Heteroatom Chemistry
Volume 16, Number 5, 2005

Reactive E=C(p-p)π-Systems 53 [1]: Reactivity Studies on Perfluoro-2-arsapropene: [2+2]-Cycloaddition Reactions and Quantum Chemical Calculations

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Received 29 November 2004; revised 8 February 2005

ABSTRACT: *The extremely labile perfluoro-2-arsapropene $F_3CAs{=}CF_2$ (**1**) has been generated by an improved pyrolysis process of $Me_3SnAs(CF_3)_2$ and found to be stabilized by the presence of hexamethyldisiloxane and tert-butylphosphaethyne, thus allowing (i) reactivity studies with alkyne derivatives like $tBuC{\equiv}P$, $(iPr)_2NC{\equiv}P$, $MeC{\equiv}CN(iPr)_2$, $HC{\equiv}COEt$ and (ii) a full NMR investigation of **1** (^{19}F, ^{13}C). Due to the instability of **1** and some of the products, the [2 + 2]-cycloaddition reactions gave the expected arsaphospha- and arsa-cyclobutene derivatives, respectively, in moderate to good yields, but in some cases contaminated with side and/or decomposition products. Unequivocal characterization of the novel compounds was accomplished by spectroscopic investigations (^1H, ^{13}C, ^{19}F, ^{31}P NMR, IR, MS) supported by comparison with the data of the more stable phosphorus analogues. An interesting isomerization was observed for the 2-dialkylamino-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutenes yielding the more stable 3-dialkylamino-2,4-difluoro-1-trifluoromethyl-1-arsa-2-phospha-3-cyclobutenes. Quantum chemical calculations [B3LYP/6-311+G(d,p)] of $HAs{=}CH_2$, $F_3CAs{=}CF_2$, and $F_3CP{=}CF_2$ were carried out to compare the length of the As=C double bond with the literature data and to elucidate substituent effects on its electronic structure.*
 Heteroatom Chem 16:406–419, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20118

INTRODUCTION

In our extensive investigations on fluorinated heteroalkenes, the extremely labile perfluoro-2-arsapropene $F_3CAs{=}CF_2$ (**1**) was of particular interest: (i) for comparison with the properties of the considerably more stable phosphorus analogue: (ii) for the study of its reactivity. Therefore, great

Dedicated to Professor Alfred Schmidpeter on the occasion of his 75th birthday.

The authors regret the much too early death of Dr. Duc Le Van, the most skilled senior scientist in the team of J. G., on September 22nd 2004 aged 53 years.

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Contract grant sponsor: Fonds der Chemischen Industrie.
Contract grant sponsor: Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme").
Contract grant sponsor: Ministerium für Wissenschaft und Forschung Nordrhein-Westfalen.

efforts were made to improve the preparation of the highly reactive As=C double bond system for which in an earlier investigation [2] the subsequent reaction to dimers and oligomers had been observed at temperatures as low as –80°C. On the other hand, a series of [4 + 2]-cycloaddition products of $F_3CAs{=}CF_2$ could be prepared by quenching the hetero-olefin immediately after its generation from the trimethyltin precursor $Me_3SnAs(CF_3)_2$ [3]. A simple route to dialkylamino derivatives of the type $F_3CAs{=}C(F)NR_2$ was found in the elimination/addition reaction of $(F_3C)_2AsH$ with secondary amines HNR_2, corresponding to the analogous behavior of $(F_3C)_2PH$ [4,5]. In the present paper, we report on an improved method for the generation of $F_3CAs{=}CF_2$, its stabilization with hexamethyldisiloxane, and the successful use of its solutions at low temperatures for [2 + 2]-cycloaddition reactions.

RESULTS AND DISCUSSION

Improvement of the Generation of **1**

The measures applied for this goal include increase of the monomer yield and prevention of dimer and oligomer formation. Both have been possible by adjusting the vapor pressure of $Me_3SnAs(CF_3)_2$ in the pyrolysis apparatus close to 10^{-3} mbar by use of an efficient vacuum pump and a Teflon valve for introducing the organotin precursor. For a productive thermal decomposition of $Me_3SnAs(CF_3)_2$, the pyrolysis tube is filled with glass wool to guarantee a longer contact time. The thermolysis is supported by the formation of the well-known polyadduct $(Me_3SnF)_n$ [6], deposited in the glass tube and on the glass wool. A critical parameter is the temperature in the pyrolysis zone. Under the conditions given above, it was adjusted to 380°C for reasonable to good yields of the monomer, which was condensed at −196°C together with a suitable solvent or the reactant in a small round bottom flask with a side-on fused NMR tube. As a suitable solvent dichloromethane or its perdeutero analogue was used. This procedure allows the condensation of arsaalkene and solvent or reactant layer by layer. The reactions are usually carried out by quick melting and mixing of the components at −78°C. The reaction mixture then can be easily transferred into the connected NMR tube.

By these measures, the yield of **1** could be increased to 50%, enough for reactivity studies with various partners. Since the [2 + 2]-self-addition of **1** is a preferred following reaction, di- and oligomerization can only be avoided by use of highly reactive partners. As a rule, several experiments at different temperatures were necessary to obtain reasonable yields of the products. The apparatus used for this preparation is shown in Fig. 1.

[2+2]-Cycloaddition Reactions of Perfluoro-2-arsapropene **1** *with Phosphaalkynes and Phosphaalkenes*

Compound **1** was expected to be particularly suitable for addition reactions. This was already indicated by the successful [4 + 2]-cycloaddition reactions of the in situ generated **1** with 1,3-dienes [3].

According to the Woodward–Hoffmann rules the [2 + 2]-cycloaddition of olefins is symmetry- allowed only photochemically [7]. However, the photochemical activation of hetero-alkenes and -alkynes is known to lead to decomposition in many cases. Such reactions, therefore, have to be activated by

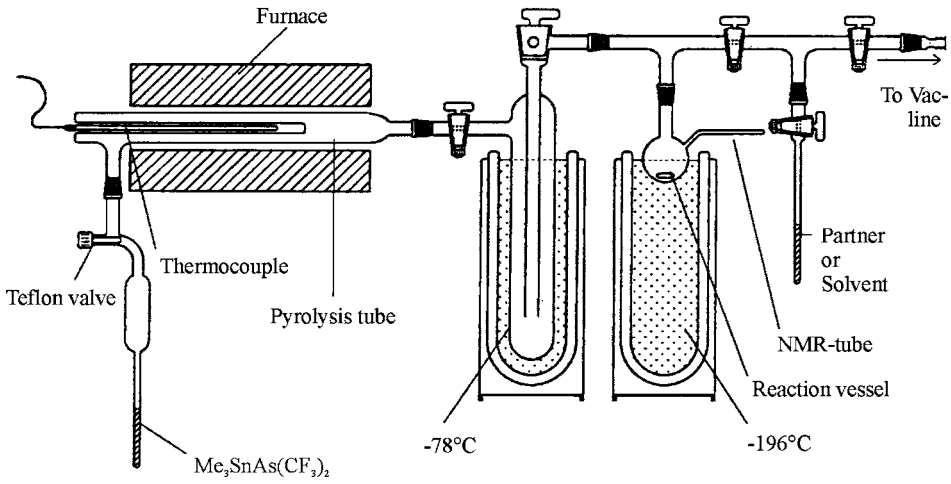


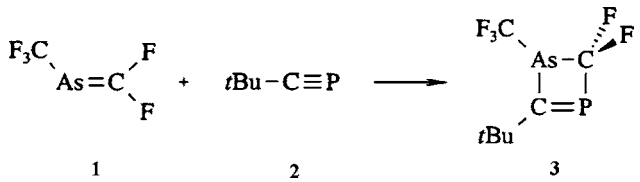
FIGURE 1 Pyrolysis apparatus for the improved preparation of perfluoro-2-arsapropene 1.

substituent effects. Due to the fluorine substituents, **1** as its phosphorus analogue is an electron-poor heteroalkene with low-lying frontier orbitals and thus expected to undergo cycloaddition reactions with electron-rich alkenes and alkynes [8]. Because heteroatoms induce a symmetry reduction of the frontier orbitals and lead to significantly different orbital coefficients, cycloaddition reactions of such alkenes often follow a nonconcerted pathway with a two-step mechanism in which neither a photochemical nor a thermal activation is necessary.

So far, only a few examples of [2 + 2]-cycloadditions of arsaalkenes are known in the literature. Besides the cyclodimerization of **1** and the more shielded derivatives $RAs{=}C(OSiMe_3)tBu$ (R = Me, Et) under UV irradiation [9], reactions of ferrioarsaalkenes like $Cp^*(CO)_2FeAs{=}C(R)NMe_2$ (R = H, Ph) with fumaric acid dimethylester and fumarodinitrile, respectively, have been described [10,11].

For the preparation of novel arsacyclobutene derivatives by [2 + 2]-cycloaddition reactions of **1**, besides activated alkenes or alkynes, heteroanalogues like phosphaalkenes or phosphaalkynes were of particular interest. Due to their electronic structure, they are highly reactive and introduce the ^{31}P NMR probe for easy detection and characterization of the resulting products.

Reaction of **1** *with Tert-butylphosphaethyne* **2**. A surprising result was obtained in an attempt to carry out this reaction. Neither during the co-condensation of **1**, obtained by the improved pyrolysis, with **2**, nor in the course of thawing and warming the reaction mixture from −78°C to room temperature was a reaction observed. Even the rapid di- and oligomerization of **1** was obviously hindered. The NMR control detected the co-existence of the two partners. Keeping the mixture below 0°C, no reaction occurred after several weeks. Only at room temperature did the expected reaction start, but with such a low rate that it came to its end only after 7 days. Additional investigations revealed that the reaction rate was dependent on the content of hexamethyldisiloxane in the sample of **2**. This is formed as a by-product of the synthesis of **2** and cannot be completely removed by vacuum condensation from mmol-scale experiments. If the sample of **2** contains only traces of hexamethyldisiloxane, the reaction with **1** already begins at 0°C, takes 4 days to finish, and gives the expected [2+2]-cycloaddition product 2-tert-butyl-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutene **3** according to Eq. (1). **3** was completely characterized by NMR (^1H, ^{13}C, ^{19}F, ^{31}P), IR, and mass spectroscopic investigations.



1 2 3 (1)

The ^{19}F NMR spectrum of **3** exhibits signals for the CF_3 and CF_2 groups, both showing characteristic patterns due to (i) the chirality of the As center and (ii) F,F and P,F couplings. The F nuclei of the CF_2 group form an AB spin-system with a $^2J_{FF(AB)}$ coupling of 261.5 Hz. The resonance at δ_F −99.6 is assigned to the atom F_B in cis-position to the CF_3 group, because it shows the larger $^4J_{FF}$ constant of 10.2 Hz. The signal δ_F −86.1, $^4J_{FF} = 4.0$ Hz is then associated with the F_A nucleus in trans-position to the CF_3 group. Both resonances exhibit a doublet of quartet structure due to coupling with the ^{31}P- and the F-atoms of the CF_3-substituent. The signal of the CF_3 group is detected as a multiplet at δ_F −49.8 containing the above given $^4J_{FF}$ couplings and a doublet splitting $^4J_{PF} = 4.0$ Hz.

The ^1H NMR spectrum shows a doublet resonance for the three equivalent methyl groups of the *t*Bu-substituent caused by a $^4J_{PH}$ coupling of 1.7 Hz. The signal of the ^1H decoupled ^{31}P nucleus exhibits a ddq pattern associated with the J_{PF} interactions discussed above. The ^{13}C NMR spectrum exhibits the expected five signals at typical δ_C values with characteristic coupling constants (see Experimental section).

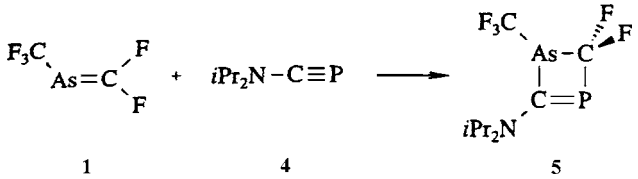
The observed NMR data are in accord with those of the analogous 1,3-diphospha-2-cyclobutene derivative [12] for which, of course, due to the second P-atom, an additional doublet splitting for all other NMR active nuclei results.

The mass spectrum of **3**, recorded on a GC/MS instrument, shows the molecular ion peak [M^+] with a relative abundance of 5% at m/z = 294 and the typical fragment peaks of [CF_3^+] (68%) and [tBu^+] (18%). On first sight unexpected is the basis peak at m/z = 119 which corresponds to the fragment [$C_4H_9C{=}PF^+$] and suggests a thermally induced rearrangement of **3** before fragmentation.

The gas phase IR spectrum of **3** was recorded after GC separation and is in agreement with the given structure (data in Experimental section).

Reaction of **1** *with Diisopropylaminophosphaethyne* **4**. This reaction was carried out as described for **2**. However, in this case cycloaddition already occurs during the co-condensation of the partners

at −196°C, indicated by a color change of the reaction mixture to brown-orange. After thawing and warming first at −78°C and then at room temperature, the reaction was almost complete, as observed by NMR control measurements of the mixture showing only small amounts of the reactants. After keeping the mixture at room temperature for 1 h, the product formation according to Eq. (2) was complete.



(2)

The cycloaddition product 2-diisopropylamino-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutene **5** is regioselectively formed in a fast reaction compared with the slow process for **2**. This can be explained by the allylic-type N—C=P system producing a more electron-rich alkyne.

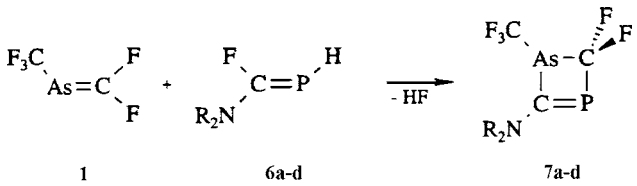
Reaction of **1** *with Phosphaalkenes of the Type HP=C(F)NR$_2$ (***6***).* These reactions are based on the former observation that compounds of type **6** usually behave as equivalents of the corresponding phosphaalkynes R$_2$N—C≡P which are formed in situ by HF elimination, but are not accessible in free form [12]. It was of interest whether dialkylaminophosphaalkynes with less bulky substituents at nitrogen react differently with **1**.

If **1** and the aminophosphaalkenes **6a–d** are cocondensed at −196°C in analogy to the above procedures with phosphaalkynes, an immediate reaction is observed. After thawing the reaction mixture changes color to an intensive red-brown, indicating a less selective reaction with formation of a greater number of by-products. Two possible pathways have to be considered:

(i) HF elimination from **6a–d** followed by the [2+2]-cycloaddition,

(ii) [2 + 2]-cycloaddition of **1** to **6a–d** followed by HF elimination.

As in the case of **4**, the reactions yield the corresponding 2-dialkyamino-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutene derivatives **7a–d** as main products as shown in Eq. (3).



6/7a: R = Me, 6/7b: R = Et, 6/7c: R = Pr ; 6/7d: NR$_2$ = Piperidine

(3)

The hydrogen fluoride formed was probably quenched to a smaller extent by addition to **1** yielding the small amounts of $(CF_3)_2AsH$, detected in the mixture, to a larger extent by reaction with **7a–d** giving insoluble ammonium salts not showing up in the NMR spectra.

Characterization of **5** *and* **7a–d**

The novel derivatives were identified and characterized by spectroscopic investigations, in particular by NMR and mass spectroscopy. The NMR results are discussed here together, since characteristic differences are expected only in the ^{1}H NMR spectra.

The ^{19}F NMR spectra generally show three signals with the intensity ratio of 3 : 1 : 1, which can be assigned to the CF_3 group and the two diastereotopic fluorine nuclei F_A and F_B of the AB spin-system in the CF_2 unit. The chemical shifts of the compounds **7a–d** are found between δ_F − 73.3 and −74.2 for the F_A and between δ_F − 84.2 and 84.7 for the F_B atoms with $^2J_{FF(AB)}$ constants between 239.0 and 246.3 Hz. The stereochemical assignment of F_A and F_B corresponds to that of the tert-butyl derivative **3**. Due to the different electronic structures of **5** and **7a–d**, the signals of the CF_2 units show a low-field shift of 12 to 15 ppm. Both signals exhibit a ddq pattern with $^2J_{PF}$ couplings between 82.8 and 89.6 Hz and $^4J_{FF}$ constants of about 4 and 10 Hz, respectively. The ^{19}F resonances of the CF_3 groups appear as dd patterns between δ_F − 50.3 and −50.7.

In the ^{1}H NMR spectra of the N-alkyl-substituents, the mesomeric interaction of the nitrogen lone pair with the π-system of the P=C-bond leads to a rotational barrier of the amino group around the C—N bond and, therefore, to a doubling of the expected signals.

The phosphorus nuclei in **7a–d** exhibit chemical shifts between 203.1 and 209.0 ppm with signal patterns ddq due to couplings with the diastereotopic F-atoms of the CF_2 group and the equivalent F-nuclei of the CF_3 substituent. The resonances of the P-atoms are, in comparison with the tert-butyl

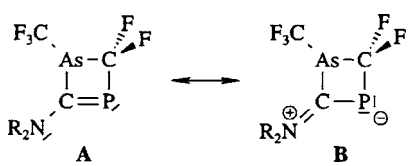
analogue, shifted to high field by about 190 ppm, due to the contribution of the zwitterionic formula **B** to the ground state of the molecules (Scheme 1).

5 and **7a–d** could not be isolated in pure form because they undergo a subsequent reaction. With the exception of the ^{13}C NMR data which could not be assigned unequivocally, the ^{1}H, ^{19}F, and ^{31}P parameters allow the clear characterization of the new arsa/phosphacyclobutenes. Mass spectra of **7a** and **7b** were recorded after gas chromatographic separation. They show the molecular ions [M^+] with intensities of 8 and 6%, respectively, in relation to the basis peaks [$M^+ - CF_3$]. Typical fragments result from splitting off F- and R_F-substituents (see Experimental section).

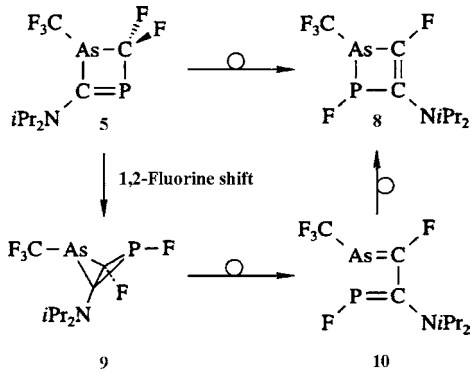
Isomerization of **5** *and* **7a–d**

When storing the arsaphosphacyclobutenes **5** and **7a–d** at room temperature, a slow decrease of the ^{19}F and ^{31}P signals together with the appearance of new characteristic patterns is observed. This is obviously due to a thermodynamically determined rearrangement which will be demonstrated here for **5**, because the analogues resulting from **7a–d** contain side- and decomposition-products making the characterization more difficult. The NMR spectra of the isomer **8** obtained from the intramolecular rearrangement of **5** exhibit new ^{19}F and ^{31}P resonances supporting the rearrangement of Scheme 2.

This conforms to the analogous isomerization of the related 2-dialkylamino-4,4-difluoro-3-trifluoromethyl-1,3-diphospha-1-cyclobutenes (alternative name: 2-dialkylamino-4,4-difluoro-3-trifluoromethyl-1,3-diphosphetes) [12]. The isomerization of **5** to 3-diisopropylamino-2,4-difluoro-1-trifluoromethyl-1-arsa-2-phospha-3-cyclobutene **8** is presumably initiated by a 1,2-fluorine migration from the CF_2 group to the neighboring P-atom. Similar 1,2- or 1,3-fluorine migrations leading to more stable systems have been observed for acyclic phosphaalkenes [13]. The primarily formed intermediate very probably is the bicyclic compound **9**, which undergoes a quick isomerization first to the 1-arsa-4-phospha-1,3-diene **10** and then to **8** (Scheme 2). The bicyclic derivative **9** is expected to be considerably



SCHEME 1

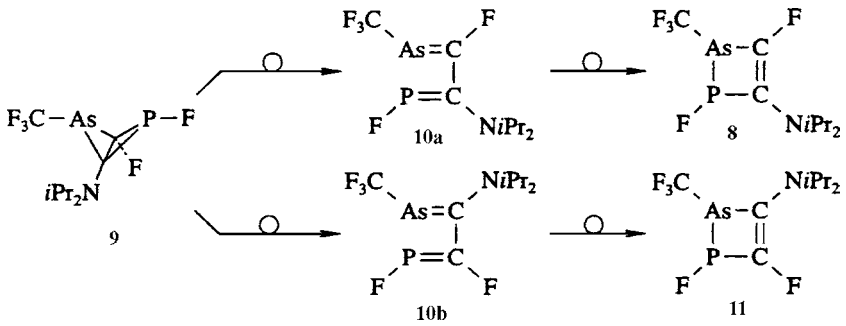


SCHEME 2

more stable than purely organic bicyclobutanes, because the heteroatoms P and As allow smaller bond angles and thus reduce the energy difference between **5** and **9** to a value below 8 kcal mol^{-1} as calculated for the above-cited diphospha analogues [12]. The last step of the rearrangement presumably is an electrocyclic reaction (valence isomerization) to yield **8**.

The spectroscopic results show that the isomerization gives **8** as the main product (90%). In addition, two by-products of 5% each are observed indicating the formation of the conformational isomer of **8**, 4-diisopropylamino-2,3-difluoro-1-trifluoromethyl-1-arsa-2-phospha-3-cyclobutene **11**, very probably via the alternative heterobutadiene derivative **10b** (Scheme 3). Attempts to grow single crystals of **8**, suitable for X-ray diffraction, failed because of the impurities and its limited stability.

8 was completely characterized by NMR, MS, and IR spectroscopic investigations. The ^{19}F NMR spectrum contains three signals with an intensity ratio of 3:1:1 for the CF_3 group and the CF and PF ring units. Due to extensive F/F and P/F couplings, the signals appear as ddd and ddq-patterns at $\delta_F - 47.3$ ($AsCF_3$), -98.1 (CF), and -175.9 (PF). The ^{31}P-resonance at δ_P 115.3 appears as doublet of pseudo-quintets, due to $^{1}J_{PF} = 990.7$ Hz and $^{3}J_{PF} = 17.1$ Hz for both CF/P-couplings (CF_3/P and CF/P). The ^{1}H-NMR spectrum at room temperature indicates two equivalent isopropyl groups with a doublet and a septet signal for the CH_3 and CH protons, respectively. This is in contrast to the doubling of signals for **5** caused by hindered rotation of the R_2N group around the C—N bond with double bond character. The mass spectrum of **8** supports the NMR spectroscopic results: The molecular ion [M^+] was detected with an intensity of 17% relative to the basis peak [$M^+ - CF_3$]. Typical fragment ions are produced by splitting off F, CF_3, and propene C_3H_6. The IR spectrum also is in good agreement with the structure



SCHEME 3

of **8**, unequivocally demonstrated by the strong $\nu_{C=C}$ band at 1593 cm^{-1}.

[2 + 2]-Cycloaddition Reactions of **1** *with 1-Diisopropylaminopropyne* **12** *and Ethoxyethyne* **14**

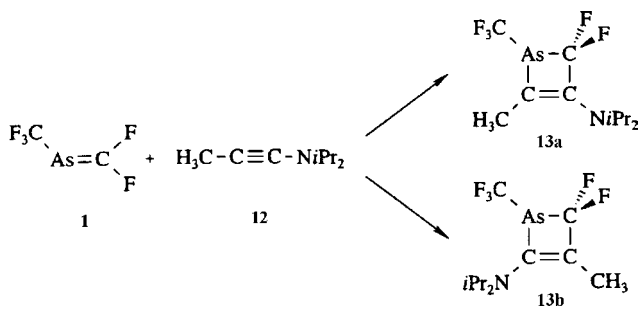
The successful cycloaddition reactions of **1** with phosphaalkynes led to the investigation of its reactivity with electron-rich alkynes like di-isopropylaminopropyne. The NMR control of the reaction mixture, after thawing the co-condensate of reactants and solvent from −196 to −78°C, indicated a fast and complete reaction within 15 min. The ^{19}F NMR spectrum is in accord with the formation of the expected [2+2]-cycloaddition product **13**. Since this product, in contrast to **5**, does not contain the ^{31}P probe the conclusive identification of the molecular structure of the main isomer was very difficult. To determine the most probable of the two isomeric structures **13a** and **13b** (Scheme 4), the analogous reaction of **1** with ethoxyethyne **14** was studied. This partner is expected to produce one or both of the isomeric structures **15a** and **15b** (Scheme 5), for which the pattern of the ^1H resonance of the CH ring-unit should allow to distinguish between the isomers.

Ethoxyethyne **14** undergoes a fast and complete reaction with **1** after thawing the co-condensate of the partners together with dichloromethane as solvent. The ^1H NMR spectrum of the product shows the typical triplet and quartet signals for the ethyl group with δ_H 2.45 and 2.90 ppm, respectively, together with a singlet at 5.62 ppm for the olefinic proton, indicating structure **15a** as the most probable one, because for the isomer **15b** coupling of the CH-unit with the fluorine nuclei of the neighboring CF_2 group should lead to a dd pattern of the signal. This assignment is supported by the cycloaddition direction observed for the reaction of electron-poor phosphalkene complexes with **14** [16]. Therefore, the analogous ring structure can also be deduced for **13a**.

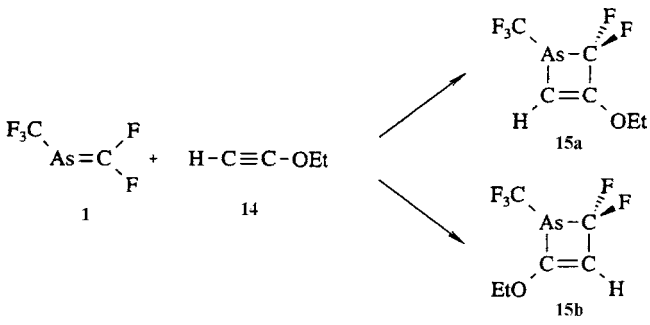
Compounds **13a** and **15a** have been identified by spectroscopic measurements, and the data of equivalent moieties correspond to those of the heteroatom derivatives **5** and **7a–d**. For **15a** the mass spectrum could be recorded after GC separation proving the molecular mass by detection of the molecular ion $[M^+]$ = 264 (7%) and the structure by typical fragment ions (see Experimental section).

Isolation and Spectroscopic Characterization of **1**

In the attempted reaction of **1** with **2**, a surprising stabilizing effect was observed depending on the concentration of hexamethyldisiloxane (bp 100°C)



SCHEME 4



SCHEME 5

which could not be completely separated from **2** (bp 62°C) by trap-to-trap vacuum condensation.

Therefore, investigations aimed at using the observed stabilizing effect for a thorough spectroscopic study were undertaken. Many of these experiments led to the polymerization of **1**, but in some cases the [D_2]dichloromethane solution of **1** was stable enough to carry out NMR measurements at room temperature. Di- and polymerization was detected only after 30 min by formation of a cloudy suspension. The complete NMR spectroscopic investigation was possible in a CD_2Cl_2 solution containing **1** and $(Me_3Si)_2O$ in equimolar amounts together with **2**, because numerous unsuccessful experiments indicated a stabilizing effect also by **2**. To avoid the self-addition and/or the polymerization of **1**, the NMR measurements were carried out at −10°C in a very dilute solution.

The ^{19}F NMR spectrum contains three signals due to the CF_3 group (δ_F −37.6, $^4J_{FF(AB)} = 10.3/17.2$) and the nonequivalent nuclei F_A and F_B of the CF_2 group (C_s symmetry). The signal of F_A in trans-position to CF_3 with δ_F 24.8 has the expected dq-pattern ($^2J_{FF(AB)} = 65.5$ Hz; $^4J_{FF(A)} = 10.3$ Hz). The better-shielded F_B in cis position to CF_3 appears at $\delta_F - 7.2$ with dq couplings of $^2J_{FF(AB)} = 65.5$ Hz and $^4J_{FF(B)} = 17.2$ Hz. Deviations of these data from those obtained earlier [2] (see Experimental section) can be attributed to the differing experimental conditions, but also indicate interactions of **1** with components of the solutions.

Because of the very low concentration of **1**, long-time measurements were necessary for a reasonable ^{13}C NMR spectrum including the coupling pattern with the fluorine nuclei. The resulting ddq ($\underline{C}F_2$) and qdd ($\underline{C}F_3$) signals with δ_F 217.0 ($^1J_{FC} = 406.0$ Hz) and δ_F 130.0 ppm ($^1J_{FC} = 330.0$ Hz) are in accord with those of $F_3CP{=}CF_2$ ($\underline{C}F_2$: δ_F 204.1 (F_A), $^1J_{FC} = 398.5$ Hz, δ_F 198.7 (F_B); $^1J_{FC} = 407.6$ Hz, and $\underline{C}F_3$: δ_F 129.7; $^1J_{FC}$ = 309.0 Hz) studied earlier [17].

Quantum Chemical Calculations of **1**, *Arsaethene and Perfluoro-2-phosphapropene*

Quantum chemical calculations have been carried out to explain the experimentally observed reactivity of **1** on the basis of its molecular and electronic structure. For this purpose, we have studied the perfluoro derivative **1** in comparison with the parent arsaethene and the corresponding perfluoro-2-phosphapropene. Furthermore, the calculated geometrical data are compared with X-ray structural results for a series of known arsaalkene derivatives to elucidate the influence of substituents on bond lengths and angles.

The As=C double bond of $HAs{=}CH_2$ has been calculated before, using the Hartree–Fock method HF/3-21G(*) [18] giving a bond length of 177.0 pm. This method is not appropriate for atoms and substituents like arsenic and fluorine introducing a great number of electrons. The basis set 6-311+G(d,p) was employed in combination with the hybrid density functional B3LYP [19]. The DFT calculations were carried out applying the program GAUSSIAN 03 [20] in order to establish the molecular structures, the natural charges, and the NAO Wiberg bond orders [21].

Structure and Charge Distribution of $HAs{=}CH_2$. The geometry and charge distribution of arsaethene are presented in Fig. 2 and Table 1. The calculated As=C bond length amounts to 178.6 pm which corresponds to a real σ + (p–p)π double bond with a bond order of 1.95. It is unaffected by inductive, mesomeric and steric substituent properties. The charges on As (+0.44*e*) and C (–0.77*e*) are consistent with the expected polarity of the double bond.

Structure and Charge Distribution of **1**. **1** is of particular interest in this study because the double bond character will considerably differ from that of $HAs{=}CH_2$ with consequences on both structure and reactivity. The quantum chemical calculation was performed for the staggered as well as for the eclipsed conformation. The results are given in Fig. 3 and Table 2.

The As=C double bond (182.1 pm) in the more stable staggered conformation (a) is found to be 2.5 pm longer than that of $HAs{=}CH_2$, and consequently the bond order is reduced to 1.66. On first sight, this result is surprising, but can be explained by π-donation from the substituents F(1) and F(2) into the π* As=C(1)-orbital, thus reducing the double bond character. This interpretation gains support

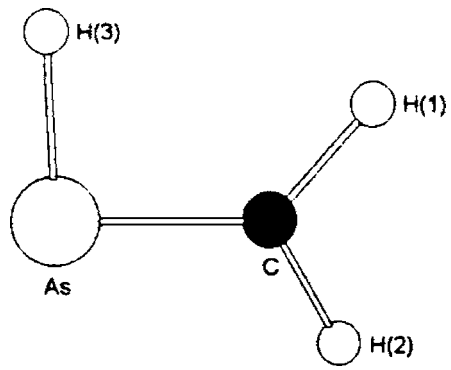


FIGURE 2 Calculated molecular structure of arsaethene, $HAs{=}CH_2$ [B3LYP/6-311+G(d,p)].

TABLE 1 Calculated Data of Arsaethene $HAs{=}CH_2$ (Total Energy, Bond Length, Bond Order, Bond Angle, Atomic Charge) by B3LYP/6-311+G(d,p) Total energy: $E_{tot} = -2275.76106$ au

Bond Length (pm)	*Bond Order*	*Bond Angle (°)*	*Atomic Charge (e)*
As–C/178.6	1.95	H(3)–As–C/ 96.0	As: +0.44
C–H(1)/108.3	0.94	As–C–H(1)/124.4	C: −0.77
C–H(2)/108.5	0.94	As–C–H(2)119.3	H(1): +0.20
As–H(3)/153.4	0.97	H(1)–C–H(2)/116.3	H(2): +0.20
			H(3): −0.08

from the shortening of the involved C(1)—F(1) and C(1)—F(2) bonds with bond orders of 0.95 vs. values of 0.88–0.89 for the C—F bonds of the CF_3 group. The As=C bond is stabilized by this interaction, and the tendency to di- and oligomerization is reduced in comparison with the hydrogen compound.

The C(1)—As—C(2) angle of 94.8° indicates a strong deviation from sp^2 hybridization and almost pure p-orbital contributions of As in the As—C σ-bonds. The lone pair of electrons on As consequently has more than 80% s-character, in accord with the small C(1)—As—C(2) bond angle. Steric interactions, causing a widening of this angle, are missing.

In contrast to $HAs{=}CH_2$ with $As(\delta+)$—$C(\delta-)$ polarity, the staggered conformation of **1** with charges of +0.43*e* (As) and +0.47*e* (C1) contains an almost nonpolar or even a slightly inversely polarized As=C bond.

To find out the thermodynamically preferred configuration, the eclipsed structure (b) of **1** was also calculated. It corresponds to the transition state of the internal rotation. The molecular structure is given in Fig. 3, and the bond parameters and the natural charges are given in Table 2.

A comparison of the data in Table 2 indicates

(i) a clear preference for the staggered conformation by 1.29 kcal mol^{-1},

(ii) a larger (3.6°) C(1)—As—C(2) angle for the eclipsed configuration due to repulsive interaction between F(1) and F(3),

(iii) smaller structural differences for the other bond lengths and angles which also can be rationalized on the basis of the discussed interactions.

Structure and Charge Distribution of Perfluoro-2-phosphapropene, $F_3CP{=}CF_2$. Since for the analogous phosphorus compound the gas phase structure has been determined by electron diffraction [22], it was of interest to calculate also its data for comparison both with the arsenic analogue and with the experimental results. Figure 4 and Table 3 present the results of the quantum chemical calculation.

In general, the calculated structures of the related phospha- and arsaalkenes show only slight differences in the molecular data, with the exception of those caused by the different radii and electronegativities of P and As. Thus the bond order of the P=C double bond is slightly higher, whereas the bond angles and bond orders of the remaining bonds show only small deviations. Due to the higher electronegativity of phosphorus, the polarity of the P=C double bond with charges of +0.40*e* for P and +0.47*e* for C(1) is a bit more strongly inverse than for As=C.

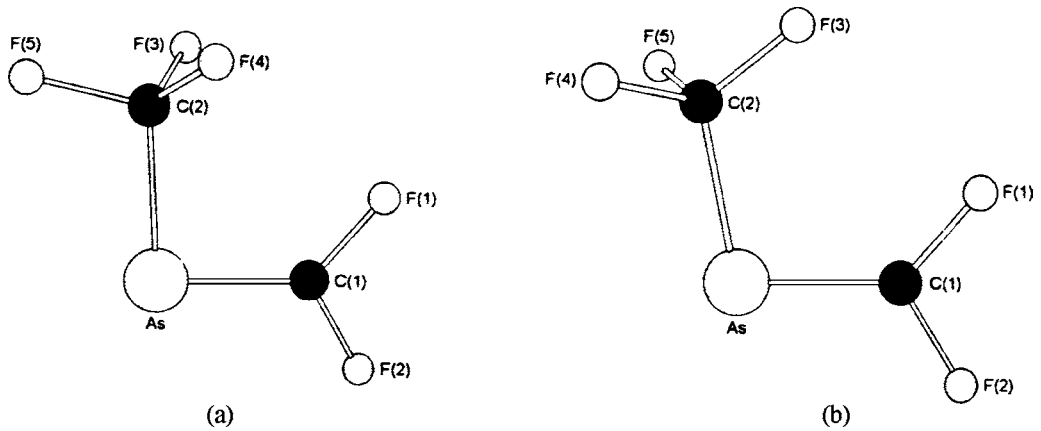


FIGURE 3 Calculated molecular structures of perfluoro-2-arsapropene 1: (a) staggered and (b) eclipsed conformation [B3LYP/6-311+G(d,p)].

TABLE 2 Calculated Data of Both the Staggered and Eclipsed Conformation of **1** by B3LYP/6-311+G(d,p): total energy: $E_{tot} = -2811.43465$ au (staggered); $E_{tot} = -2811.43259$ au (eclipsed)

	Length (pm)				*Angle (°)*		
Bond	*Staggered*	*Eclipsed*	*Bond Order Staggered*	*Group*	*Staggered*	*Eclipsed*	*Atomic charge (e^a)*
As–C(1)	182.1	182.0	1.67	C(1)–As–C(2)	94.8	98.4	As: +0.43
C(1)–F(1)	131.2	131.0	0.94	F(1)–C(1)–F(2)	109.5	109.2	C(1): +0.47
C(1)–F(2)	132.0	132.4	0.94	F(1)–C(1)–As	129.2	131.5	F(1): –0.31
As–C(2)	203.8	204.3	0.86	F(2)–C(1)–As	121.2	119.3	F(2): –0.32
C(2)–F(3)	134.8	134.1	0.89	As–C(2)–F(3)	114.0	117.7	C(2): +0.80
C(2)–F(4)	134.8	135.4	0.89	As–C(2)–F(4)	114.0	108.6	F(3): –0.35
C(2)–F(5)	135.4	135.4	0.88	As–C(2)–F(5)	106.8	108.6	F(4): –0,35
				F(3)–C(4)–F(4)	107.4	107.4	F(5): –0.36
				F(4)–C(4)–F(5)	107.2	106.7	
				F(5)–C(4)–F(3)	107.2	107.4	

[a]Data for the more stable staggered configuration.

The calculated barrier for internal rotation amounts to 1.58 kcal mol^{-1}.

The agreement between the calculated and the experimental data of $F_3CP{=}CF_2$ is also quite good, except for the angle C(1)–P–C(2): calc. 96.8°; exp. 108.8°. Because in the structures of CF_3- and $(CF_3)_2P$-substituted aminophosphaalkenes, determined by X-ray diffraction, bond angles between 95° and 97° have been detected, the angle of 108.8° for the perfluorophosphaalkene may be in error and should possibly be re-determined. [23,24].

Comparison of Calculated As=C Data with X-Ray Structural Results for a Series of Arsaalkene Derivatives. As=C bond lengths from X-ray structural work are still quite rare in the literature. Therefore, it is of interest to compare them with the calculated data and study the influence of a variety of substituents at the double bond on the bond order and the electronic structure of the molecules. Most of the presently known data are collected in Table 4.

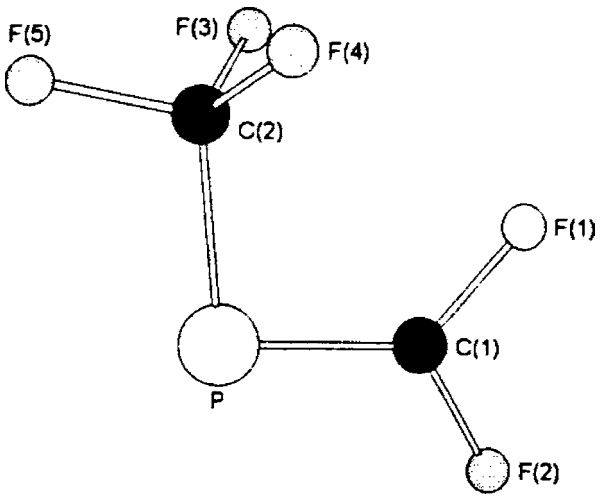


FIGURE 4 Calculated molecular structure of perfluoro-2-phosphapropene [B3LYP/6-311+G(d,p)].

The As=C bond lengths vary between 180.7 and 199.0 pm and are generally widened in comparison with that of $HAs{=}CH_2$ (178.7 pm), but in most cases are considerably shorter than typical As–C single bonds with values around 196.0 pm. As already mentioned before, the main reason for the bond enlargement is the interaction with lone pairs of electrons of substituents at the double bond. The bonds X–As involved, in general, experience a shortening. Atoms of important influence at the doubly bonded C(1) are the second row elements N > O > F. The mesomeric effect on the structure can be enhanced by steric effects of bulky substituents, so that As=C bonds even exceed in length typical single bonds. This is demonstrated by several examples in Table 4. A special effect results, if both donating and accepting groups are present at the double bond system, as demonstrated for the push/pull system with NEt_2 on C(1) and $(CF_3)_2P$ on P in the phosphaalkene derivative $(CF_3)_2PP{=}C(F)NEt_2$ [24] with a P=C length of 176.0 pm as compared to 174.4 pm for $CF_3P{=}C(F)NMe_2$ [23]. Especially, long E=C bonds are observed if the heteroatom is bound to two metal carbonyl fragments and the C-atom is substituted with two NMe_2 donor groups [34].

CONCLUSION

In spite of the experimental problems arising from the lability of perfluoro-2-arsapropene **1**, numerous interesting results could be obtained in low temperature reactions and by using the accidentally detected stabilization effect of both hexamethyldisiloxane

TABLE 3 Calculated and Experimental Data of the Staggered Conformation of Perfluoro-2-phosphapropene by B3LYP/6-311+G(d,p); total energy: $E_{tot} = -916.93371$ au

	Length (pm)				*Angle (°)*		
Bond	*Staggered*	*Experimental*	*Bond Order Staggered*	*Group*	*Staggered*	*Experimental*	*Atomic Charge (e^a)*
P–C(1)	169.5	169.0	1.71	C(1)–P–C(2)	96.8	108.8	P: +0.40
C(1)–F(1)	131.2	131.3	0.94	F(1)–C(1)–F(2)	109.5		C(1): +0.47
C(1)–F(2)	132.0	131.3	0.94	F(1)–C(1)–P	129.6	125.3	F(1): –0.30
P–C(2)	191.1	190.1	0.89	F(2)–C(1)–P	120.9	122.9	F(2): –0.31
C(2)–F(3)	134.8	134.2	0.89	P–C(2)–F(3)	114.0	114.3	C(2): +0.81
C(2)–F(4)	134.8	134.2	0.89	P–C(2)–F(4)	114.0	114.7	F(3): –0.35
C(2)–F(5)	135.3	134.2	0.88	P–C(2)–F(5)	106.8	106.7	F(4): –0,35
				F(3)–C(2)–F(4)	107.3	106.3	F(5): –0.36

[a]Data for the staggered configuration.

and **2**. Thus, [2 + 2]-cycloaddition reactions with the phosphaalkynes (**2**), (**4**), and the phosphaalkenes **6a–d** as synthetic equivalents of the corresponding phosphaalkynes have been successfully investigated yielding the novel arsaphosphacyclobutene derivatives **3, 5**, and **7a–d**. The dialkylamino compounds **5** and **7a–d** undergo an interesting intramolecular rearrangement, leading to the more stable 1-arsa-2-phospha-3-cyclobutene isomers, in the case of **5** closely studied by the characterization of the isomer **8**. As examples of electron-rich alkynes, **12** and **14** have been used as partners for **1** and are found to be highly reactive giving the expected [2 + 2]-cycloaddition products **13** and **15**, respectively. Finally, quantum chemical calculations on the heteroalkenes $HAs{=}CH_2$, $F_3CAs{=}CF_2$, and $F_3CP{=}CF_2$ were carried out to rationalize the high reactivity of **1** and to compare the calculated As=C bond lengths with X-ray structural data. This allowed us to estimate the influence of various substituents at the As=C bond on its length and electronic structure.

EXPERIMENTAL

General

Since most of the compounds used as starting materials and obtained products are volatile and toxic chemicals, a standard vacuum-line in combination with special devices and additional apparatus was employed for handling as a precaution. Solvents were purified, dried, and degassed.

TABLE 4 Experimental (X-ray) and Calculated (B3LYP/6-311+G*) As=C Bond Lengths of Arsaalkenes $R^1As{=}CR^2R^3$

$R^1As{=}CR^2R^3$			*As=C Bond Length (pm)*	
R^1	*R^2*	*R^3*	*Experimental*	*Calculated*
H	H	H	–	178.7
Mes*	2,7-di-*tert*-butylfluorenylidene		180.7 [25]	–
iPr_3Si	(–N(C_6H_{12}–)C(N–)$SiIs_2$–)$_2$		181.6 [26]	–
CF_3	F	F	–	182.1
$Cp(CO)_2Fe$	Me_3SiO	*t*Bu	182.1 [27]	–
iPr_3Si	–N(*c*C_6H_{11}–)C(N*c*C_6H_{11})$SiIs_2$–		182.7 [28]	–
CF_3	F	NH_2	–	185.8
CF_3	F	NEt_2	186.7 [4]	187.7
$Cp^*(CO)_2Fe$	NMe_2	NMe_2	187.6 [8]	–
MesAs(O)	Mes	OH	190.0 [29]	–
	–C(NMes)$SiIs_2$–	NHMes	192.1 [28]	–
	arsatrimethynecyanine cation		183.0 [30]	–
$Cp^*(CO)_2Fe$	Ph	NMe_2	184.9 [31]	–
Mes*	Br	$SiMe_3$	178.9 [32]	–
Tp′(CO)2W≡C	NMe_2	NMe_2	191.4 [33]	–
$Cp^*(CO)_2Fe[Cr(CO)_5]$	NMe_2	NMe_2	197.5 [34]	–
$Cp^*(CO)_2Fe[Fe(CO)_4]$	NMe_2	NMe_2	199.0 [34]	–
$Cp^*(CO)_2Fe[Cr(CO)_5]$	$SSiMe_3$	$SSiMe_3$	180.0 [35]	–

Starting compounds: bis(trifluoromethyl)arsanotrimethylstannane [36], **2** [37], **4** [38], and **6a–d** [38] have been prepared according to the literature. **12** and **14** are commercially available. NMR: Bruker AC 200 (^{1}H, 200.13 MHz, standard: TMS; ^{13}C, 50.32 MHz, standard: TMS; ^{19}F, 188.31 MHz, standard: CCl_3F; ^{31}P, 81.02 MHz, standard: 85% H_3PO_4). In some cases, the ^{1}H- and ^{13}C-signals of the solvents CH_2Cl_2 and CD_2Cl_2 were used as reference to determine the NMR data. GC/MS: Finnigan MAT ITD 800 spectrometer combined with a Dani gas chromatograph 8521a; column: Cp-Sil-8, 50 m, 0.32 mm, 025 μm; IE = 70 eV. GC/IR: Bruker FTIR-spectrometer IFS 48 combined with a Shimadzu GC 8A gas chromatograph; solvent: CH_2Cl_2.

General Procedure for the Preparation of **1**

A special pyrolysis apparatus (Fig. 1) has been installed for the improved generation of **1**. As a rule, the calibrated tube with a Teflon valve is charged with 5 mmol of $Me_3SnAs(CF_3)_2$ and then connected to the inlet of the furnace. The tube with the reactant and/or a suitable solvent is fixed at the end of the apparatus. Then the whole system is thoroughly evacuated, the trap and the 25 mL reaction vessel behind the furnace are cooled at −78°C and −196°C, respectively, taking care of a constant level of liquid nitrogen in the second Dewar vessel. After heating the pyrolysis tube to 380°C, the tap to the vacuum-line is closed and the Teflon valve of the $Me_3SnAs(CF_3)_2$ reservoir is opened just enough to guarantee a very low vapor density in the pyrolysis tube. The reaction is carried out in 20% portions of the precursor by closing the Teflon valve and condensing **1** completely in the reaction vessel. Next, either the reactant and/or the solvent is transferred from the respective tube into the vessel by vacuum condensation. This procedure is repeated four times until the 5 mmol amount of the precursor is used up. In the case of a reactant the co-condensation is finished with a layer of CD_2Cl_2 as suitable solvent. The reaction is then carried out by thawing the layered mixture at −78°C and stirring the resulting liquid for 15 to 60 min. The product mixture or solution is then transferred under continued cooling of the vessel into the NMR tube by turning part of the apparatus, thus allowing the liquid to run down. The NMR tube is sealed off after cooling to −196°C and used for a first control of the reaction. The following working-up procedure depends on the reaction partners involved and will be described further down for the individual [2 + 2]-reactions. Typical yield of the generation of **1**: ca. 0.5 g (2.5 mmol, 50%).

Isolation of **1** *for NMR Measurements*

Following the prescription given above with hexamethyldisiloxane as stabilizing solvent condensed in layers with **1**, the layer system is carefully thawed, then quickly mixed, cooled again with liquid nitrogen to a status still liquid, but at lower temperature than −80°C, and finally transferred into the NMR tube. Quickly frozen again at −196°C, the NMR tube is sealed under vacuum. After thawing at room temperature, **1** is only stable enough to record NMR spectra for ca. 5–10 min. The formation of dimers shows up first in the ^{19}F spectrum. To measure the ^{13}C NMR spectrum, low concentrations of **1** in a mixture of hexamethyldisiloxane and **2** were used, allowing at −10°C 30 min for recording. The ^{13}C NMR spectrum did not allow us to measure more than the $^1J_{FC}$ coupling constants.

^{19}F NMR: δ_F − 37.6 (dd, $^4J_{FF(A)} = 10.3$ Hz, $^4J_{FF(B)} = 17.2$ Hz; CF_3); 24.8 (dq, $^2J_{FF(AB)} = 65.5$ Hz, $^4J_{FF(A)} = 10.3$ Hz, F_A); −7.2 (dq, $^2J_{FF(AB)} = 65.5$ Hz, $^4J_{FF(B)} = 17.2$ Hz, F_B). ^{13}C{^{1}H} NMR: δ_C 217.0 (ddq, $^1J_{FC} = 406.0/353.0$ Hz, $\underline{C}F_2$); 130.0 (qdd, $^1J_{FC} = 330.0$ Hz, $\underline{C}F_3$). Comparison with ^{19}F NMR data obtained earlier in [D6]-dimethylether at −110°C on a 90 MHz Varian spectrometer [2]: δ_F − 41.2 (dd, $^4J_{FF(A)} = 8.5$ Hz, $^4J_{FF(B)} = 17.0$ Hz; CF_3); 6.0 (dq, $^2J_{FF(AB)} = 60.0$ Hz, $^4J_{FF(A)} = 8.5$ Hz, F_A); −11.4 (dq, $^4J_{FF(B)} = 17.2$ Hz, F_B). The observed deviations are due to differences in concentrations, temperatures, and solvents and obviously indicate interactions of **1** with the oxygen-containing compounds of the solutions.

[2 + 2]-Cycloaddtion Reactions of **1** *with Phosphaalkynes, Phosphaalkenes, and Organic Alkynes*

2-Tert-butyl-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutene **3**. The general procedure was carried out with **1** (ca. 2.5 mmol) and **2** (150 mg, 1.5 mmol) for preparing the layered system. Surprisingly, no reaction was observed during thawing and stirring for 15 min at −78°C. The reactant mixture was transferred into the NMR tube which after sealing under vacuum was slowly warmed to 0°C and stored at this temperature in the dark for several days. The end of reaction was detected by recording ^{19}F NMR spectra. In a series of experiments, we found out that the reaction time depends on the concentration of both hexamethyldisiloxane and **2**. Reaction times between four and seven days have been observed. At −20°C no reaction occurred allowing to store the mixture of reactants, if necessary, for a longer period. The product, 2-tert-butyl-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutene **3**,

was characterized by spectroscopic investigations. GC/IR: ν/cm^{-1}(rel. intensity, assignment): 2970 (42, ν_{CH}), 1653 (27), 1560 (20), 1506 (20, δ_{CH}), 1474 (18, δ_{CH}), 1458 (19, δ_{CH}), 1265 (42, $\nu_{C=P}$), 1155 (77, ν_{CF}), 1142 (79, ν_{CF}), 1115 (94, ν_{CF}), 1086 (100, ν_{CF}), 814 (51). ^{1}H NMR: δ 1.25 (d, $^4J_{PH}$ = 1.7 Hz, CH_3);[13] C{^{1}H} NMR: δ 30.2 (s, $\underline{C}H_3$), 42.3 (s, $\underline{C}CH_3$), 103.4 (2dd, $^1J_{FC}$ = 314.8 Hz, $^2J_{PC}$ = 30.5 Hz, 130.1, $\underline{C}F_2$), 130.1 (qdd, $^1J_{FC}$ = 348.0 Hz, $^3J_{F(B)C}$ = 14.6 Hz, $^3J_{F(A)C}$ = 4.5 Hz, $\underline{C}F_3$), 217.0 (qm, $^1J_{PF}$ = 57.0 Hz, $\underline{C}$=P); ^{19}F NMR: δ − 49.8 (ddd, $^4J_{FF}$ = 10.4 Hz, $^4J_{FF}$ = 4.0 Hz, $^4J_{PF}$ = 4.0 Hz, CF_3), −86.1 (ddq, $^2J_{FF(AB)}$ = 261.9 Hz, $^2J_{PF}$ = 70.0 Hz, $^4J_{FF}$ = 4.4 Hz, F(A)), −99.6 (ddq, $^2J_{FF(AB)}$ = 261.8 Hz, $^2J_{PF}$ = 72.4 Hz, $^4J_{FF}$ = 10.2 Hz, F(B)); ^{31}P{^{1}H} NMR: δ 392.2 (ddq, $^2J_{PF}$ = 70.0 Hz, $^2J_{PF}$ = 72.4 Hz, , $^4J_{PF}$ = 4.0 Hz, C=P−CF_2); GC/MS (70 eV,), *m/z* (%): 294 (5) [M^+], 175 (22) [$C_4H_9CPAs^+$], 119 (100) [C_4H_9C=PF^+], 85 (29) [$C_4H_6P^+$], 69 (68) [CF_3^+], 57 (18) [$C_4H_9^+$].

2-Diisopropylamino-4,4-difluoro-1-arsa-3-phospha-2-cyclobutene **5**. The analogously performed reaction of **1** with **4** started already during the co-condensation of the reactants at −196°C, indicated by a color change to brown-orange. After thawing of the mixture first at −78°C, then at room temperature, the reaction was complete within 1 h, giving the expected [2 + 2]-cycloaddition product **5**, which was characterized spectroscopically. ^{1}H-NMR: δ 1.20 (d, $^3J_{HH}$ = 6.0 Hz, $(CH_3)_A$), 1.24 (d,$^3J_{HH}$ = 6.4 Hz, $(CH_3)_B$), 3.41 (sept, $(CH)_A$), 3.88 (sept, $(CH)_B$); ^{19}F NMR: δ − 50.7 (ddd, $^4J_{FF}$ = 10.0 Hz, $^4J_{FF}$ = 4.2 Hz, $^4J_{PF}$ = 3.3 Hz, CF_3), −73.4 (ddq, $^2J_{FF(AB)}$ = 244.3 Hz, $^2J_{PF}$ = 82.8 Hz, $^4J_{FF}$ = 4.2 Hz, F(A)), −84.7 (ddq, $^2J_{FF(AB)}$ = 244.2 Hz, $^2J_{PF}$ = 87.0 Hz, $^4J_{FF}$ = 10.0 Hz, F_B); ^{31}P {^{1}H}-NMR: δ 203.1 (ddq, $^2J_{PF}$ = 83.7 Hz, $^4J_{PF}$ = 3.0 Hz, C=P−CF_2).

*2-Dialkylamino-4,4-difluoro-1-trifluoromethyl-1-arsa-3-phospha-2-cyclobutenes (***7a–d***)*. Dialkylamino derivatives of type **5** can be prepared also by reactions of **1** with the phosphaalkenes HP=C(F)NR_2 (R = Me, Et, Pr; NR_2 = Pip) (**6a–d**), which function as equivalents of the corresponding phosphaalkynes R_2NC≡P. The reactions were carried out with 1.5 mmol amounts as described for **4** and proceed similarly. After a reaction period of 15 min at −78°C, the resulting mixtures were kept at room temperature for 1 h and then transferred into NMR tubes for characterization. The spectra showed the signals of the expected arsaphosphacyclobutenes **7a–d** together with some by-products, mainly due to side-reactions with the eliminated hydrogen fluoride. These impurities could not be removed from the main components which, however, could be clearly characterized by NMR and in the case of **7a, b** also by GC/MS measurements.

7a: ^{1}H NMR: δ 2.95 (d, $^4J_{PH}$ = 3.0 Hz, $(CH_3)_A$), 3.08 (m, $(CH_3)_B$); ^{19}F NMR: δ − 50.4 (dd, $^4J_{FF}$ = 12.3 Hz, $^4J_{FF}$ = 3.9 Hz, CF_3); −73.7 (ddq, $^2J_{FF(AB)}$ = 242.0 Hz, $^2J_{PF}$ = 87.2 Hz, $^4J_{FF}$ = 3.9 Hz, F_A), −86.4 (ddq, $^2J_{FF(AB)}$ = 242.0 Hz, $^2J_{PF}$ = 88.5 Hz, $^4J_{FF}$ = 9.5 Hz, F_B); ^{31}P{^{1}H} NMR: δ 207.5 (dd, $^2J_{PF}$ = 88.0 Hz, C=P−CF_2). GC/MS (70 eV), *m/z* (%): 281 (8) [M^+], 212 (100) [M^+−CF_3], 162 (79) [Me_2NCPAs^+], 119 (9) [$Me_2NC_2HPF^+$], 87 (19) [Me_2NCP^+], 69 (25) [CF_3^+].

7b: ^{1}H NMR: δ 1.22 (t, $^3J_{HH}$ = 7.1 Hz, $(CH_3)_A$), 1.38 (t, $^3J_{HH}$ = 7.1 Hz, $(CH_3)_B$), 3.31 (q, $^3J_{HH}$ = 7.1 Hz, $(CH_2)_A$), 3.64 (q, $^3J_{HH}$ = 7.1 Hz, $(CH_2)_B$); ^{19}F NMR: δ − 50.3 (dd, $^4J_{FF}$ = 11.0 Hz, CF_3); −73.6 (ddq, $^2J_{FF(AB)}$ = 242, 1 Hz, $^2J_{PF}$ = 87.2 Hz, $^4J_{FF}$ = 3.9 Hz, F_A), −84.3 (ddq, $^2J_{FF(AB)}$ = 242.0 Hz, $^2J_{PF}$ = 88.5 Hz, $^4J_{FF}$ = 9.5 Hz, F_B); ^{31}P{^{1}H} NMR: δ 207.6 (dd, $^2J_{PF}$ = 88.1 Hz, C=P−CF_2). GC/MS (70 eV,), *m/z* (%): 309 (6) [M^+], 290 (6) [M^+ − F], 240 (100) [M^+−CF_3], 190 (72) [Et_2NCPAs^+], 69 (25) [CF_3^+].

7c: ^{1}H NMR: δ 0.90 (t, $^3J_{HH}$ = 7.0 Hz, $(CH_3)_A$), 0.98 (t, $^3J_{HH}$ = 7.0 Hz, $(CH_3)_B$), 1.60 (qt, $^3J_{HH}$ = 7.0 Hz, $(CH_2)_A$), 1.77 (qt, $^3J_{HH}$ = 7.0 Hz, $(CH_2)_B$), 3.25 (t, $^3J_{HH}$ = 7.0 Hz, $(CH_2)_{A'}$), 3.58 (t, $^3J_{HH}$ = 7.0 Hz, $(CH_2)_{B'}$); ^{19}F NMR: δ −50.6 (dd, $^4J_{FF}$ = 10.1 Hz, CF_3); −74.2 (ddq, $^2J_{FF(AB)}$ = 242.3 Hz, $^2J_{PF}$ = 83.6 Hz, $^4J_{FF}$ = 4.0 Hz, F_A), −84.2 (ddq, $^2J_{FF(AB)}$ = 242.1 Hz, $^2J_{PF}$ = 89.6 Hz, $^4J_{FF}$ = 10.1 Hz, F_B); ^{31}P{^{1}H} NMR: δ 209.0 (dd, $^2J_{PF}$ = 88.0 Hz, C=P−CF_2).

7d: ^{1}H NMR: δ 1.65 (m, 2H, CH_2), 1.65 (m, 4H, $2CH_2$), 3.40 (m, 4H, $2CH_2$); ^{19}F NMR: δ − 50.6 (dd, $^4J_{FF(AB)}$ = 3.8 Hz, CF_3); −73.3 (ddq, $^2J_{FF(AB)}$ = 242.0 Hz, $^2J_{PF}$ = 86.6 Hz, $^4J_{FF}$ = 4.5 Hz, F_A), −84.8 (ddq, $^2J_{FF(AB)}$ = 241.9 Hz, $^2J_{PF}$ = 89.1 Hz, $^4J_{FF}$ = 9.5 Hz, F_B); ^{31}P{^{1}H} NMR: δ 206.2 (dd, $^2J_{PF}$ = 89.4 Hz, C=P−CF_2).

3-Diisopropylamino-2,4-difluoro-1-trifluoromethyl-1-arsa-2-phospha-3-cyclobutene **8**. At room temperature **5** was found to undergo a thermodynamically determined isomerization with formation of **8** within 3 days. The resulting product mixture was transferred into a Schlenk vessel, and the volatile components pumped off at 10^{-3} mbar. **8** was characterized by spectroscopic investigations.

8: GC/IR: ν/cm^{-1}(rel. intensity, assignment): 2980 (27, ν_{CH}), 2947 (14, ν_{CH}), 2830 (9, ν_{CH}), 1593 (55, $\nu_{C=C}$), 1560 (9, ?), 1410 (9, δ_{CH}), 1375 (18, δ_{CH}), 1259 (20, δ_{CH}), 1198 (13, ν_{CF}), 1123 (100, ν_{CF}), 1032 (12, ν_{CF}). ^{1}H NMR: δ 1.20 (d, $^3J_{HH}$ = 6.5 Hz, CMe_3), 3.8 (sept, $^3J_{HH}$ = 6.5 Hz, CH); ^{19}F NMR: δ − 47.3 (ddd, $^3J_{PF}$ = 17.4 Hz, $^4J_{FF}$ = 1.8 Hz, $^4J_{FF}$ = 1.8 Hz, CF_3); −98.1 (ddq, $^3J_{PF}$ = 16.1 Hz, $^4J_{FF}$ = 1.8 Hz, CF), −175.9 (ddq, $^1J_{PF}$ = 990.4 Hz, $^4J_{FF}$ = 1.9 Hz, PF): ^{31}P{^{1}H} NMR: δ 115.3 (ddq, $^1J_{PF}$ = 990.7 Hz, $^3J_{PF}$ = 17.1 Hz,

C=P–CF_2). GC/MS (70 eV,), *m/z* (%): 337 (17) [M^+], 318 (5) [M^+–F], 268 (100) [M^+ –CF_3], 226 (41) [M^+–CF_3–C_3H_6], 184 (33) [226–C_3H_6], 69 (25) [CF_3^+].

Reactions of **1** *with* **12** *and* **14**. The electron-rich alkyne derivatives **12** and **14** (1.5 mmol in 40% hexane solution) were also reacted with **1** according to the layer-by-layer process. Immediately after thawing the solution, a complete reaction was observed by NMR control. To isolate the products the volatile components were pumped off at 10^{-1} mbar, leaving behind the arsacyclobutenes **13** and **15**, respectively. They were found to decompose already at room temperature and, therefore, were stored at −196°C.

3-Diisopropylamino-4,4-difluoro-1-trifluoromethyl-2-methyl-1-arsa-2-cyclobutene. **13a** ^{1}H NMR: δ 1.71 (d, $^3J_{HH} = 6.5$ Hz, CMe_2), 2.48 (s, CH_3), 3.61 (sept, $^3J_{HH} = 6.5$ Hz, CH); ^{19}F NMR: δ − 49.0 (dd, $^4J_{FF} = 11.1$ Hz, $^4J_{FF} = 3.6$ Hz, CF_3); −83.2 (d, $^2F_{FF(AB)} = 214.4$ Hz, $^4J_{FF} = 3.6$ Hz, F_A), −91.0 (dq, $^2J_{FF(AB)} = 214.3$ Hz, $^4J_{FF} = 10.9$ Hz, F_B).

3-Ethoxy-4,4-difluoro-1-trifluoromethyl-1-arsa-2-cyclobutene **15a** ^{1}H NMR: δ 2.45 (t, $^3J_{HH} = 7.1$ Hz, CH_3), 2.90 (q, $^3J_{HH} = 7.1$ Hz, CH_2), 5.62 (s, CH); ^{19}F NMR: δ −49.4 (d, $^4J_{FF} = 8.6$ Hz, CF_3) −81.0 (d, $^2J_{FF(AB)} = 210.7$ Hz, $^4J_{FF} = 4.6$ Hz, F_A), −89.4 (dq, $^2J_{FF(AB)} = 210.5$ Hz, $^4J_{FF} = 9.8$ Hz, F_B); GC/MS (70 eV), *m/z* (%): 264 (7) [M^+], 245 (13) [M^+–F], 236 (7) [M^+ –C_2H_4], 144 (1) [$AsCF_3^+$], 119 (6) [$F_2CC(OEt)C^+$], 91 (100) [$F_2C(OH)C^+$], 69 (6) [CF_3^+].

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