Tetraphosphacubane Chemistry: Probing Phosphorus Reactivity by Protonation, Alkylation, and Alkynylation. Formation of Novel Phosphonium Di- and Monocations in Superacid Media and Monocations with Super Electrophiles[1]

Kenneth K. Laali,*,† Manfred Regitz,*,‡ Manfred Birkel,‡ Peter J. Stang,§ and Charles M. Crittell§

Department of Chemistry, Kent State University, Kent, Ohio 44242, Fachbereich Chemie, Universität Kaiserslautern, D-6750 Kaiserslautern, Germany, and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received February 23, 1992

Tetra-*tert*-butyltetraphosphacubane (1) is diprotonated with FSO_3H-SbF_5 (1:1) (Magic acid)/SO_2 at two of the four equivalent phosphorus atoms to give a persistent diphosphonium cation 2. In FSO_3H/SO_2 or CF_3SO_3H (TfOH)/SO_2 only the monoprotonated phosphonium ion 4 was observed. Upon exothermic quenching of the Magic acid solutions of 2 apart from intact 1, oxotetraphosphacubane 3 was formed. Quenching of the FSO_3H or TfOH solutions of 4 (no SbF_5) gave intact 1 together with traces of 3. Ambient reactions of 1 with methyl triflate, trimethyloxonium tetrafluoroborate and with (trimethylsilyl)methyl triflate led to monoalkylation at phosphorus (steps 4–6, Scheme I). Reaction of 1 with propene/TfOH as an iPr^+ source gave the monocation 8 (^{31}P NMR) in competition with extensive olefin oligomerization. Crowded triisopropylsilyl triflate did not react with 1 even under forcing conditions. Similar reactions of 1 with alkynyl(phenyl)iodonium triflates led to monoalkynylation at phosphorus (step 8, Scheme I).

Introduction

The recent discovery by Regitz and co-workers that *tert*-butylphosphaacetylene tBuCP[2,3] undergoes thermal cyclooligomerization to give tetra-*tert*-butyltetraphosphacubane (1)[4,5] as a stable compound and a subsequent realization of a high-yield synthesis of 1, as well as of other derivatives of the same type having bulky substituents, by the same group[6] have now made these distorted cubelike tetramers with identical C–P bonds (X-ray analysis) available in gram quantities for further elaboration.

The ^{31}P NMR spectrum of 1 is a low-field pseudosinglet at +257.4 ppm. The ^{13}C NMR spectrum of 1 shows three absorptions (all multiplets due to phosphorus coupling) at −29.07, 21.57, and 30.64 ppm. The unusually upfield shifted multiplet at −29.07 ppm is due to four equivalent quaternary cage carbons of 1. The extreme carbon and phosphorus NMR chemical shift positions of the C–P bond are strongly indicative of phosphorus lone pair participation in the C–P cage σ bonds leading to an overall electron density shift from P to C.[8]

The nP → σP–C delocalization has been investigated by photoelectron (PE) spectroscopy.[8] In agreement with the NMR-based conclusions and PE spectroscopy, MO calculations on 1 predict a net positive charge at P and a net negative charge at C.[8]

An important predicted consequence of nP → σP–C delocalization is reduced basicity/nucleophilicity at the phosphorus atom of 1.

Initial studies by Regitz et al.[9] on P-functionalization of 1 showed only monofunctionalization by complexation with diiron nonacarbonyl and by alkylation with methyl triflate. Double functionalization was achieved with tetrachloro-*o*-benzoquinone and with alkyl azides to give cubanes with phosphorane and iminophosphorane units. Tri- and tetrafunctionalization at P was observed only in reactions with selenium and with bis(trimethylsilyl) peroxides, respectively, to give trisselonoxotetraphosphacubane and tetraoxotetraphosphacubane.[9]

In an effort to track down the limits of P-functionalization by electrophilic chemistry, the present study focuses on protonation, alkylation, and alkynylation at phosphorus and on NMR studies of the resulting phosphonium ions.

Results and Discussion

Diprotonation of 1. Slow addition of a clear solution of Magic acid/SO_2 to a slurry of 1 in SO_2 at dry ice/acetone temperature gave a light yellow, homogeneous solution upon vigorous mixing, with no indication for decomposition or polymerization.

The ^{13}P NMR spectrum of the sample at −68 °C shows two almost equivalent phosphorus signals at +180.6 ($\Delta\delta_{^{31}P}$ = −76.7) and +80.1 ppm ($\Delta\delta_{^{31}P}$ = −177.3) as pseudosinglets.

† Kent State University.
‡ Universität Kaiserslautern.
§ University of Utah.

(1) Part 68 of the series on phosphorus compounds by Regitz. For part 67 see: Lazraq, M.; Escudié, J.; Couret, C.; Bergsträsser, U.; Regitz, M. *J. Chem. Soc., Chem. Commun.*, in press.

(2) General reactivity, cf. Regitz, M.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1484. Regitz, M. *Chem. Rev.* **1990**, *90*, 191. Regitz, M.; Binger, P. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; p 58.

(3) Synthesis: Rösch, W.; Hees, U.; Regitz, M. *Chem. Ber.* **1987**, *120*, 1645.

(4) Wettling, T.; Schneider, J.; Wagner, O.; Kreiter, C. G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1013.

(5) Regitz, M. In *Heteroatom Chemistry*; Block, E., Ed.; VCH, New York, 1990; Chapter 17.

(6) Wettling, T.; Geissler, B.; Schneider, R.; Barth, S.; Binger, P.; Regitz, M., *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 758.

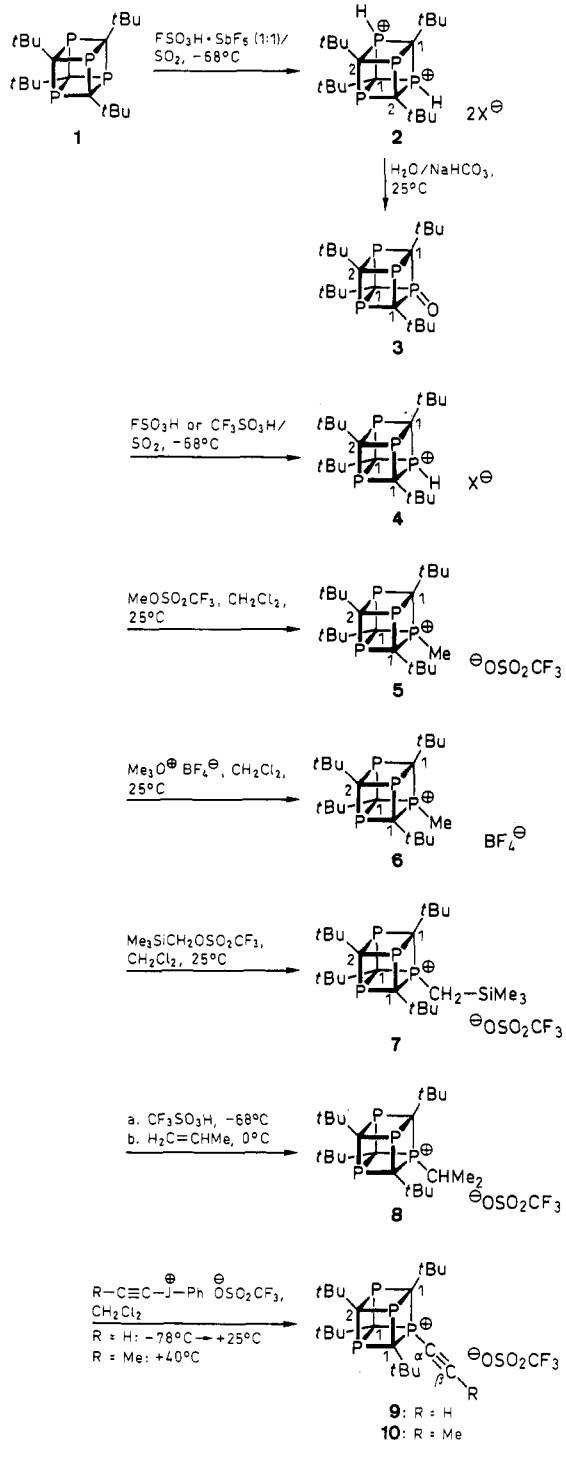
(7) Part of an AX_3Y spin system for which the calculated ^2J (^{31}P–^{31}P) = 8.52 Hz; see ref 4.

(8) Gleiter, R.; Pfeifer, K.-H.; Baudler, M.; Scholz, G.; Wettling, T.; Regitz, M. *Chem. Ber.* **1990**, *123*, 757.

(9) Birkel, M.; Schulz, J.; Bergsträsser, U.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 879.

0022-3263/93/1958-4105$04.00/0

Scheme I Protonation, Alkylation, and Alkynylation of 1.



The ^{13}C NMR spectrum at the same temperature exhibits two types of cage carbons as unresolved multiplets at 11.30 ($\Delta\delta_{^{13}C}$ = +40.3) and 36.90 ($\Delta\delta_{^{13}C}$ = +65.9) ppm, two equally prominant tBu groups with almost equally intense methyls at 23.5 and 22.3 ppm, and equally intense methines at 32.5 and 32.8 ppm as nearly overlapping pseudotriplets.

The data are consistent with diprotonation at two of the four available phosphorus centers and the formation of a diphosphonium ion **2** (Scheme I). The observed shielding at phosphorus and the accompanying deshielding of two of the four cage carbons are clear indications for electron density delocalization from C to P in the diphosphonium ion. Thus, the more upfield phosphorus signal at +80.1 ppm (P^+) and the more deshielded cage carbon signal at 36.9 ppm (C_1) are due to the "protonated P–C units", whereas the signals at 180.6 (P) and 11.3 ppm (C_2) are due to the unprotonated P–C units. This assignment is fully consistent with the NMR data on the monocations of protonation, alkylation, and alkynylation described below.

In the ^1H NMR spectrum of the ion solution (at −68 °C) two well-resolved deshielded tBu(Me) singlets are present at 1.40 ($\Delta\delta$ = 0.30) and 1.31 ($\Delta\delta$ = 0.21) ppm with a 28-Hz separation and a PH^+ absorption appearing as a broad peak at 12.3 ppm. Lowering of sample temperature at −74 °C had no noticeable effect on the PH^+ signal.

Monoprotonation of 1. When a cold solution of FSO_3H/SO_2 was slowly added to a yellow slurry of **1** in SO_2 at dry ice/acetone temperature, the tetraphosphacubane was smoothly protonated and dissolved upon mixing to give a clear pale yellow solution.

The ^{31}P NMR spectrum of the resulting solution at −68 °C shows two absorptions at +224.5 ($\Delta\delta_{^{31}P}$ = 32.9) and +86.4 ppm ($\Delta\delta_{^{31}P}$ = 171.0) in a 3:1 relative ratio as pseudosinglets, indicative of protonation of only one of the four phosphorus atoms to give a monophosphonium ion **4** (Scheme I).

The ^{13}C NMR spectrum of the sample exhibits a distinct broadened doublet at 4.10 ppm, deshielded by ca. 33 ppm compared to precursor **1**, for the three cage carbons directly bonded to PH^+ (C_1), whereas the remaining cage carbon (C_2) gives rise to a less deshielded multiplet at ca. −25 ppm ($\Delta\delta$ = 4.0).

The observed shielding at phosphorus and deshielding at carbon and a comparison of the positions of the phosphorus and carbon signals of the mono- and dication corroborate the suggested NMR assignments.

A second protonation at phosphorus (**4** → **2**) changes the ^{31}P NMR chemical shift of the unprotonated phosphorus atoms from 224.5 to 180.6 ppm corresponding to ca. 44 ppm shielding. It is plausible that enhanced deshielding of the C_1 cage carbons attached to two PH^+ centers induces lone-pair participation by the unprotonated phosphorus centers.

In the ^1H NMR spectrum of **4** the difference in the tBu(Me) proton environments is within line broadening; just one slightly broad singlet is oberved at 1.21 ppm. As observed with **2**, the PH^+ signal appears as a broad hump centered around 12.4 ppm.

Quenching of the Superacid Solution of 2 and 4. The tetraphosphacubane **1** is resistant to hydrolysis. When a $CDCl_3$ solution of **1** was treated with dilute HCl in water, **1** was recovered intact (^{31}P NMR). It was, therefore, of interest to determine if the structural integrity of the tetraphosphacubane is preserved upon quenching of the P-protonated tetraphosphacubanes.

Quenching of the Magic acid solution of the dication **2** furnished a yellow oil. Its ^{31}P NMR shows apart from intact **1** two additional phosphorus signals at +129.3 and +71.2 ppm (in a ca. 3:1 ratio). These absorptions are due to the monooxotetraphosphacubane **3**, an authetic sample of which was independently synthesized by oxidation of **1** with tBuOCl (Experimental Section). Despite the complexity of the ^{13}C NMR spectrum of the mixture of **1** and **3**, the presence of **3** was corroborated by comparison with the spectrum of the authentic oxide. Quenching of the FSO_3H or TfOH solutions of the monocation similarly

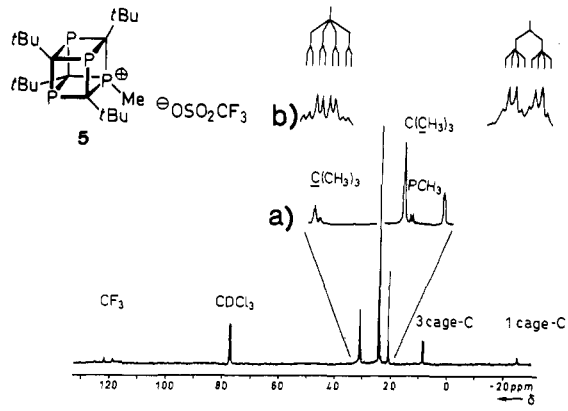


Figure 1. ^{13}C NMR spectrum of **5** [insets: (a) expansion of the indicated part of the spectrum, (b) expansion of the $-C(Me)_3$ and cage-C_2 absorptions].

furnished a yellow oil. Its ^{31}P NMR spectrum shows intact **1** and only traces of **3**.

These studies demonstrate that the oxidation observed on exothermic quenching is apparently SbF_5-catalyzed.

Alkylation of 1. Tetraphosphacubane **1** smoothly reacted with methyl triflate (Magic methyl) in methylene chloride solvent at room temperature to give the monomethylated phosphonium triflate **5** as a stable salt (Scheme I).

The ^{31}P NMR spectrum of the isolated yellow solid shows two phosphorus absorptions at 213.0 and 132.8 ppm in a 3:1 ratio. In line with the assignments of the protonated cations, the more shielded P signal at 132.8 ppm is that of the cation center. The ^{13}C NMR spectrum of **5** shows the $CP(Me)^+$ signal at 8.3 ppm whereas the remaining cage carbon (C_2) is at −25.2 ppm (Figure 1). The P^+CH_3 gives rise to a 19-Hz doublet at 23.5 ppm. The methyl protons give rise to a clear 12-Hz doublet at 3.3 ppm.

Absence of viscosity broadening in the ambient spectra of the phosphonium ions in $CDCl_3$ allows detailed observation of one-bond and long-range P–C and P–H couplings (see comparative discussion and Experimental Section).

Methylated **1** was also prepared as a stable tetrafluoroborate salt by room temperature alkylation with Me_3O^+ BF_4^- (step 5, Scheme I). Attempted dimethylation with excess alkylating agent was unsuccessful; only the monophosphonium ion was isolated.

In the absence of moisture the salts were quite stable and decomposed only at high temperatures. Interestingly, the BF_4^- salt **6** had a higher decomposition temperature (283 °C) than the triflate (200 °C).

The room-temperature reaction of **1** with (trimethylsilyl)methyl triflate similarly furnished the (trimethylsilyl)methylphosphonium cation **7** with two ^{31}P NMR signals at 129.0 and 210 ppm in a 1:3 ratio with their corresponding cage carbons at 8.5 and −25.0 ppm as multiplets and with the P^+CH_2TMS carbon at 23.7 ppm as a 19-Hz doublet.

The sterically hindered $(iPr)_3SiOTf$ failed to react with **1**, and the unreacted **1** was recovered even under forcing conditions in refluxing methylene chloride or in the absence of solvent when the reagents were heated together to 120 °C.

The propylene/TfOH system was previously used by Booth et al.[10] for isopropylation of aromatics. In a control experiment, **1** was first reacted with excess TfOH at dry ice/acetone temperature, the sample was brought to room temperature, and propene was slowly bubbled through the solution at 0°C for 5 min. An exothermic reaction occurred, and an oily red solution was obtained.

The ambient ^{31}P NMR spectrum of the TfOH solution showed, apart from unreacted **1** (a single peak at +257 ppm), two singlets at +116.4 and +238.5 ppm (in ca. 1:3 ratio). The position (and relative intensity) of these absorptions in comparison with other cations of **1** discussed above corroborate isopropylation at P to give **8**. Minor amounts of other phosphorus-containing side products (peaks between 135–136 ppm and 225–230 ppm) were also present. The ^1H NMR spectrum of the reaction mixture indicated extensive olefin oligomerization giving rise to a broad envelope of aliphatic absorptions. The observed competing triflic acid-catalyzed olefin oligomerization limits the synthetic use of this method for alkylation of **1**.

Alkynylation of 1. Presence of an activated, polarized C–C triple bond in alkynyl(phenyl)iodonium triflates enables them to act as electron-deficient alkynes toward a wide variety of nucleophiles.[11,12] Stang and Crittell[13] showed recently that alkynyl(phenyl)iodonium triflates react with Ph_3P to give stable alkynylphosphonium triflates.

In the present study, we examined the alkynylation of **1** with ethynyl- and propynyl(phenyl)iodonium triflates at room temperature in methylene chloride solvent. Formation of the alkynylphosphonium salts **9** and **10** was complete within hours (^{31}P NMR), and the alkynylphosphonium salts were isolated as stable compounds.

In agreement with the NMR observations of the protonated and alkylated phosphonium cations of **1**, the phosphorus signals of the cation centers are significantly shielded [66.4 ppm (ethynyl) and 65.2 ppm (propynyl)] as compared to the other cage phosphorus centers [213.0 ppm (ethynyl) and 207.5 ppm (propynyl)]. Opposite polarity (deshielding) is seen for the three connecting cage carbons (C_1) [11.9 ppm (ethynyl) and 13.0 ppm (propynyl)], whereas the position of the remaining cage carbon (C_2) is close to those of **1** [−22.1 ppm (ethynyl) and −22.6 ppm (propynyl)].

Comparative Discussion of the NMR Parameters of the Phosphonium Ions of 1. Characteristic NMR chemical shifts and coupling constants for the phosphonium ions of **1** are gathered in Table I for comparison.

For **5**, **6**, and **7** a two-bond P–H coupling of 12 Hz is observed between P^+ and methyl proton. With **9** a three-bond P–H coupling of 10 Hz is seen for $P^+C{\equiv}CH$. The one-bond P^+CH_3 or P^+CH_2TMS is consistently around 19 Hz. With **9** and **10**, as expected, the sp-hybridized C_α moves downfield and a much larger ^1J P^+–C results. Moreover, a ^3J P–C between the C_α-alkynyl carbon and the three remaining P centers is visible.

Among the phosphonium cations, the most deshielded cage C_1 carbon is that of the dication which is at 36.9 ppm. With phosphonium ions of alkylation **5**, **6**, and **7**, this signal is less deshielded and appears around 8.5 ppm, becoming slightly more deshielded in the case of alkynylphospho-

(10) Booth, B. L.; Haszeldine, R. N.; Laali, K. *J. Chem. Soc., Perkin. Trans. 1* **1980**, 2887.

(11) For a recent review see: Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274.

(12) Maas, G.; Regitz, M.; Moll, U.; Rahm, R.; Krebs, F.; Hector, R.; Stang, P. J.; Crittell, C. M.; Williamson, B. L. *Tetrahedron* **1992**, *48*, 3527.

(13) Stang, P. J.; Crittell, C. M. *J. Org. Chem.* **1992**, *57*, 4305.

Table I. Characteristic NMR Data on Phosphonium Ions of 1

	^{1}H NMR		^{31}P NMR		^{13}C NMR		
phosphonium ion	δ P$^+$R ($^2J_{PH}$, Hz)	δ P$^+$H	δ P	δ P$^+$	δ P$^+$R ($^1J_{PC}$, Hz)	δ C_1($^1J_{PC}$, Hz)	δ C_2($^1J_{PC}$, $^3J_{PC}$, Hz)
2		ca. 12.3	180.6	80.1		36.9	11.3
4		ca. 12.4	224.5	86.4		4.1	ca. −25
5	3.3		213.0	132.8	23.5	8.3	−25.2
	(12)				(19)	(40.5)	(29, 6.9)
6	3.3		214.0	132.3	23.1	8.4	−25.1
	(12)				(18.7)	(40.9)	(29, 7.0)
7	3.3		210.0	129.0	23.7	8.5	−25.0
	(12)				(19)	(41.2)	
9	6.99		213.0	66.4	70.2	11.9	−22.1
	($^3J_{PH}$ = 10)				(38)	(45.6)	(33.2, 7.0)
10	2.70		207.5	65.2	67.7	13.0	−22.6
	($^3J_{PH}$ = 5.3)				(51.8)		(33.2, 7.3)

nium ions **9** and **10**. The ^1J P–C between C_1 and P$^+$ is ca. 41 Hz in the alkylated cations and ca. 45 Hz with **9**. A ^1J P–C between C_1 and the three remaining phosphorus centers is not detected.

The C_2 cage carbons, on the other hand, appear as doublet of quartets by coupling to both types of phosphorus environments. The magnitude of ^1J P$^+$–C_2 coupling is somewhat larger in the alkynylphosphonium ions as compared to the alkylation cations.

The relative position and intensity of the phosphorus signals of the phosphonium mono- and dications of **1** provide unambiguous assignments for the two phosphorus environments. The P$^+$ center in the alkynylphosphonium monocations is more shielded relative to that in the alkylation cations.

Protonation of 5. In preliminary studies we have found that the P-methylated tetra-*tert*-butyltetraphosphacubane **5** is diprotonated in FSO_3H·SbF_5(1:1)/SO_2ClF or in HF·SbF_5(1:1)/SO_2ClF at dry ice/acetone temperature to give a persistent trication exhibiting just three shielded phosphorus absorptions at 80.3, 117.2, and 116.7 ppm in a 1:1:2 ratio in the ^{31}P NMR (P$^+$Me, PH$^+$, and P$^{\delta+}$··H··P$^{\delta+}$ respectively) and two further deshielded cage carbon absorptions (relative to **5**) at 60.6 (C_1) and 16.1 ppm (C_2) in the ^{13}C NMR. We are continuing our stable ion studies with **5** and with other alkylated and alkynylated tetra-*tert*-butyltetraphosphacubanes.

Summary and Conclusions

Stable phosphonium ions of **1** were formed by protonation in superacids by alkylation with super electrophiles and by alkynylation with alkynyl(phenyl)iodonium triflates.

Phosphorus lone pair participation in the P–C bonds of tetraphosphacubane **1** is manifested in the observed lack of reactivity at phosphorus beyond the monophosphonium cation stage. Only with Magic acid could we observe diprotonation of **1**. These reactions point to a dramatic difference in phosphorus reactivity between **1** and phosphines. The present investigation suggests that further synthetic elaboration of tetraphosphacubane by cycloaddition and ylide chemistry via the phosphonium cations formed by reaction with super electrophiles should be achievable.

Experimental Section

Tetra-*tert*-butyltetraphosphacubane **1**[4,6] and ethynyl- and propynyl(phenyl)iodonium triflates[12] were synthesized according to published procedures. *tert*-Butyl hypochlorite was prepared according to the literature.[14] Methyl triflate and Me_3O^+ BF_4^- were commercial products.

FSO_3H (Allied), CF_3SO_3H (TfOH) (Aldrich), and SbF_5 (Aldrich) were freshly distilled in an all-glass distillation unit under dry nitrogen at atmospheric pressure.

Anhydrous SO_2 (Linde) was used as received. The solvents were rigorously dried.

FSO_3H·SbF_5 (1:1) (Magic acid) was freshly prepared by direct transfer of SbF_5 (27.6 g, 127.4 mmol) under a fast flow of dry nitrogen into a preweighed, dried, Nalgene bottle and by subsequent slow addition of FSO_3H (12.7 g; 1.0 mol equiv) which was transferred and preweighed inside a second Nalgene bottle under nitrogen. The resulting mixture was mixed (vortex) until a clear, homogeneous liquid resulted (exothermic).

The low-temperature NMR spectra were recorded on a GN-300 wide-bore instrument using a 5-mm H/C switchable probe and a 10-mm broad-band probe for ^{31}P measurements. Typically, the probe was cooled to ca. −68 °C while shimming on an acetone-d_6 sample. The cold ion solution was quickly inserted into the cold probe and the sample spun for 2–3 min prior to data collection. Internal CD_2Cl_2 was used as lock for all nuclei and as reference for carbon and proton spectra. The phosphorus spectra were referenced relative to external 85% H_3PO_4. Typically, a 3-s delay time was employed in the carbon spectra and a 2-s delay in phosphorus spectra. Due to its highly diagnostic nature and sensitivity, the ^{31}P spectra were recorded first, and the sample was ejected and cooled to dry ice/acetone temperature while the H/C switchable probe was installed. The probe was then shimmed on acetone-d_6 and cooled down as before; once the desired temperature was attained, the cold sample was introduced and the carbon/proton data were collected. The ambient NMR spectra of the alkylated cations were recorded on Bruker AM400 and Bruker WP200 instruments using $CDCl_3$ as solvent. IR spectra were recorded on a Perkin-Elmer 710B, a Perkin-Elmer 310, and a Beckman IR 20A spectrophotometer.

General Procedure for Stable Ion Generation by Protonation (Steps 1 and 3, Scheme I). The tetraphosphacubane **1** (ca. 30 mg) was placed inside a 10-mm NMR tube, cooled to dry ice/acetone temperature, and diluted with SO_2 (ca. 0.5 mL) under a dry nitrogen atmosphere. The superacid (ca. 1 mL) was transferred under nitrogen into a second 10-mm NMR tube, cooled, and diluted with SO_2 (1:1 v/v). The clear cold homogeneous acid was slowly poured into the cold substrate with efficient mixing until homogeneous (vortex). A cold aliquot of the resulting solution was transferred [either via a precooled pipet (liquid SO_2) or directly) into a 5-mm NMR tube immersed in a dry ice/acetone bath and kept under a nitrogen atmosphere. Cold CD_2Cl_2 (ca. 8 drops) was then added (vortex), and the sample was kept at dry ice/acetone temperature until the NMR spectra were recorded as described.

Quenching Experiments. Ion quenching experiments were done by careful pouring of the contents of the 5-mm NMR tubes into ice/sodium bicarbonate. Methylene chloride was added, and the organic phase was extracted twice. The combined extracts were dried ($MgSO_4$) and filtered, and the solvent was slowly evaporated. The resulting yellow oil was taken up in $CDCl_3$

(14) Teeter, H. M.; Bell, E. W. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 125.

and directly examined by NMR at ambient temperature (→ 3 and unchanged 1).

Oxidation of 1 with tBuOCl (Synthesis of Authentic 3). In a Schlenk pressure tube equimolar amounts of tetraphosphacubane[6] 1 (400 mg) and tBuOCl (108 mg) in diethyl ether (20 mL) were kept at 100 °C for 4 days. The solvent was then removed under vacuum and the yellowish residue washed with pentane and purified by "bulb to bulb sublimation" (200 °C/10^{-3} mbar) to yield 308 mg (74%). 3: mp 264 °C; IR (KBr) 2920 (s), 2860 (w), 1460 (s), 1360 (m), 1230 (vs, br), 790 (m), 750 (m) cm^{-1}; ^1H NMR δ (tBu) 1.13 (s, 27H), 1.02 (tBu) (s, 9H); ^{13}C NMR δ (C_1) 41.1 (d, $^1J_{P,C}$ = 41.3 Hz), (tBu) 32.1 (m), (tBu) 30.9 (m), (tBu) 26.2 (s), (tBu) 20.8 (s), (C_2) −24.2 (m); ^{31}P NMR δ 124.7 (s, 3P), 66.6 (s, 1P); MS (EI, 70 eV) *m/z* 416 (M, 100), 401 (14), 231 (14), 169 (42), 57 (17). Anal. Calcd for $C_{20}H_{36}OP_4$: C, 57.68; H, 8.71. Found: C, 57.4; H, 8.5.

Alkylation Experiments. (a) With Methyl Triflate (Step 4, Scheme I). Methyl triflate (164 mg, 1.0 mmol) was slowly added to a solution of tetraphosphacubane 1 (400 mg, 1.0 mmol) in dry methylene chloride (15 mL) at room temperature. After 4 days, the solvent was removed under vacuum and the yellow solid washed with dry pentane and dried under vacuum to give 5 (536 mg; 95%): mp 200 °C dec; IR (KBr) 2980 (s), 2960 (w), 1470 (s), 1395 (m), 1370 (m), 1280 (br vs), 1220 (s), 1150 (s), 1035 (s), 840 (s), 745 (s), 635 (s) cm^{-1}; ^1H NMR δ (PCH_3) 3.3, (d, $^2J_{PH}$ = 12 Hz), (tBu) 1.2 (s, 27H), (tBu) 1.1 (s, 9H); ^{13}C NMR δ (CF_3) 121.2 (q, $^1J_{CF}$ = 318.1 Hz), (tBu) 31.0 (m), (tBu) 30.5 (dq, $^2J_{PC}$ = 10.5 Hz, $^4J_{PC}$ = 4.5 Hz), (tBu) 24.0 (s), (PCH_3) 23.5 (d, $^1J_{PC}$ = 19 Hz), (tBu) 20.7 (q, $^3J_{PC}$ = 6 Hz), (C_1), 8.3 (d, $^1J_{PC}$ = 40.5 Hz), (C_2) −25.2 (dq, $^1J_{PC}$ = 29.0 Hz, $^3J_{PC}$ = 6.9 Hz); ^{31}P NMR δ 213.0 (s, 3P), 132.8 (s, 1P). Anal. Calcd for $C_{22}H_{39}F_3O_3P_4S$: C, 46.77; H, 6.90. Found: C, 46.6; H, 6.8.

(b) With Me_3O^+ BF_4^- (Step 5, Scheme I). To a solution of 1 (649 mg, 1.6 mmol) in dichloromethane (10 mL) was added Me_3O^+ BF_4^- (240 mg, 1.6 mmol), and the mixture was stirred at room temperature for 24 h. The solvent was removed in vacuum, and the remaining solid was washed with dry pentane and vacuum dried to give **5a** as colorless crystals (731 mg; 90%): mp 283 °C dec; IR (KBr) 2925 (s), 2860 (w), 1460 (s), 1365 (s), 1280 (m), 1230 (s), 1050 (br vs), 840 (s), 790 (m), 740 (s) cm^{-1}; ^1H NMR δ (PCH_3) 3.30 (d, $^2J_{PH}$ = 12 Hz), (tBu) 1.20 (s, 27H), (tBu) 1.12 (s, 9H): ^{13}C NMR δ (tBu) 31.0 (m), (tBu) 30.6 (dq, $^2J_{PC}$ = 10.7 Hz, $^4J_{PC}$ = 4.6 Hz), (tBu) 24.0 (s), (PCH_3) 23.15 (d, $^1J_{PC}$ = 18.7 Hz), (tBu) 20.8 (q, $^3J_{PC}$ = 5.9 Hz), (C_1) 8.4 (d, $^1J_{PC}$ = 40.9 Hz), (C_2) −25.1 (dq, $^1J_{PC}$ = 29.0 Hz, $^3J_{PC}$ = 7.0 Hz); ^{31}P NMR δ 214.4 (s, 3P), 132.3 (s, 1P). Anal. Calcd for $C_{21}H_{39}BF_4P_4$: C, 50.22; H, 7.76. Found: C, 50.0; H, 7.7.

(c) With (Trimethylsilyl)methyl Triflate (Step 6, Scheme I). To tetraphosphacubane 1 (330 mg, 0.8 mmol) was slowly added at room temperature a solution of (trimethylsilyl)methyl triflate (0.2 mL, 0.8 mmol) in methylene chloride (10 mL). The reaction mixture was kept at 40 °C for 1 week, and the solvent was subsequently removed under vacuum. The resulting colorless powder was rinsed with dry pentane and dried under vacuum (498 mg, 95%): ^1H NMR δ (PCH_2TMS) 3.2 (d, $^2J_{PH}$ = 12 Hz), (tBu) 1.1 (s, 27H), (tBu) 1.0 (s, 9H), (TMS) 0.1 (s, 9H); ^{13}C NMR δ (CF_3) 120.0 (q, $^1J_{CF}$ = 315.3 Hz), (tBu) 31.1 (m), (tBu) 30.6 (m), (tBu) 24.2 (s), (PCH_2TMS) 23.7 (d, $^1J_{PC}$ = 19.0 Hz), (tBu) 20.7 (q, $^3J_{PC}$ = 7.0 Hz), (C_1) 8.5 (d, $^1J_{PC}$ = 41.2 Hz), (TMS) 1.5 (s), (C_2) −25.0 (m); ^{31}P NMR δ 210.0 (s, 3P), 129.0 (s, 1P). Anal. Calcd for $C_{25}H_{47}F_3O_3P_4SSi$: C, 47.16; H 7.44. Found: C, 47.0; H 7.4.

Alkynylation Experiments. (a) With Ethynyl(phenyl)-iodonium Triflate (Step 8, Scheme I). Tetraphosphacubane 1 (60 mg 0.15 mmol) was dissolved in 10 mL of freshly distilled, degassed methylene chloride and cooled to −78 °C, and ethynyl-(phenyl)iodonium triflate (56.7 mg, 0.15 mmol) was added all at once. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h under nitrogen giving a bright orange solution. The reaction was checked by ^{31}P NMR which showed it to be complete. Diethyl ether was then added slowly to precipitate the product which was then filtered, washed several times with ether, and dried in vacuo giving slightly yellow crystals (58 mg, 67%): mp 170–171 °C: IR (KBr) 3101, 3076, 2954, 2861, 2027 (C≡C), 1470, 1396, 1368, 1280 (OTf), 1257 (OTf), 1238 (OTf), 1224, 1155 (OTf), 1030, 823, 778, 753, 744, 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ (HC≡C) 6.99 ($^3J_{PH}$ = 10 Hz), (tBu) 1.14 (27H), (tBu) 1.06 (9H); ^{13}C NMR ($CDCl_3$) δ (βC) 125.90 ($^3J_{PC}$ = 5.3 Hz, $^1J_{CH}$ = 266.5 Hz), (OTf) 120.62 ($^1J_{CF}$ = 320 Hz), (αC) 70.15 ($^1J_{PC}$ = 38.0 Hz, $^3J_{PC}$ = 2.5 Hz, $^2J_{CH}$ = 47.6 Hz), (tBu) 31.2 (m), (tBu) 31.1 (m), (tBu) 23.42 (d, J_{PC} = 45.6 Hz; t, J_{PC} = 5.6 Hz), (tBu) 20.89 (q, J_{PC} = 6.2 Hz), (Cl) 11.94 (d, J_{PC} = 45.6 Hz; t, J_{PC} = 5.6 Hz), (C2) −22.08 (d, J_{PC} = 33.2 Hz; q, J_{PC} = 7 Hz); ^{31}P NMR ($CDCl_3$) δ 213.0 ($^3J_{PP}$ = 6 Hz, 3P), (PC≡CH) 66.4 ($^2J_{PP}$ = 6 Hz); ^{19}F NMR ($CDCl_3$) δ −78.6 ppm. Anal. Calcd for $C_{23}H_{37}P_4SO_3F_3$: C, 48.09; H, 6.49. Found: C, 47.75; H, 6.51.

(b) With Propynyl(phenyl)iodonium Triflate (Step 8, Scheme I). Tetraphosphacubane 1 (80 mg, 0.20 mmol) and propynyl(phenyl)iodonium triflate (86.2 mg, 0.22 mmol) were added to a thick-walled glass tube (volume = 16 mL). Freshly distilled CH_2Cl_2 (8 mL) was added and the solution was degassed by the freeze–thaw method (3×). The contents were then frozen under vacuum, and the glass tube was flame sealed. The reaction was then stirred in the dark for 2 weeks at 40 °C. The tube was opened, and the product was concentrated by rotary evaporation. Diethyl ether was added carefully to precipitate the product which was then filtered, washed several times with ether, and dried in vacuo giving yellow crystals (76 mg, 65%): mp 162–164 °C: IR (KBr) 2962, 2933, 2869, 2200 (C≡C), 2119, 1469, 1396, 1273 (OTf), 1233 (OTf), 1224 (OTf), 1160 (OTf), 1031, 756, 746, 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ (CH_3) 2.70 (d, $^3J_{PH}$ = 5.3 Hz), (tBu) 1.14 (27 H), (tBu) 1.06 (9 H); ^{13}C NMR ($CDCl_3$) δ (βC) 135.58 ($^2J_{PC}$ = 10 Hz), (OTf) 120.83 (J_{CF} = 321 Hz), (αC) 67.66 (d, J_{PC} = 51.8 Hz; t, 2.6 Hz), (tBu) 31.3 (m), (tBu) 31.1 (m), (tBu) 23.64 (m), (tBu) 20.9 (q, J_{PC} = 6.2 Hz), (Cl) 12.99 (m), (Me) 7.58 (d, $^3J_{PC}$ = 3.6 Hz), (C2) −22.55 (d, J_{PC} = 33.2 Hz; t, J_{PC} = 7.3 Hz); ^{31}P NMR ($CDCl_3$) δ 207.47 (d, 3P, $^2J_{PP}$ = 5.4 Hz), (PC≡CH) 65.24 (q, 1P, $^2J_{PC}$ = 5.4 Hz); ^{19}F NMR ($CDCl_3$) δ −78.4 ppm. Anal. Calcd for $C_{24}H_{39}P_4SO_3F_3$: C, 48.98; H, 6.68. Found: C, 49.13; H, 6.77.

Acknowledgment. K.K.L. thanks KSU for research support and the Ohio Academic Challenge Program for purchasing funds for the GN-300 NMR instrument used for the stable ion studies. M.R. is grateful to the Volkswagen-Stiftung and the Fonds der Chemischen Industrie for generous financial support. Support at Utah from the NCI of NIH (2R01CA16903) is also greatfully acknowledged.