 2) unambiguously allow to assign to this the structure Ph₃Sn-P=C=N-SiPh₃. Note that both 5 and 6 decompose slowly in solution, likely in a redox process similar to thermal decomposition of 4, and could not be obtained in pure nor crystalline form.

The reaction between Na(18-crown-6)[1] with triphenylborane in DFB gave rise to a major ³¹P{¹H}-NMR signal at $\delta(^{31}\text{P}) = -289$ ppm ($J_{\text{P,Si}} = 55$ Hz) and a broad signal at $\delta(^{31}\text{P}) = -283$ ppm of very low intensity which could not be assigned. The major compound is [Na(18-crown-6)(DFB)][Ph₃Si-P=C=N-BPh₃], Na(18-C-6)[7]. Layering the reaction solution with hexane afforded crystals of this product.^[27] In the anion [7]⁻, the boryl group binds to the nitrogen atom. As expected, the P-C bond (1.73 Å) is shorter than in the anion [1]⁻, but significantly longer than in the neutral phospho-aza-allene 4. The sodium atom has a weak contact to the phosphorus center (Na-P distance 3.07 Å) and is furthermore loosely attached to one fluorine center of DFB (Na-F distance 2.61 Å). The central P=C=N-B unit is again almost linear (P1-C1-N1 174°, C1-N1-B1 173°).

Na(18-crown-6)[1] reacts also with heteroallenes such as mesityl isocyanate or 1,3-di-p-tolylcarbodiimide as electrophiles to give Na(18-C-6)[8] and Na(18-C-6)[9] as products, respectively. ³¹P{¹H}-NMR of Na(18-C-6)[8] shows a broad resonance at $\delta(^{31}\text{P}) = -101$ ppm at room temperature in THF or DFB as solvent. Crystallisation from DFB gave single crystals suitable for XRD. The structure of Na(18-C-6)[8] is displayed in Figure 2C.^[27] Anion [8]⁻ is a phospho-cyanourea derivative^[25] with a short C-N bond (1.15 Å), an elongated P=C double bond (1.77 Å), and an almost linear PCN unit (173°). The ¹³C-NMR resonance of the C2 carbon in [8]⁻ is

Table 2: Spectroscopic data for adducts 4–6.

	4	5	6
$\delta(^{31}\text{P})$ in ppm	-295	-292	-328
$\delta(^{29}\text{Si})$ NSi in ppm	-23	-23	-28
$\delta(^{13}\text{C})$ PCN in ppm	170	172	169
$J_{\text{P,C}}$ in Hz	89	95	101

observed at $\delta(^{13}\text{C}) = 138$ ppm ($^1J_{\text{PC}} = 105$ Hz) which is very similar to the data found in $[\mathbf{1}]^-$. Note that the reaction between $\text{Mes-N}=\text{C}=\text{O}$ and the neutral phosphazaaallene, $\text{Ph}_3\text{Si-P}=\text{C}=\text{N-SiPh}_3$ ($\mathbf{4}$) gives a product with the same NMR data as seen for $\text{Na}(18\text{-C-6})[\mathbf{8}]^-$ indicating that $[\mathbf{8}]^-$ with a solvated $[\text{Ph}_3\text{Si}]^+$ as counter cation is formed as a product. The broadening of the ^{31}P -NMR resonance seen in solutions of $[\mathbf{8}]^-$ is likely due to a silatropic rearrangement whereby the N-bound Ph_3Si group in $[\text{Ar}(\text{Ph}_3\text{Si})\text{N}-(\text{C}=\text{O})-\text{P}-\text{CN}]^-$ is transferred to the oxygen center of the $\text{C}=\text{O}$ group to give $[\text{ArN}=\text{C}(\text{OSiPh}_3)-\text{P}-\text{CN}]^-$. Indeed the calculated energy difference between both isomers is only 1.4 kcal mol $^{-1}$ and the broad coalescence signal splits into two broad signals at 175 K (Supporting Information Figure S35).

A similar adduct, $\text{Na}(18\text{-crown-6})[\mathbf{9}]$ ($\delta(^{31}\text{P}) = -120$ ppm, $\delta(^{13}\text{C}) = 134$ ppm, $^1J_{\text{PC}} = 105$ Hz) is obtained from the reaction between $\text{Na}(18\text{-crown-6})[\mathbf{1}]^-$ and bis(*p*-tolyl)carbodiimide. The salt $\text{Na}(18\text{-crown-6})[\mathbf{9}]$ can be viewed as a phosphorus analogue of dicyandiamide [or 2-cyanoguanidine, $\text{H}_2\text{N}(\text{C}=\text{NH})(\text{NHCN})$]^[3a,26]. The structure of $\text{Na}(18\text{-crown-6})[\mathbf{9}]$ is shown in Figure 2D.^[27] The bond distances within the PCN unit closely resemble those of $[\mathbf{8}]^-$, with a P1-C1 distance of 1.77 Å and a C1-N1 distance of 1.15 Å. The only significant structural difference between $[\mathbf{8}]^-$ and $[\mathbf{9}]^-$ is the P-C-N angle which is closer in $[\mathbf{9}]^-$ (168°) likely because of steric repulsion between the *p*-tolyl substituent at N2 and the bulky $[\text{Na}(18\text{-crown-6})]^+$ cation which coordinates to the cyano group (Na-N1 distance 2.35 Å).

In summary, a convenient synthesis to a cyano-(silyl)phosphide, $[\text{P}(\text{SiPh}_3)(\text{CN})]^-$, $[\mathbf{1}]^-$, has been developed which in contrast to its heavier congeners, $[\text{P}(\text{EPh}_3)(\text{CN})]^-$ (E = Ge, Sn), is stable as salt with $[\text{Na}(18\text{-C-6})]^+$ as counter cation. Counterintuitively, the silyl group binds to the phosphorus center in the thermodynamically most stable isomer although the energy difference to the constitutional (expected) isomer $[\text{P}=\text{C}=\text{NSiPh}_3]^-$ is very small. In reactions with R_3ECl , 1-phospha-3-aza-allenes $\text{R}_3\text{E-P}=\text{C}=\text{N-SiPh}_3$ are obtained, even though calculations indicate that the major contributor to the electronic ground of $[\mathbf{1}]^-$ is the phosphide and not allenide form. Other possible isomers such as $(\text{Ph}_3\text{Si})(\text{R}_3\text{E})\text{P}-\text{C}\equiv\text{N}$ or $(\text{Ph}_3\text{Si})(\text{R}_3\text{E})\text{N}-\text{C}\equiv\text{P}$ are thermodynamically slightly less stable and their formation from $\text{R}_3\text{E-P}=\text{C}=\text{N-SiPh}_3$ via a 1,3- R_3E shift may be severely kinetically hindered. Reactions with electrophilic organic allenes such as isocyanates or carbodiimides allow to access new phosphacyanurea or phosphacyanoguanidine derivatives. All salts represent new functional groups in organophosphorus chemistry which may allow to prepare P,C,N conjugated molecules and materials.

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Conflict of Interest

The authors declare no conflict of interest.

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