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C-Protonation of Adamantylphosphaacetylene (1-AdC$\equiv$P) and *tert*-Butylphosphaacetylene (tBuC$\equiv$P) in Superacids: Phosphavinyl Cation Generation and Trapping To Form Phosphaalkenes, Formation of Isomeric Boron-Containing Spirocyclic Betaines by Reaction of 1-AdC$\equiv$P with B(OTf)$_3$, and Theoretical Studies on Protonation of MeC$\equiv$P

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Low-temperature protonations of 1-adamantylphosphaacetylene (1-AdC$\equiv$P, **1**) and *tert*-butylphosphaacetylene (tBuC$\equiv$P, **2**) were examined in various superacid media, namely FSO$_3$H/SO$_2$ClF, FSO$_3$H/SO$_2$, CF$_3$SO$_3$H (TfOH)/SO$_2$ClF, FSO$_3$H·SbF$_5$ (4:1)/SO$_2$, FSO$_3$H·SbF$_5$ (1:1)/SO$_2$, and TfOH$_2^+$B(OTf)$_4^-$/SO$_2$ClF. In SbF$_5$-free systems initial C-protonation to an incipient phosphavinyl cation **5** ($\lambda^2\sigma^1$-P) is followed by rapid gegenion trapping (FSO$_3^-$, OTf$^-$) to furnish cleanly the corresponding phosphaalkenes **15**, **17** and **20** in the *Z* configuration (anti stereochemistry of addition). P-Protonation ($\rightarrow$ **6a** $\leftrightarrow$ **6b**) was never observed. The derived isomeric spirocyclic cations (**18**/**19**) are formed as minor byproducts. With SbF$_5$-containing superacids or TfOH$_2^+$B(OTf)$_4^-$ despite lower counterion nucleophilicity, **5** is still not persistent. Moreover phosphaalkene products are unstable in these media and give complex product mixtures. Reaction of **1** with B(OTf)$_3$ gives two isomeric spirocyclic betaines (**22**/**23**), which were characterized by multinuclear NMR. Attempts to observe the initial step of the reaction, namely formation of **21** prior to cycloaddition chemistry, by low-temperature NMR were unsuccessful. For comparison, in model studies the protonation of MeC$\equiv$P (**3**) was probed at the RHF/6-31G* and subsequently at the MP2/6-311+G** levels of theory. Structures and energies of the derived fluorophosphaalkenes formed by a hypothetical F$^-$ quenching of the cation were also examined at the RHF/6-31G* level. At the higher level the calculations predict a slightly bent hydrogen-bridged structure for the cation.

Introduction

Vinyl cations such as **4** (Figure 2) are established intermediates in protonation (alkylation) of alkynes with superacids (super electrophiles).[2-5] Two well-known reactions of the incipient vinyl cation generated in superacid media are alkyl migration to give allyl cations and dimerization to form stable cyclobutenyl cations. Addition of FSO$_3$H to terminal alkynes forming vinyl fluorosulfates (with *E*/*Z* ratios about 4:1)[3] is usually extremely rapid even at −120 °C. Formation of the bis(fluorosulfate) is slower and occurs at higher temperatures (−20 °C).[3]

Increasing vinyl cation stability by β-silyl substitution or effective π-conjugation with vinyl, aryl, ferrocenyl, or cyclopropyl groups allows their direct observation under persistent ion conditions.[6-10] Contrary to vinyl cations which have been extensively probed, the phosphorus analogue of vinyl cation, namely the phosphavinyl cations (P$^+$, $\lambda^2\sigma^1$-P as in **5**, or C$^+$, $\lambda^3\sigma^2$-P as in **6b**), is elusive (Figure 3).

Theoretical studies of charge distribution in phosphaalkynes[11] and previous experimental work on HCl addition to RC$\equiv$P, showing specific addition with protonation occurring twice at the alkyne carbon,[12,13] suggested to us that under controlled conditions generation of **5** by low-temperature protonation of phosphaacetylenes should be feasible.

In this connection, Regitz et al. showed recently that Lewis acids such as AlCl$_3$ and AlBr$_3$ react with **1** and **2** (1:3 molar ratios, respectively) according to Scheme 1 to give the corresponding spirocyclic betaines **11**/**12** as single isomers.[14] The X-ray structure of **12** has been reported.[14] GaCl$_3$ and AlI$_3$ react similarly.[15] These reactions all point to the intermediacy of phosphavinyl betaines **7** and **8**, showing that the Lewis acid preferentially attacks at carbon.

The 1:1 reactions of **1** with BCl$_3$ leads to the 1,2-addition product (**13**) with *Z* stereochemistry for addition

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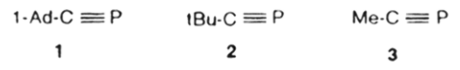


Figure 1. Phosphaalkyne protonation substrates **1** and **2** and theoretical model **3**.

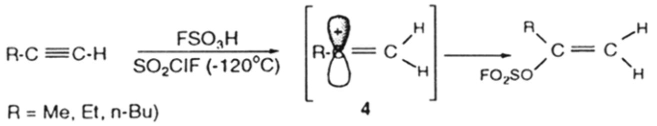


Figure 2. Protonation of alkynes.

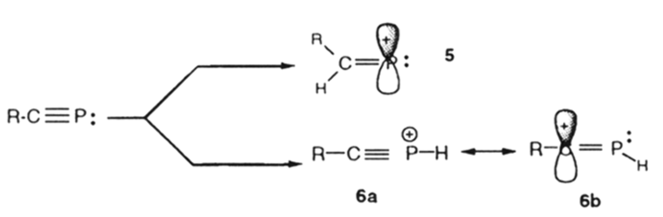
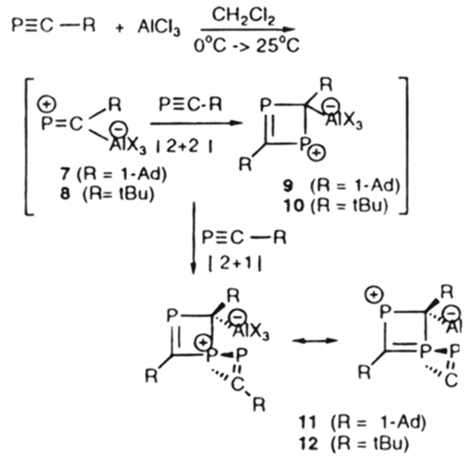
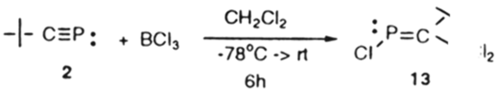


Figure 3. Possible modes of protonation of phosphaalkynes.

Scheme 1. Reaction of AlX_3 with Phosphaalkynes 1 and 2



Scheme 2. Reaction of BCl_3 with

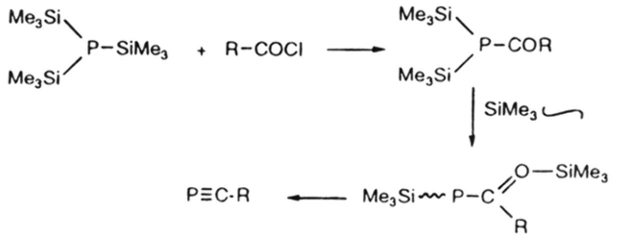


(*E* configuration)[15] (Scheme 2). Improved preparative methods for efficient synthesis of various phosphacetylenes developed by Regitz and co-workers[16-19] (Scheme 3) provided access to gram quantities of **1** and **2** and was the impetus for the present investigation.

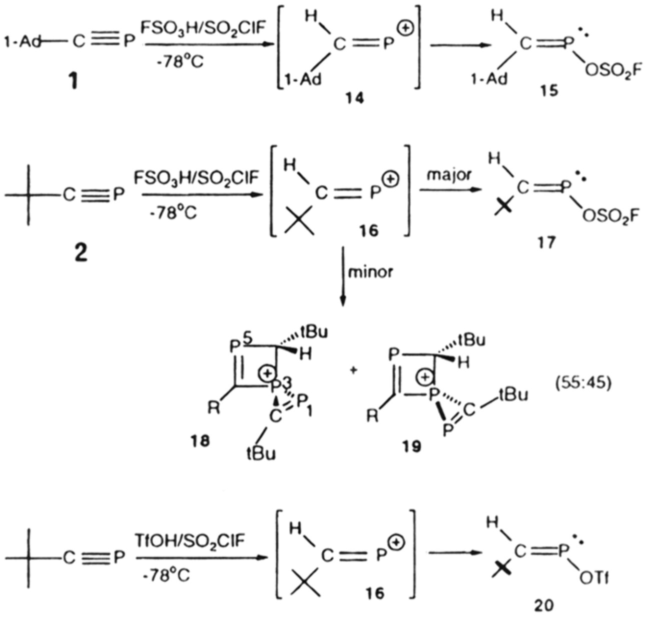
Results and Discussion

Protonation Studies on 1 (Scheme 4 and Table 1). The crowded phosphaalkyne **1** does not react with FSO$_3$H/SO$_2$ at dry ice/acetone temperature. However when the NMR sample is slowly warmed to ca −50 °C (efficient mixing), it dissolves smoothly to give a yellow-orange solution whose ^{1}H NMR exhibits a distinct low-field doublet at 8.91 ppm (1H) with a two-bond PH coupling constant of 14.4 Hz, clearly showing that *C-protonation* had occurred. The C≡P carbon in the $\{^1H\}^{13}C$ NMR spectrum is a doublet at 196.8 ppm with a one-bond PH coupling constant of 57.2 Hz.

Scheme 3. Strategy for Efficient Synthesis of Phosphaalkynes



Scheme 4. Protonation of 1 and 2 in Superacids



That the product is the covalent fluorosulfate **15** and not the cation **14** is apparent from the ^{31}P NMR spectrum showing just one resonance at 336.6 ppm, typical of phosphaalkenes. The latter appears as a 9.5 Hz doublet in the proton-decoupled spectrum and changes to a distorted doublet of doublets on H-coupling. This establishes a three-bond PF coupling constant of 9.5 Hz and a two-bond PH coupling constant of 14.0 Hz.

The presence of the *Z* stereochemistry in **15** is deduced based on the magnitudes of $^2J_{PH}$ (14.4 Hz) and $^2J_{PC}$ couplings (38.8 Hz).[18] Replacing SO$_2$ for the less nucleophilic SO$_2$ClF gave the same results. Complete NMR data are gathered in Table 1.

We subsequently used FSO$_3$H·SbF$_5$ (4:1) in SO$_2$ClF or SO$_2$ solvent in the hope that **14** would be persistent in the presence of more bulky, less nucleophilic counterions. Again the initial reaction was smooth, with protonation taking place only at ca. −50 °C.

The ^{31}P NMR spectrum of the sample, however, showed a complex mixture of products among which traces of **15** and small amounts of the derived spirocyclotrimer cation (two isomers) could be identified (see protonation of **2**).

Hence, in higher acidity superacids, the phosphaalkene addition product is subject to numerous secondary reactions and does not survive. A complex mixture of products was also formed when **1** was reacted with TfOH$_2^+$B(OTf)$_4^-$/SO$_2$ClF superacid.

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Table 1. NMR Data for 15, 17, and 20

phosphaalkene product	solvent/temp (°C)	^{1}H NMR	^{13}C NMR	^{31}P NMR
15	$FSO_3H{\cdot}SO_2$/−70 or $FSO_3H{\cdot}SO_2ClF$/−70	8.91 (d, $^{2}J_{PH}$ = 14.4 Hz; PCH) 2.09 (brs; Ad) 1.72 (brs; Ad)	196.8 (d, $^{1}J_{PC}$ = 57.2 Hz, $^{1}J_{CH}$ = (158.3 Hz; *C*H) 41.5 (d, $^{3}J_{PC}$ = 14.3 Hz; Ad-C_β) 39.5 (d, $^{2}J_{PC}$ = 38.8 Hz; Ad-C_α) 35.4 (s; Ad-C_δ) 27.4 (d, $^{4}J_{PC}$ = 1.8 Hz; Ad-C_γ)	336.6 (d, $^{3}J_{PF}$ = 9.5 Hz, $^{2}J_{PH}$ = 14.0 Hz)
17	$FSO_3H{\cdot}SO_2ClF$/−70	8.9 (d, $^{1}J_{PH}$ = 14.4 Hz) 1.10 (pseudo-s)	197.5 (d, $^{1}J_{PC}$ = 57.8 Hz) 37.4 (d, $^{2}J_{PC}$ = 14.7 Hz) 29.3 (d, $^{3}J_{PC}$ = 13.8 Hz)	331.7 (d, $^{3}J_{PF}$= 8.6 Hz)
17	$FSO_3H{\cdot}SO_2$/−70	9.08 (d, $^{2}J_{PH}$ = 14.6 Hz) 1.18 (d, $^{4}J_{PH}$ = 3.3 Hz)	197.5 (d, $^{1}J_{PC}$ = 57.8 Hz) 37.4 (d, $^{2}J_{PC}$ = 14.7 Hz) 29.3 (d, $^{3}J_{PC}$ = 13.8 Hz)	
20	CF_3SO_3H/SO_2ClF/−70	8.93 (d, $^{2}J_{PH}$ = 14.7 Hz) 1.13 (d, $^{4}J_{PH}$ = 3.0 Hz)	197.4 (d, ^{1}J = 59.3 Hz) 37.3 (d, $^{2}J_{PC}$ = 14.4 Hz) 29.3 (d, $^{3}J_{PC}$ = 13.0 Hz)	

Table 2. NMR Data for 22/23 and 18/19

spirotricyclic betaine (or cation)	^{31}P NMR	^{13}C NMR	^{1}H NMR	^{11}B NMR
22	412.5 (d, $^{3}J_{PP}$ = 36.8 Hz; P_5) 264.9 (dd, $^{1}J_{PP}$ 254.4 Hz, $^{3}J_{PP}$ = 36.8 Hz; P_1) −104.4 (d, $^{1}J_{PP}$ = 254.4 Hz, P_3)	233.2 (dd, $^{1}J_{PC}$ = 51 Hz, $^{1}J_{PC}$ = 84 Hz, C_4) 205.4 (dd, $^{1}J_{PC}$ = 7.5 Hz, $^{1}J_{PC}$ = 67 Hz; C_2) 118.3 (9, $^{1}J_{CF}$ = 318.0 Hz; CF_3) 65.0 (m; C_6) 41.8−44.3 (Ad-C_β) 37.8−38.9 (Ad-C_α) 35.1−36.0 (Ad-C_δ) 28.0−28.9 (Ad-C_δ)	8.3−1.6 (m)	−3.0 (s) ($\Delta\delta = -7.11$)
23	408.2 (d, $^{3}J_{PP}$ = 32.4 Hz; P_5) 266.7 (dd, $^{1}J_{PP}$ = 241.3 Hz, $^{3}J_{PP}$ = 32.4 Hz; P_1) −97.2 (d, $^{1}J_{PP}$ = 241.3 Hz; P_3)	70.8 (m, C_6) all others as above	8.3−1.6 (m)	−3.0 (s) ($\Delta\delta = -7.11$)
18	413.4 (d, $^{3}J_{PP}$ = 34.2 Hz; P_5) 263.5 (dd, $^{1}J_{PP}$ = 254.1 Hz, $^{3}J_{PP}$ = 33.7 Hz; P_1) −93.0 (d, $^{1}J_{PP}$ = 253.1 Hz; P_3)			
19	410.7 (d, $^{3}J_{PP}$ = 32.7 Hz; P_5) 270.0 (dd, $^{1}J_{PP}$ = 242 Hz; P_1) −85.0 (d, $^{1}J_{PP}$ = 244.5 Hz; P_3)			

Protonation of 2 (Scheme 4 and tables). Reaction of the less crowded phosphacetylene **2** with superacids is more rapid as compared to **1**. Thus addition of a cold solution of FSO_3H/SO_2ClF to a solution of **2** in SO_2ClF at −78 °C gives a distinct red color on contact which changes to a persistent orange-red solution within seconds. The ^{1}H NMR spectrum recorded at −70 °C shows a low-field resonance at 8.90 ppm (1H) appearing as a 14.4 Hz doublet due to a two-bond PH coupling and a slightly deshielded tBu group at 1.10 ppm as a pseudosinglet. The data indicate formation of covalent **17** rather than its precursor cation **16**.[20]

In the ^{13}C NMR spectrum, the alkene $C{\equiv}P$ carbon is at 197.5 ppm, appearing as a 57.8 Hz doublet in the proton-decoupled spectrum. Both tBu carbon resonances (at 37.4 and 29.3 ppm) appear as doublets due to phosphorus coupling.

The ^{31}P NMR spectrum shows just one resonance at 331.7 ppm, typical of phosphaalkenes. The presence of a three-bond PF coupling of 8.6 Hz provides further support for the formation of covalent **17**. As in **15**, the magnitudes of $^{1}J_{PH}$ and $^{2}J_{PC}$ coupling constants establish the *Z* stereochemistry for **17**.

It is conceivable that the initially observed red color stems from **16** (see also the theoretical study for more insight), which is rapidly quenched with the counterion (→ **17**). The presence of minor amounts of isomeric spirocyclotrimer cations **18/19** (55:45 ratio; ca. 10%) is apparent in the ^{31}P NMR spectrum (Table 2 and later discussion).

Protonation of **2** with FSO_3H/SO_2 similarly gave **17**. Whereas the ^{13}C NMR spectra were essentially identical, the ^{1}H resonances in SO_2 were slightly more downfield. Thus the C*H* was observed as a 14.6 Hz doublet at 9.08 ppm and the tBu absorption was seen at 1.18 ppm, appearing as a resolved 3.3 Hz doublet due to four-bond coupling to phosphorus. Low-temperature reaction of **2** with $TfOH/SO_2ClF$ gave initially the triflate **20** (Table 1). Prolonged reaction times gave a complex mixture of products (^{31}P NMR).

In a control experiment protonation of **2** was also examined in FSO_3D (ca. 60% deuterium content)/SO_2. As expected, the low-field doublet resonance for C*H* was reduced substantially in the ^{1}H NMR spectrum. The ^{31}P NMR spectrum examined several hours later indicated extensive formation of secondary products, among which the isomeric spirocyclic cations were discernible (two isomers in a 60:40 ratio).

Protonation of **2** was also effected with $FSO_3H{\cdot}SbF_5$ (4:1)/SO_2, $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2ClF, and $TfOH_2^+B(OTf)_4^-$/SO_2ClF. In all cases rapid reactions occurred at dry ice/acetone temperature, and a complex mixture of products was formed, among them only minor amounts of **17** (or **20**). The isomeric spirocyclic cations could also be seen.

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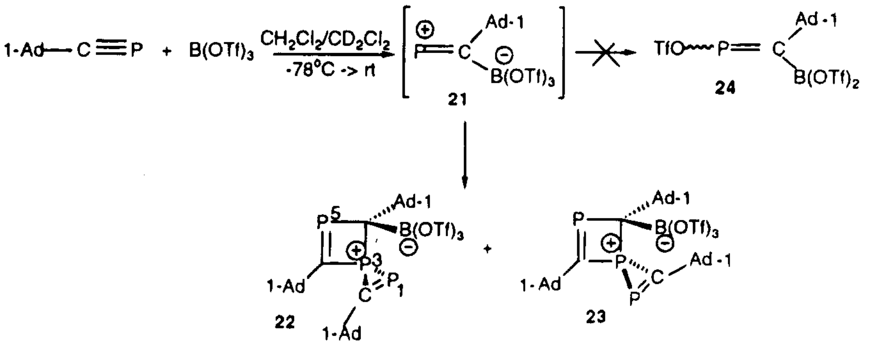
(20) In agreement with the outcome of our superacid protonation studies, a very recent X-ray diffraction study on **2** published after submission of this manuscript (Antipin, M. Y.; Cherenega, A. N.; Lysenko, K. A.; Struchkov; Y. T.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1995**, 505) shows that there is excess electron density on the alkyne carbon.

Scheme 5. Reaction of 1 with B(OTf)$_3$



Reaction of 1 with B(OTf)$_3$ (Scheme 5, Table 2). The 1:1 reaction of BCl$_3$ according to Scheme 2 gives **13**. We have now found that **1** reacts with boron tris(triflate) according to Scheme 5 to give a yellow oil after removal of solvent. Multinuclear NMR data for this oil clearly establish the formation of two isomeric spirocyclic betaines **18/19** in a 4:1 ratio. Therefore, contrary to BCl$_3$ addition to tBuC≡P (Scheme 2), the reaction product of **1** with B(OTf)$_3$ is not **24**; spirocyclotrimerization occurs instead (→ **22** and **23**).

As previously discussed for the AlCl$_3$ reaction,[14] the three phosphorus resonances in each case appear in very different environments. The one-bond P_3−P_1 couplings are 254.7 and 241.3 Hz, respectively. In addition, a three-bond coupling is seen between P_1 and P_5, but there is no two-bond coupling between P_3 and P_5. The ^{11}B NMR spectrum gives a singlet at −3.0 ppm for the tetracoordinated boron ($W_{1/2}$ = 45 Hz; rt; CD_2Cl_2).

Whereas the C_4 and C_2 resonances are identical for the two isomers, there are two different sp^3-hybridized C_6 carbon resonances at 65.0 ppm (**22**) and 70.8 ppm (**23**), both as multiplets. In the AlX$_3$-derived betaines, the C_4 carbon peak is not observable[14] but that for the GaCl$_3$ derivative was observed at 71.3 ppm (appearing as a doublet; $^1J_{CP}$ = 61.0 Hz).[15] The data are gathered in Table 2.

In an attempt to observe **21** directly, **1** was mixed with B(OTf)$_3$ in CH_2Cl_2/CD_2Cl_2 at dry ice/acetone temperature, and the progress of reaction was monitored by ^{31}P NMR as a function of temperature. 1-AdC≡P (**1**) remained unreacted up to −20 °C, above which **22/23** appeared without any resonances being detected for the intermediate products. It appears that attack of B(OTf)$_3$ on the crowded **1** has a high activation barrier, and any conversion to **21** is followed by instant cycloaddition. There is, therefore, no buildup of **21** in the reaction.

Finally, in an attempt to extend the scope of spirocyclization of phosphaalkynes, the 3:1 reactions of **1** with TfOH (a) and Tf$_2$O (b) were examined: (a) When TfOH was added to **1** in CH_2Cl_2 solvent at dry ice/acetone temperature and the temperature was slowly raised to rt, the color changed to yellow-orange. Removal of solvent gave an orange oil. Its ambient ^{31}P NMR spectrum showed a complex mixture of products, among them the isomeric spirocyclotrimers (peaks at 497, 435, −154, and −159 ppm), and some tetraadamantyltetraphosphacubane (240 ppm singlet) could be seen. (b) Similar reaction of **1** with Tf$_2$O gave a colorless solution whose ^{31}P NMR spectrum indicated only unchanged **1** (singlet at −65.4 ppm).

Theoretical Studies. To gain more insight into the structure and energies of protonated phosphaacetylenes, we used ab initio theory at the RHF/6-31G* level to calculate the energies of C-protonated and P-protonated **3**. We also examined the energies and geometries of the isomeric phosphaalkenes formed by a hypothetical F$^-$ quenching of the C-protonated cation as models for the fluorosulfates and triflates formed in superacid media.

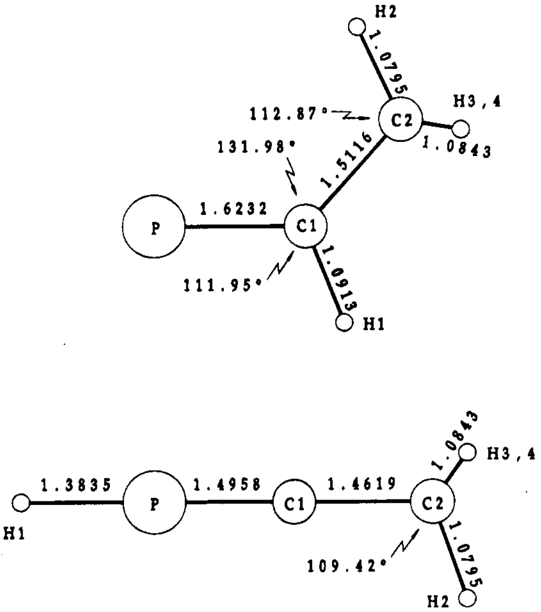


Figure 4. RHF/6-31G*-calculated structures for the C-protonated and P-protonated **3** (bond lengths and angles are displayed).

Figure 4 displays the calculated structures for the cations with bond lengths and angles shown; charges are given in Figure 5. These studies suggested a strong preference (45.23 kcal/mol) for C-protonation over P-protonation. Subsequent frequency calculations at this level showed however that whereas the C-protonated cation had no imaginary frequencies, the linear P-protonated cation produced two imaginary frequencies, suggesting that it cannot be a true minimum on the potential energy surface. At the RHF/6-31G* level of theory, Gaussian-92 gave the same energy as Gaussian-90 for the C-protonated ion, −418.441 582 au (see supporting information). When the level is raised to RHF/6-311+G**, the energy is lowered by 0.042 002 au or 26.4 kcal/mol for this ion. At the MP2/6-311+G** level, no linear P-protonated ion could be found, and two different starting geometries led to an unsymmetrical hydrogen-bridged structure with the proton closer to the C than the P atom. The bridged ion has an energy of −418.876 566 au, which is 0.392 982 au or 246.6 kcal/mol above the C-protonated ion at the RHF/6-311+G** level, but no MP2 correction was done on the calculation for this species. Figures 6 and 7 illustrate bond lengths/

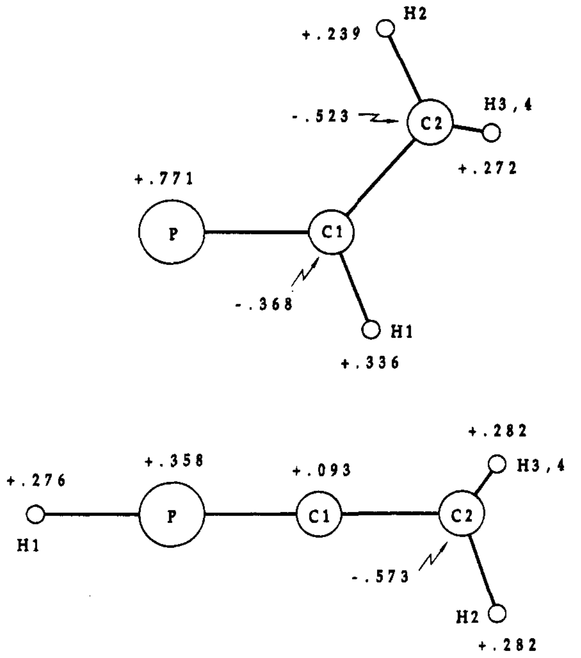


Figure 5. RHF/6-31G*-calculated charges for C-protonated and P-protonated open cations.

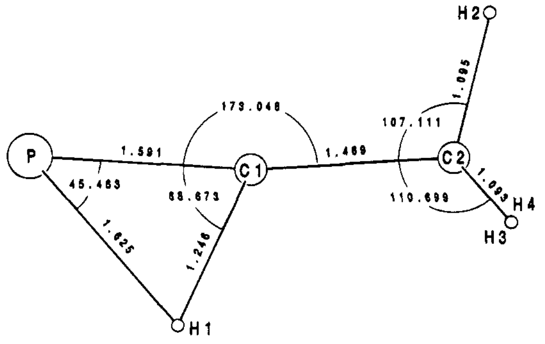


Figure 6. RHF/6-311+G**-calculated bond lengths and angles for the bridged cation.

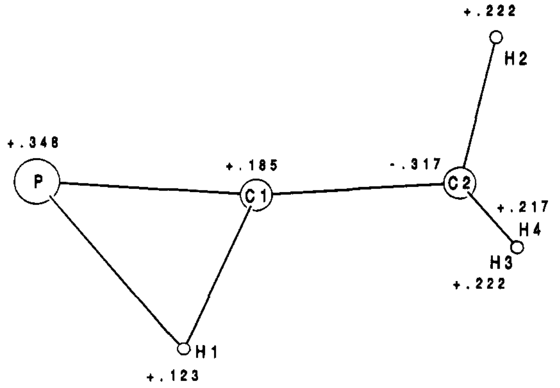


Figure 7. RHF/6-311+G**-calculated charges for the bridged cation.

angles and the charges for the bridged ion. The noteworthy features are rather long P−H and C−H bonds (1.625 and 1.246 Å, respectively), with the latter being longer than that in the C-protonated open cation (1.091 Å). The extent of the positive charge at phosphorus is nearly twice as large as that on the alkyne carbon. The calculated PC bond length for the bridged ion (1.591 Å) is in between the experimental values for P−C in phosphaalkenes (1.67 Å)[14] and P≡C bond of MeC≡P (1.544 Å),[21] arguing against a mere π-complex.

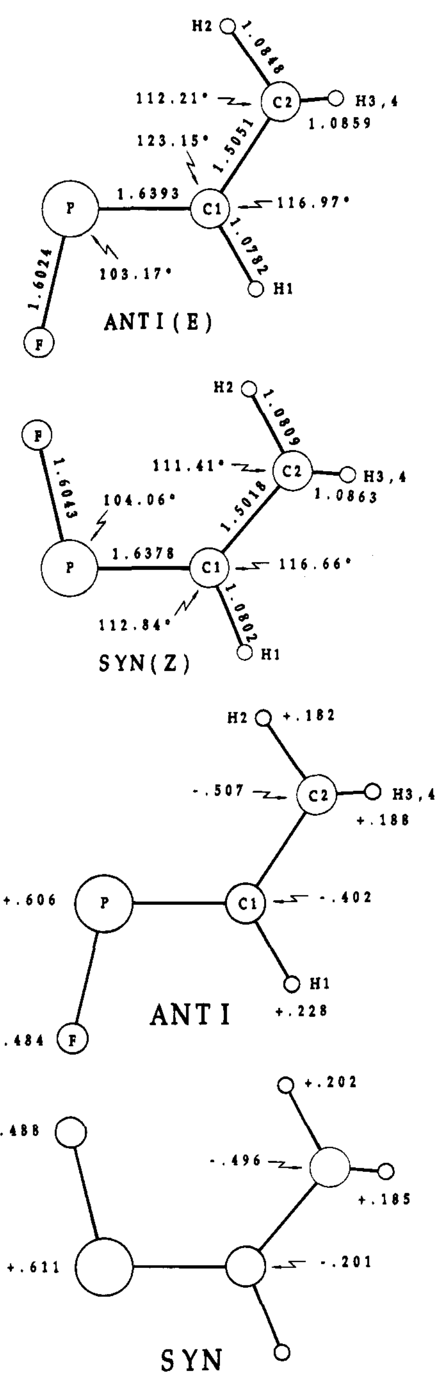


Figure 8. RHF/6-31G*-calculated structures for the fluorophosphaalkenes. (a) Bond lengths and angles are displayed. (b) Charges are shown.

When the phosphavinyl cation is quenched with F$^-$, the resulting fluorophosphaalkene can exist in the *E* (anti) or the *Z* (syn) configuration. The ab initio calculations at the RHF/6-31G* level predict (Figure 8) that the latter is favored by only 1.17 kcal/mol.

Comparison of the bond lengths between the C-protonated phosphavinyl cation and the fluorophosphaalkene is instructive. Whereas quenching of the cation causes little change in the C−P and C−C bond lengths, a slight shortening of the PC−H(Me) bond occurs in the fluoro derivative (from 1.091 to 1.080 Å). In the *Z* (syn) isomer the methyl CH bonds and the PC−H(Me) are all about equivalent. It is tempting to take the observed lengthen-

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[21] Kroto, H. W.; Nixon, J. F.; Simmons, N. P. C. *J. Mol. Spectrosc.* **1979**, *77*, 270.

ing of the PC−H(Me) bond in the cation as evidence for hyperconjugation between the C−H (Me) and the P^+ in a structure such as **5**.

Summary

Direct observation of the phosphavinyl cation **5** formed by C-protonation of phosphaacetylenes **1** and **2** was not achieved under a variety of conditions in superacid media. Instead, rapid quenching furnished the fluorosulfates or the triflates exclusively (NMR limit) in the *Z* configuration. Although BCl_3 reacts with **1** to give the 1,2-addition product (with *E* configuration), reaction of $B(OTf)_3$ with **1** gave instead the novel boron-containing isomeric spirotricyclic betaines **22/23**.

Whereas at the RHF/6-31G* level a C-protonated cation is a true minimum, a P-protonated linear cation is not. At the MP2/6-311+G** level the most stable structure is an unsymmetrical hydrogen-bridged cation. The experimental observation of exclusive anti addition (NMR) is quite compatible with a bridged intermediate. The 1.17 kcal/mol calculated difference in the relative stabilities of *Z*/*E* fluorophosphaalkenes (at the RHF/6-31G* level) does not appear significant enough to explain the observed stereochemical preference.

Experimental Section

FSO_3H (Allied), CF_3SO_3H (Aldrich), and SbF_5 (Fluorochem) were freshly distilled in an all-glass distillation apparatus under dry argon. The superacids were prepared according to general procedures previously described.[22,23] Triflic anhydride (Aldrich) was stored over P_2O_5 in the cold.

The carbon and proton NMR data were obtained with a 5 mm switchable C/H probe, whereas a 10 mm broadband probe was used for phosphorus and boron NMR. The procedures for the low-temperature NMR work were analogous to those reported previously.[22-24]

For RHF/6-31G* calculations the Gaussian-90 package was used; the MP2/6-311+G** calculations were done with Gaussian-92. Initial geometries were calculated using the PC-MODEL molecular mechanics program (Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076). Using the MP2/6-311+G* basis set we performed calculations with two different starting geometries: the linear P-protonated and the bent C-protonated cation. In both cases the resulting minimized structure was the slightly bent hydrogen-bridged cation.

To test which change in the calculation method was responsible for the change in geometry, we recalculated the structure starting with the C-protonated geometry but omitted the MP2 correction; the resulting optimized geometry was identical to the bent bridged ion but as expected the energy was higher.

The phosphaalkynes **1** and **2** were prepared according to Scheme 3. Details of their syntheses have already been published by Regitz et al.[17,18]

Boron Tris(triflate).[25,26] In a 3-necked flask equipped with a magnetic stirrer bar, an argon gas inlet, a pressure-equalizing dropping funnel, and a gas outlet was placed ca. 75 mL of dry Freon-113. The flask was cooled to just above the freezing point of Freon (ca. −37 °C) with a cold bath. Liquid BCl_3 (5 mL, 6.7 g) was condensed into a cold Nalgene measuring cylinder and poured directly into the flask under argon. After stirring, triflic acid (5 mL, 8.6 g; 3 molar equiv) was charged into the dropping funnel, diluted with some Freon (ca. 10 mL), and added dropwise to BCl_3 with efficient stirring. Evolution of HCl was rapid. Stirring was continued for some time after the HCl evolution was ceased, while the flask was flushed with dry argon and the temperature raised to ambient. Removal of solvent under high vacuum gave a viscous oil which was washed with dry Freon and evacuated again to give $B(OTf)_3$ as a light gray solid. It was stable for several months when refrigerated under argon.

Protonation of 1-AdC$\equiv$P with FSO_3H/SO_2. Solid 1-AdC$\equiv$P (167 mg, 0.91 mmol) was charged into a 10 mm NMR tube, cooled in a dry ice/acetone bath, and slurried with liquid SO_2 (ca. 1 mL) under dry argon. FSO_3H (ca. 1 mL) was charged into a second NMR tube, cooled, and diluted with SO_2 (1 mL) under dry argon. The cold superacid was slowly added with mixing to the 1-AdC$\equiv$P/SO_2 at dry ice/acetone temperature. No reaction occurred under these conditions. The sample was vigorously mixed (vortex) while the temperature was allowed to rise slowly. The substrate dissolved at ca. −50 °C to give a clear yellow solution. A cold aliquot was transferred directly into a precooled 5 mm tube fully immersed in a dry ice/acetone bath. Precooled CD_2Cl_2 (7 to 8 drops) was added, and the sample was vigorously mixed, flushed with dry argon, and quickly examined by NMR at −70 °C.

Protonation of tBuC$\equiv$P (2) with FSO_3H/SO_2ClF. Liquid tBuC$\equiv$P (164 mg, 1.64 mmol) was charged into a 10 mm NMR tube under argon, cooled, and diluted with SO_2ClF (ca. 0.5 mL). In a second 10 mm NMR tube FSO_3H (1 mL) was diluted with SO_2ClF (1 mL) under argon at dry ice/acetone temperature. Both tubes were fully immersed in a dry ice/acetone bath for 2 to 3 min, following which the acid was directly poured into **2** with mixing under argon. A red color developed on contact which became red-orange within seconds on vortex mixing. The persistent red-orange solution was quickly transferred into a precooled 5 mm tube as described above. Spectra were recorded within minutes of preparation usually at −70 °C.

Reaction of 1 with Boron Tris(triflate). $B(OTf)_3$ (195 mg, 0.43 mmol) was added to a solution of **1** (76 mg, 0.43 mmol) in dry CH_2Cl_2 at dry ice/acetone temperature under argon. The temperature was subsequently allowed to rise slowly to rt, whereupon a yellow solution resulted. The solvent was removed and the residue dissolved in CD_2Cl_2 for ambient temperature NMR studies.

In another experiment, $B(OTf)_3$ (65 mg, 0.14 mmol) was added to **1** (75 mg, 0.41 mmol) in CH_2Cl_2/CD_2Cl_2 solvent at dry ice/acetone temperature. The progress of the reaction was monitored by ^{31}P NMR starting at −75 °C.

Reaction of 1 with TfOH. **1** (130 mg, 0.73 mmol) was charged into a Schlenk pressure tube, dissolved in dry CH_2Cl_2, and cooled in a dry ice/acetone bath under argon. TfOH (37 mg, 0.24 mmol, 0.0214 mL) was added with stirring, and the tube was sealed. The temperature was slowly brought to rt to give an orange solution. Removal of solvent under vacuum gave an orange oil which was examined by ^{31}P NMR at rt.

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Supporting Information Available: Tables of energies, initial and optimized Z-matrix, and frequencies for the hydrogen-bridged and the open C-protonated **3** (3 pages). This material is contained in libraries on microfiche, immediately follows the article in the microfilm edition of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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