ELSEVIER

Journal of Organometallic Chemistry 529 (1997) 177–187

Journal of Organometallic Chemistry

Synthesis, structure and isomerization of fluorine-containing 1,2-dihydro-1,3-diphosphetes [1]

Joseph Grobe [a,*,2], Duc Le Van [a], Burkhardt Broschk [a], Marianne Hegemann [a], Bettina Lüth [a], Gerd Becker [a], Matthias Böhringer [b], Ernst-Ulrich Würthwein [c]

[a] *Anorganisch-Chemisches Institut der Westfälischen Wilhelms-Universität, Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany*
[b] *Institut für Anorganische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*
[c] *Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität, Corrensstraße 40, D-48149 Münster, Germany*

Received 5 April 1996; revised 3 June 1996

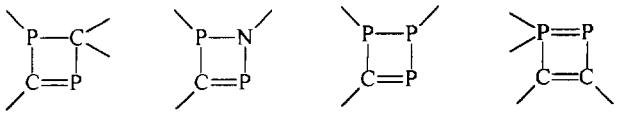
Abstract

Reaction of perfluoro-2-phosphapropene **1** with phosphaalkynes of the type RC≡P (**2**) smoothly yields the formal [2 + 2] cycloaddition products, 1,2-dihydro-1,3-diphosphetes $\overline{RC{=}P-\,-CF_2-\,-PCF_3}$ (R = Me_2N (**3a**), Et_2N (**3b**), $^iPr_2N$ (**3c**), ^{t}Bu (**3d**)). Instead of the not isolable aminophosphaalkynes $Me_2NC{\equiv}P$ and $Et_2NC{\equiv}P$, the precursors $HP{=}C(F)NR_2$ are successfully used as synthetic equivalents. The results of a single-crystal X-ray analysis of **3a** almost exactly agree with the structural data of an ab initio calculation. The elongated sp^2 CP distance in **3a** (exp. 173.7(2) pm, calc. 171.4 pm) is due to the interaction of the Me_2N lone pair with the PC (p–p)π bond. Surprisingly, the sterically unshielded derivatives **3a** and **3b** at 25 °C undergo an interesting rearrangement to the thermodynamically more stable 1,2-dihydro-1,2-diphosphetes $\overline{RC{=}C(F)-\,-P(CF_3)-\,-PF}$ (R = Me_2N (**6a**), Et_2N (**6b**)) via a 1,2-fluorine shift, an electrocyclic ring opening to a 1,4-diphosphabutadiene intermediate and an intramolecular [2 + 2] cycloaddition. This mechanism is supported by high level ab initio calculations.

Keywords: Fluorophosphaalkene; Phosphaalkynes; Cycloaddition; 1,2-Dihydro-1,3-diphosphetes; 1,2-Dihydro-1,2-diphosphetes; Isomerization

1. Introduction

During the last five years extensive studies of cycloaddition reactions of phosphaalkynes RC≡P have been performed [2] leading to a series of novel phosphaheterocycles. Of particular interest is the extension of the class of unsaturated four-membered phosphorus–carbon ring systems of types **I** to **IV**. For reviews see Ref. [3]. For $1\lambda^3\sigma^2,3\lambda^3\sigma^3$-diphosphetenes (**I**) see Refs. [4–8] and Refs. [9–11] for further derivatives with $1\lambda^3\sigma^2,3\lambda^3\sigma^3$ diphosphete structure elements; Ref. [6] contains a preliminary account of this work. For azadiphosphetine (**II**) see Ref. [12]. For 1,2,3-triphosphetenes (**III**) see Ref. [13] and for a report on the first 1,2-dihydro-1,2,3-triphosphetene-tungsten complex see [14]. For $1\lambda^5 3\lambda^3$-diphosphete (**IV**) see Ref. [15].



I **II** **III** **IV**

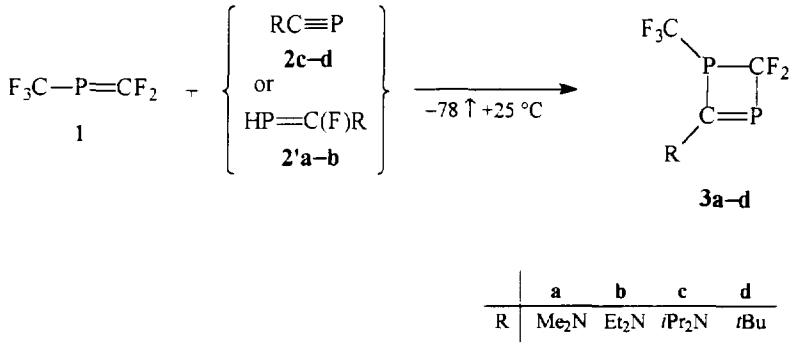
As a rule, for the preparation of such compounds *tert*-butylphosphaethyne has been used as the starting material, and thus the substituent pattern on the sp^2-C atom was limited. Derivatives with heteroatom groups on the four-membered ring are rare. Therefore, we have investigated the reactivity of perfluoro-2-phosphapropene $F_3C{-}P{=}CF_2$ (**1**) with phosphaalkynes RC≡P (R = Me_2N (**2a**), Et_2N (**2b**), $^iPr_2N$ (**2c**), ^{t}Bu (**2d**)) [6], a study which parallels that of Niecke and coworkers [8] on the formal [2 + 2] cycloaddition of 2-[isopropyl(tri-

* Corresponding author.

[1] Dedicated to Professor Dr. W. Jeitschko on the occasion of his 60th birthday.

[2] Reactive $E = C(p{-}p)\pi$ systems, Part 44. Part 43: see Ref. [1].

PII S0022-328X(96)06579-5



Scheme 1.

methylsilyl)amino]phosphaethyne with *P*-halogeno silylphosphaalkenes.

Here we report both on the formation and structure of novel fluorine-containing diphosphetenes of type **I** and on the interesting isomerization of the two labile derivatives **3a** and **3b**.

2. Synthesis and spectroscopic investigations of 1 $\lambda^3\sigma^2$,3 $\lambda^3\sigma^3$-diphosphetes 3a–3d

When perfluoro-2-phosphapropene **1** is added by vacuum condensation to an equimolar amount of di(isopropyl)aminophosphaethyne **2c** in dichloromethane, a quick reaction of the unsaturated phosphorus compounds takes place on warming up the solution from −78 to 25 °C. Immediate control by ^{19}F and ^{31}P NMR measurements clearly indicates an almost quantitative formation of a (1:1) adduct. The unavoidably concurring di- and oligomerisation [16] of **1** only plays a minor part in the reaction. After fractional condensation to remove the solvent and traces of the diphosphetane $(F_3CPCF_2)_2$, the pure 1,2-dihydro-1,3-diphosphete **3c** is obtained by sublimation in 35% yield as a colourless, crystalline compound.

For the reaction of **1** with the not isolable aminophosphaalkynes $Me_2NC{\equiv}P$ (**2a**) and $Et_2NC{\equiv}P$ (**2b**) [17], the easily accessible precursors $HP{=}C(F)NR_2$ (**2'a**, **2'b**) are used as synthetic equivalents. From reactivity studies on these phosphaalkenes it was known that in some cases, e.g. formation of 1,2,3-triphosphetenes [13] by reaction with the cyclotetraphosphane $(F_3CP)_4$, they yield products derived from the corresponding phosphaalkynes [18]. This allows a simple preparation of the diphosphetenes **3a** and **3b** in 40 to 45% yields [3] (Scheme 1). In this process, obviously the resulting phosphaheterocycles act as HF acceptors, since NMR control measurements show that both starting compounds react completely without formation of HF addition products.

In a similar manner the *tert*-butylphosphaethyne **2d** reacts with **1** at room temperature to give **3d**. However, the [2 + 2] cycloaddition is much slower in this case (ca. 5 days) and, therefore, is accompanied by the self-addition of **1**.

While the derivatives **3c** and **3d** are inert for weeks at 25 °C even in organic solvents, **3a** and **3b** undergo a rearrangement in polar solvents, indicated by a colour change to yellow (see below). The possible dimerization by a [2 + 2] addition of the P=C bonds of two diphosphetene molecules was not observed.

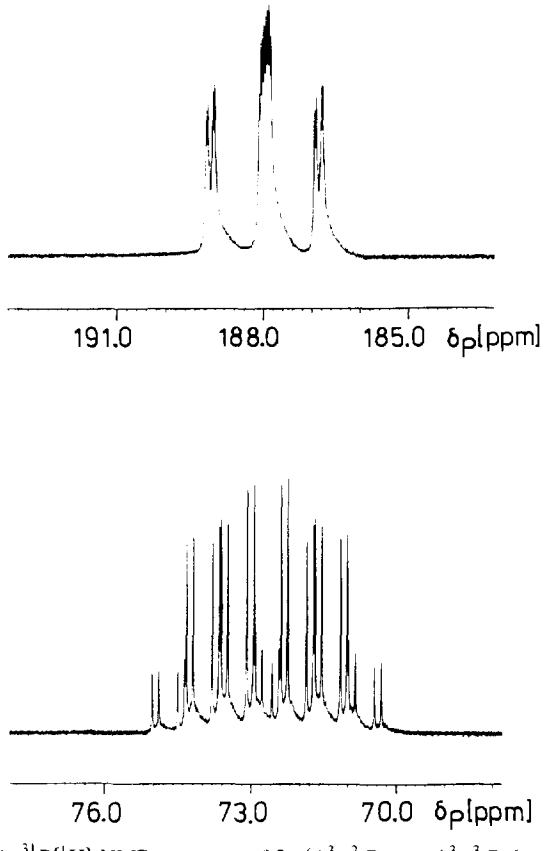


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of **3a** ($\lambda^3\sigma^2$-P: top, $\lambda^3\sigma^3$-P: bottom).

[3] Higher yields of isolated **3a,b** in comparison with **3c** are due to their higher volatility.

The diphosphetenes **3a** to **3d** were characterized by elemental analysis and spectroscopic investigations as well as by an X-ray diffraction study of **3a**. The mass spectra generally show the molecular mass peak M^+ with relatively high intensity. The fragment ion $[M^+ - CF_3 - CF_2]$ in most cases is the basis peak of the spectrum.

In the ^{19}F NMR spectra the resonance of the CF_2-group results from an AB-spin system and appears in the expected region between −80 and −110 ppm with typically large F_A, F_B coupling constants of 255 Hz for **3a** to **3c** and 273.5 Hz for **3d** [19]. A remarkable high field shift of 12 ppm for F_A and 16 ppm for F_B, compared with the *C*-amino-substituted compounds, is observed for the ^{t}Bu-derivative **3d**.

The $^{31}P\{^1H\}$ NMR spectra of **3a** to **3d** result from AX spin systems with dddq-patterns due to J(P,P) and J(P,F) couplings (Fig. 1). The resonance of the σ^3-P atoms of **3a** to **3d**, as expected, is found in the high field region (δ_P = 72.7–86.0) and shows little variation, while the signal of the two-coordinated phosphorus in **3d** (δ_P = 370.5) experiences a large low field shift relative to the amino-substituted compounds **3a** to **3c** (δ_P = 182.8–188.1). A similar substituent effect was recently observed for the 1,2,3-triphosphetenes [13]. Thus the δ_P-values of the σ^2-P atoms in **3a** to **3c** correspond to literature data of other sp^2-C amino-substituted analogues [8], while the chemical shift of σ^2-P in **3d** agrees with those of the ^{t}Bu diphosphetenes [7]. However, the ^2J(P,P) coupling constants of 11.4 to 13.9 Hz are distinctly smaller than the characteristic values of about 90 Hz [7] or 120 Hz [8] (depending on the substituents on the P_2C_2-ring) of known 1,2-dihydro-1,3-diphosphetes; but, they are in accord with the data of σ^3-P acyl-substituted analogues (16.2 to 16.9 Hz) [4].

The $^{13}C\{^1H\}$ resonance of the sp^2-C atom in **3a** to **3c** appears as a dd-pattern at low field (δ_C = 182.3 to 187.8) with typically large $^1J(\sigma^2$-P,C) values of 52.0 to 61.2 Hz [4–8,20] and $^1J(\sigma^3$-P,C) constants of 30.5 to 35.4 Hz. The ^{13}C signals of the alkyl substituents on nitrogen, in agreement with the corresponding ^1H NMR spectra, show up at different chemical shifts at 25 °C and may be due to hindered rotation of the dialkylamino group around the sp^2-CN bond.

3. Crystal and molecular structure of the 1,2-dihydro-1,3-diphosphete 3a

The low temperature crystal structure determination of **3a** confirms its molecular constitution as already deduced from the NMR spectra (Fig. 2).

With endocyclic torsional angles [22] between 8 and 9° (e.g. P(1)–C(4)–P(3)–C(2) +8.8°; P(1)–C(2)–P(3)–C(4) −8.4°), the four-membered ring skeleton of the 1,2-dihydro-1,3-diphosphete is almost planar; the positions of both the phosphorus (P(1) +6.5; P(3) +6.8 pm) and carbon atoms (C(2) −6.3; C(4) −7.1 pm) deviate only insignificantly from their least squares plane. Angular sums of 359.9° and 359.7° indicate trigonal planar coordination for the atoms N(4) and C(4); a torsional angle of just 3.7° for P(3)–C(4)–N(4)–C(42) shows the dimethylamino group to be coplanar with the four-membered ring skeleton. Compared with standard values of 143 pm [23] and 167 pm [4,24] for an N(sp^2)–C(sp^2) and a P=C bond length [4] respectively, the intramolecular distances within the characteristic N(4)–C(4)=P(3) fragment are found to be shortened to a value of 132.8 pm (Table 1) on the one hand and to be elongated to 173.7 pm on the other hand.

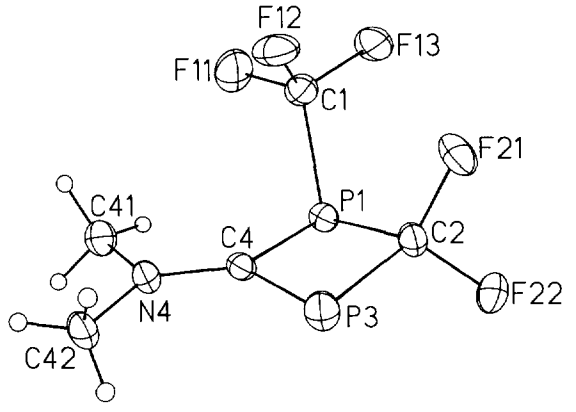


Fig. 2. Molecular model of compound **3a** with the atomic numbering scheme employed. Thermal ellipsoids of the heavier atoms with 25% probability, circles of arbitrary size for the hydrogen atoms [21].

These structural features may be interpreted in terms of strong electronic interactions between the free p-electron pair at nitrogen and the P=C π-system; as a consequence, the a priori positive net partial charge of phosphorus atom P(3), which is further increased by the adjacent CF_2 group, will be reduced. In **3a** the deviation of N(sp^2)–C(sp^2) and P=C bond lengths from standard values, however, is found to be much larger than in *P-tert*-butyl(dimethylamino)methylidene-phosphane, for which intramolecular distances of 134.8 and 170.4 pm within the N–C=P fragment have been determined together with angular sums of 359.0° and 359.9° for nitrogen and carbon respectively [25]. These differences in bond lengths indicate an *increased* shift of electron density towards the two-coordinated phosphorus of **3a**. Finally, it should be noted that a comparable elongation of the P=C bond is generally observed in *C*-amino-sub-

[4] Bond lengths of 167.9 and 167.2 pm have respectively been determined for, e.g., the analogous 1,2-dihydro-1,3-diphosphete ^{t}BuC(O)P−−C(^{t}Bu)OSiMe$_3$−−P=C–OSiMe$_3$ [4] and the corresponding unit of a tricyclic tetramer of *tert*-butylphosphaethyne with two dihydrophosphete rings [10].

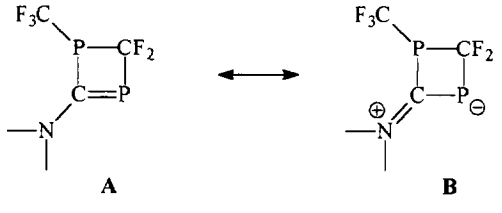
Table 1
Selected bond lengths (pm) and angles (deg) for compound **3a**. For experimentally determined bond lengths and angles not specified in the table, ranges are given below [a]

	Exp.	Calc. [b]		Exp.	Calc. [b]
P(1)–C(1)	189.3(2)	189.0	C(1)–P(1)–C(2)	100.9(1)	104.2
P(1)–C(2)	188.5(2)	188.0	C(1)–P(1)–C(4)	101.1(1)	100.2
P(1)–C(4)	182.6(2)	183.6	C(2)–P(1)–C(4)	79.1(1)	79.3
C(2)–P(3)	185.9(2)	187.5	P(1)–C(2)–P(3)	95.5(1)	94.9
C(2)–F(21)	136.9(2)	134.3	P(1)–C(2)–F(21)	115.5(1)	114.1
C(2)–F(22)	137.6(2)	134.4	P(1)–C(2)–F(22)	112.8(1)	111.7
P(3)–C(4)	173.7(2)	171.4	P(3)–C(2)–F(21)	115.6(1)	115.5
C(4)–N(4)	132.8(2)	133.0	P(3)–C(2)–F(22)	114.7(1)	115.1
C(1)–F(11)	135.1(3)	133.5	F(21)–C(2)–F(22)	103.3(1)	105.5
C(1)–F(12)	132.9(3)	131.7	C(2)–P(3)–C(4)	82.1(1)	82.6
C(1)–F(13)	133.4(2)	132.1	P(1)–C(4)–P(3)	102.1(1)	102.3
N(4)–C(41)	145.9(3)	(H: 99.6)	P(1)–C(4)–N(4)	127.7(1)	125.3
N(4)–C(42)	146.0(3)	(H: 99.7)	P(3)–C(4)–N(4)	129.9(1)	132.9
			C(4)–N(4)–C(41)	112.0(2)	(H: 122.0)
			C(4)–N(4)–C(42)	118.2(2)	(H: 121.2)
			C(41)–N(4)–C(42)	117.7(2)	(H,H: 116.8)

[a] P(1)–C(1)–F(1*n*) 109.6(2)–115.7(1); F(1*n*)–C(1)–F(1*n'*) 106.2(2)–107.7(2); C(41)–H(41*n*) 95.(3)–99(3); C(42)–H(42*n*) 87(3)–96(4); N(4)–C(4*m*)–H(4*mn*) 104(3)–115(2); H(4*mn*)–C(4*mn'*) 96(3)–121(3); $m = 1,2$; $n,n' = 1,2,3$; $n \neq n'$.
[b] (6-31 + G*//6-31 + G*).

stituted phosphaalkene fragments of unsaturated phospha-heterocycles [8,13] [26,27] or in R_2N-conjugated 1.3-diphosphapropenes [28].

The structural data of **3a** discussed above are in accord with the NMR spectroscopic observation of hindered rotation of the dimethylamino group showing up in two different multiplets at room temperature, both in the ^1H and the $^{13}C\{^1H\}$ spectrum. Owing to the complexity of the signals, however, the barrier of rotation could not be determined. Hence, the mesomeric structure **B** contributes considerably to the ground state of **3a** (see formula below).



With the exception of the P(1)–C(4) distance (182.6 pm), which corresponds very well to the P–C(sp^2) standard of 183 pm, the bonds P(1)–C(1) and P(1)–C(2) are found to be strongly elongated to values of 189.3 pm and 188.5 pm respectively. This observation is in good agreement with molecular parameters recently obtained from a low temperature crystal structure determination of centrosymmetric tetrakis(trifluoromethyl)diphosphane [29] with average P–C and C–F distances of 188.3 pm and 131.7 pm respectively.

In the past, several research groups [30–32] have studied the problem of elongated P–CF_3 bonds and introduced terms such as 'altruistic covalent interactions' [30,31] or 'counter-intuitive orbital mixing' [31] to describe this phenomenon. We suggest that this elongation can be explained by electrostatic repulsion between the positively charged phosphorus and carbon atoms, for the latter due to the −I-effect of the adjacent fluorine atoms [32]. Consequently, P–CF_x bonds are expected to be shortened both by decreasing the number x of fluorine substituents and the net charge on phosphorus, e.g. by a mesomeric effect as discussed above. In keeping with this expectation, the P(3)–C(2) bond

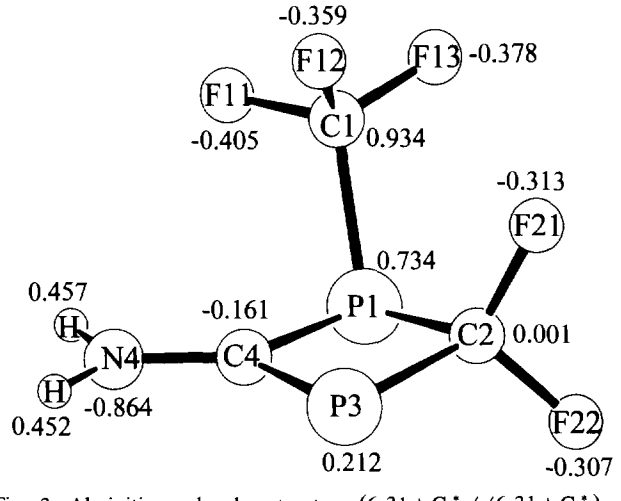


Fig. 3. Ab initio molecular structure (6-31 + G*//6-31 + G*) of compound **3'** with total atomic charges (Mulliken population analysis); Crystallographic numbering: see Fig. 2.

adopts a length of only 185.9 pm. Furthermore, the difference of 3.5 pm for the average C–F bond lengths of the CF_3 and CF_2 groups of **3a** (133.8 vs. 137.3 pm) corresponds very well with the observed increase of C–F distances in the series of $CH_{4-x}F_x$ molecules from 131.7 (CF_4) [33] to 138.2 pm (CH_3F) [34].

The experimentally deduced model for the electronic structure of **3a** to **3c** is strongly supported by ab initio calculations (6-31 + G*//6-31 + G* basis set) for the parent compound **3'**, where the NMe_2 substituent has been exchanged for NH_2. In Table 1 the calculated bond lengths and angles are given next to the results of the crystal structure determination, and they demonstrate an excellent correspondence. Fig. 3 shows the Mulliken charges for **3'**, which are in full agreement with the arguments given above.

4. Isomerization of 3a and 3b to the 1,2-dihydro-1,2-diphosphetes 6a and 6b

As mentioned above, the originally colourless solution of **3a** or **3b** in di- or trichloromethane slowly changes to yellow-brown (amber-like), possibly under the influence of diffuse day-light. ^{19}F NMR measurements show a continuous decrease of the resonances of **3a** or **3b** together with the appearance of three new signals with chemical shifts for CF_3P, FC and FP groups (intensity ratio of 3:1:1). Both the typical $^1J(P,F)$ coupling constants of 1003.3 or 1007.2 Hz and the ddqd-pattern of the PF-signals indicate a 1,2-fluorine shift as the first step of the isomerization. A complete transformation under the given conditions is observed for **3a** after about 4 weeks, and for **3b** after 6 weeks. The resulting products are obtained as yellow oils.

The mass spectra of the isomers show the same molecular masses as **3a** or **3b**, but different fragmentation patterns and peak intensities, e.g. basis peak for **3a**: $m/z = 118$ [$M^+ - CF_3 - CF_2$], basis peak for **6a**: $m/z = 168$ [$M^+ - CF_3$]. The ^{19}F NMR spectra exclude the possible isomerization of **3a** or **3b** by ring-opening to the corresponding 1,3-diphosphabuta-1,3-dienes. This result gains support from the fact, that the thermally allowed conrotatory ring-opening of 1,2-dihydro-1,3-diphosphete to give *Z*- or *E*-1,3-diphosphabutadiene, according to ab initio MP2/6-31G* calculations [35], is endothermic by 12.71 kcal mol^{-1} for *Z* and 13.17 kcal mol^{-1} for *E*. So far, only the reverse ring closure reaction of 1,3-diphosphabutadienes has been detected [4].

All obtainable spectroscopic information on the constitution of the isomerization products of **3a** or **3b** are in accord only with the structure of the 1,2-dihydro-1,2-diphosphetes $F_3CP--C(F)=C(NR_2)--PF$ (R = Me (**6a**), Et (**6b**)). Structurally relevant data are ase follows.

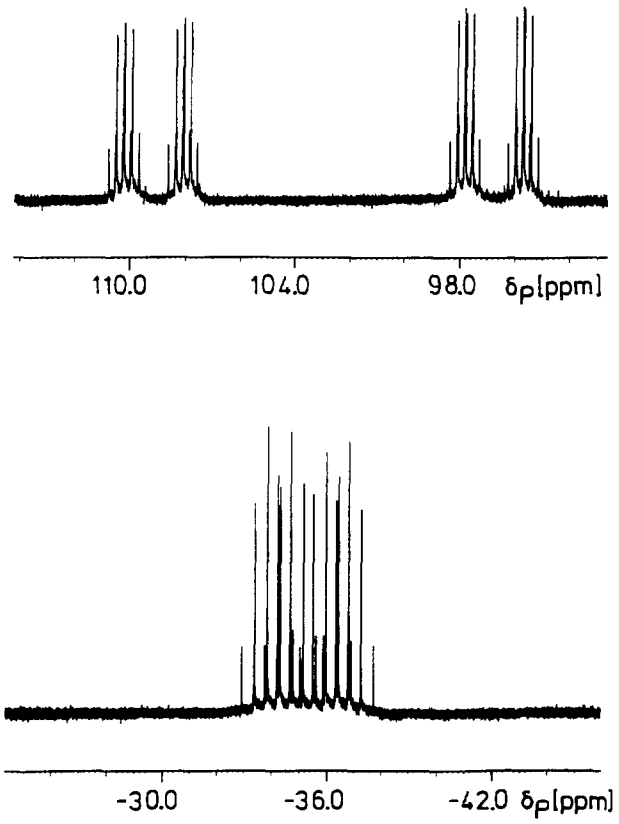


Fig. 4. $^{31}P\{^1H\}$ NMR spectrum of **6a** (product of the isomerization of **3a**; signal of *P*F: top, *P*CF_3: bottom).

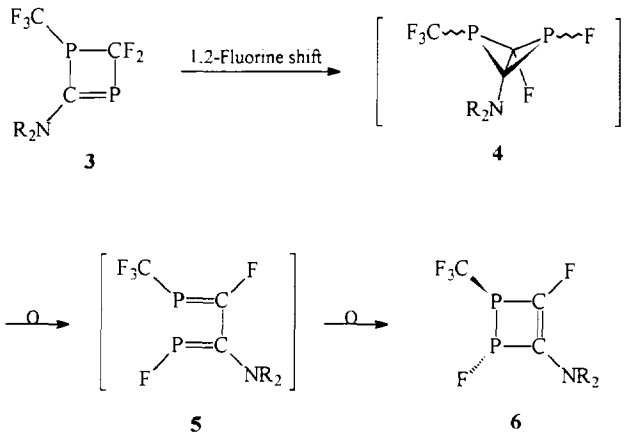
(i) The ^{19}F chemical shift of the CF group at $\delta_F = -118.5$ ppm is clearly indicative for the bonding of fluorine to an sp^2-C atom [36] in an olefinic, but not in a phosphaalkene fragment with $\delta_F(FC=P) = +9$ to -50 ppm [37]. The couplings of the CF-group with the PF-unit are small ($J(P,F) = 24.8$ (**6a**) or 24.9 Hz (**6b**), $J(F,F) = 0.4$ (**6a**) or 0.5 Hz (**6b**)), thus excluding a direct bond between CF and PF.

(ii) The ^{31}P NMR signals of **6a** and **6b** show up at chemical shifts δ_P typical for three-coordinated, fluorine-containing phosphorus compounds (high field relative to **3a** or **3b**, Fig. 4). The $^1J(P,P)$ coupling constants amount to ca. 172 Hz and are considerably larger than those of P^{t}Bu- or PPh-substituted 1,2-diphosphetenes [38], but are in agreement with those of P–CF_3 analogues [39].

(iii) Important structural arguments for **6a** or **6b** arise from the $^{13}C\{^1H\}$ NMR spectra, since $\delta(CF)$ values of 124.1 (**6a**) or 123.5 ppm (**6b**) and $\delta(CNR_2)$ of 142.3 (**6a**) or 139.8 ppm (**6b**) can be attributed neither to phosphaalkene [5] [40] nor to 2,4-diphosphabicyclobutane structures [6] [41]. The δ_C-values only correspond to

[5] Typical chemical shifts for the sp^2-hybridized carbon atoms in phosphaalkene compounds: $\delta_C = 170–210$.

[6] Only one compound containing the 2,4-diphosphabicyclobutane unit as part of the structure is known; δ_C (bridgehead-carbon) = 70.



(**a** : R = Me , **b** : R = Et)

Scheme 2.

spectroscopic results for olefinic C-atoms. This interpretation is strongly supported by the fact that the rotational barrier of the R_2N groups observed in **3a** or **3b** no longer exists in the isomers **6a** or **6b**.

(iv) The structures suggested for **6a** and **6b** gain further support by the observed C=C valence frequencies $\tilde{\nu} = 1636$ (**6a**) and 1622 cm^{-1} (**6b**) in the IR spectra being characteristic for 1,2-diphosphetenes [4,42].

The unusual transformation of the 1,2-dihydro-1,3-diphosphetes **3a** and **3b** to the corresponding 1,2-dihydro-1,2-diphosphetes **6a** and **6b** presumably is initiated by a 1,2-fluorine migration. Similar 1,2- or 1,3-fluorine shifts, in general leading to more stable systems [43], have been observed for acyclic phosphaalkenes. The primarily generated intermediates very probably are the bicyclic compounds **4** (Scheme 2), which undergo a very quick isomerization first to the 1,4-diphosphabuta-1,3-dienes **5** and then to the 1,2-dihydro-1,2-diphosphetes **6** (R = Me (**6a**), Et (**6b**)). The valence isomerization from **5** to **6** has been previously reported by Appel et al. [4]. Isolation of 1,4-diphosphabuta-1,3-dienes is only possible with bulky substituents like 2,4,6-tri-*tert*-butylphenyl (supermesityl) on the P atoms [44].

It is of particular interest that recently Niecke et al. [45] were able to fully characterize a sterically stabilized orbital isomer of a 2,4-diphosphabicyclobutane derivative in the form of the diradical 1,3-diphosphacyclobutane-2,4-diyl. The formation of an analogous species as the primary intermediate during the transformation of **3a** and **3b** to **6a** and **6b** respectively seems very unlikely, because, according to Ref. [45], in this case the isomerization would produce a phosphinocarbene and not the 1,4-diphosphabuta-1,3-dienes as precursors of **6a** or **6b**.

Further support for the interpretation in Scheme 2 comes from a report of Zenneck and coworkers [46] on the surprising transformation of a coordinated $1\lambda^3\sigma^2,3\lambda^3\sigma^2$-diphosphete by reaction with C_2Cl_6 giv-

Table 2
Ab initio total energies, relative energies, dipole moments and zero point energies for **3′–6′**

No.	6-31 + G*//6-31 + G* (au)	E_{rel} (kcal mol^{-1})	ZPE (kcal mol^{-1})	Dipole Moments (Debye)	MP2/6-31 + G*//6-31 + G* (au)	E_{rel} (kcal mol^{-1})
3′	−1347.81767(0)	22.41	41.80	5.046	−1349.45955	19.29
4′	−1347.79488	36.71	41.50	2.179	−1349.44743	26.89
5′	−1347.82284	19.16	41.37	2.971	−1349.47121	11.97
6′	−1347.85338	0.00	41.75	3.402	−1349.49029	0.00

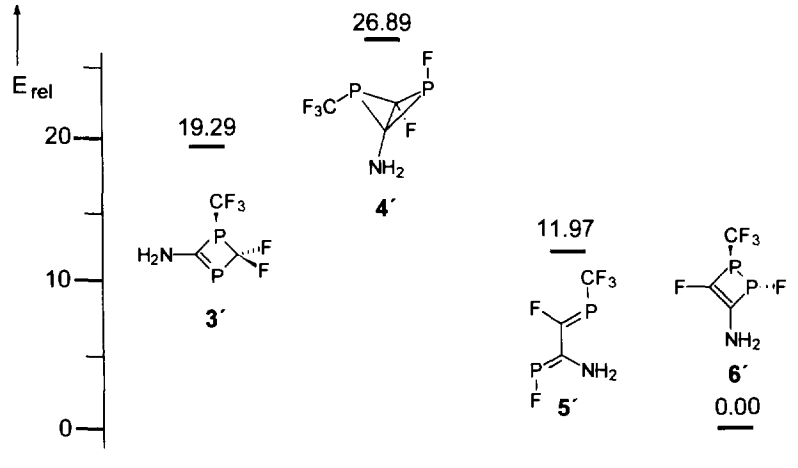


Fig. 5. Relative energies (kilocalories per mole) for the intermediates of the **3′** → **6′** isomerization (MP2/6-31 + G*//6-31 + G*).

ing the corresponding 1,2-dichloro-1,2-diphosphet-3-ene.

According to the spectroscopic results, the three-step reaction from **3a** or **3b** to **6a** or **6b** (Scheme 2) is strictly stereospecific; only one of the possible stereoisomers is formed. This conclusion is in accord with the earlier observation that *C*-amino-substituted trifluoromethyl phosphaalkenes, in contrast to compounds with $P{=}C(F)CR_3$ or $P{=}CF_2$ units, are not capable of cycloaddition reactions [47].

The proposed reaction mechanism is also supported by high level ab initio calculations (Table 2 and Fig. 5). The 6-31 + G* basis set of the GAUSSIAN 94 [48] series of programs was used for the geometry optimizations (only the conformers lowest in energy are discussed). Effects of electron correlation were estimated using second-order Moller–Plesset theory [49]. The character of the stationary points was determined by frequency analyses. Although we were not yet able to localize the transitions states on the potential energy hyperface, the relative energies of the proposed intermediates **3′**, **4′**, **5′** and **6′** (using NH_2-groups instead of NR_2), which all correspond to minima, agree well with the observed isomerization; (details of the calculations (GAUSSIAN 94 archive entries) may be obtained from E.-U.W. upon request). It is noteworthy that the bicyclic system **4′** is calculated to be only by ca. 8 kcal mol^{-1} higher in energy than **3′**, thus supporting the idea of an initial 1,2-fluorine shift as the key step of the reaction cascade. **4′** then is converted in two quite exothermic steps into **6′**, the final and stable product of the reaction sequence.

5. Conclusion

Perfluoro-2-phosphapropene **1**, accessible in preparative amounts, exhibits a high reactivity towards phosphaalkynes RC≡P giving 1,2-dihydro-1,3-diphosphetes. In the case of the sterically unshielded derivatives with $R = Me_2N$ (**3a**) or Et_2N (**3b**) on the sp^2-C atom, for the first time an interesting isomerization was observed yielding the thermodynamically more stable 1,2-dihydro-1,2-diphosphetes **6a** or **6b**. This transformation is of particular interest because it demonstrates once again the strong tendency to stabilize fluorine containing E=C systems by fluorine migration, and because it adds a new aspect to the chemistry of unsaturated four-membered phosphorus–carbon ring systems by proving an especially high stability for 1,2-dihydro-1,2-diphosphete isomers.

6. Experimental

All reactions were carried out using a standard vacuum line. 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. Perfluoro-2-phosphapropene [16], phosphaalkenes $HP{=}C(F)NR_2$ [17] di(isopropyl)aminophosphaethyne [17] and *tert*-butylphosphaethyne [50] have been prepared according to literature prescriptions.

Apparatus. For elemental analyses: Perkin–Elmer Analyser 240. NMR: Bruker AC 200 (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. IR: Nicolet Impact 400, Bruker IFS 48.

6.1. Standard procedure for the preparation of the 1,2-dihydro-1,3-diphosphetes 3a–d

1.5 mmol of the phosphaalkyne $^iPr_2NC{\equiv}P$ (**2c**) or of the phosphaalkyne precursors $HP{=}C(F)NMe_2$ (**2′a**) and $HP{=}C(F)NEt_2$ (**2′b**), respectively, 5 ml CH_2Cl_2 and 225 mg (1.5 mmol) $F_3CP{=}CF_2$ (**1**) are transfered into a thoroughly dried and evacuated 50 ml Schlenk vessel by vacuum condensation. The reaction starts on warming the mixture from −78 to 0 °C and is accompanied by a colour change to yellow-orange. After stirring the solution for some minutes at 25 °C, the mixture is cooled again to −78 °C and the solvent pumped off. The 1,2-dihydro-1,3-diphosphetes **3a** to **3c** are isolated from the yellow-brown residues by vacuum sublimation (10^{-3} mbar) at 25 °C to a cold finger at −78 °C. They are obtained as colourless crystalline solids of low melting points. The analogous reaction of **1** with *tert*-butylphosphaethyne **2d** is carried out in an ampoule equipped with break seals and an NMR-tube. ^{19}F and ^{31}P NMR measurements are used to control the process which is found to be complete after 5 days. The product **3d** is isolated from the mixture by trap-to-trap condensation at −55 °C, while small amounts of the diphosphetane $(F_3CPCF_2)_2$ are collected in the trap at −196 °C.

Note: the starting compound $^tBuC{\equiv}P$ (**2d**) has to be thoroughly purified, since even traces of hexamethyldisiloxane from the preparation of **2d** slow down the cyclocodimerization with **1** considerably.

Derivatives **3c** and **3d** are inert compounds and can be kept at room temperature, whereas **3a** and **3b** have to be stored in pure form or in organic solvents at −30 °C.

Yields: **3a** (47%), **3b** (42%), **3c** (34%), **3d** (65%).

6.2. 2-Dimethylamino-4,4-difluoro-3-trifluoromethyl-1λ³σ²,3λ³σ³-diphosphete 3a

^1H NMR (CD_2Cl_2, 25 °C): δ = 3.03 (dt, $^4J(P,H)$ = 2.9, $^6J(F,H)$ = 1.2 Hz, 3H, CH_3), 3.14 (br.m, 3H, CH_3). $^{19}F\{^1H\}$NMR (CD_2Cl_2, 25 °C): δ = −57.4 (dddd,

^2J(P,F) = 57.2, ^4J(F,F) = 12.0, 3.8, ^4J(P,F) = 2.7 Hz, 3F, CF_3), −78.7(dddq, $^2J(F_A, F_B)$ = 254.6, ^2J(P,F) = 156.9, 87.8, ^4J(F,F) = 3.9 Hz, 1F, F_A of CF_2), −94.3 (dddq, $^2J(F_A, F_B)$ = 254.6, ^2J(P,F) = 93.4, 43.1, ^4J(F,F) = 12.1 Hz, 1F, F_B of CF_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 188.1 (dddq, ^2J (P,F) = 93.2, 87.8, ^2J(P,P) = 11.4, ^4J(P,F) = 2.6 Hz, 1P, *P*=C), 72.8 (dqdd, ^2J(P,F) = 156.4, 57.2, 43.2, ^2J(P,P) = 11.4 Hz, 1P, *P*CF_3). $^{13}C\{^1H\}$NMR (CD_2Cl_2, 25 °C): δ = 41.9 (dd, *J*(F,C), *J*(P,C) = 12.7, 2.4 Hz, *C*H_3), 44.3 (brdm, *J*(F,C), *J*(P,C) = 11.5 Hz, *C*H_3), 115.1 (ddddq, ^1J(F,C) = 307.4, 287.4, ^1J(P,C) = 30.5, 6.5, ^3J(F,C) = 2.0 Hz, *C*F_2), 128.4 (qddddd, ^1J(F,C) = 324.9, ^1J(P,C) = 67.5, ^3J(P,C) = 13.4, ^3J(F,C) = 3.2, 1.7 Hz, *C*F_3), 186.2 (dd, ^1J(P,sp^{2}C) = 53.4, ^1J(P,sp^{3}C) = 35.44 Hz, *C*=P). Selected IR and MS data: IR(pentane): ν = 1533 (m); 1409 (s), 1160 (ws), 1145 (ws), 1107 (ws), 1076 (ws); (ν(CF)), 863 (w) cm^{-1}. MS (70 eV, EI): *m/z*(%) = 237 (18) [M^+], 168 (38) [$M^+ - CF_3$], 118 (100) [$M^+ - CF_3 - CF_2$], 87 (25) [$M^+ - F_3CPCF_2$]. Anal. Found: C, 25.29; H, 2.52; N, 5.98. $C_5H_6F_5NP_2$ (237.05). Calc.: C, 25.33; H, 2.55; N, 5.91%.

6.3. 2-Diethylamino-4,4-difluoro-3-trifluoromethyl-1λ^{3}σ^2,λ^{3}σ^3-diphosphetene **3b**

^1H NMR (CD_2Cl_2, 25 °C): δ = 1.21 (t, ^3J(H,H) = 7.1 Hz, 3H, CH_3), 1.24 (t, ^3J(H,H) = 7.3 Hz, 3H, CH_3), 3.32 (q, ^3J(H,H) = 7.1 Hz, 2H, CH_2), 3.39 (q, ^3J(H,H) = 7.3 Hz, 2H, CH_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = −56.1 (dddd, ^2J(P,F) = 56.2, ^4J(F,F) = 12.4, 3.8, ^4J(P,F) = 2.6 Hz, 3F, CF_3), −79.1 (dddq, $^2J(F_A, F_B)$ = 254.4, ^2J(P,F) = 158.7, 88.0, ^4J(F,F) = 5.5 Hz, 1F, F_A of CF_2), −93.3 (dddq, $^2J(F_A, F_B)$ = 254.4, ^2J(P,F) = 94.2, 40.7, ^4J(F,F) = 12.8 Hz, 1F, F_B of CF_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 187.6 (dddq, ^2J(P,F) = 94.8, 87.2, ^2J(P,P) = 12.2, ^4J(P,F) = 2.4 Hz, 1P, *P*=C), 72.7 (dqdd, ^2J(P,F) = 157.0, 56.8, 41.4, ^2J(P,P) = 12.2 Hz, 1P, *P*CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 9.9 (d, ^4J(P,C) = 4.2 Hz, *C*H_3), 13.5 (s, *C*H_3), 45.6 (dd, ^3J(P,C) = 11.2, 1.8 Hz, *C*H_2),49.6 (d, ^3J(P,C) = 12 Hz, *C*H_2), 115.3 (ddddq, ^1J(F,C) = 306.0, 287.0, ^1J(P,C) = 30.5, 6.7, ^3J(F,C) = 2.0 Hz, *C*F_2), 127.0 (qddd, ^1J(F,C) = 324.3, ^1J(P,C) = 61.8, ^3J(F,C) = 13.7, 2.4, ^3J(P,C) = 2.4 Hz, *C*F_3), 187.8 (ddddq, ^1J(P,sp^{2}C) = 53.0, ^1J(P,sp^{3}C) = 32.1, ^3J(F,C) = 13.8, 11.1, 2.7 Hz, *C*=P). IR spectrum (GC-IR): ν = 2985 (m), 2947 (m), 2889 (w), 1502 (s), 1464 (m), 1448 (m), 1387 (w), 1362 (m), 1286 (m), 1250 (w), 1167 (s), 1153 (vs), 1111 (vs), 1086 (s), 1038 (m), 870 (w) cm^{-1}. MS (70 eV, EI): *m/z*(%) = 265 (48) [M^+], 246 (6) [$M^+ - F$], 208 (5) [$M^+ - 3F$], 196 (99) [$M^+ - CF_3$], 146 (100) [$M^+ - CF_3 - CF_2$], 115 (6) [$C_5H_{10}NP^+$], 69 (90) [CF_3^+]. Anal. Found: C, 31.88; H, 3.89; N, 5.38. $C_7H_{10}F_5NP_2$ (265.10). Calc.: C, 31.72; H, 3.80; N, 5.28%.

6.4. 2-Di(isopropyl)amino-4,4-difluoro-3-trifluoromethyl-1λ^{3}σ^2,3λ^{3}σ^3-diphosphete **3c**

^1H NMR ($CDCl_3$, 25 °C): δ = 1.21 (d, ^3J(H,H) = 6.5 Hz, 3H, CH_3), 1.27 (d, ^3J(H,H) = 6.5 Hz, 3H, CH_3), 1.41 (d, ^3J(H,H) = 7.0 Hz, 3H, CH_3), 1.43 (d, ^3J(H,H) = 7.0 Hz, 3H, CH_3), 3.64 (dsept, ^3J(H,H) = 6.5, ^4J(P,H) = 6.4 Hz, 1H, CH), 3.87 (dsept, ^3J(H,H) = 7.0, ^4J(P,H) = 3.0 Hz, 1H, CH). ^{19}F NMR ($CDCl_3$, 25 °C): δ = −57.7 (dddd, ^2J(P,F) = 52.6, ^4J(F,F) = 12.9, 3.0, ^4J(P,F) = 3.0 Hz, 3F, CF_3), −79.7 (dddq, $^2J(F_A,F_B)$ = 256.0, ^2J(P,F) = 156.7, 84.0, ^4J(F,F) = 3.7 Hz, 1F, F_A of CF_2), −94.5 (dddq, $^2J(F_A,F_B)$ = 256.0, ^2J(P,F) = 92.2, 42.2, ^4J(F,F) = 12.9 Hz, 1F, F_B of CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 182.8 (dddq, ^2J(P,F) = 92.2, 84.0, ^2J(P,P) = 13.9, ^4J(P,F) = 2.7 Hz, 1P, *P*=C), 80.0 (dqdd, ^2J(P,F) = 156.7, 52.6, 42.2, ^2J(P,P) = 13.9 Hz, 1P, *P*CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −30 °C): δ = 16.0 (d, ^4J(P,C) = 11.3 Hz, *C*H_3), 18.3 (d, ^4J(P,C) = 13.7 Hz, *C*H_3), 19.7 (s, *C*H_3), 20.2 (s, *C*H_3), 50.0 (s, *C*H), 60.9 (d, ^3J(P,C) = 18 Hz, *C*H), 116.8 (dddd, ^1J(F,C) = 303.5, 285.3, ^1J(P,C) = 33.4, 6.9 Hz, *C*F_2), 127.1 (qdd, ^1J(F,C) = 324.7, ^1J(P,C) = 63.2, ^3J(F,C) = 13.5 Hz, *C*F_3), 182.3 (dddd, ^1J(P,sp^{2}C) = 61.2, ^1J(P,sp^{3}C) = 30.5, ^3J(F,C) = 12.1 Hz, *C*=P). IR spectrum (GC-IR): ν = 2978 (s), 2936 (m), 2876 (w), 1505 (s), 1454 (m), 1389 (w), 1374 (m), 1344 (m), 1193 (m), 1155 (s), 1122 (vs), 1056 (s), 1035 (m), 982 (m), 954 (m), 880 (w), 846 (vw), 805 (w), 737 (vw), 668 (w), 582 (w), 546 (w), 496 (w), 472 (m), 456 (w) cm^{-1}. MS (70 eV, EI): *m/z*(%) = 293 (62) [M^+], 278 (4) [$M^+ - CH_3$], 274 (5) [$M^+ - F$], 250 (6) [$M^+ - C_3H_7$], 224 (96) [$M^+ - CF_3$], 174 (100) [$M^+ - CF_3 - CF_2$], 143 (36) [$M^+ - F_3CPCF_2$], 69 (18) [CF_3^+]. Anal. Found: C, 36.75; H, 4.80; N. 4.79. $C_9H_{14}F_5NP_2$ (293.16). Calc.: C, 36.87; H, 4.81; N, 4.78%.

6.5. 2-tert-Butyl-4,4-difluoro-3-trifluoromethyl-1λ^{3}σ^2,3λ^{3}σ^3-diphosphete **3d**

^1H NMR (C_6D_6, 25 °C): δ = 1.25 (d, ^4J(P,H) = 6.2 Hz, CH_3). ^{19}F NMR (C_6D_6, 25 °C): δ = −56.7 (dddd, ^2J(P,F) = 62.3, ^4J(F,F) = 12.7, 3.0, ^4J(P,F) = 3.0 Hz, 3F, CF_3), −91.1 (dddq, $^2J(F_A,F_B)$ = 273.5, ^2J(P,F) = 148.6, 73.3, ^4J(F,F) = 3.4 Hz, 1F, F_A of CF_2), −111.0 (dddq, $^2J(F_A, F_B)$ = 273.5, ^2J(P,F) = 75.0, 36.2, ^4J(F,F) = 12.8 Hz, 1F, F_B of CF_2). $^{31}P\{^1H\}$ (C_6D_6, 25 °C): δ = 370.5 (dddq, ^2J(P,F) = 75.0, 73.3, ^2J(P,P) = 12.3, ^4J(P,F) = 2.8 Hz, 1P, *P*=C), 86.0 (dqdd, ^2J(P,F) = 148.6, 62.4, 36.3, ^2J(P,P) = 12.3 Hz, 1P, *P*CF_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ = 29.7 (dd, ^3J(P,C) = 10.3, 8.1 Hz, *C*H_3), 126.5 (qdd, ^1J(F,C) = 323.4, ^1J(P,C) = 61.0, ^3J(F,C) = 4.9 Hz, *C*F_3); resonances of the CF_2-group and the sp^2-C atom were not observed owing to unfavourable signal to noise ratios

and multiple hetero-couplings. MS (70 eV, EI): m/z(%) = 250 (20) [M^+], 200 (6) [$M^+ - CF_2$], 131 (35) [$C_6H_9PF^+$, $C_5H_9P_2^+$], 119 (69) [CF_3PF^+], 100 (36) [CF_3P^+], $C_5H_9P^+$], 85 (77) [$C_4H_6P^+$], 69 (100) [CF_3^+], 57 (39) [$C_4H_9^+$]. Anal. Found: C, 33.56; H, 3.59. $C_7H_9F_5P_2$ (250.09). Calc.: C, 33.62; H, 3.63%.

6.6. Isomerization of 3a,b to the 1,2-dihydro-1,2-diphosphetes 6a,b

The isomerization of **3a** and **3b** is carried out at 25 °C in CD_2Cl_2 solution and is followed by NMR measurements. The formation of intermediates according to Scheme 2 is not observed; obviously they are only present in undetectable concentrations. After 4 weeks (**3a**) or 6 weeks (**3b**) the rearrangement is complete, yielding **6a** and **6b** respectively as the only products. They are isolated by trap-to-trap condensation at 10^{-3} mbar (−78/−196 °C) and are collected in the trap at −78 °C. At room temperature they form yellow oils with a pungent smell.

6.7. 1,3-Difluoro-2-trifluoromethyl-4-dimethylamino-1,2-diphosphet-3-ene 6a

^{1}H NMR (CD_2Cl_2, 25 °C): δ = 3.08 (d, ^5J(F,H) = 1.3 Hz, CH_3). ^{19}F NMR (CD_2Cl_2, 25 °C): δ = −52.67 (dddd, ^2J(P,F) = 37.1, ^3J(P,F) = 21.3, ^4J(F,F) = 2.4, 0.8 Hz, 3F, CF_3), −118.45 (ddqd, ^2J(P,F) = 67.8, ^3J(P,F) = 24.8, ^4J(F,F) = 0.8, 0.4 Hz, 1F, CF), −178.37 (ddqd, ^1J(P,F) = 1007.2, ^2J(P,F) = 37.7, ^4J(F,F) = 2.4, 0.4 Hz, 1F, PF). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 102.9 (ddqd, ^1J(P,F) = 1007.1, ^1J(P,P) = 172.5, ^3J(P,F) = 21.4, 24.4, 1P, *P*F), −35.3 (dqdd, ^1J(P,P) = 171.8, ^2J(P,F) = 37.4, 67.8, ^2J(P,(P)F) = 37.0 Hz, 1P, *P*CF_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 40.7 (dd, ^3J(P,C), ^4J(F,C) = 4.4, 1.9 Hz, *C*H_3), 124.1 (ddddq, ^1J(F,C) = 347.1, ^1J(P,C) = 41.5, ^2J(P,C) = 40.0, ^3J(F,C) = 6.0, 1.0 Hz, *C*F), 129.1 (qdddd, ^1J(F,C) = 326.0, ^1J(P,C) = 83.2, ^2J(P,C) + ^3J(F,C) = 7.0 Hz, *C*F_3), 142.3 (dm, ^1J(P,C) = 41.0 Hz, *C*NMe_2). IR (pentane, selected): ν = 1636 (s) (ν(C=C)); 1166 (s), 1125 (vs), 1118 (s) [ν(CF)], 767 (s) cm^{-1}. MS (70 eV, EI): m/z(%) = 237 (29) [M^+], 168 (100) [$M^+ - CF_3$], 125 (10) [$M^+ - F_3CPC$], 118 (6) [$M^+ - CF_3 - PF$], 99 (25) [$M^+ - CF_3 - PF - F$], 69 (20) [CF_3^+].

6.8. 1,3-Difluoro-2-trifluoromethyl-4-diethylamino-1,2-diphosphet-3-ene 6b

^{1}H NMR (CD_2Cl_2, 25 °C): δ = 1.19 (t, ^3J(H,H) = 7.1 Hz, 6H, CH_3), 3.36 (q, ^3J(H,H) = 7.1 Hz, 4H, CH_2). ^{19}F NMR (CD_2Cl_2, 25 °C): δ = −52.83 (dddd, ^2J(P,F) = 36.9, ^3J(P,F) = 21.4, ^4J(F,F) = 2.5, 0.9 Hz, 3F, CF_3), −118.56 (ddqd, ^2J(P,F) = 69.3, ^3J(P,F) = 24.9, ^4J(F,F) = 0.8, 0.5 Hz, 1F, CF), −177.65 (ddqd, ^1J(P,F) = 1003.2, ^2J(P,F) = 38.9, ^4J(F,F) = 2.5, 0.5, 1F, PF). ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 103.4 (ddqd, ^1J(P,F) = 1003.3, ^1J(P,P) = 171.6, ^3J(P,F) = 21.5, 24.9 Hz, 1P, *P*F), −34.9 (ddqd, ^1J(P,P) = 171.6, ^2J(P,F) = 69.3, 36.9, ^2J(P,(P)F) = 38.8 Hz, 1P, *P*CF_3). ^{13}C{^{1}H} NMR: δ = 13.9 (s, *C*H_3), 45.4 (d, ^3J(P,C), ^4J(F,C) = 3.9 Hz, *C*H_2), 123.5 (dddq, ^1J(F,C) = 350.0, ^1J(P,C) = 44.0, ^2J(P,C) = 38.0, ^3J(F,C) = 4.8 Hz, *C*F),

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for compound **3a**

Atom	X (×10^4)	Y (×10^4)	Z (×10^4)	U_{eq}
P(1)	3863(1)	2184(1)	4464(1)	359(2)
C(1)	4454(1)	1321(3)	3642(1)	504(5)
F(11)	4423(1)	−451(2)	3630(1)	846(5)
F(12)	4121(1)	1843(3)	2874(1)	714(5)
F(13)	5316(1)	1768(2)	3818(1)	702(4)
C(2)	3799(1)	4599(2)	4209(1)	410(3)
F(21)	4335(1)	5152(2)	3686(1)	601(3)
F(22)	4061(1)	5643(2)	4896(1)	615(4)
P(3)	2579(1)	4616(1)	3772(1)	466(2)
C(4)	2716(1)	2360(1)	3881(1)	327(3)
N(4)	2127(1)	1074(2)	3672(1)	414(3)
C(41)	2344(2)	−787(3)	3786(2)	556(5)
C(42)	1225(1)	1538(4)	3243(1)	535(5)
	X (×10^3)	Y (×10^3)	Z (×10^3)	U (×10^{-1})
H(411)	288(2)	−99(4)	418(2)	68(8)
H(412)	187(2)	−144(4)	399(2)	68(8)
H(413)	239(2)	−131(5)	326(2)	96(11)
H(421)	95(3)	45(7)	311(3)	132(16)
H(422)	97(2)	236(5)	348(2)	77(9)
H(423)	126(3)	222(5)	276(3)	106(13)

Equivalent isotropic U_{eq} values are defined as one-third of the trace of the orthogonalized U_{ij} tensor [54].

128.5 (qd, $^1J(F,C) = 328.4$, $^1J(P,C) = 82.6$ Hz, CF_3), 139.8 (dm, $^1J(P,C) = 38.9$ Hz, sp^2-CN). IR spectrum (GC-IR): $\nu = 2981$ (m), 2945 (m), 2887 (m), 1622 (s), 1464 (w), 1384 (m), 1375 (sh, m), 1251 (m), 1211 (w), 1163 (s), 1132 (vs), 1100 (m), 1001 (w), 767 (s), 667 (w) cm^{-1}. MS (70 eV, EI): $m/z(\%) = 265$ (35) [M^+], 246 (30) [$M^+ - F$], 196 (85) [$M^+ - CF_3$], 177 (6) [$M^+ - CF_3 - F$], 146 (100) [$M^+ - CF_3 - PF$], 115 [Et_2CCF^+], 69 (32) [CF_3^+].

6.9. Crystal structure determination of **3a**

Crystal data: $C_5H_6F_5NP_2$; $M = 237.05$, m.p. -48°C; monoclinic, space group $C2/c$ (No. 15 [51]; $a = 1526.9(7)$; $b = 761.7(3)$, $c = 1650.8(6)$ pm, $\beta = 101.56(3)$°, $V = 1881.0 \times 10^{-30}$ m^3; $Z = 8$; $D_c = 1.674 \times 10^3$ kg m^{-3}; μ(Mo Kα) = 493 m^{-1}. A cylindric colourless crystal was grown at low temperature (−49.5°C)in a capillary of 0.3 mm diameter directly from the liquid; the procedure applied has already been described in the literature [52,53]. Intensities of 2745 independent reflections within a range of $2 \leq 2\theta \leq 55°$ ($-7 \leq h \leq 21$; $-10 \leq k \leq 10$, $-23 \leq l \leq 22$) were measured at -100 ± 2 °C on a Syntex $P2_1$ four circle diffractometer ($\lambda = 71.069$ pm; Wyckoff scan with a width of 0.8° in ω). After a data reduction as usual and corrections for a varying crystal volume exposed to the x-ray beam, but not for absorption, the phase problem could be solved with statistical methods, and the structure model was refined on the basis of F^2 and statistical weights from the measurement, using the crystallographic program packages SHELXTL PLUS., Rel. 4.0 [54] and SHELXL-93 [21]. In the final stages of the structure determination with anisotropic U_{ij}-parameters for the heavier atoms, all hydrogen atoms were located in a difference Fourier map; their positions and isotropic U-values could be reasonably refined (see Table 3) ($wR2 = 0.1352$; $R1 = 0.0442$ with $I > 2\sigma(I)$; GOF = 1.046 on the basis of 142 variables; maximum height of 0.48×10^{30} and maximum hole of -0.51×10^{30} e m^{-3} in the final difference Fourier map).

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CDS-59322.

Acknowledgements

We thank the Fond der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme") and the Ministerium für Wissenschaft und Forschung Nordrhein-Westfalen for generous financial support of our work.

References

[1] J. Grobe, D. Le Van, J. Winnemöller, B. Krebs and M. Läge, *Z. Naturforsch. Teil B:, 51* (1996) 778.
[2] (a) M. Regitz, in M. Regitz and O.J. Scherer (eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, 1990, p. 58; in D. Enders, H.J. Gais and W. Keim (eds.), *Organic Synthesis via Organometallics*, Vieweg, Braunschweig, 1993, p. 93. (b) H. Memmersheimer and M. Regitz, in U.H. Brinker (ed.), *Advances in Carbene Chemistry*, JAI Press, 1994, p. 185. (c) M. Regitz, A. Hoffmann and U. Bergsträsser, in P.J. Stang and F. Diederich (eds.), *Modern Acetylene Chemistry*, VCH, Weinheim, 1995, p. 173. (d) R. Streubel, *Angew. Chem., 107* (1995) 251; *Angew. Chem. Int. Ed. Engl., 34* (1995) 198. (e) J.F. Nixon, *Chem. Soc. Rev., 24* (1995) 319.
[3] (a) F. Mathey, C. Charrier, N. Maigrot, A. Marinetti, L. Ricard and N.H. Tran Huy, *Comments Inorg. Chem., 13* (1992) 61. (b) S. Kummer and U. Zenneck, in A. Padwa (ed.), *Comprehensive Heterocyclic Chemistry*, Vol. 1, Elsevier, Oxford, 2nd edn., 1996, Chapter 1.40, in press. (c) E. Fluck and B. Neumüller, in H. W. Roesky (ed.), *Rings, Cluster and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989, p. 195.
[4] R. Appel, V. Barth and F. Knoch, *Chem. Ber., 116* (1983) 938.
[5] G. Becker, W. Becker, R. Knebel, H. Schmidt, U. Hildebrand and M. Westerhausen, *Phosphorus Sulfur, 30* (1987) 349.
[6] J. Grobe, A. Armbrecht, T. Grosspietsch, M. Hegemann and D. Le Van, *12th Int. Conf. on Phosphorus Chemistry, Toulouse, France, July 1992*, Poster II-31; *Phosphorus Sulfur Silicon, 77* (1993) 245.
[7] B. Breit and M. Regitz, *Chem. Ber., 126* (1993) 1945.
[8] R. Streubel, M. Frost, M. Nieger and E. Niecke, *Bull. Soc. Chim. Fr., 130* (1993) 642.
[9] E. Lindner, C. Haase, H.A. Mayer, M. Kemmler, R. Fawi and M. Steinmann, *Angew. Chem., 105* (1993) 1521; *Angew. Chem. Int. Ed. Engl., 32* (1993) 1424.
[10] B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P.B. Hitchcock, M. Hofmann, P. Binger, J.F. Nixon, P. von R. Schleyer and M. Regitz, *Angew. Chem., 107* (1995) 485; *Angew. Chem. Int. Ed. Engl., 34* (1995) 484.
[11] P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann and C. Krüger, *Angew. Chem., 107* (1995) 2411; *Angew. Chem. Int. Ed. Engl., 34* (1995) 2227.
[12] P.B. Hitchcock, R.M. Matos, M.F. Meidine, J.F. Nixon, B.F. Trigo Passos, D. Barion and E. Niecke, *J. Organomet. Chem., 461* (1993) 61; E. Niecke and D. Barion, *Tetrahedron Lett., 30* (1989) 459.
[13] H. Pucknat, J. Grobe, D. Le Van, B. Broschk, M. Hegemann, B. Krebs and M. Läge, *Chem. Eur. J., 2* (1996) 208.
[14] R. Streubel, L. Ernst, J. Jeske and P.G. Jones, *J. Chem. Soc. Chem. Commun.*, (1995) 2113.
[15] R. Armbrust, M. Sanchez, R. Reau, U. Bergsträsser, M. Regitz and G. Bertrand, *J. Am. Chem. Soc., 117* (1995) 10785.
[16] J. Grobe and D. Le Van, *Angew. Chem., 96* (1984) 716; *Angew. Chem. Int. Ed. Engl., 23* (1984) 710.
[17] J. Grobe, D. Le Van, B. Lüth and M. Hegemann, *Chem. Ber., 123* (1990) 2317.
[18] J. Grobe, D. Le Van and B. Lüth, unpublished results.
[19] J. Grobe, D. Le Van, W. Meyring, B. Krebs and M. Dartmann, *J. Organomet. Chem., 346* (1988) 361.
[20] G. Becker and O. Mundt, *Z. Anorg. Allg. Chem., 462* (1980) 130; G. Becker, W. Uhl and H.J. Wessely, *Z. Anorg. Allg. Chem., 479* (1981) 41.
[21] G.M. Sheldrick, SHELXL-93, *Program for Crystal Structure Determination*, University of Göttingen, 1993.
[22] R.S. Cahn, C. Ingold and V. Prelog, *Angew. Chem., 78* (1966) 413, *Angew. Chem. Int. Ed. Engl., 5* (1966) 385.

[23] G. Becker, M. Böhringer, R. Gleiter, K.-H. Pfeifer, J. Grobe, D. Le Van and M. Hegemann, *Chem. Ber., 127* (1994) 1041.
[24] E. Wiberg, *Hollemann–Wiberg Lehrbuch der Anorganischen Chemie*, de Gruyter, Berlin, 81.–90. edn., 1976, p. 129; see also, e.g.: O. Mundt, G. Becker, W. Uhl, W. Massa and M. Birkhahn, *Z. Anorg. Allg. Chem., 540–541* (1986) 319.
[25] G. Becker, O. Mundt and M. Mayer, unpublished results.
[26] E. Niecke, R. Streubel, M. Nieger and D. Stalke, *Angew. Chem., 101* (1989) 1704; *Angew. Chem. Int. Ed. Engl., 28* (1989) 1673.
[27] M. Soleilhavoup, A. Baceiredo, F. Dahan and G. Bertrand, *J. Chem. Soc. Chem. Commun.*, (1994) 337.
[28] R. Appel, F. Knoch, B. Laubach and R. Sievers, *Chem. Ber., 116* (1983) 1873.
[29] G. Becker, O. Mundt and M. Sachs, unpublished results.
[30] C.J. Marsden and L.S. Bartell, *Inorg. Chem., 15* (1976) 2713; C.J. Marsden, *Inorg. Chem., 23* (1984) 1703.
[31] M.-H. Whangbo and K.R. Stewart, *Inorg. Chem. 21* (1982) 1720 and references cited therein.
[32] H. Hayd, H. Savin, A. Stoll, H. Preuss and G. Becker, *J. Mol. Struct. (Theochem), 165* (1988) 87 and references cited therein.
[33] C.W. Hoffmann and R.L. Livingston, *J. Chem. Phys., 21* (1953) 565.
[34] K.-H. Hellwege, in A. M. Hellwege (ed.), *Landolt–Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie, Gruppe II*, Vol. 7, Springer, Berlin, 1976.
[35] S.M. Bachrach and M. Liu, *J. Org. Chem., 57* (1992) 2040.
[36] S. Berger, S. Braun and H.O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, Vol. 4, *^{19}F-NMR-Spektroskopie*, Thieme, 1994, p. 29.
[37] J. Grobe, D. Le Van, J. Schulze and J. Szameitat, *Phosphorus Sulfur, 28* (1986) 239; J. Grobe, M. Hegemann and D. Le Van, *Z. Naturforsch. Teil B:, 45* (1990) 148.
[38] C. Charrier, J. Guilhem and F. Mathey, *J. Org. Chem., 46* (1981) 3; C. Charrier, N. Maigrot, F. Mathey, F. Robert and Y. Jeannin, *Organometallics, 5* (1986) 623; L. Ricard, N. Maigrot, C. Charrier and F. Mathey, *Angew. Chem., 99* (1987) 590; *Angew. Chem. Int. Ed. Engl., 26* (1987) 548.
[39] I.G. Phillips, R.G. Ball and R.G. Cavell, *Inorg. Chem., 27* (1988) 2269.
[40] R. Appel and F. Knoll, *Adv. Inorg. Chem., 33* (1989) 259.
[41] Y. Kobayashi, S. Fujino, H. Hamana, I. Kumadaki and I. Hanzawa, *J. Am. Chem. Soc., 99* (1977) 8511.
[42] (a) W. Mahler, *J. Am. Chem. Soc., 86* (1964) 2306; (b) G. Becker, W. Becker and G. Uhl, *Z. Anorg. Allg. Chem., 518* (1984) 21.
[43] J. Grobe, D. Le Van and J. Nientiedt, *New J. Chem., 13* (1989) 363; J. Grobe, D. Le Van, U. Althoff and G. Lange, *Chem. Ber., 125* (1992) 567; J. Grobe and D. Le Van, *Chem. Ber., 123* (1990) 1047.
[44] R. Appel, J. Hühnerbein and N. Siabalis, *Angew. Chem., 99* (1987) 810; *Angew. Chem. Int. Ed. Engl., 26* (1987) 779.
[45] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger and W. W. Schoeller, *Angew. Chem., 107* (1995) 640; *Angew. Chem. Int. Ed. Engl., 34* (1995) 555; see also: W.W. Schoeller and U. Tubbesing, *Chem. Ber., 129* (1996) 419.
[46] F. Knoch, S. Kummer and U. Zenneck, *Synthesis*, (1996) 265; see also: P. Binger, T. Wettling, R. Schneider, R. Zurmühlen, U. Bergsträßer, J. Hoffmann, G. Mass and M. Regitz, *Angew. Chem., 103* (1991) 208; *Angew. Chem. Int. Ed. Engl., 30* (1991) 207.
[47] J. Grobe, D. Le Van, N. Nientiedt, B. Krebs and M. Dartmann, *Chem. Ber., 121* (1988) 655.
[48] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez and J.A. Pople, GAUSSIAN 94, Revision B.2, 1995 (Gaussian, Inc. Pittsburgh, PA).
[49] C. Møller and M.S. Plesset, *Phys. Rev., 46* (1934) 618; J.S. Binkley and J.A. Pople, *Int. J. Quantum Chem., 9* (1975) 229.
[50] G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch. Teil B:, 36* (1981) 16; G. Becker, H. Schmidt and G. Uhl, *Inorg. Synth., 27* (1990) 249.
[51] Th. Hahn (ed.), *International Tables for Crystallography, Space-Group Symmetry*, Vol. A, Kluwer Academic, Dordrecht, 3nd edn., 1992.
[52] A. Simon, H.-J. Deiseroth, E. Westerbeck and B. Hillenkötter, *Z. Anorg. Allg. Chem., 423* (1976) 203.
[53] O. Mundt, H. Riffel, G. Becker and A. Simon, *Z. Naturforsch. Teil B:, 43* (1988) 952.
[54] G.M. Sheldrick, *Program system* SHELXTL PLUS, Rel. 4.0, 1989 (Siemens Analytical X-ray Instruments, Inc., Madison, WI, USA).