Electrophilic Chemistry of Tetraphosphacubane: Novel Monophosphonium Ions of Ethylation, Benzylation, Acylation, and Adamantylation, Di- and Triphosphonium Ions of Acylation/Alkylation and Alkylation/Protonation, and Monoprotonation of Tetraoxo- and Tetrathioxotetraphosphacubane†

Kenneth K. Laali,*,‡ Bernhard Geissler,§ Manfred Regitz,*,⊥ and John J. Houser∥

Department of Chemistry, Kent State University, Kent, Ohio 44242, Fachbereich Chemie, Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663, Germany, and Department of Chemistry, University of Akron, Akron, Ohio 44325-3601

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Ethyl triflate and benzyl triflate (via $PhCH_2Cl/AgOTf$) react with the tetraphosphacubane **2a** at room temperature to give the phosphonium salts **6** and **7**. The P-adamantylated monocation **8** was obtained by the ambient temperature reaction of **2a** with 1-$Ad^+SbCl_6^-$. P-Acylation of **2a** with $MeCO^+SbCl_6^-$ gives **9**, whereas the diphosphonium salt **11** is cleanly obtained by ambient temperature acylation of **6**, adamantylation of **6** with 1-Ad^+ is less selective, forming **13** in a mixture. Protonation of **6** with $FSO_3H{\cdot}SbF_5$ (1:1) (magic acid)/SO_2 gives a ca. 1:1 mixture of dication **14** and trication **15**. The trication becomes more prominant with time or by an increase in temperature. Protonation of **5** similarly gives a mixture of **16** and **17**, but the disappearance of **16** is very rapid. With HF/SbF_5 (1:1)/SO_2ClF only triphosphonium cation **17** is detected. Protonation of **6** with $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2 leads to near exclusive formation of **14**; only traces of **15** are detected. Tetraoxo- and tetrathioxotetraphosphacubanes **4a, 4b** are only monoprotonated in Magic acid/SO_2 (→ **18** and **19**). PM3 calculations on protonation of tetramethyltetraphosphacubane **21** as model are also reported.

Introduction

Thermal cyclooligomerization of tBuC≡P is nonselective yielding a mixture containing **2a** in low yield (~10%). Chemoselective synthesis of **2a** and **2b** was subsequently achieved using the tricyclic zirconium complex **3** by reaction with hexachloroethane (Figure 1), providing gram quantitites (**3a,b** → **2a,b**) for further studies.[1,2]

Photoelectron spectroscopy,[3] ab initio calculations,[3] and NMR spectroscopy[4] support the notion that nP → σ P–C delocalization occurs in tetraphosphacubane, a chemical manifestation of which is decreased nucleophilicity/basicity at phosophorus.[3,5]

In our previous studies,[6] mono- and diprotonation of **1** in superacid media was demonstrated. Some examples of monoalkylation and monoalkynylation were also provided.

The present study is an extensive survey of ambient-temperature reactions of onium ions and carbocation salts with **2a,b** (Figure 1), namely ethylation with EtOTf, benzylation with $PhCH_2OTf$, adamantylation with 1-Ad^+-$SbCl_6^-$, and acylation with $MeCO^+$ $SbCl_6^-$. Further ambient P-acylation and P-adamantylation of the alkylation monocations (**5** and **8**) are shown with $MeCO^+$ and 1-Ad^+ as electrophiles, and the first examples of protonated tetraoxo- and tetrathioxotetraphosphacubane (**4b**, **4a**) are provided.

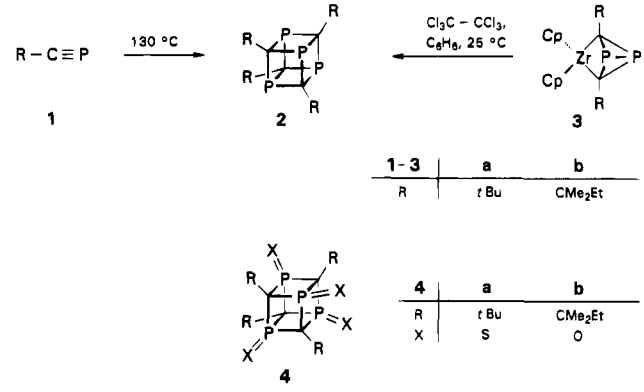

Figure 1. The tetraphosphacubane substrates.

We also demonstrate that despite decreased reactivity at phosphorus, further P-protonation of the P-ethylated and P-methylated tetraphosphacubane (**5** and **6**) to give di- (SO_2 solvent) and triphosphonium ions (SO_2ClF solvent) is possible with FSO_3H/SbF_5 (1:1). Multinuclear NMR data for the phosphonium cations are obtained, and the key features compared. We also discuss the protonation of tetramethyltetraphosphacubane **21** by PM3 (mono- through tetraprotonation).

Results and Discussion

(1) Ethylation, Benzylation, and Adamantylation (Scheme 1). Tetraphosphacubane **2a** reacts smoothly

† Novel Phosphonium Cations. 2. For part 1, see ref 6. Organophosphorus Compounds. 93. For part 92, see: Mo, X. B.; Birkel, M.; Regitz, M. *Heteroatom Chem.* **1994**, *5*, in press.

‡ Kent State University.

§ Visiting Postdoctoral Fellow from Kaiserslautern at KSU.

⊥ University of Kaiserslautern.

∥ University of Akron.

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(1) Regitz M. in *Organic Synthesis via Organometallics*, proceedings of the Fourth Symposium in Aachen, July 1992; Enders, D., Gais, H. J., Keim, W. Eds.; 1992 and related references cited therein.

(2) (a) Wettling, T.; Geissler, B.; Schneider, R.; Barth, S. Binger, P.; Regitz, M. *Angew Chem., Int. Ed. Engl.* **1992**, *31*, 758. (b) Regitz, M. In *Heteroatom Chemistry*, Block, E., Ed.; VCH: New York, 1990; Chapter 17.

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

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

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

(6) Laali, K. K.; Regitz, M.; Birkel, M.; Stang, P. J.; Crittell, C. M. *J. Org. Chem.* **1993**, *58*, 4105.

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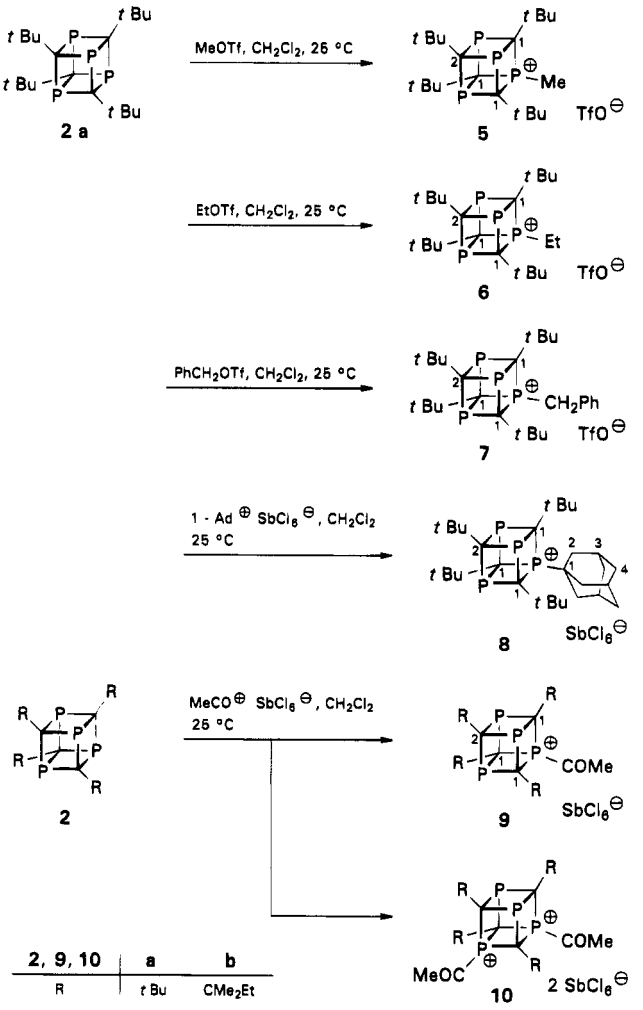
Scheme 1. Methylation, Ethylation, Benzylation, and Adamantylation of 2a and Acylation of 2b



with ethyl triflate (EtOTf) at rt to give after 3 days a ca. 90% yield of the monophosphonium salt **6** isolated as a yellow crystalline product. It shows two resonances in the ^{31}P NMR at 215.8 (3P) and 143.4 ppm (P^+) as pseudosinglets. Their positions compare closely with those of the methylated analog **5** (213.0 and 132.8 ppm). The two types of cage carbons appear as multiplets at 10.0 (C_1) and −25.6 ppm (C_2). Coupling of the P^+-*Et* group to phosphorus is seen both in the ^{13}C and ^1H NMR. Attempted P/P diethylation of **1** with EtOTf/BCl_3 (2 equiv) was unsuccessful.

Room-temperature reaction of **2a** with benzyl triflate ($PhCH_2OTf$) formed in situ via the reaction of $PhCH_2Cl$ with AgOTf[7a] gave the P-benzylated analog **7** for which two ^{31}P resonances are observed at 219.3 (3P) and 132.6 ppm (1P), appearing as doublet and quartet, respectively, due to P−P coupling. Such cage P−P coupling is not observable with the P-ethylated and P-methylated salts. The diagnostic benzylic hydrogens appear at 4.88 ppm in the ^1H NMR spectrum as a doublet ($^2J_{PH}$ = 10 Hz). In the ^{13}C NMR spectrum, the benzylic carbon is seen at 47.5 ppm with a $^1J_{CP}$ of 33.0 Hz. This value is twice as large as $^1J_{CP}$ in the P^+-CH_2CH_3 group. Carbon resonances for the Ph group appear as doublets and the cage carbons as two multiplets at 13.1 and −25.7 ppm.

Monoadamantylation of **2a** could be achieved by stirring the tetraphosphacubane with 1-Ad$^+SbCl_6^-$ in CH_2Cl_2 solvent at rt for 3 days to give **8** as a yellow solid. Oxidation to the tetraphosphacubane monooxide is a side reaction (ca. 15% from ^{31}P NMR). The two types of phosphorus resonances for **8** are at 198.1 (3P) and 86.4 ppm (1P), appearing as a doublet and a quartet, respectively, with $^2J_{PP}$ = 17.1 Hz. This P−P coupling is considerably larger than that for **7**. It appears that increasing steric crowding causes geometrical distortions in the cubic structure which in turn affects the P−P coupling. The 1-Ad-P^+ phosphorous resonance (86.4 ppm) is substantially more upfield than those of the alkylated and benzylated analogs **5**−**7** (in the region where P^+−H resonances were observed for the mono- and diprotonated analogs).[6] The bridgehead carbon is at 41.2 ppm with $^1J_{PC}$ = 41.5 Hz. Comparison of the ^1J PC at P^+ for **6**, **7**, and **8** shows increasing coupling constants with increased steric crowding [14.4 (for **6**), 33.0 (for **7**), and 41.5 (for **8**)]. There is little change in the positions of the C_1 cage carbons for **7** and **8**.

(2) Acylation (Scheme 1). Under strictly anhydrous conditions, **2b** is selectively monoacylated with MeCO$^+$-$SbCl_6^-$ in CH_2Cl_2 solvent at rt to give **9b** (ca. 75% yield after 3 days stirring). The ^{31}P NMR spectrum of **9b** exhibits two resonances at 194.5 (3P) and 84.2 (1P), appearing as a doublet and a quartet, respectively (J = 18 Hz), due to P−P coupling. Both the position of P^+-COMe phosphorus resonance and the magnitute of the P−P coupling for **9b** are close to those observed for **8**. The *Me*CO is a singlet at 2.13 ppm in the ^1H NMR spectrum; its CO group appears as a multiplet at 191.3 ppm in its ^{13}C NMR spectrum (by coupling to two different cage P centers). The cage carbons give rise to two multiplets at −18.0 (C_2) and 9.0 ppm (C_1). Two types of *tert*-pentyl groups are seen (3:1 ratio) in the ^{13}C NMR.

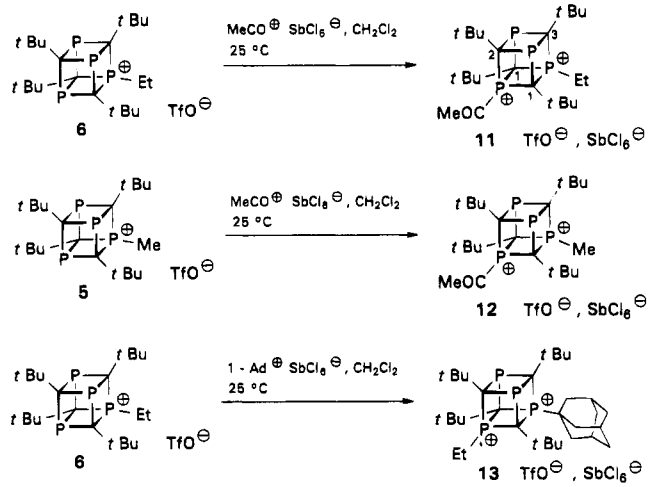
A similar reaction of **2a** with MeCO$^+SbCl_6^-$ was less selective. The ^{31}P NMR spectrum of the reaction mixture showed apart from **9a** (70%), some tetraphosphacubane monooxide[6] (20%) and minor amounts of P/P diacylated dication **10a** (10%). The lattter exhibits two ^{31}P resonances at 30.7 and −18.0 ppm (1:1), both as 5.3 Hz triplets ($^2J_{PP}$). The extent of oxidation was variable in different runs: in one case, only minor amounts of **9a** were formed and the tetraphosphacubane monooxide increased to ca. 40%. A significant portion of the reaction mixture was a P/P-difunctionalized tetraphosphacubane (60%), having two ^{31}P resonances at 30.7 and −9.9 ppm (1:1; both as triplets with ^2Jpp = 7.1 Hz), assigned to the tetraphosphacubane bis(oxide). In an independent experiment we found that the latter can be obtained [^{31}P NMR: 34.3 and −15.2 (1:1)] as a byproduct in the oxidation of **2a** with bis(trimethylsilyl) peroxide ($Me_3Si)_2O_2$ (1 equiv).

Due to a lack of reproducibility, the acetyl cation salt/methylene chloride approach is unsuitable for selective synthesis of the dioxotetraphosphacubane.

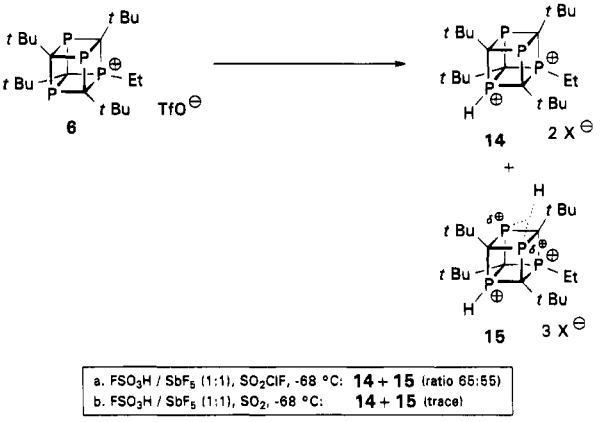
(3) Synthesis of Diphosphonium Salts 11−13 by Ambient-Temperature Acylation and Adamantylation of 5−6 (Scheme 2). The P-ethylated triflate salt **6** reacts cleanly with MeCO$^+SbCl_6^-$ in dry CH_2Cl_2 at rt to furnish the diphosphonium salt **11** as a yellow solid in quantitative yield after 4 days.

The ^{31}P NMR spectrum of **11** exhibits three resonances at 85.6 (1P), 62.4 (2P), and 49.0 ppm (1P) as a doublet of triplet, a pseudotriplet, and a doublet of triplets, respectively. The assignment of pseudotriplet at 62.6 ppm to the remaining two cage P centers is unambiguous ($^2J_{P^+-P}$ = 9.9 Hz). For the two remaining 1P signals, assignment of the 85.6 ppm resonance to P^+-Et and 49.0 ppm resonance to P^+-COMe are based on comparison with **12**

Scheme 2. Acylation and Adamantylation of 6 and Acylation of 5



Scheme 3. Low-Temperature Protonation of 6 and 5 in Superacid Media



(see below). Analysis of these doublet of triplets shows that $^2J_{P^+-P^+}$ is twice as large compared to $^2J_{P^+-P}$ coupling (22.8 compared to 9.4 and 10.2 Hz respectively).

As expected, there are three cage-C multiplets [12.8 (C_3), 47.1 (C_2), and 69.4 (C_1)] and three tBu groups (2:1:1 ratio) in the ^{13}C NMR. The P^+-*C*OMe appears as a broad singlet at 182.3 ppm, which is slightly more upfield compared to the CO in **9**.

Dication salt **11** appears indefinitely stable when refrigerated; attempts are underway to obtain its X-ray crystal structure.

Surprisingly, P-acylation of **5**, with $MeCO^+SbCl_6^-$ was sluggish, yielding a mixture of desired dication **12** (ca. 60%) and unreacted **5**. The ^{31}P resonances for **12** were at 61.7 (2P), 53.7 (1P), and 49.2 ppm (1P). The assignment of 49.2 ppm resonance to P^+-COMe was thus assured (see above). Attempts to force the reaction to completion by adding excess $MeCO^+SbCl_6^-$ were unsuccessful.

Chemoselective P-adamantylation of **6** with $1\text{-}Ad^+SbCl_6^-$ could not be achieved. The desired diphosphonium cation **13** was obtained in ca. 35% yield in a mixture containing unreated **6** and several unidentified tetraphosphacubane derivatives. The ^{31}P spectrum of **13** exhibited three resonances at 86.2 (1P), 61.9 (2P), and 49.0 ppm (1P). These are very close to the resonances for **11**, suggesting that P-adamantylation and P-acetylation effects on ^{31}P shifts are nearly the same for the two dications. The $^2J_{P-P}$ coupling patterns are also similar.

(4) Protonation of P-Alkylated Monocations 5 and 6 in Superacid Media (Scheme 3). In the context of our previous studies,[6] we briefly mentioned the protonation of **5** in $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2ClF and in $HF{\cdot}SbF_5$ (1:1)/SO_2ClF leading to the novel trication **17**. We have now studied **6** (and **5**) in detail and find that the nature of the cosolvent (SO_2ClF versus SO_2) has an impact on protonation:

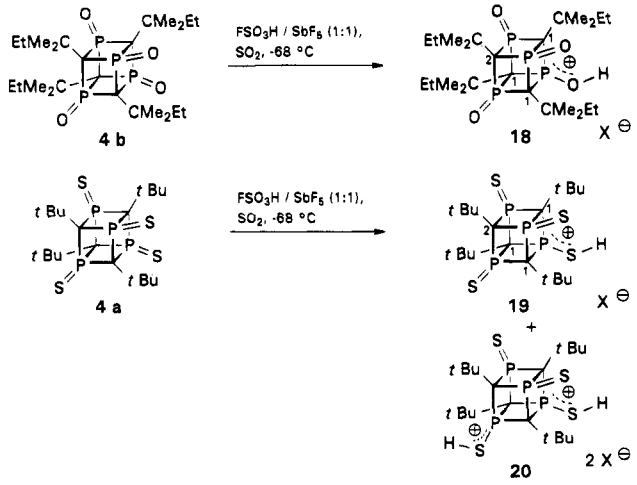
When a cold solution of $FSO_3H{\cdot}SbF_5$ (1:1) (Magic acid)/SO_2 is added to a solution of **6** in SO_2 (dry ice/acetone temperature), the P/P ethylated/protonated dication **14** is formed, showing three phosphorus resonances at 170.2 (2P), 136.4 (P^+−Et), and 81.2 (P^+−H). The latter shows a $^1J_{P^+-H}$ of 467 Hz (with decoupler off). Both P^+ centers appear as doublet of triplets with $^2J_{P^+-P^+} = 34.5$ and ^2J P^+-P = 11.2 and 12.1 Hz. This trend is analogous to that for **11** and **13**. In the ^{13}C NMR there are three cage-C carbons, the most downfield of which is a multiplet (C_1) at 39.9 ppm. The most upfield cage-C (C_3) appears as a doublet of doublet. As was the case with the mono- and diprotonated **2a** we previously studied,[6] the P-*H* resonance is not observed in the ^1H NMR spectrum of **14**.

The same reaction in the less nucleophilic SO_2ClF gave apart from **14** a new phosphonium ion with three (more upfield) phosphorus resonances at 117.0 (2P), 114.8 (1P), and 79.5 ppm (1P) (spectra recorded at −80 °C). The 117.0 ppm 2P resonance appears as a doublet of doublets (29.7 and 13.4 Hz) and remains unchanged when the decoupler is off. The 114.8 ppm 1P resonance appears as a doublet of triplets (29.6 and 13.2 Hz) and collapses into a broad hump when the decoupler is off. The 79.5 ppm 1P resonance appears as a pseudoquartet (30.0 Hz) and remains unchanged when the decoupler is turned off. On this basis the 79.5 ppm resonance is assigned to P^+−Et and the 114.8 ppm resonance to P^+−H.

The ^{13}C NMR spectrum of the mixture gives apart from the expected resonances for **14** (discussed earlier), three new, more deshielded, cage-C carbons at 61.9, 37.9, and 17.4 ppm (2:1:1 ratio; multiplets), a distinctly more deshielded P^+−Et(Me) doublet at 8.35 ppm ($^2J_{CP} = 6.8$ Hz), and additional tBu resonances. The observed trend of more shielded phosphorus and more deshielded cage-carbon environments suggests a trication structure for the second ion. On the basis of the chemical shift arguments, a P/P-diprotonated/P-ethylated cation is inconsistent with the data, whereas a structure like **15** fullfils all the requirements. Thus formation of a 4e/3C bond at two phosphorus centers is tentatively suggested.[7b] Lack of change in the doublet of doublets appearance of this resonance on H-decoupling suggests a rather weak P−H−P interaction. There is no exchange broadening in the phosphorus spectra to suggest an average structure by rapid proton exchange. Collapse of the doublet of triplet resonance for P^+−H center on H-decoupling rather than splitting into a doublet (as was observed with **14**) suggests that the P^+−H bond state is different from that in **14**. Prolonged storage of the sample at dry ice/acetone temperature led to a slow decrease of **14** and

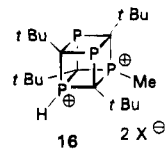
(7) (a) Booth, B. L.; Haszeldine, R. M.; Laali, K. *J. Chem. Soc., Perkin. Trans. 1* **1980**, 2887. (b) Whereas crude molecular models of tetraphosphacubane skeleton suggest that the presumed relative orientation of phosphorus lone pairs should be unsuitable for $P^{\delta+}$−H−$P^{\delta+}$ 4e/3C bond formation, the nP → σ PC delocalization process may influence this picture. In any case, our experimental data do not appear compatible with "averaging" due to rapid exchange (we thank one of the reviewers for insightful comments on this issue). (c) The 116.7 ppm value in ref 6 is an unnoticed printing error.

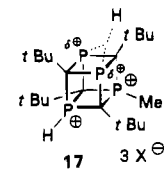
Scheme 4. Low-Temperature Protonation of 4a and 4b in Magic Acid/SO_2



increase in **15**. The observed changes corroborated the relative assignments of the phosphorus resonances. Likewise, changes observed in the relative intensities of the ^{13}C resonances corroborated the assignments made for **15**. Increased concentration of **15** increased the viscosity of the sample. Samples reaching 80–90% of **15** rapidly polymerized in the probe, forming a gel. Therefore a ^{13}C NMR spectrum of pure **15** could not be obtained.

Protonation of **5** with $FSO_3H{\cdot}SbF_5$ (1:1)/SO_2ClF gave a mixture of **16** and **17**, but the disappearance of **16** was much more rapid (compared to **16**). In $HF{\cdot}SbF_5$ (1:1)/SO_2ClF only **17** was observed, which subsequently polymerized. The trication **17** exhibited three phosphorus resonances at 117.2 (2P), 106.7[7c] (1P), and 80.3 (1P). The latter appeared as a distorted 33 Hz pseudoquartet. Other resonances appeared as pseudosinglets. The ^{13}C NMR spectrum of **17** shows the P^+–Me as a distinct doublet at 21.4 ppm. The cage carbon positions at 60.6, 38.1, and 16.0 (2:1:1; all multiplets) are in close agreement to those assigned to **15**.


16 2 X⊖


17 3 X⊖

(5) Protonation of the Tetraphosphacubane Tetraoxide (4b) and Tetrasulfide (4a) (Scheme 4). Regitz et al. have shown[8] that P-oxidation in **2a** or **2b** to give **4a** (with sulfur/Et_3N) or **4b** (with 4 equiv of $(Me_3Si)_2O_2$) brings about a dramatic change in the P–C bonding situation.[8] Thus the unusually deshielded phosphorus resonances and extremely shielded cage-carbon resonances observed in **2a,b**[2,4] change to normal values for phosphine oxides (or sulfides). In this regard it was of interest to examine the protonation of **4a,b** for comparison with our previous studies with **2a**.

Surprisingly, tetraphosphacubane tetraoxide **4b** is not fully protonated in FSO_3H/SO_2 at −60 °C. The resulting clear yellow solution exhibited a single resonance in the ^{31}P NMR spectrum deshielded by just 7 ppm relative to **4b**.

The O-protonation could only be effected with FSO_3H/SbF_5 (1:1)/SO_2 to give **18**. The reaction takes place immediately at dry ice/acetone temperature, forming a clear yellow solution. The resulting monocation exhibits two ^{31}P resonances at 26.4 (3P) and −33.7 ppm (1P), appearing as a doublet and a quartet, respectively, with $^2J_{P,P} = 91.3$ Hz. Two cage carbons are seen as multiplets at 120.7 (C_2) and 59.9 ppm (C_1). The cage-C in **4b** is a multiplet at 111.2 ppm.

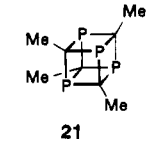
The two-bond P–P coupling in **18** is significantly larger than those observed for phosphonium cations of **2a** and **2b**. The *tert*-pentyl groups appear broad in the ^1H NMR spectrum, and a separate $PO\mathit{H}^+$ resonance is not seen.

Protonation of **4a** was remarkably slow in FSO_3H/SbF_5 (1:1)/SO_2 solvent and required raising of temperature to ca. −40 °C for the substrate to dissolve in the superacid. Its ^{31}P NMR spectrum exhibits two major resonances at 63.2 (3P) and −38.4 (1P) both as pseudosinglets and two minor absorptions at 68.2 and −33.0 ppm (1:1) accounting for ca. 10% of the reaction mixture. No unreacted **4a** remains (^{31}P absorption of **4a** itself is at 19.0 ppm). The major product is assigned to **19**, and the minor one to the diprotonated analog **20**. The $PS\mathit{H}^+$ resonance was detectable as a broad peak in the ^1H NMR centered at 5.6 ppm. The cage-C resonances are at 88.4 (C_2) and 47.7 (C_1) ppm. The latter is *shielded* by 47 ppm relative to the precursor. The tBu groups appear broad in the ^{13}C spectrum.

(6) Theoretical Studies of Protonation. The X-ray crystal structure of **2a** has been determined by Regitz et. al.,[4] confirming its distorted cubic geometry. The average P–C bond length is 1.881 Å; the P–C–P, C–P–C, and P–C–C angles are 94.4°, 85.6°, and 122.2°. Bachrach and Perriott[9] carried out an ab initio study on unsubstituted tetraphosphacubane at the HF/6-31G* level and obtained a geometry which agreed very closely with the X-ray structure of the *tetra-tert*-butyl-substituted species. Their calculated C–P bond length and P–C–P and C–P–C bond angles were 1.885 Å and 94.97° and 84.81°, respectively. They attribute the calculated 100 kcal/mol decrease in ring strain energy compared to cubane to the ability of phosphorus to accommodate small angles, allowing the angles about carbon to exceed 90°, and to a significant ionic character of the C–P bond.[9]

We have used PM3 to study the unsubstituted tetraphosphacubane and find a $\Delta H_f°$ of 65.8 kcal/mol, making it the most stable among the possible $C_4H_4P_4$ isomers. The PM3 geometry is likewise in close agreement with the aforementioned X-ray structure, with an average C–P bond length of 1.896 Å and P–C–P and C–P–C angles of 94.9° and 85.0°, respectively. PM3 likewise predicts a very polar C–P bond ($Q_P = +0.51$; $Q_C = -0.68$).

We carried out PM3 calculations on tetramethyltetraphosphacubane **21** and its mono-, di-, tri-, and tetraprotonated forms as models for the corresponding tetra-*tert*-butyl systems (Table 1 and supplementary material). We


21

find that in the phosphonium ions, the C–P^+ bonds are

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

(9) Bachrach, S. M.; Perriott, L. M. *Tetrahedron Lett.* **1993**, *34*, 6365.

Table 1. PM_3 Calculations on Protonation of 21

substrate	$\Delta H_f°$ (KCal/mol)	$\Delta\Delta H_f°$	Selected Charges			
			P^+	P	$C-(P^+)_n$	$C-(P)_n$
21	67.22			+0.517		−0.613
P-protonated **21**	212.57	145.35	+1.854	+0.791	−0.95	−0.745
					$n = 1$	$n = 3$
P,P-diprotonated **21**	438.58	371.36	+2.042	+1.041	−1.213	−1.056
					$n = 2$	$n = 2$
P,P,P-triprotonated **21**	747.66	680.44	+2.202	+1.266	−1.39	−1.289
					$n = 3$	$n = 1$
P,P,P,P-tetraprotonated **21**	1142.94	1075.72	+2.338		−1.448	

shorter and the C−P bonds (with one exception) are longer than the C−P bonds in the unprotonated **21** or in **2a**. Note that in several cases there are two groups of bonds of the same type, $C-P^+$ or C−P (see the supplementary material for more detailed assignments). In all cases the highly polarized nature of the cage C−P bond is evident. The amount of C-P charge separation increases with progressive protonation, and the negative charge on carbon increases even for those carbons not directly bonded to a protonated phosphorus.

A Comparison of the Shielding/Deshielding Trends for the Cage C−P in the Studied Cations. In accord with our previous observations with the mono- and diprotonated **2a** and monoalkylated (monoalkynylated) **2a**,[6] the monophosphonium ions of ethylation (**6**), benzylation (**7**), adamantylation (**8**), and acylation (**9**) show that the phosphorus resonances move upfield and cage-carbon resonances move downfield from their original extreme positions in **2a**. The magnitudes of these shifts are the greatest for the $C-P^+$ bonds. These shifts are opposite to the calculated charge densities (see Table 1).

The ethylation/acylation dication **11** provides an extreme example of shielding at phosphorus and deshielding at cage carbons.

A rather different situation is seen in **18** and **19**, for which both the protonated PO and the attached cage-C_1 carbons are strongly shielded relative to the precursors, instead the remaining phosphorus centers and cage-C_2 are deshieled.

Experimental Section

Chemoselective synthesis of **2a,b** was according to Regitz et al.[2a] Synthesis of **5** was previously reported by us.[6] The tetraoxo and tetrathioxo derivatives were prepared by oxidation of **2a** (or **2b**) with $(TMS)_2O_2$ and with S_8/Et_3N, respectively, according to Regitz et al.[5]

Methyl and ethyl triflate (both Aldrich) were distilled prior to use.

Benzyl triflate was prepared in situ from AgOTf (Aldrich) and benzyl chloride at rt according to ref 7a.

FSO_3H (Allied) and SbF_5 (Aldrich) were distilled in an all-glass distillation unit under dry nitrogen. SO_2ClF (Aldrich) and anhydrous SO_2 (Linde) were used as received.

Preparation of FSO_3H/SbF_5 (1:1) and HF/SbF_5 (1:1) were according to the general procedures previously reported.[6]

For the synthesis of 1-$Ad^+SbCl_6^-$ and $MeCO^+SbCl_6^-$ salts, the procedures of Olah et al.[10,11] were modified as follows:

Adamantyl chloride (0.684 g, 4.0 mmol) was dissolved in dry CH_2Cl_2 (ca. 50 ml). The solution was cooled to dry ice/acetone temperature, and $SbCl_5$ (0.51 mL, 1 equiv) was added under a dry nitrogen atmosphere. The temperature was brought to rt, and after 1 h the solution was cooled again (dry ice/acetone bath) to crystallize 1-$Ad^+SbCl_6^-$ out of solution. The liquid was removed with a pipet and the white solid dried under vaccum (yield ca. 80%). For $MeCO^+SbCl_6^-$ preparation, the procedure was similar except that the Lewis acid was added at O °C. The salt precipitated from methylene chloride as a white solid. It was filtered under nitrogen, washed with a small amount of CH_2Cl_2, and dried under vaccum.

The NMR spectra were all recorded on a GE-GN300 instrument. A 10 mm broad-band probe was used for the phosphorus spectra, whereas a 5 mm C/H switchable probe was used for carbon and proton data. The procedures for the low-temperature NMR work were analogous to our previous work.[6]

PM3 calculations were carried out using MOPAC **7** running under OS/2. We are grateful to Dr. Henry A. Kushka of The University of Akron (retired) for providing this program.

General Procedure for the Room-Temperature Synthesis of Phosphonium Salts 6−9 and 11−13. The experiments were carried out on 80−100 mg scale in Schlenk pressure tubes under argon (or dry nitrogen). The tetraphosphacubane substrate was dissolved in rigorously dried methylene chloride, the triflate or the cation salt (usually 1.1 molar equiv) was added directly under argon with efficient stirring at rt, and the Schlenk tube was sealed. After 2−3 days the solvent was removed under vaccum, and the residue (usually yellow) was washed with hexane and dissolved in $CDCl_3$ for NMR studies. **2a** and **2b** are nicely soluble in hexane and give yellow solutions even at very high dilution. The hexane wash from the reactions was found to be colorless in almost all cases, showing that no unreacted tetraphosphacubane remained.

For synthesis of **7**, after dissolving **2a** in methylene chloride, AgOTf was added under argon followed by benzyl chloride (1 equiv each) whereupon AgCl was quickly formed and increased with time. The reaction was complete (^{31}P NMR) after overnight stirring at rt.

General Procedure for Stable Ion Generation. Typically, 100 mg of the substrate was placed inside a 10 mm NMR tube cooled to dry ice/acetone temperature diluted with SO_2 (or SO_2ClF) under argon.

The NMR tube was capped and was fully immersed into the cold bath. The superacid (ca. 1 mL) was charged into a second NMR tube (quartz tube for $HF{\cdot}SbF_5$) and was diluted with SO_2 or SO_2ClF (ca. 1 mL), flushed with argon, and capped. Vigorous vortex mixing of the cold superacid solution gave a clear homogeneous solution. The NMR tube containing the cold superacid was slowly poured into the cold substrate while shaking the NMR tube in dry ice/acetone bath. Vigorous vortex mixing followed, giving a clear yellow solution. A cold aliquot was quickly transferred under argon into a 5 mm NMR tube immmersed in dry ice/acetone bath. Precooled CD_2Cl_2 (8−10 drops) was added (vortex). The cold NMR samples were examined within 1−2 h of preparation.

Multinuclear NMR (and Microanalysis) Data for the Phosphonium Cations. Phosphonium ion 6: ^{31}P NMR ($CDCl_3$) δ 215.8 (s, 3P), 143.4 (s, 1P); ^{13}C NMR ($CDCl_3$) δ (OTf) 119.4 (q, $^1J_{CF}$ = 317.5 Hz), (P^+-*C*H_2-) 33.0 (dd, $^1J_{PC}$ = 14.4 Hz, $^3J_{PC}$ = 1.6 Hz), (C_1-*C*Me_3) 31.6 (m), (C_2-*C*Me_3) 31.1 (dd, $^4J_{PC}$ = 10.8 Hz, $^2J_{PC}$ = 5.1 Hz), (C_1-C*Me*$_3$) 24.6 (m), (C_2-C*Me*$_3$) 21.4 (pseudoquartet, J_{PC} = 5.7 Hz), (C_1) 10.0 (m), (P^+-CH_2*C*H_3) 7.9 ($^2J_{PC}$ = 5.4 Hz), (C_2) −25.6 (m); ^1H NMR ($CDCl_3$)δ (P^+-*C*H_2-) 4.11 (dq, $^3J_{HH}$ = 8.4 Hz, $^2J_{HP}$ = 10.1 Hz), (P^+-CH_2-*C*H_3) 2.28 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 11.6 Hz), (tBu) 1.68 (s, 27H), (tBu) 1.56 (s, 9H). Anal. Calcd for $C_{23}H_{41}P_4SO_3F_3$: C, 47.75; H, 7.14. Found: C, 47.65; H, 7.30.

Phosphonium ion 7: ^{31}P NMR ($CDCl_3$) δ 219.3 (d, $^2J_{PP}$ = 4.3 Hz, 3P), 132.6 (q, $^2J_{PP}$ = 4.3 Hz, 1P); ^{13}C NMR ($CDCl_3$) δ

(10) Olah, G. A.; Svoboda, J. J.; Ku, A. T. *Synthesis* **1973**, 492.
(11) Olah, G. A.; Lin, H. C.; Germain, A. *Synthesis* **1974**, 895.

(Ph) 131.4 (d, J_{PC} = 5.3 Hz), (Ph) 130.0 (d, J_{PC} = 3.6 Hz), (Ph) 129.6 (d, J_{PC} = 3.0 HZ), (ipso-C) 124.7 (d, $^2J_{PC}$ = 10.6 Hz), (CF_3) 119.6 (q, $^1J_{CF}$ = 319 Hz), (P^+-CH_2Ph) 47.5 (d, $^1J_{PC}$ = 33.0 Hz), (C_1-CMe_3) 31.9 (m), (C_2-CMe_3) 31.1 (m), (C_1-CMe_3) 24.5 (m), (C_2-CMe_3) 21.6 (pseudoquartet, J_{PC} = 5.5 Hz), (C_1) 13.1 (m), (C_2) −25.7 (m); ^{1}H NMR ($CDCl_3$) δ (Ph) 7.55−7.40 (m, 5H), (P^+-CH_2Ph) 4.88 (d, $^2J_{PH}$ = 10.0 Hz, 2H), (tBu) 1.14 (s, 27H), (tBu) 1.05 (s, 9H). Anal. Calcd for $C_{28}H_{43}P_4SO_3F_3$: C, 52.49; H, 6.76. Found: C, 52.44; H, 7.0.

Phosphonium ion 8: ^{31}P NMR ($CDCl_3$) δ 198.1 (d, $^2J_{PP}$ = 17.1 Hz, 3P), 86.4 (q, $^2J_{PP}$ = 17.1 Hz, 1P); ^{13}C NMR ($CDCl_3$) δ (Ad-C_2) 47.7 (s), (Ad-C_1) 41.2 (d, $^1J_{PC}$ = 41.5 Hz), (Ad-C_4) 35.5 (s), (Ad-C_3) 31.6 (s), (C_1-CMe_3) 32.8 (m), (C_2-CMe_3) 32.0 (m), (C_1-CMe_3) 24.7 (d, $^3J_{PC}$ = 11.1 Hz), (C_2-CMe_3) 21.1 (pseudoquartet, J_{PC} = 5.8 Hz), (C_1) 12.6 (m), (C_2) −20.6 (m); ^{1}H NMR (Ada) 2.10 (br, s), (Ad) 1.64 (br, s), (tBu) 1.23 (s, 27H), (tBu) 1.08 (s, 9H). Anal. Calcd for $C_{30}H_{51}P_4Cl_6Sb$: C, 41.4; H, 5.90. Found: C, 39.3; H, 6.7.

Phosphonium ion 9: ^{31}P NMR ($CDCl_3$) δ 194.5 (d, $^2J_{PP}$ = 18.0 Hz; 3P), 84.2 (q, $^2J_{PP}$ = 18.0 Hz; 1P); ^{13}C NMR ($CDCl_3$) δ (CO) 191.3 (m), (C_1-CMe_2Et) 42.3(m), (C_2-CMe_2Et) 38.3 (m), (C_1-$CMe_2CH_2CH_3$) 36.0 (m), (C_2-$CMe_2CH_2CH_3$) 35.2 (m), (C_1-CMe_2Et) 30.0 (m), (C_2-CMe_2Et) 26.1 (m), (C_1-$CMe_2CH_2CH_3$) 20.9, (C_2-$CMe_2CH_2CH_3$) 16.8 (m), (C_1) 9.0 (m), (COMe) 8.3 (s) (C_2) −18.0 (m); ^{1}H NMR ($CDCl_3$) δ COMe 2.13 (s, 3H), (CH_2) 1.55 (s, 8H), (CH_3) 1.17 (5, 18H), (CH_3) 1.04 (s, 6H), (CH_2CH_3) 0.94 (t, 12H).

Phosphonium ion 11: ^{31}P NMR ($CDCl_3$) δ (P^+-Et) 85.6 (dt, J_{PP} = 22.8 and 9.4 Hz), (2P) 62.4 (pseudotriplet, J_{PP} = 9.9 Hz), (P^+-COMe) 49.0 (dt, J_{PP} = 22.8 and 10.2 Hz); ^{13}C NMR ($CDCl_3$) δ (CO) 182.3 (br, s), (CF_3) 119.1 (q, J_{CF} = 318.5 Hz), (C_1) 69.4 (m), (C_2) 47.1 (m), (C_1-CMe_3) 34.8 (m), (CMe_3) 33.1 (m), (CMe_3) 32.7 (m), (P^+-CH_2) 29.7 (d, $^1J_{PC}$ = 23.3 Hz), (C_1-CMe_3) 28.3 (m), (CMe_3) 26.2 (m), (CMe_3) 24.0 (m), (COMe) 20.6 (s), (C_3) 12.8 (m), (P^+-CH_2CH_3) 8.4 (d, $^2J_{PC}$ = 12.8 Hz); ^{1}H NMR ($CDCl_3$) δ (Et) 3.32 (m, 2H), (COMe) 2.27 (s, 3H), (Et) 1.74 (dt, $^3J_{PH}$ = 23.7 Hz, J_{HH} = 6.7 Hz), (C_1-CMe_3) 1.26 (s, 18H), (CMe_3) 1.17 (s, 9H), (CMe_3) 1.13 (s, 9H).

Phosphonium ion 13: ^{31}P NMR ($CDCl_3$) δ 86.2 (dt, 1P, $^2J_{PP}$ = 22.3 Hz, $^2J_{PP}$ = 8.3 Hz), 61.9 (pseudotriplet, 2P, $^2J_{PP}$ = 9.3 Hz), 49.0 (dt, 1P, $^2J_{PP}$ = 22.3, $^2J_{PP}$ = 10.4 Hz).

Phosphonium ion 14: ^{31}P NMR (FSO_3H·SbF_5/SO_2) δ 170.2 (pseudotriplet, 2P, $^2J_{PP}$ = 11.2 Hz), (P^+-Et) 136.4 (dt, $^2J_{PP}$ = 34.5 Hz, $^2J_{PP}$ = 12.1 Hz), (P^+-H) 81.2 (dt, $^2J_{PP}$ = 34.5 Hz, $^2J_{PP}$ = 10.8 Hz, $^1J_{PH}$ = 467 Hz); ^{13}C NMR (FSO_3H·SbF_5/SO_2) δ (CF_3) 114.8 (q, J_{CF} = 276.5 Hz), (C_1) 39.9 (m), (C_1-CMe_3) 33.1 (m), (CMe_3) 32.5 (m), (CMe_3) 31.7 (m), (P^+-CH_2CH_3) 31.6 (m), (C_1-CMe_3) 24.4 (s), (CMe_3) 23.2 (s), (CMe_3) 21.7 (s), (C_2) 16.1 (m), (C_3) 8.5 (dd, J_{CP} = 26 Hz and 39 Hz), (P^+-CH_2CH_3) 7.6 (d, $^2J_{CP}$ = 6.8 Hz); ^{1}H NMR (FSO_3H·SbF_5/SO_2) δ (P^+-CH_2CH_3) 3.71 (br m), (P^+-CH_2CH_3) 1.92 (dt), (tBu) 1.40 (s, 18H), (tBu) 1.31 (s, 9H), (tBu) 1.27 (s, 9H).

Phosphonium ion 15: ^{31}P NMR (FSO_3H·SbF_5/SO_2ClF) δ 117.0 (dd, 2P, $^2J_{PP}$ = 29.7 and 13.4 Hz), (P^+-H) 114.8 (dt, $^2J_{PP}$ = 29.6 and 13.2 Hz); (P^+-Et) 79.5 (pseudoquartet, J_{PP} = 30.0 Hz); ^{13}C NMR δ (C_1) 61.9 (m) (cage-C) 37.9 (m), (C_1-CMe_3) 36.5 (br,s), (P^+-CH_2-CH_3) 34.5 (m), (CMe_3) 33.6 (br,s), (CMe_3) 33.4 (br, s), (CMe_3) 24.9 (s), (CMe_3) 24.2 (s), (CMe_3) 23.7 (s), (cage-C) 17.4 (m), (P^+-CH_2CH_3) 8.35 (d, $^2J_{CP}$ = 6.8 Hz).

Phosphonium ion 17: ^{31}P NMR (FSO_3H·SbF_5/SO_2ClF) δ 117.2 (2P), 106.7 (1P), 80.3 (pseudoquartet, $^2J_{PP}$ = 33 Hz); ^{13}C NMR δ (C_1) 60.6 (m), (cage-C) 38.1 (m), (C_1-CMe_3) 36.1 (br, s), (CMe_3) 33.1 (m), (CMe_3) 34.2 (m), (CMe_3) 25.9 (s), (CMe_3) 23.7 (s), (CMe_3) 23.4 (s), (P^+-Me) 21.4 (d, $^1J_{CP}$ = 17.6 Hz), (cage-C) 16.0 (m).

Phosphonium ion 18: ^{31}P NMR (FSO_3H·SbF_5/SO_2) δ 26.4 (d, 3P, $^2J_{PP}$ = 91.3 Hz), −33.7 (q, 1P, $^2J_{PP}$ = 91.3 Hz); ^{13}C NMR δ (cage-C) 120.7 (m), (cage-C) 59.9 (m), (CMe_2Et) 47.7 (m), ($CMe_2CH_2CH_3$) 35.8 (m), (CMe_2Et) 25.0 (s), ($CMe_2CH_2CH_3$) 8.2 (s); ^{1}H NMR ($CMe_2CH_2CH_3$) 1.87 (unresolved), (C$Me_2CH_2CH_3$) 1.45 (unresolved), ($CMe_2CH_2CH_3$) 1.07 (unresolved).

Phosphonium ion 19: ^{31}P NMR (FSO_3H·SbF_5/SO_2) δ 63.2 (s, 2P), −38.9 (s, 1P); ^{13}C NMR δ (C_1) 88.4 (m), (C_2) 47.7 (m), (C_2-CMe_3) 41.5 (s), (C_1-CMe_3) 37.6 (m), (C_1-CMe_3) 29.1 (br, s), (C_2-CMe_3) 26.7 (br, s); ^{1}H NMR δ (CMe_3) 1.60 (s, 9H), (CMe_3) 1.25 (s, 27H), (PSH) 5.6 (br, 1H).

Phosphonium ion 20: ^{31}P NMR (FSO_3H·SbF_3/SO_2) δ 68.2 (s, 2P), −33.0 (s, 2P).

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Supplementary Material Available: PM3 structures for **21** and its mono-, di-, tri-, and tetra-P-protonated cations with bond lengths and bond angles shown on the figures; ^{31}P, ^{13}C, and ^{1}H NMR spectra of **6**, **7**, and **11**; ^{31}P and ^{1}H NMR spectra of **8** and **9b** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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