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Synthesis and Structure of $K^+[^iPrN{=}C{=}P]^-$, a 1-Aza-3λ^3-phospha-3-allenide[†]

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2-Isopropyl(trimethylsilyl)amino-1λ^3-phosphaalkyne **1** reacts with potassium *tert*-butoxide to form potassium 1-isopropyl-1-aza-3λ^3-phospha-3-allenide (**2**). This compound was structurally characterized as the corresponding 18-crown-6 ether complex **3**. The molecular structure of **1** was also determined in order to compare the bonding situation in the anion and the neutral λ^3-phosphaalkyne. Compound **3** contains a nitrogen–carbon–phosphorus group for which the parameters were shown by X-ray structural analysis and quantum chemical calculations to lie between the extrema $N{-}C{\equiv}P$ and $N{=}C{=}P$, suggesting reactivity typical of an ambident anion. This is indeed the case, as subsequent reaction of **2** with chlorotrimethylsilane at nitrogen regenerates the λ^3-phosphaalkyne **1**; with chlorotriphenylsilane the new derivative **4** is formed. In contrast, chlorotrimethylstannane reacts at phosphorus, giving the 1-aza-3λ^3-phosphaallene isopropyliminomethylidene(trimethylstannyl)phosphane **5**.

Introduction

Since the synthesis of the thermally stable *tert*-butyl-λ^3-phosphaalkyne in 1981,[1] the chemistry of λ^3-phosphaalkynes $R{-}C{\equiv}P$ has become a well-developed field.[2] Several other stable alkyl- and aryl-λ^3-phosphaalkynes, notably where R = 1-adamantyl,[3] 2,4,6-trimethylphenyl (Mes)[4] and 2,4,6-tri-*tert*-butylphenyl (Mes*),[5] have been subsequently synthesized and their chemical properties investigated. A few heteroatom-substituted λ^3-phosphaalkynes have also been obtained and characterized, but these are either thermally unstable (R = Me_3Si,[6] $Me_3Si{-}O$,[7] F,[8] Cl[9]) or highly reactive (notably $(dme)_2Li{-}O{-}C{\equiv}P$,[10] $[(dme)_3Li]^+$-$[S{-}C{\equiv}P]^-$ [11]), restricting the scope of the investigations into their chemistry. Very recently the compounds $[Ph_4P][(F_3C)_3B{-}C{\equiv}P]$ and $[Ph_4P][(F_3C)_3B{-}C{\equiv}As]$ have been reported;[12] their unusually high thermal stability will probably open a new chapter in λ^3-phosphaalkyne and λ^3-arsaalkyne chemistry.

The nitrogen-substituted hetero-λ^3-phosphaalkynes are known to have a quite different reactivity when compared to the alkyl- and aryl-substituted compounds due to the influence of the heteroatom lone pair on the charge distribution in the multiple bond.[13,14]

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[†] Dedicated to Prof. Hubert Schmidbaur on the occasion of his 70th birthday.

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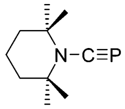

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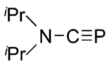

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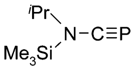


1

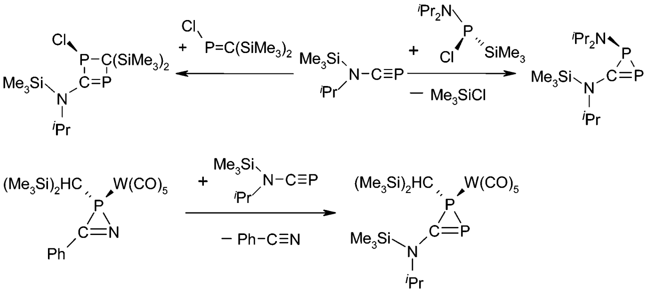
2-(2,2,6,6-Tetramethylpiperidino)-1λ^3-phosphaalkyne (**A**)[15] and the thermally unstable 2-(diisopropylamino)-1λ^3-phosphaalkyne (**B**)[16] have both been structurally characterized. No reactions, however, have been reported for the former, whereas several products of the latter are known: Grobe et al. treated $^{i}\mathrm{Pr_2N{-}C{\equiv}P}$ with diazo compounds,[14,17] and Hahn and co-workers treated it with Arduengo carbenes[13] to give five-membered heterocycles. Furthermore, Grobe et al. reacted $^{i}\mathrm{Pr_2N{-}C{\equiv}P}$ with $\mathrm{F_3C{-}P{=}CF_2}$ to furnish a 1,2-dihydro-1λ^3,3λ^3-diphosphete via [2+2] cycloaddition; they also studied the methylation of the λ^3-phosphaalkyne as well as reactions with chalcogens and with several metal complexes.[18] In contrast, although 2-isopropyl(trimethylsilyl)amino-1λ^3-phosphaalkyne **1** shows a remarkably high thermal stability,[19] to our knowledge, only three investigations by Niecke, Streubel and co-workers into the chemistry of this compound have been carried out to date; typical reactions are shown in Scheme 1.[20]

The lack of intensive studies into **1** is surprising, especially when considering the additional possibility of modifying one of the substituents of the *λ^3-phosphaalkyne itself*, namely the trimethylsilyl group. Here we present the crystal structure of **1**, the synthesis and reactivity of the 1-aza-3λ^3-phospha-3-allenide anion **2** formed by reaction of **1** with potassium *tert*-butoxide, the structure of the corresponding 18-crown-6 ether complex **3**, and the preparation of the triphenylsilyl derivative **4**.[21]

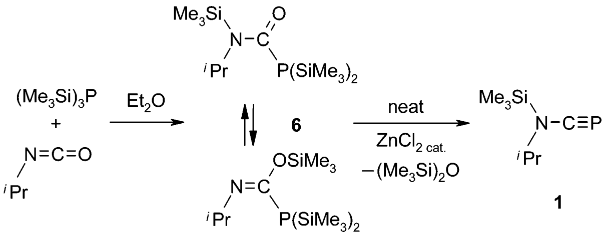
Results and Discussion

2-Isopropyl(trimethylsilyl)amino-1λ^3-phosphaalkyne (1). The synthesis of compound **1** was originally reported by Appel and Poppe.[19] During our studies we have observed that the elimination of hexamethyldisiloxane using catalytic amounts of powdered sodium hydroxide in tetraethylene glycol dimethyl ether (tetraglyme) leads to variable yields for this step (between 4 and 45%); for this reason other potential elimination catalysts, such as tetra-*n*-butylammonium fluoride[3] or aluminum trichloride[4] were investigated. Anhydrous zinc chloride was finally chosen, which results in reproducible yields for this step of about 50% and avoids the need to use a solvent (Scheme 2).

Scheme 1. Reactivity of Compound **1**



Scheme 2. Synthesis of **1**



The structure of λ^3-phosphaalkyne **1** was then determined by X-ray diffraction (Experimental Section, Table 2) using a single crystal that had been prepared by zone-melting the compound (mp −42 ± 2 °C) in a 0.3-mm capillary.[22] The molecule is characterized by a crystallographically imposed mirror plane containing the P–C–N group and the atoms C1, Si, and C21 (Figure 1). The linearity of the P–C–N group (178.68(10)°) compares well with that of 2-(2,2,6,6-tetramethylpiperidino)-1λ^3-phosphaalkyne (**A**) (178.9(1)°)[15b] and diisopropylamino-1λ^3-phosphaalkyne (**B**) (179.2(2)°).[16b] This is also true of the P,C bond length (1.5578(4) Å, cf. 1.559(2), 1.552(2) Å), but the distance is longer than that of $^{t}\mathrm{Bu{-}C{\equiv}P}$ (1.536(2), 1.542(2) Å).[23] Similarly, the neighboring C,N bond length (1.315(2) Å) compares well with those of the other two structurally characterized amino-substituted λ^3-phosphaalkynes (1.316(2) and 1.312(3) Å), but is drastically shortened with respect to the standard value corrected for $\mathrm{C}_{sp}{-}\mathrm{N}_{sp^2}$ (1.40 Å).[24] This lengthening of the P,C triple

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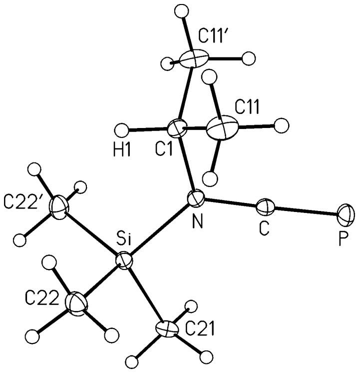
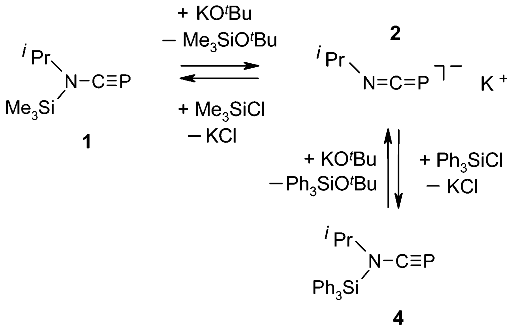


Figure 1. Molecular structure of the heteroatom-substituted λ^3-phosphaalkyne **1** (30% probability ellipsoids). Selected bond lengths and angles are presented in Table 1.

bond and a shortening of the neighboring C,N single bond along with the trigonal planar environment of the nitrogen atom (sum of angles 360.0°) indicates a strong electronic interaction of the nitrogen lone pair with the π-system of the C≡P group. Without doubt, this interaction contributes considerably to the thermal stability of compound **1**. It seems to be much higher than in λ^3-phosphaalkyne **B**, and, in our opinion, might be further attributed to steric and electronic effects of the trimethylsilyl substituent at nitrogen (Si−N 1.7738(11) Å).

Potassium 1-Isopropyl-1-aza-3λ^3-phospha-3-allenide (2) and the 18-Crown-6 Complex 3. Compound **2** was synthesized quantitatively by dropwise addition of λ^3-phosphaalkyne **1** to a solution of one equiv of potassium *tert*-butoxide in dry, oxygen-free THF at −50 °C under argon (Scheme 3). The reaction mixture was allowed to warm to room-temperature overnight; after removal of solvent and volatile *tert*-butoxytrimethylsilane under vacuum, the product could be isolated as a yellow powder and characterized by NMR spectroscopy.

Scheme 3. Synthesis and Reactions of $K^+[{}^iPrN{=}C{=}P]^-$ (**2**)



The conversion of compound **1** to the anion **2** is accompanied by a large upfield shift of the ${}^{31}P\{{}^1H\}$ signal from −137.6 (C_6D_6)[25] to −228.4 ppm (THF-d_8), indicating an at least partial localization of negative charge at phosphorus. In our opinion the electronic situation resembles that of 2-amino-1-λ^3-phosphaalkenes.[26] Whereas the P,C π bond of the parent compound $H{\sim}P{=}CH_2$ has been shown by quantum chemical methods to be essentially nonpolar, the π electron density of the amino-substituted derivative $H{\sim}P{=}C(H)NH_2$ was calculated to be inverted with a substantial negative charge at phosphorus and a positive one at nitrogen. For this class of λ^3-phosphaalkenes, upfield shifted ${}^{31}P\{{}^1H\}$ signals are also typical.

Table 1. Selected Experimental and Calculated Bond Lengths (Å) and Angles (deg)

	$\mathbf{1}_{exp}$	$\mathbf{1}_{calc}{}^a$	$\mathbf{3}_{exp}$	$[{}^iPr{-}N{=}C{=}P]^{-\,b}$
C−P	1.558(1)	1.5721	1.603(3)	1.6256
N−C	1.315(2)	1.3261	1.248(5)	1.2638
C1−N	1.499(2)	1.5036	1.490(6)	1.4574
Si−N	1.7738(11)	1.8038		
N−C−P	178.68(10)	179.70	174.8(3)	177.95
C1−N−C	117.01(10)	118.14	119.3(4)	121.17
C−N−Si	123.48(9)	121.75		

[a] B3LYP/6-31+G(d,p), −962.04041 au. [b] B3LYP/6-31+G(d,p), −552.77259 au.

To obtain crystals for further structural characterization, one equiv of 18-crown-6 was added to a THF solution of **2**; after cooling to 5 °C for one week, yellow tablets of complex **3** had deposited. The ${}^{31}P\{{}^1H\}$, ${}^{13}C\{{}^1H\}$, and ${}^1H$ chemical shifts and corresponding coupling constants are almost identical to those of the crown ether-free product **2**. Extremely large isotope shifts are characteristic for λ^3-phosphaalkynes; to verify this for compounds **2** and **3**, detailed NMR experiments have already been carried out and published along with those of the λ^3-phosphaalkyne $(dme)_2K{-}O{-}C{\equiv}P$.[25]

As shown by an X-ray structural analysis on complex **3**, the potassium cation and the N=C=P unit lie on a mirror plane which dissects the isopropyl group and the 18-crown-6 ligand at atoms O1 and O4. The potassium ion is found 0.589 Å above the average plane of the oxygen atoms of the crown ether. The N=C=P unit lies such that both the N=C and C=P bonds can interact in an η^3 fashion with the potassium cation and is slightly tilted by 6.9° with respect to the plane of the crown ether. The NCP angle (174.8(3)°) is less than the 180° expected for cumulative double bonds. Since the nitrogen and phosphorus atoms are both characterized by relatively high negative partial charges (see below) and nonbonding electron pairs, the observed deviation from linearity might be a consequence of Coulomb interactions between cation and anion. However, as this deviation from linearity is slight, it is expected to be far too small as to affect the bonding situation. Further bond lengths and angles are summarized in Table 1.

The bonding situation in the anion can be best described as lying between two extrema, namely a (phosphanetriylmethyl)amide and an iminomethylidenephosphanide (1-aza-3λ^3-phospha-3-allenide), depending on the formal localization of the negative charge at either nitrogen or phosphorus (Figure 3). From a very elementary viewpoint, the mesomeric amide form is favored by the higher electronegativity of nitrogen (N, 3.07, P, 2.06),[27] but is disadvantageous with

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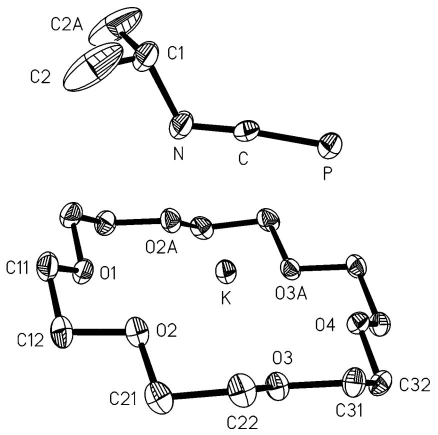


Figure 2. Molecular structure of complex **3** (30% probability ellipsoids, hydrogen atoms omitted for clarity). For bond distances and angles see Table 1. Selected contact distances and angles: N···K 3.207(4), C···K 3.041(4), P···K 3.404(1), K···O 2.818(2) to 2.898(2) Å; P−C···K 88.7(1), C−P···K 63.3(1), C−N···K 71.1(2), O···K···O 58.76(4) to 58.57(5)°.

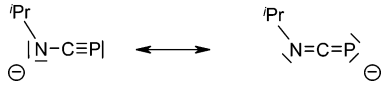
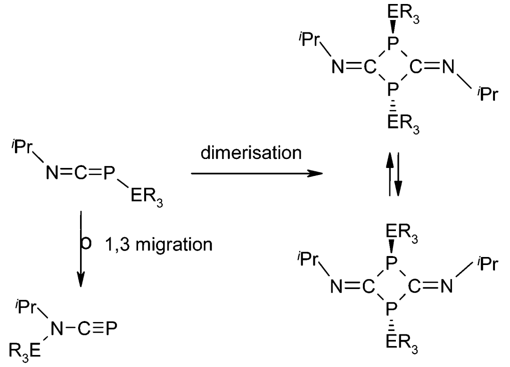


Figure 3. Mesomeric amide and phosphanide forms of the anion of compound **2**.

respect to the formation of a phosphorus−carbon triple bond. In contrast, the phosphanide form is characterized by the conversion of a nitrogen−carbon single bond (average bond energy 72.80 kcal mol^{-1}) to an energetically more stable double bond (147 kcal mol^{-1})[28] and a reduction of the phosphorus−carbon bond order. In the case of the (18-crown-6)-potassium complex, the major IR band is found at 1734 cm^{-1}, which lies between values determined for RR′N−C≡P (1588,[19] 1608,[15a] 1642[16a] cm^{-1}) and RN=C=PR′ molecules (1830 to 1915 cm^{-1}).[29] All these frequencies have been assigned to the asymmetric N−C−P stretch.[29]

Furthermore, the intermediate bonding situation is also clearly reflected in the P,C and N,C distances of the anion. As can be seen in Table 1, the P,C bond of complex **3** (1.603(3) Å) is elongated with respect to the P,C triple bond in the λ³-phosphaalkyne **1** (1.558(1) Å), and shortened with respect to the corresponding P,C distances of the 1-aza-3λ³-phosphaallenes Mes*−N=C=P−Ph (1.651(3) Å)[30b] and Mes*−N=C=P−C_6H_4-4-Cl (1.642(5) Å).[30c] Correspondingly, the situation is reversed for the C,N bond: the carbon−nitrogen bond in **3** (1.248(5) Å) is shorter than that of **1** (1.315(2) Å) and longer than those of Mes*−N=C=P−Ph (1.209(4) Å) and Mes*−N=C=P−C_6H_4-4-Cl (1.214(6) Å). The above data thus clearly show a bonding situation lying between N−C≡P and N=C=P forms.

Scheme 4. Modes of Stabilizing 1-Aza-3λ³-phosphaallenes



Molecules containing a N=C=P unit normally stabilize via dimerization of the C=P bond (Scheme 4)[31] unless bulky groups are present.[30] The anion **2** is, however, remarkably stable as the monomer; no significant change was observed in $^{31}P\{^1H\}$ NMR spectra obtained over a period of many months, and the compound only decomposes at temperatures above 168 °C. This stability is due in part to the negative charge preventing oligomerization, which has also been observed for the compounds $(dme)_2Li{-}O{-}C{\equiv}P$[10] and $[(dme)_3Li]^+[S{-}C{\equiv}P]^-$[11] and very recently for the anions $[(F_3C)_3B{-}C{\equiv}P]^-$ and $[(F_3C)_3B{-}C{\equiv}As]^-$.[12]

Quantum Chemical Calculations for 2. To further confirm the nature of the λ³-phosphaalkyne **1** and of the $[{}^iPr{-}N{=}C{=}P]^-$ anion derived from it, structural parameters in the gas phase were calculated by complete geometry optimizations utilizing the DFT method B3LYP/6-31+G(d,p) as implemented in the GAUSSIAN98 series of programs.[32] Both structures observed in the solid state (Figures 1 and 2) correspond to minima on the potential energy surface calculated for the gas phase. The theoretical data compare well with the parameters determined in the X-ray structural analyses, and are also summarized in Table 1. For the $[{}^iPr{-}N{=}C{=}P]^-$ anion a gauche conformation with respect to the N−C1 bond (torsional angle C−N−C1−H 40.03°) is calculated to be more stable than the C_s structure by 1.72 kcal mol^{-1}.

Additionally, calculated natural population analysis charges[33] were determined for λ³-phosphaalkyne **1** and

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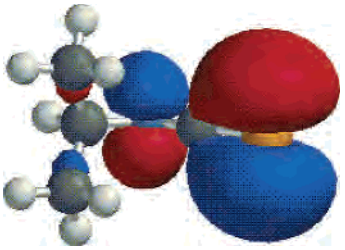

Figure 4. Depiction of the HOMO of the [^{i}PrN=C=P]$^{-}$ anion (C_s structure, RHF/6-31 G*) generated with the program Titan (ref 35).

the [^{i}Pr−N=C=P]$^{-}$ anion. Whereas for compound **1** values of −0.887 at N, −0.306 at C, and +0.306 at P reflect the electronegativity of the elements involved, in the [^{i}Pr−N=C=P]$^{-}$ anion a charge distribution of −0.665 at N, −0.156 at C, and −0.274 at P suggests that it may be regarded as an ambident anion. Thus, whereas hard electrophiles would be expected to attack preferentially at the nitrogen center, the largest HOMO coefficient of the anion is found at phosphorus (Figure 4), and along with a significant negative charge at this atom, the possibility of the anion also reacting with soft electrophiles via attack at phosphorus is also conceivable.[34]

Reactivity of 2. To establish the chemical behavior of the 1-aza-3λ^3-phospha-3-allenide **2**, reactions with hard electrophiles such as chlorotriorganylsilanes were carried out. Addition of one equiv of chlorotrimethylsilane in THF, followed by removal of solvent in vacuo, extraction into hexane, and filtration to remove potassium chloride leads back to compound **1**, as confirmed by comparing spectroscopic data with those of an authentic sample. This result agrees very well with the quantum chemical calculations.

Similarly, chlorotriphenylsilane reacts with compound **2** to form the analogous λ^3-phosphaalkyne **4**. This is converted back to the 1-aza-3λ^3-phospha-3-allenide **2** when treated with an equimolar amount of potassium *tert*-butoxide, as expected (Scheme 3). As described in detail for compound **4** in the Experimental Section, after filtration and removal of the solvent cyclopentane, an oil remained, which was subsequently used for NMR spectroscopic studies. Cooling a solution of the oil in hexane to +5 °C for 5 days, however, resulted in the precipitation of a yellow powder. The ^{1}H NMR spectrum and an elementary analysis showed this powder to contain 2-isopropyl(triphenylsilyl)amino-1λ^3-phosphaalkyne **4** which had cocrystallized with two and a half equiv of hexane.

To confirm that the triphenylsilyl substituent is bound to nitrogen and not phosphorus requires a comparison of the pertinent NMR data of derivative **4** with those of the trimethylsilyl compound **1**[25] (in brackets): ^{31}P{^{1}H} −129.5 ppm (−137.6), $^{3}J_{PSi}$ = 3.1 Hz (3.5), ^{13}C{^{1}H} 154.1 ppm (153.9), $^{1}J_{CP}$ = 21.4 Hz (18.2). Furthermore, the position of the IR band at 1588 cm^{-1} is identical to that reported for **1**.[19] Thus 1-aza-3λ^3-phospha-3-allenide **2** indeed reacts with hard electrophiles to form amino-λ^3-phosphaalkynes. The possibility that the silyl group attacks at phosphorus first and then rapidly migrates to nitrogen in order to form the energetically favored λ^3-phosphaalkyne (Scheme 4) is considered unlikely but cannot be discounted.

As deduced from quantum chemical calculations, soft electrophiles such as chlorotriorganylstannanes are expected to attack at phosphorus. Indeed, the reaction of compound **2** with chlorotrimethylstannane in THF at −50 °C furnished isopropyliminomethylidene(trimethylstannyl)phosphane ^{i}Pr−N=C=P−SnMe$_3$ (**5**). The ^{31}P{^{1}H} NMR spectrum exhibits a singlet at −267.9 ppm accompanied by one set of ^{119}Sn and ^{117}Sn satellites. The influence of tin can be seen in the considerable upfield shifting of the signal relative to other known RN=C=PR′ compounds (−99 to −135 ppm, R, R′ = alkyl, aryl).[29] The large $^{1}J_{PSn}$ coupling constant (719.5 Hz) proves the existence of a direct phosphorus−tin bond, and strong, broad bands at 1908 and 1879 cm^{-1} in the IR spectrum are typical for a N=C=P group.[29] Further investigations into this highly reactive species as well as the isolation and crystal structure of the homologous triphenylstannyl derivative, which is stabilized by rapid dimerization according to Scheme 4, will be the subject of a future publication.

In our opinion, the results described above clearly indicate that the 1-aza-3λ^3-phospha-3-allenide anion **2** has to be considered as the connecting link between two classes of compound, namely iminomethylidenephosphanes and 2-amino-1λ^3-phosphaalkynes. Interestingly, the close relationship between these has very recently been corroborated by quantum chemical calculations on the hydrogen derivatives; the two parent compounds H−P=C=N−H and P≡C−NH$_2$ differ in energy by merely 0.27 kcal mol^{-1}.[36]

Conclusions

The removal of the trimethylsilyl group of the λ^3-phosphaalkyne **1** with potassium *tert*-butoxide provides a facile route to the 1-aza-3λ^3-phospha-3-allenide anion **2**, the first representative of this type of compound to be characterized. It contains a nitrogen−carbon−phosphorus group for which the parameters were shown by X-ray structural analysis and quantum chemical calculations to lie between the extrema N−C≡P and N=C=P; this suggests the possibility of dual modes of reactivity. Indeed, reaction with hard electrophiles at nitrogen opens the way to new heteroatom substituted λ^3-phosphaalkynes such as derivative **4**, whereas with softer electrophiles, attack at phosphorus leads to 1-aza-3λ^3-phosphaallenes. Investigations into the latter are currently underway with trialkyl- and triaryltin chlorides and will be published in due course.

Experimental Section

Solvents were dried with sodium/benzophenone (THF) or lithium aluminum hydride (cyclopentane, *n*-hexane) and distilled under argon; other chemicals were used as received and all reactions

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were carried out under argon using standard Schlenk techniques. NMR spectra were recorded on Bruker AM 200, AC 250, and AM 400 MHz spectrometers, elementary analyses were carried out using a Perkin-Elmer Series II Analyzer 2400, IR spectra were obtained with a Perkin-Elmer Paragon 1000 PC IR spectrophotometer, and the Raman spectrum was recorded on a Dilor ISA XY 500 instrument. Melting points (uncorrected) were determined using a Büchi apparatus, with samples sealed in capillaries under argon.

Synthesis of 1. ^{i}PrNCO (9.5 mL, 96.7 mmol) and $(Me_3Si)_3P$ (25 mL, 86.1 mmol) were combined in diethyl ether (30 mL) under argon, resulting in a slight cooling of the pale yellow solution. After the mixture had been stirred at room temperature for 5 days, the solvent was removed under vacuum and the product was distilled (54−55 °C/ 5•10^{-3} mmHg) to give a slightly yellow- or green-tinged liquid (29−31 mL, **6**) consisting of the isomers ^{i}Pr(Me_3Si)NC(O)P($SiMe_3$)$_2$ and ^{i}PrN═C($OSiMe_3$)P($SiMe_3$)$_2$). $ZnCl_2$ (2 g) was then heated to 120 °C under vacuum (10^{-3} mmHg) for 2 h in a two-necked 100-mL round-bottomed flask fitted with a pressure-equalizing dropping funnel and a Claisen condenser leading to a Schlenk tube followed by a cold trap cooled with liquid nitrogen. After the $ZnCl_2$ had cooled to room temperature, liquid **6** was then added dropwise via the dropping funnel, resulting in a yellow coloration that darkened with time. After 12 to 18 h the solution was dark yellow to orange-red; $(Me_3Si)_2O$ was then distilled into the cold trap (40−60 °C/2−5 mmHg) followed by ^{i}Pr(Me_3Si)NCP (**1**) into the Schlenk tube (70 °C/0.6 mmHg; total yield based on $(Me_3Si)_3P$: 5.6 g, 38%).

Synthesis of K[^{i}PrNCP] (2). Compound **2** was synthesized by dropwise addition of **1** (1 mL, 0.872 g, 5.033 mmol) to a stirred solution of one equiv of potassium *tert*-butoxide (0.565 g, 5.035 mmol) in dry, oxygen-free THF (20 mL) at −50 °C under argon. The solution then darkened and was allowed to warm to room-temperature overnight. The solvent and *tert*-butoxytrimethylsilane formed were removed under vacuum to give potassium 1-isopropyl-1aza-3λ^3-phospha-3-allenide **2** quantitatively as a yellow powder, mp 168 °C (dec). Solutions of the product in THF (typically ca. 2.5 mol L^{-1}), can be stored at 5 °C for many months without significant decomposition (controlled by $^{31}P\{^1H\}$ NMR).

NMR data for **2** (THF-d_8): $^{31}P\{^1H\}$ (161.995 MHz, 27 °C) δ −228.4 ppm (s, br). ^1H (250.134 MHz, 25 °C) δ 3.27 (sept, 1H, $^3J_{HH}$= 6.4 Hz, C*H*(CH_3)$_2$); 1.06 ppm (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ (62.896 MHz, 27 °C) δ 177.9 (d, $^1J_{CP}$ = 47.8 Hz, *C*P); 51.6 (d, $^3J_{CP}$ = 9.9 Hz, *C*H(CH_3)$_2$); 24.6 ppm (s, CH(*C*H$_3$)$_2$).

Synthesis of [(18-Crown-6)K][^{i}PrNCP] (3). One equivalent of 18-crown-6 (665 mg, 2.516 mmol) was added to a 2.514 mol L^{-1} solution of **2** (1.00 mL) diluted with THF to 10 mL under argon. After one week at 5 °C, yellow tablets suitable for X-ray crystallographic analysis had deposited. Yield 771 mg (76%), mp 114 °C (dec). Anal. Calc. for $C_{16}H_{31}KNO_6P$: C, 47.63; H, 7.74; N, 3.47. Found: C, 47.35; H, 7.86; N, 3.24.

NMR data for **3** (THF-d_8): $^{31}P\{^1H\}$ (161.995 MHz, 27 °C) δ −226.1 ppm (s). ^1H (250.134 MHz, 25 °C) δ 3.67 (s, 24H, 18-crown-6); 3.22 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*(CH_3)$_2$); 1.04 ppm (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ (62.896 MHz, 25 °C) δ 178.8 (d, $^1J_{CP}$ = 45.8 Hz, *C*P); 71.0 (s, 18-crown-6); 51.9 (d, $^3J_{CP}$ = 10.9 Hz, *C*H(CH_3)$_2$); 24.9 ppm (s, CH(*C*H$_3$)$_2$). IR (Nujol mull, NaCl plates, cm^{-1}): 1714 s, 1694 s, 1463 s, 1353 s, 1345 s, 1283 m, 1247 m, 1228 m, 1163 m, 1105 s br, 963 s, 838 s, 737 m, 722 m, 578 w, 546 m, 527 w. Raman (crystal, cm^{-1}): 1709 w, 1696 m, 1468 s, 1270 s, 1145 m, 1138 m, 1071 w, 978 m, 870 s, 829 m, 549 s.

Table 2. Crystallographic Data for **1** and **3**

	1	**3**
empirical formula	$C_7H_{16}NPSi$	$C_{16}H_{31}KNO_6P$
molecular mass	173.27	403.49
temp/K	173(2)	173(2)
space group	$P2_1/m$	$Pmn2_1$
a/Å	7.285(3)	14.3655(19)
b/Å	10.067(4)	8.8715(12)
c/Å	8.103(2)	8.4647(16)
β /deg	112.21(2)	
F(000)	188	432
V/Å^3	550.2(3)	1007.88(3)
μ/mm^{-1}	0.302	0.348
ρ_{calcd}/g cm^{-3}	1.046	1.242
Z	2	2
crystal dimensions/mm	Ø 0.3 × 0.4	0.4 × 0.4 × 0.4
θ range for data collection/deg	2.72−30.02	2.30−29.99
GOF^a	1.083	1.029
No. of reflections	3887	4133
unique reflections (N_0)	1689	2027
No. of parameters (N_p)	89	124
R_{int}	0.0263	0.042
$R_1{}^b$	0.0296	0.0349
wR_2 ($I > 2\sigma(I)$)^c	0.0858	0.0817

^{a} GOF = $[\Sigma(w(|F_0| - |F_c|)^2/(N_0 - N_p)]^{1/2}$. ^{b} $R_1 = (\Sigma|F_0| - |F_c|)/\Sigma|F_0|$. ^{c} $wR_2 = [\Sigma(w(|F_0|^2 - |F_c|^2)^2)/\Sigma(w(F_0{}^2)^2)]^{1/2}$, $w = 1/[\sigma^2(F_0{}^2) + (xP)^2 + yP]$, where $P = (F_0{}^2 + 2F_c{}^2)/3$; x = 0.0557, y = 0.0442 (**1**); x = 0.0551, y = 0.0559 (**3**).

Synthesis of ^{i}Pr(Ph_3Si)NCP (4). Dropwise addition of a 2.517 mol L^{-1} solution (1.00 mL) of potassium 1-isopropyl-1-aza-3λ^3-phospha-3-allenide (**2**) to a stirred solution of chlorotriphenylsilane (742 mg, 2.517 mmol) in THF (30 mL) under argon at −50 °C resulted in a color change from dark to bright yellow. This solution was allowed to warm to room temperature overnight; after removal of solvent in vacuo a yellow glassy solid remained. Cyclopentane (25 mL) was then added and the resulting suspension was stirred, filtered to remove potassium chloride, and then concentrated, whereupon the remaining potassium chloride separated. After further filtration the solvent was stripped completely to give a yellow oil, which was then used for IR and NMR studies. When, however, *n*-hexane was added and the solution was then cooled to +5 °C, **4** precipitated as a yellow powder cocrystallizing with hexane (633 mg, 44%; mp 162−3 °C). Anal. Calc. for $C_{22}H_{22}NPSi{\cdot}2.5C_6H_{14}$: C, 77.30; H, 9.99; N, 2.44. Found: C, 77.44; H, 9.94; N, 1.93 (hexane was observed in an ^1H NMR spectrum of the analytical sample).

NMR data for **4** (THF-d_8): $^{31}P\{^1H\}$ (161.995 MHz, 27 °C) δ −129.5 ppm (s). $^{29}Si\{^1H\}$ (79.495 MHz, 27 °C) δ −9.27 ppm (d, $^3J_{PSi}$ = 3.05 Hz). ^1H (250.134 MHz, 25 °C) δ 7.1−7.9 (m, 15H, *Ph*$_3$Si); 3.07 (dsept, 1H, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 1.1 Hz, C*H*(CH_3)$_2$); 1.20 ppm (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ (62.896 MHz, 25 °C) δ 154.1 (d, $^1J_{CP}$ = 21.4 Hz, *C*P); 136.5 (s, *o*-*C*$_6$H$_5$); 132.1 (s, *ipso*-*C*$_6$H$_5$); 130.7 (s, *p*-*C*$_6$H$_5$); 128.3 (s, *m*-*C*$_6$H$_5$); 50.0 (d, $^3J_{CP}$ = 6.6 Hz, *C*H(CH_3)$_2$); 20.9 ppm (s, CH(*C*H$_3$)$_2$). IR (Nujol mull, NaCl plates, cm^{-1}): 1588 w, 1429 s, 1118 s, 1091 m, 890 w, 712 s, 703 s, 518 s.

X-ray Structure Determination. Crystals of **1** were obtained by zone-melting the pale-yellow compound neat (mp −42 ± 2 °C) in a 0.3-mm capillary, while X-ray quality crystals of **3** were obtained from THF at 5 °C after a week as large yellow tablets (Table 2). Reflections were obtained using a Siemens P4 four-circle diffractometer with Mo Kα radiation and a graphite monochromator. Structures were solved by direct methods and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 with the programs SHELXTL Plus (data reduction), SHELXS (structure solving), and SHELXL (structure refinement).[37] Psi-scan absorption correction was carried out for **1**. The hydrogen atoms of **3** were added in calculated positions, included in the final stage of refinement, and allowed to ride on their respective carbon atoms.

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Supporting Information Available: Crystallographic data in CIF format for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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