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Novel Diphosphetene Derivatives by Reactions of Di(isopropyl)aminophosphaethyne with Chalcogens or Halogens†

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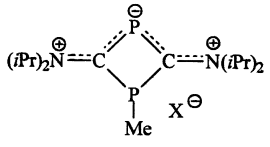
Abstract—The $1\lambda^3\sigma^2,3\lambda^5\sigma^4$-diphosphetene derivatives **6a**, **6b** are formed in quantitative yields by reactions of di(isopropyl)aminophosphaethyne **1a** with sulphur and selenium, respectively, at 25°C. **6a** is also produced slowly from **1a** and CS_2. The *tert*-butylphosphaalkyne P≡C–*t*Bu (**1b**), however, does not react with sulphur or selenium, but undergoes a slow reaction with CS_2 to give the five-membered heterocycle 3,5-di-*tert*-butyl-1-thia-2,4-diphosphole as one of the main products. Halogenation of **1a** using SO_2Cl_2, Br_2 or I_2 as reagents leads to the $1\lambda^3\sigma^2,3\lambda^3\sigma^3$-diphosphetenium salts **9a**–**9c**. X-ray diffraction studies of **6a** and **6b** prove that the easy formation of the four-membered diphospha-heterocycles is obviously governed by electronically delocalized phosphaallyl units within the unsaturated rings. © 1999 Elsevier Science Ltd. All rights reserved.

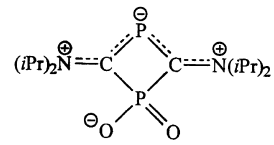
Introduction

Phosphaalkynes of the type P≡C–R (e.g. R=*t*Bu, Ad, Mes) serve as valuable synthetic tools in organophosphorus chemistry,[1,2] in particular, with respect to the preparation of saturated or unsaturated compounds with ring or cage structures.[3,4] Replacement of the alkyl or aryl substituent R at the sp-hybridized carbon atom by an amino group NR_2 with a strong +M effect leads to considerable changes in reactivity and opens additional synthetic possibilities.[5] In quite a number of reactions carried out under similar conditions and with analogous partners aminophosphaalkynes give rise to other products than P≡C–R precursors. Some typical experimental results are presented here as examples:

1. The reactions of P≡C–R and P≡C–N(*i*Pr)$_2$ (**1a**), respectively, with 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene, in general, yield 1,3,5,7-tetraphosphabarrelene derivatives for R=*t*Bu or *i*Pen, whereas with **1a** the 1,3,4,7-tetraphosphasemibullvalene valence isomer with R=N(*i*Pr)$_2$ is formed in quantitative yield.[6]
2. **1a** reacts with methylating agents like CH_3I or $CH_3OSO_2CF_3$ to give the $1\lambda^3,3\lambda^3$-diphosphetenium cation **2** with a stable phosphaallyl building unit.[7] P≡C–R compounds do not react in a similar manner. Becker et al.,[8] however, have shown that P≡C–*t*Bu (**1b**) adds bromine to the triple bond followed by cleavage of the resulting PC single bond giving PBr_3 as one of main products.
3. Oxidation of **1a** by air in the presence of catalytic amounts of CuCl unexpectedly yields the $1\lambda^3,3\lambda^5$-diphosphetene derivative **3**.[9] Structural investigations of the resulting phospha-heterocycle have shown, that **3** like **2** contains a conjugated phosphaallyl system in the four-membered ring.[10] In addition, **3** can be described as a compound isolobally related to the rare binuclear complexes **4**.[11] Again, this surprising reaction of **1a** with oxygen was not observed for the phosphaalkynes P≡C–R. On the other hand, a remarkable analogy to the formation of **3** was found by Becker and coworkers[12] for the π-donor substituted diphosphetenes **5a**, **5b** produced from the λ^3-phosphaalkyne P≡C–OLi(dme)$_2$ with sulphur and selenium, respectively.



2 (X = I, CF_3SO_3)



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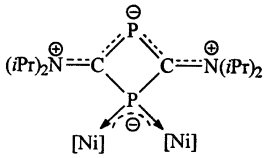

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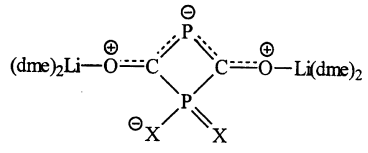
[Ni] = $Ni(CO)_3$; $Ni(CO)_2PR_3$



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(**a**: X = S, **b**: X = Se)

Keywords: phosphaalkynes; 1,3-diphosphetenes; 1-thia-2,4-diphosphole.

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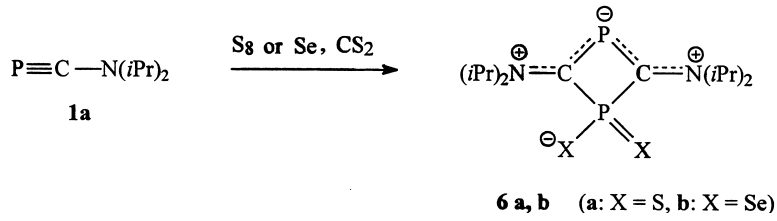


Scheme 1.

The deviating reactivity of aminophosphaalkynes from the broadly studied behaviour of the alkyl and aryl analogues led us to investigate the reactions of P≡C–N(iPr)$_2$ (**1a**) with chalcogens and halogens in some detail. Here we report on the interesting results.

Reaction of P≡C–N(iPr)$_2$ (1a) with Chalcogens

1a reacts at room temperature in CS_2 solution with one equivalent of sulphur or selenium to give the diphosphetene derivatives **6a**, **6b** within 2–3h in quantitative yields. They can be isolated in the form of yellow orange crystals (Scheme 1). The analogous reaction with tellurium in CS_2, however, was unsuccessful, but after several days at 25°C formed the sulphur containing diphosphetene **6a** as the only product indicated by the characteristic ^{31}P and ^{13}C resonances showing up in the mixture besides the signals of unreacted **1a**. Obviously a slow reaction takes place between **1a** and CS_2 as the source for sulphur. A separate experiment with **1a** in CS_2 confirmed this result with the additional information that—as expected—the reaction with the dissolved sulphur is much quicker.

Composition and constitution of the novel compounds **6a** and **6b** have been determined by NMR [^{1}H, ^{13}C, ^{31}P, ^{77}Se (**6b**)] and mass spectra, and finally proved by X-ray diffraction analyses of **6a** and **6b**. For both derivatives the ^{1}H and ^{13}C NMR spectra reveal the non-equivalence of the *N*-isopropyl groups due to hindered rotation of the N(iPr)$_2$ substituents around the (P)C–N bond. The ^{31}P{^{1}H} NMR spectra show two doublets of a typical AX spin system expected for 1λ^3,3λ^5-diphosphetenes. The resonances of the $\lambda^3\sigma^2$ phosphorus atoms are detected at low field (**6a**: δ=96.9; **6b**: δ=92.1) and do not differ strongly from the values of the $\lambda^5\sigma^4$ P-atoms at δ=86.8 (**6a**) and δ=53.6 (**6b**). The corresponding ^2J(P,P) coupling constants amount to 18.2 (**6a**) and 22.4Hz (**6b**), respectively, and thus are in accord with the data of **2**,[7] **3**,[9] and **4**.[11] The high-field resonance of **6b** is accompanied by characteristic ^{77}Se satellites with ^1J(P,Se)=688.0Hz. This value was confirmed in the ^{77}Se NMR spectrum at δ_{Se}=185.3. The crystal structure analyses of **6a** and **6b** are in excellent agreement with the NMR data and verify the conclusion that both chalcogen atoms are bound to only one of the phosphorus atoms in the four-membered ring (Fig. 1).

In both structures the 1λ^3,3λ^5-diphosphetene skeleton is nearly coplanar with the NC_2 fragments of the amino substituents. The units PS_2 and PSe_2, respectively, are arranged perpendicularly to the skeleton plane. The angles SPS and SePSe amount to 121.16(3) and 121.39(7)°, respectively. The electronic structure of the PX_2 fragments (X=S, Se) provides for a fairly uniform charge distribution and leads to only small differences of the PS (**6a**) and PSe (**6b**) distances, which correspond very well to literature data[13] for thio- or seleno-phosphoranes R_3P=X [X=S: (1.954Å); Se: (2.093Å)], and also for Mes*P(=S)$_2$[14] (1.90Å) or the diselenophosphorane derivative Ph_3P=C(Ph)–P(=Se)$_2$[15] [2.079(2) and 2.081(2)Å] (see Table 1).

Whereas the $\lambda^5\sigma^4$ PC distances of 1.804–1.841Å are in the range of PC single bonds, the $\lambda^3\sigma^2$ PC bond lengths of 1.769–1.783Å indicate a bond order >1 and so considerable double bond character. The mesomeric contribution of the lone pair of electrons on the N(iPr)$_2$ substituents shows up both in the planar structure of the NC_3 units (sum of bond angles: 359.92 and 360.01°) and in the drastic shortening of the C1–N1 and C2–N2 distance (1.287–1.303Å) reaching almost the typical double bond length of 1.27Å. The

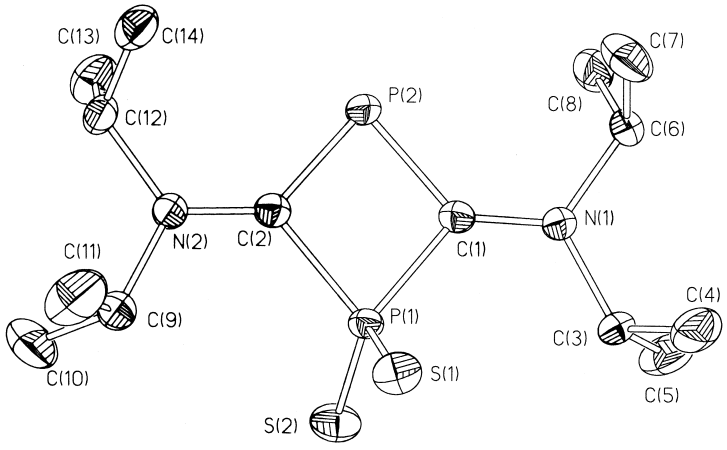


Figure 1. Molecular structure of **6a**.

Table 1. Selected bond lengths (Å) and angles (degrees) for **6a** (E=S) and **6b** (E=Se)

Bond lengths	**6a**	**6b**	Angles	**6a**	**6b**
P(1)–C(1)	1.839(2)	1.829(6)	C(1)–P(1)–C(2)	79.62(7)	79.2(3)
P(1)–C(2)	1.839(2)	1.841(5)	C(1)–P(1)–E(1)	111.28(5)	111.4(2)
P(2)–C(1)	1.783(2)	1.782(6)	C(1)–P(1)–E(2)	113.27(5)	113.1(2)
P(2)–C(2)	1.777(2)	1.769(5)	C(2)–P(1)–E(1)	113.12(5)	113.3(2)
P(1)–E(1)	1.9557(6)	2.109(2)	C(2)–P(1)–E(2)	111.02(5)	110.9(2)
P(1)–E(2)	1.9536(6)	2.109(2)	E(1)–P(1)–E(2)	121.16(3)	121.4(7)
N(1)–C(1)	1.299(2)	1.302(7)	C(1)–P(2)–C(2)	82.82(7)	82.4(3)
N(1)–C(3)	1.497(2)	1.497(6)	P(1)–C(1)–P(2)	98.66(7)	99.2(3)
N(1)–C(6)	1.496(2)	1.496(6)	P(1)–C(1)–N(1)	127.67(11)	127.6(4)
N(2)–C(2)	1.303(2)	1.300(6)	P(2)–C(1)–N(1)	133.64(11)	133.2(4)
N(2)–C(9)	1.493(2)	1.491(7)	P(1)–C(2)–P(2)	98.90(8)	99.2(3)
N(2)–C(12)	1.497(2)	1.512(7)	P(1)–C(2)–N(2)	127.56(12)	126.8(4)
			P(2)–C(2)–N(2)	133.54(12)	134.1(4)

bonding situation in **6a**, **b** obviously corresponds to that in derivatives **2**–**4**, i.e. it is determined by the electronically stabilized structural unit NCPCN and can be rationalized by the mesomeric forms **A** to **C** (Scheme 2). A very similar description applies to the $1\lambda^3,3\lambda^5$-diphosphetenes **5a**, **b**.[12]

^{31}PNMR control measurements during the preparation of **6a**, **b** only in case of the reaction of **1a** with selenium pointed to an intermediate which was quickly transformed to **6b**. Immediately after the start of the reaction two AX doublets at δ_P=129.8 and 124.6 with ^2J(P,P)=33.4Hz were detected in the ^{31}PNMR spectrum in addition to the resonances of **1a** and **6b**. A plausible explanation for this result is the formation of the monoseleno diphosphetene **7**. Because of the fast following reaction leading to **6b** this intermediate could not be isolated even in a further reaction of **1a** with only 0.5 equivalents of selenium. **7** can be considered as product of a formal [2+2] cycloaddition of **1a** with the first step intermediate [Se=P≡C–N(*i*Pr)$_2$]. A similar sequence of steps can be assumed for the analogous formation of the sulphur compound **6a**.

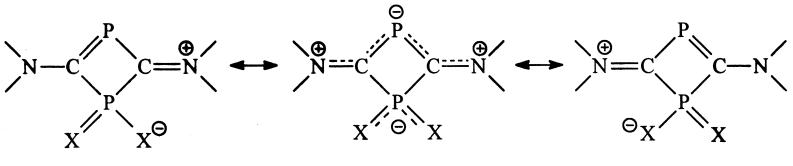
To elucidate the influence of the π-donor substituent NR_2 on the reactivity of aminophospha-ethynes with chalcogens the related reactions of *tert*-butylphosphaethyne **1b** are of particular interest. In order to avoid problems which could be caused by the reactivity of CS_2, benzene was used as solvent for the experiments with sulphur or selenium. Neither at 25°C nor by heating the reaction mixture at 70°C for several hours an attack of the phosphaalkyne **1b** by the chalcogens could be detected. Even the addition of triethylamine to activate the degradation of the S_8 molecules was unsuccessful. On the other hand, **1b** reacts with CS_2 already at room temperature indicated by a colour change from colourless over yellow to red. Complete reaction of **1b** was observed within 3days yielding a mixture of products. The main component (25%, relative to **1b**) was characterized by ^{31}P and ^{13}C NMR spectra to be the known 3,5-di-*tert*-butyl-1-thia-2,4-diphosphole **8**.[16] The NMR control experiments have also shown that at the beginning of the reaction **8** is the only detectable product and that the composition of the reaction mixture does not change if sulphur or selenium is added to the CS_2 solution.

Consequently, the sulphur necessary for the formation of **8** has to be supplied by the solvent CS_2. A possible, but not established pathway is presented in Scheme 3. The frequently postulated, but so far not detectable thiocarbonyl phosphinidene [:P–C(=S)*t*Bu] could well be one of the highly reactive intermediates.[17]

The difference in reactivity of **1a** and **1b** with CS_2 (**1a→6a**; **1b→8**) can be attributed to the distinct polarity of the P≡C bond. While the charge distribution in P≡C–*t*Bu is mainly determined by the electronegativity values of carbon (2.5) and phosphorus (2.1), the aminophosphaalkyne **1a** exhibits a polarity strongly influenced by the delocalization of the lone pair of electrons on nitrogen into the π-system resulting in a large contribution of the zwitterionic form **B** (Scheme 4) to the electronic ground-state of the molecule.[5a] Therefore, an inverse attack of one of the sulphur atoms of CS_2 on the P≡C fragment in **1a** or **1b** seems plausible.

Reaction of P≡C–N(*i*Pr)$_2$ (1a) with Halogens

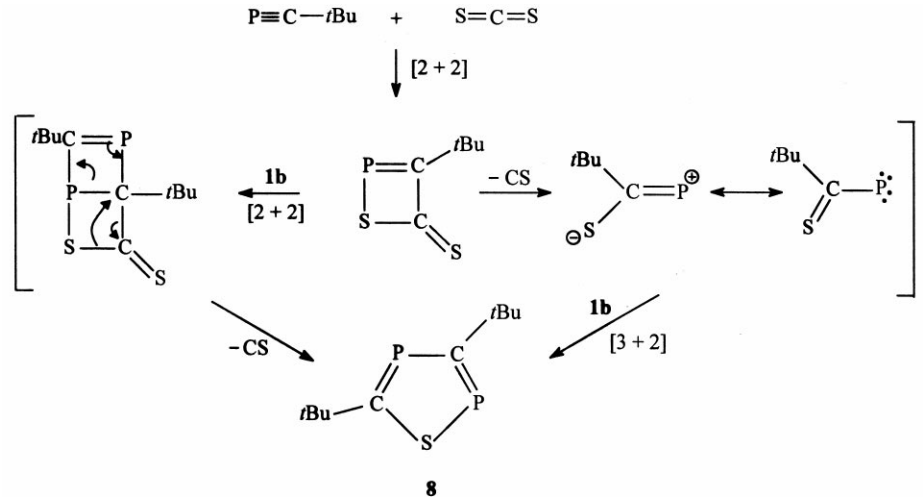
The addition of SO_2Cl_2, Br_2 or I_2 to **1a**, in general, produces the corresponding diphosphetenium cations **9a**–**9c** in good



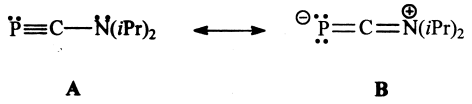
A **B** **C**

(X = O, S, Se)

Scheme 2.



Scheme 3.



Scheme 4.

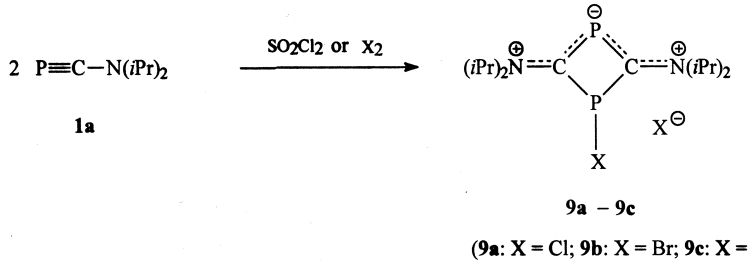
yields. The complete degradation with formation of PX_3, which is observed for P≡C–*t*Bu (**1b**), is of some importance only in case of the chlorination of **1a** (Scheme 5).

In contrast to the chlorinated derivative **9a**, compounds **9b** and **9c** are stable at room temperature even in chloroform or dichlormethane solutions and have been characterized by multinuclear NMR and mass spectroscopic investigations. Very probably, **9a** decomposes by following reactions with SO_2Cl_2 yielding a complex mixture of products and, therefore, could not be isolated. One of the decomposition products is PCl_3.

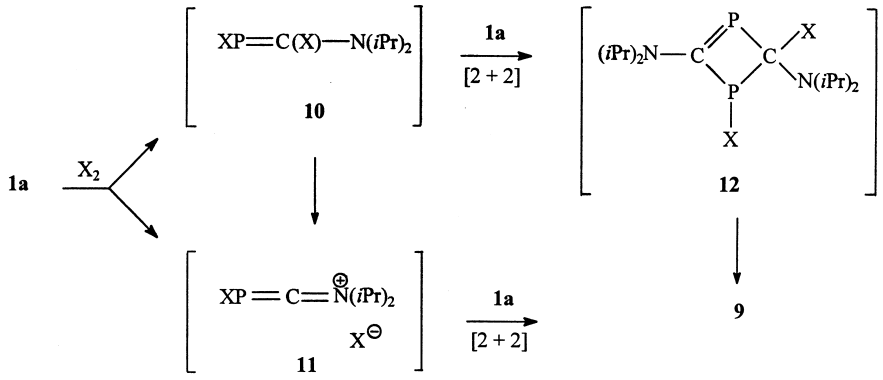
Similar to the diphosphetenium derivatives **2** the salt-like compounds **9a**–**9c** generally show two doublets of the AX spin system in the $^{31}P\{^1H\}$ NMR spectra. The signals of the $\lambda^3\sigma^2$ phosphorus atom of the iodine compound **9c** (δ_P=192.2) are shifted to low field as compared to the chlorine or bromine systems **9a** (δ_P=123.4) or **9b** (δ_P=123.2). On the other hand, the δ_P-values of the $\lambda^3\sigma^3$ P-atoms vary only in a small range as a function of X (δ_P=62.3–90.4). The ^2J(P,P) coupling constants amount to 23.1–54.0Hz and thus are larger than in the derivatives of type **2**, but considerably smaller than those of the related 2,4-bis(triphenylphosphoranediyl)-1,3-diphosphetenium salts[18] (ca. 120Hz).

The formation of **9a**–**9c** occurs so quickly that intermediates on the way to the final products could not be detected by NMR spectroscopy. Two possible pathways are considered in Scheme 6. In the first step the addition of X_2 to the aminophosphaethyne leads either to a *cis*/*trans* mixture of the corresponding 1,2-dihalogenophosphaalkenes **10** (as reported for **1b**) or by heterolytic cleavage of X_2 at the positive ammonium center of form **B** (Scheme 4) to an electrophilic attack of X^+ at the negatively charged P-atom to give intermediates of type **11**. For the next step a formal [2+2] cycloaddition of **10** or **11** with **1a** is suggested, furnishing either the heterocyclic systems **12** or the final products **9**. In the case of **12** dissociation of X^- is necessary, but conceivable under the π-donor effect of the $(iPr)_2N$ group. Pathways according to Scheme 6 gain support from the fact that phosphaalkenes are known to be reactive partners in [2+2] cycloaddition reactions of phophaalkynes forming 1,2-dihydro-1,3-diphosphetes.[5c,19] Since **1a** spontaneously reacts with methylating agents like CH_3I or $CH_3OSO_2CF_3$, affording the diphosphetenium salts **2**,[7] we favour the shorter route **1a→11→9** as the more likely sequence.

In conclusion, the work presented in this paper is a valuable contribution both to the chemistry of unsaturated four-membered diphospha heterocycles, especially to the rare



Scheme 5.



Scheme 6.

representatives of $1\lambda^3,3\lambda^5$-diphosphetenes, and to the class of cyclic phosphaallyl cations. It clearly demonstrates the differences in reactivity between alkyl- and amino-substituted phosphaalkynes induced by the R_2N π-donor.

Experimental

General

All experiments were carried out under argon (or by using a standard vacuum line) in anhydrous solvents. Reaction vessels were either Schlenk flasks or ampoules with several break seals and an NMR tube. Solvents and deuterated compounds for NMR measurements were carefully dried and degassed. NMR: Bruker AC 200 (200.13MHz, ^{1}H, standard: TMS; 50.32MHz; ^{13}C, standard: TMS; 81.02MHz; ^{31}P, standard: 85% H_3PO_4), Bruker AM 360 (68.68MHz; ^{77}Se, standard: $(CH_3)_2Se$). MS: Model CH 5 MAT Finnigan. Elemental analyses: Perkin Elmer CHN-Analysator 240. The phosphaalkynes P≡C–N(*i*Pr)$_2$ (**1a**),[20] P≡C–*t*Bu (**1b**)[21] were prepared according to the literature.

General procedure for the preparation of the $1\lambda^3,3\lambda^5$-diphosphetene derivatives 6a, b

36.5mg (1.14mmol) sulphur or 90.0mg (1.14mmol) selenium were placed in an ampoule with break seals and an NMR tube together with 5mL CS_2. 160mg (1.12mmol) of di(isopropyl)amino-phosphaethyne **1a** were then introduced by vacuum condensation at −196°C. On warming up to room temperature the mixture was continuously stirred and afterwards transfused into the NMR tube. NMR measurements at 25°C indicated a complete reaction of **1a** and the quantitative formation of the $1\lambda^3$, $3\lambda^5$-diphosphetene derivatives **6a** or **6b** after 2–3h. After evaporation of the solvent in vacuo, **6a** or **6b** was obtained as an orange red powder (**6a**: 372mg, 1.06mmol, 95% yield; **6b**: 462mg, 1.04mmol, 93% yield). Crystals of **6a** or **6b** were obtained on cooling the pentane solution at −30°C. Their quality was sufficient for a single crystal X-ray structure analysis.

1,1-Dithioxo-2,4-bis(diisopropylamino)-1,3-diphosphetene (6a). ^{1}H NMR (C_6D_6, 25°C): δ=1.0–1.5 (m, 24H, CH_3), 3.7 (m, 2H, CH), 5.2 [dsept, ^3J(H,H)=7.0, ^4J(P,H)=2.0Hz, 2H, CH]. ^{13}C{^{1}H} NMR (C_6D_6, 25°C): δ=20.1 (m, *C*H$_3$), 51.0 [d, ^3J(P,C)=7.9Hz, *C*H], 60.5 [d, ^3J(P,C)=14.4Hz, *C*H], 209.1 [dd, ^1J(P,C)=60.0 and 44.0Hz, P=*C*]. ^{31}P{^{1}H} NMR (C_6D_6, 25°C): δ=86.8 [d, ^2J(P,P)=18.2Hz, λ^5 P], 96.9 [d, ^2J(P,P)=18.2Hz, λ^3 P]. EI-MS (70eV, selected), *m/z* (%): 350 (54) [M$^+$], 318 (4) [M$^+$−S], 307 (5) [M$^+$−CH(CH$_3$)$_2$], 286 (100) [M$^+$−2S]. $C_{14}H_{28}N_2P_2S_2$ (350.44): calcd. C 47.98, H 8.05, N 7.99; found C 48.06, H 8.13, N 7.73.

1,1-Diselenoxo-2,4-bis(diisopropylamino)-1,3-diphosphetene (6b). ^{1}H NMR (C_6D_6, 25°C): δ=1.21 [d, ^3J(H,H)=7.1Hz, 12H, CH_3], 1.34 [d, ^3J(H,H)=7.1Hz, 12H, CH_3], 3.70 [dsept, ^3J(H,H)=7.1, ^4J(P,H)=2.7Hz, 2H, CH], 5.35 [dsept, ^3J(H,H)=7.1, ^4J(P,H)=2.5Hz, 2H, CH]. ^{13}C{^{1}H} NMR (C_6D_6, 25°C): δ=18.8 (s, *C*H$_3$), 19.5 [d, ^4J(P,C)=8.1Hz, *C*H$_3$], 51.3 [d, ^3J(P,C)=7.1Hz, *C*H], 59.0 [d, ^3J(P,C)=15.4Hz, *C*H], 199.1 [dd, ^1J(P,C)=61.8 and 29.4Hz, P=*C*]. ^{31}P{^{1}H} NMR (C_6D_6, 25°C): δ=53.6 [dd$_{Se}$, ^2J(P,P)=22.4, ^1J(P,Se)=688.0Hz, λ^5 P], 92.1 [d, ^2J(P,P)=22.4Hz, λ^3 P]. ^{77}Se NMR: 185.3 [d, ^1J(P,Se)=687.0Hz]. EI-MS (70eV, selected, based on ^{80}Se), *m/z* (%): 446 (26) [M$^+$], 366 (12) [M$^+$−Se], 286 (100) [M$^+$−2Se], 223 (11) [(Pr$_2$NCPSe$^+$]. $C_{14}H_{28}N_2P_2Se_2$ (444.24): calcd. C 37.85, H 6.35, N 6.31; found C 37.99, H 6.31, N 6.29.

General procedure for the preparation of the $1\lambda^3$, $3\lambda^5$-diphosphetenium salts 9a–9b

To a solution of 0.5mmol SO_2Cl_2 or the halogens (Br_2, I_2) in dichloromethane (2mL), prepared in an ampoule with break seals and an NMR tube, 145mg (1.0mmol) di(isopropyl)-aminophosphaethyne **1a** were added by vacuum condensation at −196°C. The mixture was stirred during a warming-up period of ca. 1h to reach room temperature. NMR control measurements indicated a complete consumption of **1a** and the formation of the corresponding 1,3-diphosphetenium salts **9a**–**9c**. In case of **9a** some side products (e.g. PCl_3) were detected by ^{31}P NMR measurements. After evaporation of the solvent in vacuo and recrystallization (from acetonitrile or toluene), **9b** and **9c** were obtained as pale yellow powders (**9b**: 124.8mg, 0.28mmol, 56% yield; **9c**: 167.3mg, 0.31mmol, 62% yield). Due to the air and moisture sensitivity of **9b** and **9c** reliable analytic data could not be obtained. However, their identity was proved by the NMR and MS data including the simulation of isotopic patterns. This is exemplified for **9b** by comparison of measured and calculated intensities for the overlapping

Table 2. Crystallographic data and parameters of the crystal structure determinations

Compound	**6a**	**6b**
Empirical formula	$C_{14}H_{28}N_2P_2S_2$	$C_{14}H_{28}N_2P_2Se_2$
Fw	350.44	444.24
Crystal size (mm)	0.23×0.20×0.26	0.20×0.22×0.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.635(2)	10.635(2)
b (Å)	13.081(2)	13.081(2)
c (Å)	14.919(3)	14.919(3)
β (°)	108.53	108.53
V (Å^3)	1967.9(6)	1967.9(6)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.183	1.499
μ (mm^{-1})	0.427	3.914
F(000)	752	896
Temperature (K)	173(2)	153(2)
θ (degrees)	10–17	10–17
Index ranges	$0\le h\le 13$	$0\le h\le 12$
	$0\le k\le 16$	$0\le k\le 15$
	$-19\le l\le 18$	$-17\le l\le 16$
No. of reflns measd	4528	3388
No. of indep rflns with $I>2\sigma(I)$	3448	1829
No. of parameters	293	181
$R1$ (obs. data)	0.0319	0.0407
$wR2$ (obs. data)	0.0841	0.0749
$R1$ (all data)	0.0410	0.0831
$wR2$ (all data)	0.0866	0.807
GooF on F^2	1.024	0.807
Resid. electron density (eÅ^{-3})	+0.353/−0.337	+0.763/−0.379

peaks $[M^+]$/$[M^+-H]$ as well as for the basis peak $[M^+-Br]$.

1-Chloro-2,4-bis(diisopropylamino)-1,3-diphosphetenium chloride (9a). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25°C): δ=72.8 [d, ^2J(P,P)=23.1Hz, *P*Cl], 123.4 [d, ^2J(P,P)=23.1Hz, *P*=C].

1-Bromo-2,4-bis(diisopropylamino)-1,3-diphosphetenium bromide (9b). ^1H NMR (CD_3CN, 25°C): δ=1.6–1.7 (m, 24 H, CH_3), 4.6 [sept, ^3J(H,H)=6.4Hz, 2H, CH], 4.7 [sept, ^3J(H,H)=6.7Hz, 2H, CH]. $^{31}P\{^1H\}$ NMR (CD_3CN, 25°C): δ=90.4 [d, ^2J(P,P)=54.0Hz, *P*Br], 123.2 [d, ^2J(P,P)=54.0Hz, *P*=C]. EI-MS (70eV), $[M^+]$ and $[M^+-H]$, *m*/*z* (%) calcd. for ratio 1:1/found: 443 (10.80)/(10.22), 444 (12.62)/(11.70), 445 (23.11)/(19.19), 446 (24.85)/(24.45), 447 (14.19)/(16.48), 448 (12.38)/(14.43), 449 (1.89)/(1.78), 450 (0.14)/(–); $[M^+-Br]$, *m*/*z* (%) calcd./found: 365 (42.75)/(43.42), 366 (7.19)/(7.00), 367 (42.41)/(42.29), 368 (7.07)/(6.61), 369 (0.56)/(0.68), 370 (0.03)/(–).

1-Iodo-2,4-bis(diisopropylamino)-1,3-diphosphetenium iodide (9c). ^1H NMR ($CDCl_3$, 25°C): δ=1.46 [d, ^3J(H,H)=6.6Hz, 3 H, CH_3], 1.53 [d, ^3J(H,H)=6.5Hz, 6 H, CH_3], 1.54 [d, ^3J(H,H)=6.9Hz, 3 H, CH_3], 3.58 [dsept, ^3J(H,H)=6.5, ^4J(P,H)=6.5Hz, 2H, CH], 4.16 [dsept, ^3J(H,H)=7.0, ^4J(P,H)=7.0Hz, 1H, CH], 4.42 [dsept, ^3J(H,H)=6.6, ^4J(P,H)=1.9Hz, 1H, CH]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ=16.3 (s, *C*H_3), 17.0 (s, *C*H_3), 20.0 [d, ^4J(P,C)=6.0Hz, *C*H_3], 21.5 [d, ^4J(P,C)=5.4Hz, *C*H_3], 49.0 (s, *C*H), 55.8 (s, *C*H), 59.4 [d, ^3J(P,C)=20.7Hz, *C*H], 61.8 [d, ^3J(P,C)=31.8Hz, *C*H], 185.9 [dd, ^1J(P,C)=90.7 and 4.4Hz, P=*C*]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ=62.3 [d, ^2J(P,P)=41.1Hz, *P*I], 192.2 [d, ^2J(P,P)=41.1Hz, *P*=C]. EI-MS (70eV, selected), *m*/*z* (%): 413 (10) $[M^+-I]$, 286 (13) $[M^+-2I]$, 243 (2) $[M^+-2I\text{-}C_3H_7]$, 143 (4) $[i\text{Pr}_2\text{NCP}^+]$, 128 (100) $[i\text{Pr}_2\text{NCP}^+-CH_3]$.

X-Ray structural analyses of 6a, 6b

Single crystals of good quality were obtained by crystallization from pentane solution. X-ray data of **6a** and **6b** were collected with a Syntex $P2_1$ diffractometer (Mo K_α radiation); structure solution by direct methods (SHELXS-86[22]) and structure refinement by SHELXL-93.[23] Crystallographic data are given in Table 2. Data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC-136868 (6a) and -136869 (6b) and can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1233)336-033; e-mail: teched@chemcrys.cam.ac.uk).

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