1,2,3-Triphosphetenes, First Examples of a New Class of Phosphorus Heterocycles**

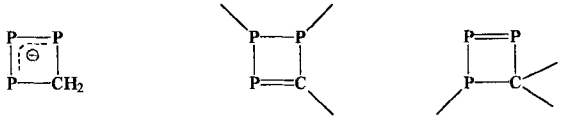
Heike Pucknat, Joseph Grobe,* Duc Le Van, Burkhardt Broschk, Marianne Hegemann, Bernt Krebs, and Mechtild Läge

Abstract: Hitherto unknown 1,2,3-triphosphetenes RC=P-PCF_3-PCF_3 (**3a–d**) are formed as main products in reactions of phosphaalkynes R-C≡P [R = *i*Pr_2N (**1a**), *t*Bu (**1b**), Me_2EtC (**1c**), 1-methylcyclohexyl (**1d**)] with the cyclotetraphosphane $(PCF_3)_4$ (**2**). According to NMR results the CF_3 groups in **3a–d** have a *trans* disposition; an X-ray diffraction study of **3a** confirms this structure. The P–P bond lengths in **3a** are equal [2.201(2) and 2.204(2) Å] and correspond to single bonds. A considerable shortening is observed for the sp^2-C–N bond (1.336 Å) which, together with the elongation of the P=C bond (1.746 Å), indicates effective π donation of the lone pair on nitrogen. Surprisingly, **3a** can be prepared in quantitative yields by reaction of the PP ylide $Me_3P{=}PCF_3$ (**6**) with **1a** (molar ratio: 2:1). In contrast, the corresponding reactions of **6** with the alkyl-substituted phosphaalkynes **1b–d** lead to the novel phosphorus ylides $Me_3P{=}C(R)$-P-PCF_3-PCF_3-PCF_3 [R = *t*Bu (**10a**), Me_2EtC (**10b**), 1-methylcyclohexyl (**10c**)] in good yields. In their molecular ground-state structures, determined by X-ray diffraction, the lone pair on the phosphano P atom prefers the *syn* position with respect to the ylidic P=C bond. An unusual lengthening of the sp^2-C–C bond [1.553(4) (**10a**), 1.543(6) (**10b**), 1.551(4) Å (**10c**)] to values typical for sp^3-C/sp^3-C distances is observed.

Keywords
heterocycles · insertion reactions · phosphaalkynes · phosphorus ylides · triphosphetenes

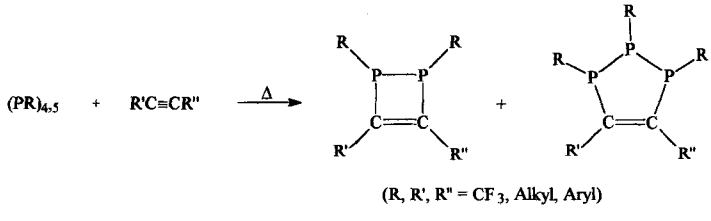
Introduction

The triphosphacyclobutenide ion **I**, produced and spectroscopically (^{31}P NMR) detected by Baudler et al.,[2] seems to be the only unsaturated four-membered triphosphaheterocyclic system reported to date.[3] Uncharged 1,2,3-triphosphetenes with P–C (**II**) or P–P (**III**) π bonds are also unknown.[4] Recent



I **II** **III**

studies of [2+2] cycloaddition reactions of phosphaalkynes[5] with heteroalkenes like phospha-[6–9] or silaalkenes[10] suggest that a successful synthesis of system **II** might be achieved by using reactive diphosphenes. According to earlier reports by Mahler,[11] Schmidt[12] and others,[13–15] diphosphene intermediates clearly play an important role in reactions of cyclophosphanes $(PR)_{4,5}$ with alkynes to yield 1,2-diphosphetenes and 1,2,3-triphospholenes (Scheme 1). Since phosphaalkynes and alkynes in some respect show similar properties, we recently decided to investigate the reactions of phosphaalkynes R-C≡P (**1a–d**) with trifluoromethylcyclophosphanes $(PCF_3)_n$ (n = 4, 5) and the phosphorus ylide $Me_3P{=}PCF_3$ (**6**), respectively. Here we report on the interesting results obtained.



Scheme 1.

Results and Discussion

Synthesis and Characterization of the 1,2,3-Triphosphetenes 3a–d: Phosphaethyne **1a** reacted with $(PCF_3)_4$ (**2**) in a 2:1 molar ratio in THF at 25 °C. Within 7 h **2** had been completely consumed (detected by ^{19}F NMR), and **3a** formed as the main product (ca. 70% yield relative to **1a**) (Scheme 2). The 1,2,3-triphosphetene **3a** was characterized by elemental analysis (C, H, N), spectroscopically and by single-crystal X-ray diffraction. In addition to **3a**, small amounts of the expected 1,2,3,4-tetraphospholene **4** were formed, but could not be isolated in pure form from the reaction mixture. The alkyl-substituted phos-

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[**] Reactive E=C(p–p)π Systems, Part 41. Part 40: see ref. [1].

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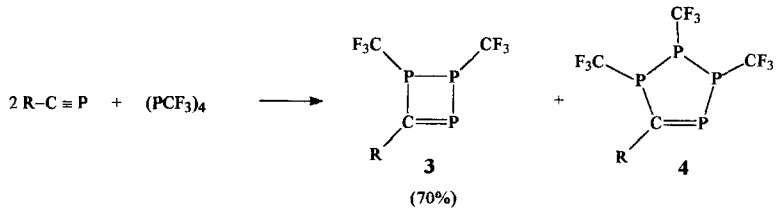


1,3	a	b	c	d
R	iPr$_2$N	tBu	Me$_2$EtC	Me

Scheme 2.

phaalkynes **1b–d** undergo similar reactions with **2** affording high yields of the derivatives **3b–d**. The only difference to **1a** is that a longer reaction time (ca. 24 h) is required. A much lower reactivity is observed under similar conditions in reactions of cyclopentaphosphane $(PCF_3)_5$ (**5**) with the phosphaalkynes to give the 1,2,3-triphosphetene derivatives.

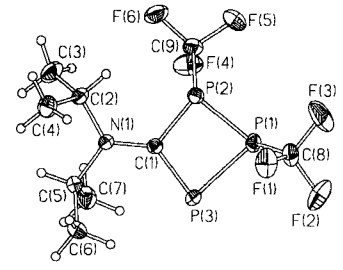
The novel heterocycles **3a–d** are stable at room temperature and in the usual organic solvents, provided that air is excluded. Dimerization by [2+2] addition of the P=C units of two triphosphetene molecules was not observed. Identity and structure of the new compounds were confirmed by spectroscopic investigations. The mass spectra generally show a molecular ion peak of relatively high intensity. The fragment ion $[M^+ - CF_3]$ is very often the base peak. The ^{19}F NMR spectra consist of two groups of signals, a low-field resonance with a chemical shift δ_F between -46.2 and -49.9 for the F_3CP-P unit and a high-field resonance between -53.2 and -55.2 for the F_3CP-C fragment. The coupling pattern dddq is due to the interactions with the three nonequivalent ^{31}P atoms and the second CF_3 group. An unusually low value of 1.2 Hz is observed for the $^3J(PF)$ coupling to the σ^2, λ^3-P atom.

The $^{31}P\{^1H\}$ NMR spectra of **3a–d** result from an AMX spin system. The complex coupling pattern can be interpreted and the coupling constants established from the spectra by using decoupling experiments and NMR simulation programs. As expected the resonances of the σ^2, λ^3-P atoms are found in the low-field region ($\delta_P = 117.5-318.9$) with typical $^1J(\sigma^2\text{-P}/\sigma^3\text{-P})$ values of 185–200 Hz.[16] The signals of the σ^3, λ^3-P nuclei appear at higher field with only small variations. A strong influence of the amino group is observed on the σ^2, λ^3-P resonance of **3a** causing an upfield shift of about 200 ppm relative to the signals of the C-alkyl compounds **3b–d**. The $^1J(\sigma^3\text{-P}/\sigma^3\text{-P})$ couplings in **3a–d** (100–120 Hz) are distinctly larger than those of tBuP or PhP diphosphetenes,[13] but agree very well with coupling constants of the corresponding CF_3P compounds.[14] Together with literature results[13, 14] they point to a *trans* arrangement of the CF_3 groups in **3a–d**, a hypothesis proved to be correct for **3a** by X-ray diffraction.

Further support for the molecular structures of **3a–d** emerges from $^{13}C\{^1H\}$ NMR investigations. Thus the resonance of the phosphaalkene carbon atom with ddd splitting is observed in the expected low-field region ($\delta_C = 185.4-229.7$) with typically large $^1J(\sigma^2\text{-P/C})$ coupling constants of 68.3–81.7 Hz.[7, 17] The special influence of the amino group on the bonding in **3a** shows up in a 20 ppm upfield shift of the sp^2-C resonance relative to those of the alkyl substituted analogues **3b–d** and a larger $^1J(\sigma^2\text{-P/C})$ coupling (by about 10 Hz). The ^{13}C NMR signals of the isopropyl substituents on the nitrogen atom of **3a** appear separately; this indicates chemical nonequivalence due to hindered rotation of the amino group about the sp^2-C–N bond.

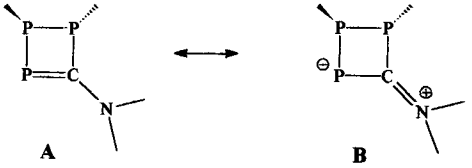
Crystal and Molecular Structure of the Triphosphetene 3a: The crystal structure analysis of **3a** confirms the composition and the molecular structure (Fig. 1) deduced from the NMR studies.

As expected the P_3C ring skeleton is nonplanar; the angle between the vectors of the P=C and the P–P bond is 20.7°. The P–P bond lengths are almost identical (2.201(2) and 2.204(2) Å) and correspond to a P–P single bond. The result of equal lengths for σ^2-P/σ^3-P and σ^3-P/σ^3-P bonds is in agreement with literature data of both acyclic and cyclic diphospha compounds.[16a, 18, 19] The C(2)C(5)N(1)C(1)P(2)P(3) framework of **3a** is comparable to that of the 1*H*-diphosphirene (iPr)Me$_3$SiN-C=P-P-NiPr$_2$ described by Niecke et al.[19] The planarity of this portion of the molecule (deviation from planarity: 0.048 Å), the short C(1)–N(1) bond and the elongation of the P(3)–C(1) bond [1.746(2) Å] support the view that the amino group acts as an effective π-electron donor and that the mesomeric form **B** makes a considerable contribution to the ground-state structure of **3a**.



3a

Fig. 1. Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.201(2), P(1)–P(3) 2.204(2), P(2)–C(1) 1.827(2), P(3)–C(1) 1.746(2), N(1)–C(1) 1.336(2), N(1)–C(2) 1.484(2), N(1)–C(5) 1.488(2), P(1)–C(8) 1.880(2), P(2)–C(9) 1.896(2); P(1)–P(3)-C(1) 85.62(6), P(3)-C(1)-P(2) 104.69(8), C(1)-P(2)-P(1) 83.84(6), P(2)-P(1)-P(3) 79.89(4), P(2)-C(1)-N(1) 124.5(1), P(3)-C(1)-N(1) 130.5(1), C(1)-N(1)-C(2) 121.4(2), C(1)-N(1)-C(5) 121.7(1), C(2)-N(1)-C(5) 116.8(1).

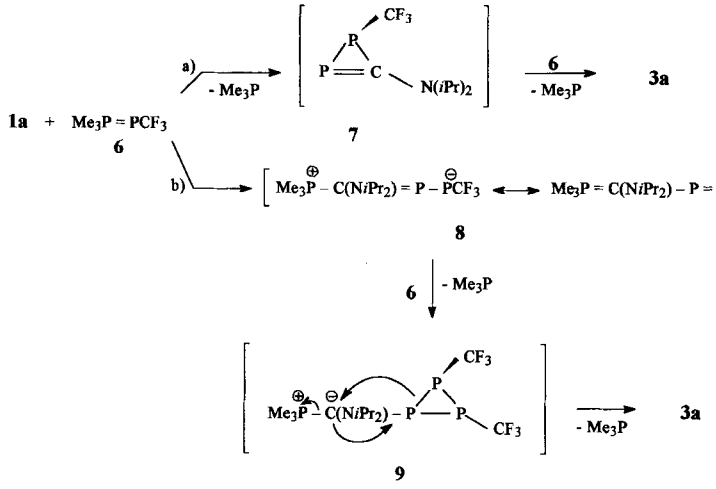


As in the known 1,2-diphosphetenes,[13, 14] the CF_3 substituents on P(1) and P(2) occupy *trans* positions. The torsional angle is 137.6°. The iPr groups are twisted so as to avoid close intramolecular contacts. Their geometrical arrangement resembles the conformation of the iPr$_2$N group in phosphaalkyne **1a**[20] and several other compounds derived from it.[21]

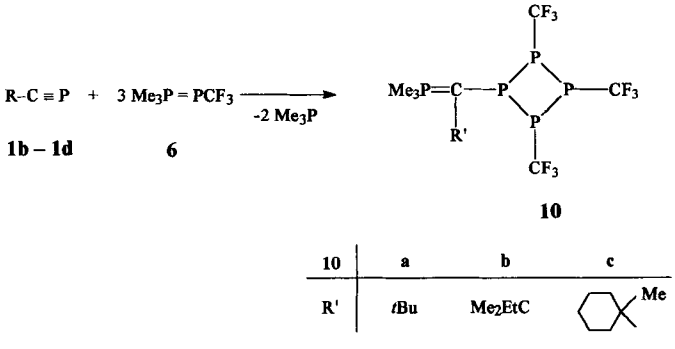
Phosphorus Ylides Me$_3$P=C(R)-P-PCF$_3$-PCF$_3$-PCF$_3$ (10a–c): In 1989 Fritz et al.[22] reported on reactions of the PP ylide adduct tBu$_2$P-P=P(Br)tBu$_2$ · LiBr with 2,3-dimethyl-1,3-butadiene (DMB) and cyclohexene. The products obtained point to the intermediate formation of the diphosphene [tBu$_2$P-P=P-PtBu$_2$] and/or the phosphinidene [tBu$_2$P-P̈:]. Our investigations of the generation and reactivity of the trifluoromethyl-substituted diphosphene [$F_3CP=PCF_3$] or phosphinidene [F_3C-P̈:][23] led us to the observation that the analogous reaction of the PP ylide $Me_3P=PCF_3$ (**6**)[24] with DMB exclusively yields the phospholene derivative H_2C-C(Me)=C(Me)-CH_2-PCF_3.[15] These diverging results caused us to study the reactions of **6** with the phosphaalkynes **1a–d**.

The reaction of **1a** with **6** (molar ratio: 1:2) took a surprising course to give the 1,2,3-triphosphetene **3a** in quantitative yield and, therefore, is particularly suited for the preparation of this

heterocycle. Even on changing the stoichiometry of **1a**/**6** to 1/1, no intermediate could be detected by NMR measurements. This allows us to make some conclusions with respect to the mechanism. As the formation of the diphosphene $F_3CP{=}PCF_3$ from **6** seems unlikely under the reaction conditions, the pathways shown in Scheme 3 can be considered as possible mechanisms for the formation of **3a**. According to course (a) the addition of **6** to **1a** followed by the loss of Me_3P yields the 1*H*-diphosphirene **7**, which quickly takes up an additional CF_3P unit into the PP bond to form **3a**. Support for this hypothesis comes from the known insertion of $[F_3C\text{-}\ddot{P}{:}]$ into the E–E bond (E = P, As) of diphosphanes or diarsanes.[25] Route (b) begins with the insertion of **1a** into the P–P bond of **6**, thereby transforming **6** to the PC ylide **8**, which adds another molecule of **6** to give **3a** by ring expansion and Me_3P elimination. There is good evidence that route (b) is more plausible than (a), because the reactions of **6** with the phosphaalkynes **1b–d** lead to the phosphorus ylides **10a–c** as main products (yields of 60–70%). By-products can be largely limited by adjusting the molar ratio **1b–d**:**6** to 1:3 (Scheme 4).



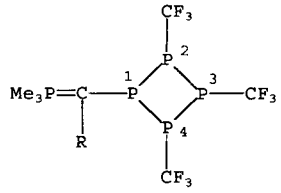
Scheme 3. Possible mechanisms for the formation of **3a** from **1a** and **6**.



Scheme 4.

The novel compounds **10a–c** are attacked by oxygen to give Me_3PO as one of the oxidation products. They were characterized spectroscopically. The ^{19}F NMR spectra consist of two complex signals at $\delta = -47$ and -51 with an intensity ratio of 1:2. In the corresponding $^{31}P\{^1H\}$ NMR spectra five interacting resonances are observed, which can be attributed to the different ^{31}P nuclei by decoupling experiments (Table 1). With the exception of the Me_3P signal, all other resonances show complicated multiplet structures due to numerous PP and PF couplings of the extremely complex spinsystem.

Table 1. ^{19}F and ^{31}P NMR data [a] of compounds **10a–c**.



	10a	**10b**	**10c**
^{19}F NMR			
CF_3P^3	−47.5 (dt, 3F) $^2J(P,F) = 56.5$ $^3J(P,F) = 9.0$	−47.8 (dtd, 3F) $^2J(P,F) = 55.5$ $^3J(P,F) = 9.9$ $^4J(P,F) = 3.0$	−46.2 (dt, 3F) $^2J(P,F) = 57.0$ $^3J(P,F) = 9.2$
$CF_3P^{2,4}$	−51.2 (dm, 6F) $^2J(P,F) = 45.6$	−51.6 (dm, 6F) $^2J(P,F) = 45.8$	−50.0 (dm, 6F) $^2J(P,F) = 44.0$
$^{31}P\{^1H\}$ NMR			
Me_3P	8.4 (d) $^2J(P,P) = 248.8$	8.5 (d) $^2J(P,P) = 250.4$	10.5 (d) $^2J(P,P) = 251.9$
P^1	1.2 (m)	2.6 (m)	5.2 (m)
P^2, P^4	−69.4 (m)	−67.6 (m)	−70.0 (m)
P^3	−94.8 (m)	−94.2 (m)	−93.1 (m)

[a] ^{19}F (188.31 MHz, CD_2Cl_2, CCl_3F as external reference), ^{31}P (81.01 MHz, CD_2Cl_2, 85% H_3PO_4 as external reference), *J* in Hz; **10a** in C_6D_6.

Clear proof for the structures of the crystalline compounds **10a–c** was obtained by single-crystal X-ray diffraction (see below). With reference to the chemistry of low-coordinate phosphorus compounds and phosphorus ylides, the formation of **10a–c** can be plausibly explained as follows: The multistep process starts with the insertion of a phosphaalkyne into the P=P bond of **6** (Scheme 5). Reaction of the intermediate **11** with an additional molecule of **6** yields the three-membered cyclophosphane derivative **12** after Me_3P elimination. Like $(PCF_3)_3$, **12** is a labile system,[26] which is stabilized by further addition of a CF_3P unit from **6** to produce the ylides **10a–c**.

The different behaviour of the related intermediates **9** (Scheme 3) and **12** (Scheme 5) is caused by the π-donating properties of the amino group in **9**. It is known from experimental[27] and theoretical studies[28] that π-donor substituents like NR_2, OR or F destabilize PC ylides. Therefore, compounds of the type $R_3P{=}C(X)R'$ (X = π-donor group) exhibit an increased tendency to dissociate to R_3P and $[{:}C(X)R']$. Intermediate **9** belongs to this class of ylide derivatives and spontaneously releases Me_3P. The resulting carbene then inserts into the neighbouring PP bond of the cyclotriphosphane fragment to give **3a**.

The reactions of the phosphaalkynes **1a–d** with the PP ylide **6** demonstrate for the first time the ability of σ^1, λ^3-P≡C species to insert into double bonds between σ^4, λ^5-P and σ^2, λ^3-P, probably via intermediates formed by [2+2] cycloaddition followed by ring opening.

Crystal and Molecular Structures of the P Ylides 10a–c: The crystallographic data of **10a–c** are given in Table 2. Figure 2 shows the molecular structures as determined from single-crystal structure analyses. As expected the different alkyl substituents on the ylidic C atom only slightly affect the molecular structure.

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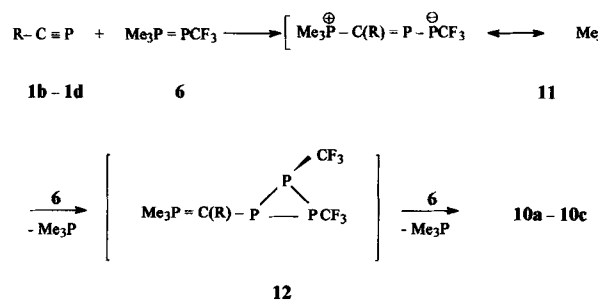
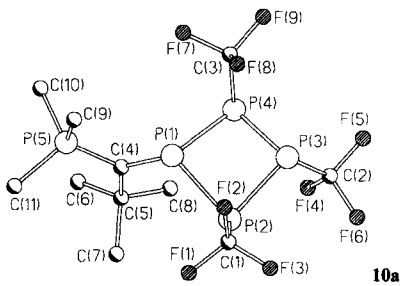
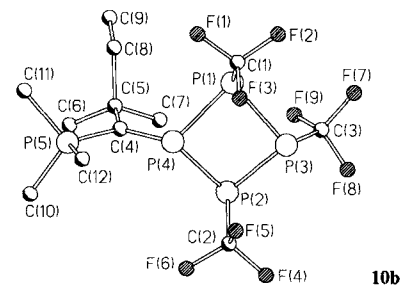


Scheme 5.





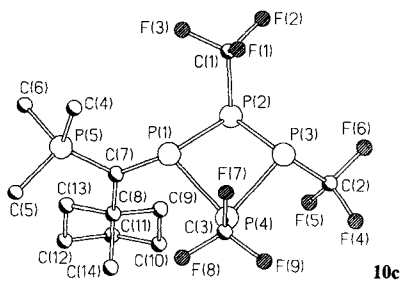


Fig. 2. Molecular structures of **10a–c**.

Table 2. Selected bond lengths (Å) and bond angles (°) for Compounds **10a–c**.

	10a	**10b**	**10c**
$d[\lambda^5, \sigma^4$ P–C(ylide)]	1.736(5)	1.749(4)	1.737(3)
$d[\lambda^3, \sigma^3$ P–C(ylide)]	1.734(5)	1.728(4)	1.735(3)
d(P–P)	2.258(2)	2.259(2)	2.250(2)
	2.221(2)	2.213(2)	2.212(2)
	2.212(2)	2.212(2)	2.210(2)
	2.290(2)	2.272(2)	2.296(2)
d[C(ylide)–C]	1.553(7)	1.543(6)	1.551(4)
∢PPP	85.2(1)	86.0(1)	83.0(1)
	86.4(1)	87.0(1)	85.6(1)
	84.7(1)	85.7(1)	84.2(1)
	83.7(1)	84.5(1)	82.8(1)
∢C(ylide)	110.3(3)	109.4(2)	109.9(2)
	122.0(3)	121.3(3)	121.9(2)
	127.6(3)	129.2(3)	127.8(2)

The new phosphorus ylides exhibit the following common structural characteristics:

1) The geometries around the ylidic P=C unit are tetrahedral and trigonal-planar as expected.

2) Both sp^2-C–P bond lengths are approximately equal; the σ^4, λ^5-P–C bond length of between 1.736(5) and 1.749(4) Å is significantly longer than typical for P ylides (1.63 to 1.71 Å).[29]

3) The molecular structures of **10a–c** can be described as a combination of two known structural units, namely, phosphano substituted phosphonium ylides[30] and cyclotetraphosphanes.[31, 32] Thus, the phosphano centres in **10a–c** show trigonal-pyramidal geometries as expected for $R_3P{=}CH{-}PR'_2$ compounds.[30] The lone pair on phosphorus occupies the *syn*, or (*Z*), position relative to the P=C bond (Fig. 3). According to a theoretical study[33] the phosphano lone pair is expected to take up either the *syn* (*Z*) or the *anti* (*E*) position perpendicular to the p (or π) orbital of the ylidic C atom.

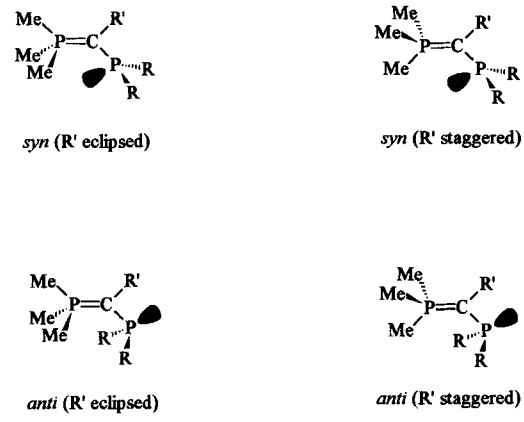


Fig. 3. Possible conformations of monophosphano-substituted phosphonium ylides.

In the three structures presented in Figure 2, the alkyl substituent on the sp^2-C atom generally takes up a staggered orientation relative to the methyl groups at the phosphonium centre and to the CF_3P groups bound to the phosphano P. Consequently, of the two possible *syn* conformations, only the structure with eclipsed positions of the phosphano lone pair and one of the methyl groups at the phosphonium P atom is observed.

4) A surprising elongation is found for the sp^2-C–C bonds [1.553(4) (**10a**), 1.543(6) (**10b**), 1.551(4) (**10c**) Å], which are now very close in length to sp^3-C/sp^3-C bonds;[34] these bonds differ distinctly from those in other P ylides.[35, 36] This deviation very probably is due to the steric interaction of the alkyl groups with the cyclotetraphosphane fragment.

5) The structural parameters of the cyclotetraphosphane fragment of the molecules **10a–c** mirror the *d*(PP), *d*(PC) and internal angles of $(PCF_3)_4$.[31] On the other hand, the (sp^2-C)P–P bond lengths of 2.250(2) to 2.296(2) Å are considerably longer than typical single bonds (2.20 Å).

Conclusion

The reported efficient synthesis of the 1,2,3-triphosphetenes (according to Scheme 2) once more demonstrates the close relationship between phosphaalkyne and alkyne chemistry. The novel compounds are the first examples of a new class of unsat-

urated four-membered phosphaheterocycles, which will open a broad field of interesting preparative work in organoelement and coordination chemistry by making use of the different reactive sites of the molecules.

Experimental Procedure

All reactions were carried out using a standard vacuum line. Reaction vessels were either Schlenk flasks or ampoules with serveral break seals and an NMR tube. Solvents and deuterated compounds for NMR measurements were carefully dried and degassed. Bis(isopropylamino)phosphaethyne (**1a**) was prepared by a procedure described recently [37]. Literature preparations were used for the syntheses of the phosphaalkynes **1b–d** [38,39], the cyclophosphanes $(PCF_3)_{4,5}$ [40] and the PP ylide $Me_3P{=}PCF_3$ (**6**) [24].

Apparatus: For elemental analyses: Perkin-Elmer Analyser 240. NMR: Bruker AC200 (200.13 MHz, ^1H, Standard: TMS; 188.31 MHz, ^{19}F, Standard: CCl_3F; 81.02 MHz, ^{31}P, Standard: 85% H_3PO_4; 50.32 MHz, ^{13}C, Standard: TMS). MS: Model CH 5 MAT-Finnigan.

Preparation of the 1,2,3-Triphosphetenes (3a–d): The best method for the preparation of the amino substituted triphosphetene **3a** is the reaction of **1a** with the ylide $Me_3P{=}PCF_3$ (**6**) in a 1:2 molar ratio. The derivatives **3b–d** could only be obtained by reacting phosphaalkynes **1b–d** with the cyclotetraphosphane $(PCF_3)_4$ (**2**).

1,2-Bis(trifluoromethyl)-4-di(isopropyl)amino-1,2,3-triphosphetene (3a): $(PCF_3)_4$ (451 mg, 1.13 mmol) was transferred into a Schlenk flask (100 mL, thoroughly dried by heating under vacuum) and treated with Me_3P (342 mg, 4.5 mmol) at room temperature with stirring. The PP ylide **6** was formed quantitatively in an exothermic reaction indicated by a colour change to yellow. After 30 min dry degassed diethyl ether (ca. 5 mL) and iPr_2N-C≡P (**1a**) (322 mg, 2.25 mmol) were introduced by vacuum condensation. The mixture was stirred at 20 °C for 24 h and then separated by trap-to-trap condensation (cooling baths at 0 and −196 °C). **3a** was condensed at 0 °C in form of pale yellow crystals. After dissolution in *n*-pentane it was recrystallized at −30 °C. Yield: 70%. ^1H NMR ($CDCl_3$, 25 °C): δ = 3.82 (sept., $^3J(H,H)$ = 6.8 Hz, 2H; CH), 1.49 (d, $^3J(H,H)$ = 6.4 Hz, 3H; CH_3), 1.47 (d, $^3J(H,H)$ = 6.4 Hz, 3H; CH_3), 1.22 (d, $^3J(H,H)$ = 6.5 Hz, 3H; CH_3), 1.16 (d, $^3J(H,H)$ = 6.4 Hz, 3H; CH_3); ^{19}F NMR ($CDCl_3$, 25 °C): δ = −49.9 (dddq, $^2J(P,F)$ = 40.5, $^3J(P,F)$ = 23.5, $^3J(P,F)$ = 1.2, $^5J(F,F)$ = 1.2 Hz, $PPCF_3$), −53.6 (dddq, $^2J(P,F)$ = 38.7, $^3J(P,F)$ = 20.3, $^4J(P,F)$ = 3.1, $^5J(F,F)$ = 1.2 Hz, $CPCF_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 117.5 (ddqq, $^1J(P,P)$ = 195.1, $^2J(P,P)$ = 44.2, $^3J(P,F)$ = 1.2, $^4J(P,F)$ = 3.1 Hz, P=C), 7.7 (ddqq, $^1J(P,P)$ = 106.8, $^2J(P,P)$ = 44.2, $^2J(P,F)$ = 38.7, $^3J(P,F)$ = 23.5 Hz, $CPCF_3$), −111.6 (ddqq, $^1J(P,P)$ = 195.1, 106.8, $^2J(P,F)$ = 40.5, $^3J(P,F)$ = 20.3 Hz, PPP); ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.1 (d, $^4J(P,C)$ = 10.8 Hz, CH_3), 20.9 (s, CH_3), 51.3 (s, CH), 57.7 (d, $^3J(P,C)$ = 19.2 Hz, CH), 129.5 (dddq, $^1J(F,C)$ = 325.5, $^1J(P,C)$ = 68.8, $^2J(P,C)$ = 7.1 Hz, CF3), 132.5 (ddq, $^1J(F,C)$ = 324.1, $^1J(P,C$ = 84.9, $^2J(P,C)$ = 7.2 Hz, CF3), 185.4 (ddd, $^1J(P,C)$ = 81.7, 24.8, $^2J(P,C)$ = 15.4 Hz, C=P); MS (70 eV, EI): *m/z* (%): 343 (44) [M^+], 274 (82) [$M^+ - CF_3$], 143 (29) [$M^+ - P_2C_2F_6$], 43 (100) [$C_3H_7^+$]. $C_9H_{14}F_6NP_3$ (343.1): calcd C 31.48, H 4.08 N 4.08; found C 32.22, H 4.09, N 4.11 (the rather large deviations of the experimental C values are very probably due to the difficult combustion and the air sensitivity of fluorine-containing organophosphorus compounds).

3b–3d: These compounds were prepared by the same general procedure, described here for **3b**. $(PCF_3)_4$ (320 mg, 0.80 mmol) was transferred into a carefully dried ampoule equipped with several break seals. Phosphaalkyne **1b** (160 mg, 1.60 mmol) was introduced by vacuum condensation, and the evacuated ampoule sealed off with liquid N_2 cooling. The reaction started when the compounds were melted and mixed, reflected in a colour change to yellow. The mixture was allowed to warm to room temperature over 3–4 h. Over this period it turned orange. NMR control measurements indicated complete reaction with formation of the 1,2,3-triphosphetene **3b** (main product) and the corresponding 1,2,3,4-tetraphosphole (by-product). Isolation of **3b** was achieved by vacuum condensation with traps at −30 and −196 °C. The light yellow triphosphetene **3b** was collected in the −30 °C trap, while the nonvolatile phosphole remained in the reaction vessel as an orange oily residue. Yields of **3b–3d**: 50–60%.

1,2-Bis(trifluoromethyl)-4-*tert*-butyl-1,2,3-triphosphetene (3b): ^1H NMR (C_6D_6, 25 °C): δ = 0.95 (ddd, $^4J(P,H)$ = 1.5, 1.0, $^5J(P,H)$ = 0.25, CH_3); ^{19}F NMR (C_6D_6, 25 °C): δ = −46.9 (dddq, $^2J(P,F)$ = 41.5, $^3J(P,F)$ = 18.6, 1.0, $^5J(F,F)$ = 1.0 Hz, $PPCF_3$), −55.2 (dddq, $^2J(P,F)$ = 48.2, $^3J(P,F)$ = 17.1, $^4J(P,F)$ = 2.8, $^5J(F,F)$ = 1.0 Hz, $CPCF_3$); $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 311.3 (ddqq, $^1J(P,P)$ = 186.6, $^2J(P,P)$ = 50.1, $^3J(P,F)$ = 1.3, $^4J(P,F)$ = 1.0 Hz, P=C), −18.2 (ddqq, $^1J(P,P)$ = 101.4, $^2J(P,P)$ = 47.9, $^2J(P,F)$ = 41.4, $^3J(P,F)$ = 18.2 Hz, $CPCF_3$), −100.7 (ddqq, $^1J(P,P)$ = 182.4, 100.9, $^2J(P,F)$ = 41.4, $^3J(P,F)$ = 17.1 Hz, PPP); ^{13}C NMR (C_6D_6, 25 °C): δ = 28.9 (ddd, $^3J(P,C)$ = 10.4, 3.9, $^4J(P,C)$ = 1.1 Hz, CH_3), 44.5 (dd, $^2J(P,C)$ = 8.0 Hz, CCH_3), 128.3 (dddq, $^1J(F,C)$ = 319.2, $^1J(P,C)$ = 69.6, $^2J(P,C)$ = 7.9 Hz, CF_3), 130.6 (ddq, $^1J(F,C)$ = 325.1, $^1J(P,C)$ = 73.8, $^2J(P,C)$ = 7.8 Hz, CF_3), 228.7 (ddd, $^1J(P,C)$ = 68.3, 40.1, $^2J(P,C)$ = 18.0 Hz, C=P); MS (70 eV, EI): *m/z* (%): 300 (10) [M^+], 231 (98) [$M^+ - CF_3$], 69 (100) [CF_3^+]; $C_7H_9F_6P_3$ (300.1): calcd C 28.02, H 3.02; found C 27.85, H 2.90.

1,2-Bis(trifluoromethyl)-4-(2,2-dimethylbutyl)-1,2,3-triphosphetene (3c) was produced from $(PCF_3)_4$ (320 mg, 0.80 mmol) and a 0.9:1 mixture of **1c** and hexamethyldisiloxane (469 mg, corresponding to 1.60 mmol of **1c**). ^1H NMR (CD_2Cl_2, 25 °C): δ = 1.65 (dq, $^3J(H,H)$ = 7.49 Hz, 2H, CH_2), 1.27 (dd, $^3J(H,H)$ = 10.08, $^4J(P,H)$ = 0.79 Hz, 6H, $C(CH_3)_2$), 0.92 (t, $^3J(H,H)$ = 7.49 Hz, 3H, CH_3); ^{19}F NMR (CD_2Cl_2, 25 °C): δ = −46.2 (dddq, $^2J(P,F)$ = 41.5, $^3J(P,F)$ = 18.7, $^3J(P,F)$ = 1.1, $^5J(F,F)$ = 1.1 Hz, $PPCF_3$), −54.1 (dddq, $^2J(P,F)$ = 48.2, $^3J(P,F)$ = 17.5, $^4J(P,F)$ = 2.5, $^5J(F,F)$ = 1.1 Hz, $CPCF_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 317.9 (ddqq, $^1J(P,P)$ = 185.3, $^2J(P,P)$ = 49.3, $^3J(P,F)$ = 1.1, $^4J(P,F)$ = 2.5 Hz, P=C); −15.4 (ddqq, $^1J(P,P)$ = 119.9, $^2J(P,P)$ = 49.3, $^4J(P,F)$ = 48.2, $^3J(P,F)$ = 18.7 Hz, $CPCF_3$), −97.4 (ddqq, $^1J(P,P)$ = 185.3, $^2J(P,P)$ = 119.9, $^2J(P,F)$ = 41.5, $^3J(P,F)$ = 17.5 Hz, PPP); ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 8.65 (dd, $^4J(P,C)$ = 6.91 Hz, CH_2CH_3), 26.15 (ddd, $^3J(P,C)$ = 13.43, $^4J(P,C)$ = 4.54 Hz, $C(CH_3)_2$), 34.45 (dd, $^4J(P,C)$ = 7.46 Hz, CH_2CH_3), 48.32 (dd, $^2J(P,C)$ = 13.82, $^3J(P,C)$ = 6.91 Hz, $C(CH_3)_2$), 128.13 (dddq, $^1J(F,C)$ = 325.61, $^1J(P,C)$ = 72.95, $^2J(P,C)$ = 9.36, CF_3), 130.45 (ddq, $^1J(F,C)$ = 322.12, $^1J(P,C)$ = 67.40, $^2J(P,C)$ = 5.73 Hz, CF_3), 228.6 (dddq, $^1J(P,C)$ = 70.84, 38.31, $^2J(P,C)$ = 14.0, $^3J(F,C)$ = 2.1 Hz, C=P); MS (70 eV, EI): *m/z* (%): 314 (17) [M^+], 245 (93) [$M^+ - CF_3$], 99 (42) [$M^+ - CH_3$], 83 (42) [$C_6H_{11}^+$]; $C_8H_{11}F_6P_3$ (314.1); calcd C 30.59, H 3.53; found C 29.45, H 3.48 (the rather large deviations of the experimental C values are very probably due to the difficult combustion and the air sensitivity of fluorine containing organophosphorus compounds).

1,2-Bis(trifluoromethyl)-4-(1-methylcyclohexyl)-1,2,3-triphosphetene (3d) was obtained by reaction of $(PCF_3)_4$ (320 mg, 0.80 mmol) and **1d** (224 mg, 1.60 mmol). ^1H NMR (CD_2Cl_2, 25 °C): δ = 1.0–2.18 (m, 10H, cyclohexyl), 1.25 (s, 3H, CH_3); ^{19}F NMR (CD_2Cl_2, 25 °C): δ = −46.2 (dddq, $^2J(P,F)$ = 41.35, $^3J(P,F)$ = 18.75, $^3J(P,F)$ = 1.08, $^5J(F,F)$ = 1.08 Hz, $PPCF_3$), −54.05 (dddq, $^2J(P,F)$ = 47.6, $^3J(P,F)$ = 17.9, $^4J(P,F)$ = 3.5, $^5J(F,F)$ = 1.08 Hz, $CPCF_3$), $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 318.9 (ddqq, $^1J(P,P)$ = 186.6, $^2J(P,P)$ = 49.3, $^3J(P,F)$ = 1.1, $^4J(P,F)$ = 3.5 Hz, P=C), −15.9 (ddqq, $^1J(P,P)$ = 119.5, $^2J(P,P)$ = 49.5, $^2J(P,F)$ = 47.6, $^3J(P,F)$ = 18.8 Hz, $CPCF_3$), −93.0 (ddqq, $^1J(P,P)$ = 186.6, $^4J(P,P)$ = 119.5, $^2J(P,F)$ = 41.4, $^3J(P,F)$ = 17.9 Hz, PPP); ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 22.6 (dd, $^4J(P,C)$ = 11.3, $^5J(P,C)$ = 3.8 Hz, C-3 cyclohexyl), 25.8 (s, C-4 cyclohexyl), 36.3 (ddd, $^3J(P,C)$ = 11.8, $^4J(P,C)$ = 4.8 Hz, CH_3), 37.3 (dd, $^3J(P,C)$ = 8.9 Hz, C-2 cyclohexyl), 48.1 (dd, $^2J(P,C)$ = 12.8 Hz, C-1 cyclohexyl), 128.1 (dddq, $^1J(F,C)$ = 325.2, $^1J(P,C)$ = 74.1, $^2J(P,C)$ = 10.6 Hz, CF_3), 130.1 (ddq, $^1J(F,C)$ = 322.1, $^1J(P,C)$ = 67.7, $^2J(P,C)$ = 5.6 Hz, CF_3), 229.7 (dddq, $^1J(P,C)$ = 72.1, 39.9, $^2J(P,C)$ = 14.3, $^3J(F,C)$ = 2.01 Hz, C=P); MS (70 eV, EI): *m/z* (%) = 340 (12) [M^+], 271 (69) [$M^+ - CF_3$], 69 (100) [CF_3^+].

Synthesis of the Phosphorus Ylides 10a–c: The PP ylide $Me_3P{=}PCF_3$ (**6**) (792 mg, 4.5 mmol) was prepared as described for the synthesis of **3a**. The phosphaalkyne **1b** (1.5 mmol) was added to the resulting ether solution (5 mL) in the Schlenk flask by vacuum condensation. The reaction mixture was then warmed to 20 °C and mixed with a magnetic stirrer. At the beginning of the reaction, the mixture slowly changed from yellow to red-orange. For the purpose of isolating the product **10a** all volatile compounds of the mixture were pumped off into a −196 °C trap. The orange oily residue was taken up in dry degassed *n*-pentane (ca. 2–3 mL) and kept in a refrigerator at −30 °C. After 3 d pale yellow crystals of **10a** separated from the red-orange solution and were collected for further investigations. Compounds **10b** and **10c** were produced similarly from **6** (792 mg, 4.5 mmol) and **1c** and **1d**, respectively (1.5 mmol). Yields: 60–70%. The new compounds were characterized by NMR spectroscopy (Table 1) and X-ray diffraction studies (Table 2).

X-ray Crystal Structure Analyses [41] of **3a, 10a–c**:

3a: $C_9H_{14}F_6NP_3$; M_r = 343.14, crystal dimensions: 0.17 × 0.23 × 0.18 mm, monoclinic, space group $P2_1/c$, a = 14.052(7), b = 6.157(3), c = 17.558(8) Å, β = 104.28(4)°, V = 1472.1 Å^3, Z = 4, D_c = 1.557 Mg m^{-3}, μ = 0.454 mm^{-1}. Measurements: SYNTEX $P2_1$, radiation: $Mo_{K\alpha}$ (λ = 0.71073 Å), T = 150 K, 2θ range: 4.0–54°, index ranges: $0 \le h \le 17$, $0 \le k \le 7$, $-21 \le l \le 22$. Reflections collected: 3604, independent reflections: 3235 [R(int) = 0.0176]. Data/restraints/parameters: 3234/0/228. Solution: direct methods. Refinement method: Full-matrix least-squares on F^2 (SHELXL-93 [42]). R indices (all data): R_1 = 0.0343, wR^2 = 0.0733; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0274, wR^2 = 0.0674.

10a: $C_{11}H_{18}F_9P_5$, M_r = 476.1, crystal dimensions: 0.15 × 0.18 × 0.20 mm, monoclinic, space group $P2_1/c$, a = 8.515(4), b = 24.072(9), c = 10.359(4) Å, β = 108.80(3)°, V = 2010 Å^3, Z = 4, D_c = 1.57 g cm^{-3}. Measurements: SYNTEX $P2_1$, radiation: $Mo_{K\alpha}$ (λ = 0.71073 Å), T = 150 K, 2θ range: 4–54°, reflections collected: 4412, reflections with $I > 2\sigma(I)$: 2911. Solution: direct methods, SHELXTL PLUS, full-matrix least squares, all non-hydrogen atoms from E-map, H atoms from difference Fourier synthesis, isotropic temperature factors. R_1 = 0.0558, R_2 = 0.552.

10b: $C_{12}H_{20}F_9P_5$, M_r = 491.14, crystal dimensions: 0.22 × 0.12 × 0.15 mm, orthorhombic, space group $Pbca$, a = 15.086(5), b = 14.163(4), c = 20.047(6) Å,

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$Z = 8$, $D_c = 1.523\ Mg\,m^{-3}$, $V = 4283\ Å^3$, $\mu = 0.498\ mm^{-1}$. Measurements: SYNTEX $P2_1$ radiation: $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 150$ K, 2θ range: 5.0–54°, index ranges: $0 \le h \le 19$, $0 \le k \le 20$, $0 \le l \le 26$. Reflections collected: 4691, independent reflections: 4691 [R(int) = 0.0000]. Solution: direct methods. Refinement: full-matrix least-squares on F^2 (SHELXL-93 [42]). Data/restraints/parameters: 4691/0/235. R indices (all data): $R_1 = 0.1189$, $wR^2 = 0.1548$; Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0594$, $wR^2 = 0.1247$.

10c: $C_{14}H_{22}F_9P_5$, $M_r = 516.17$, crystal dimensions: $0.22 \times 0.15 \times 0.08$ mm, monoclinic, space group $P2_1/n$, $a = 10.860(4)$, $b = 13.805(4)$, $c = 15.014(6)$ Å, $\beta = 98.69(3)°$, $V = 2225.1$ Å^3, $Z = 4$, $D_c = 1.541\ Mg\,m^{-3}$, $\mu = 0.483\ mm^{-1}$. Measurements: SYNTEX $P2_1$, radiation: $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 150$ K, 2θ range: 4.0–54°, index ranges: $0 \le h \le 13$, $0 \le k \le 17$, $-19 \le l \le 18$. Reflections collected: 5139, independent reflections: 4885 [R(int) = 0.0289]. Solution: direct methods. Refinement: full-matrix least-squares on F^2 (SHELXL-93 [42]). Data/restraints/parameters: 4883/0/341. R indices (all data): $R_1 = 0.0802$, $wR^2 = 0.1072$; Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0450$, $wR^2 = 0.0905$.

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