Derivatives of the Phosphaalkyne Tetramer 1,2,5,6-Tetraphosphatricyclo[4.2.0.0^{2,5}]octadiene: Phosphonium Ions of Alkylation (EtOTf) and Acylation ($MeCO^+$ $SbCl_6^-$), and Mono- and Diprotonation with Superacids; Synthesis of the 1-Monooxo, 1-Monothioxo, 1-Tosylimino, and 1,5-Ditosylimino Derivatives†

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Received December 13, 1994®

Tricyclooctadiene **5** reacts with ethyl triflate and acetyl cation hexachloroantimonate at room temperature to give the corresponding P-ethylated and P-acylated phosphonium salts **6** and **8**. P-Adamantylation (with 1-AdCl/$SbCl_5$ complex) is not chemoselective, forming **7** in a mixture. The low temperature protonation of **5** with FSO_3H/SO_2ClF and FSO_3H/SbF_5 (1:1)"magic acid"/SO_2ClF gave the mono- and diphosphonium ions **9** and **10**, respectively. The monooxo and monothioxo derivatives of **5** (**11** and **12**) were prepared by oxygenation with $(TMS)_2O_2$ and sulfuration with S_8/Et_3N, respectively. Finally the Staudinger reaction of **5** with 1 and 2 equiv of *p*-tosyl azide gave the mono- and 1,5-bis(*p*-tosylimino) derivatives **13** and **14**, respectively. Multinuclear NMR data of the resulting compounds are discussed and compared.

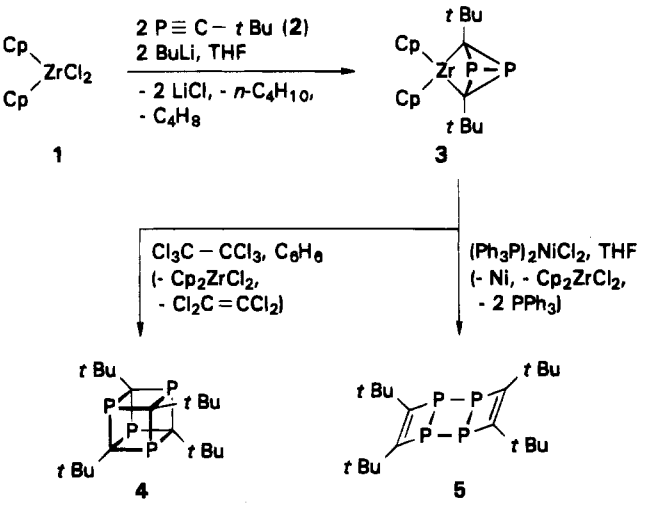
Introduction

The zirconocenephosphaalkyne dimer complex **3**[1] (Scheme 1) is the starting material for chemoselective synthesis of the tetraphosphacubane skeleton **4**[2] and its P-functionalized derivatives.[3] When **3** is gently heated in the presence of $(Ph_3P)_2NiCl_2$ in THF the tricyclooctadiene **5**, another cyclotetramer of **2**, is formed.[4,5] The ^{31}P NMR spectrum of **5** consists of just one resonance at −23.4 ppm (appearing as a singlet); the olefinic carbons appear as a multiplet at 172.4 ppm in the ^{13}C NMR spectrum. The four tBu groups are equivalent; both tBu(C) and tBu(Me) show phosphorus coupling. Finally, the ^1H NMR shows one tBu(Me) singlet at 1.44 ppm. The P/C chemical shifts are dramatically different from those of tetraphosphacubanes which show extremely deshielded phosphorus and a highly shielded cage-C environment[2,6] and appear rather normal for a trivalent-tricoordinated P-center.

The X-ray crystal structure analysis of **5** confirms that it exists in the anti configuration in the solid state.[4,5] Theoretical studies on **5** have also been carried out.[4]

In relation to our previous studies, probing phosphorus reactivity in the tetraphosphacubane skeleton by protonation studies in superacid media and by reaction with various super electrophiles,[7,8] the present article deals with the phosphonium ions derived from **5**[9] and its controlled oxidation to obtain the monoxo-, monothioxo-, and mono- and bis(*p*-tosylimino) derivatives. The NMR characteristics of the resulting phosphonium cations and the oxidized derivatives are compared and discussed.

Scheme 1. Chemoselective Syntheses of 4 and 5 via 3



Results and Discussion

Ethylation (and adamantylation) of 5 (Scheme 2). The ambient temperature reaction of **5** with 1.1 equiv of ethyl triflate leads to the P-ethylated phosphonium triflate **6** (Scheme 2) (ca. 90% conversion by ^{31}P NMR).

† Novel phosphorus cations. Part 3. For Part 2 see reference 8. Organophosphorus compounds. Part 82. For Part 81 see: Veeck, W. G.; Regitz, M. in *Comprehensive Organic Functional Group Transformations*; Moody, C., Ed.; Pergamon: Oxford, 1995; Vol 5, in press.

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® Abstract published in *Advance ACS Abstracts,* May 1, 1995.

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

(4) Geissler, B.; Barth, S.; Bergsträsser, U.; Slany, M.; Durkin, J.; Hitchcock, P. B.; Hofmann, M.; Binger P.; Nixon, J. F.; von Ragué Schleyer, P.; Regitz, M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484.

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

(8) Laali, K. K.; Geissler, B.; Regitz, M.; Houser, J. J. *J. Org. Chem.* **1995**, *60*, 47.

(9) Minor amounts of Ph_3P, the byproduct of **3** → **5** transformation, was present in the sample of **5** used in this study.

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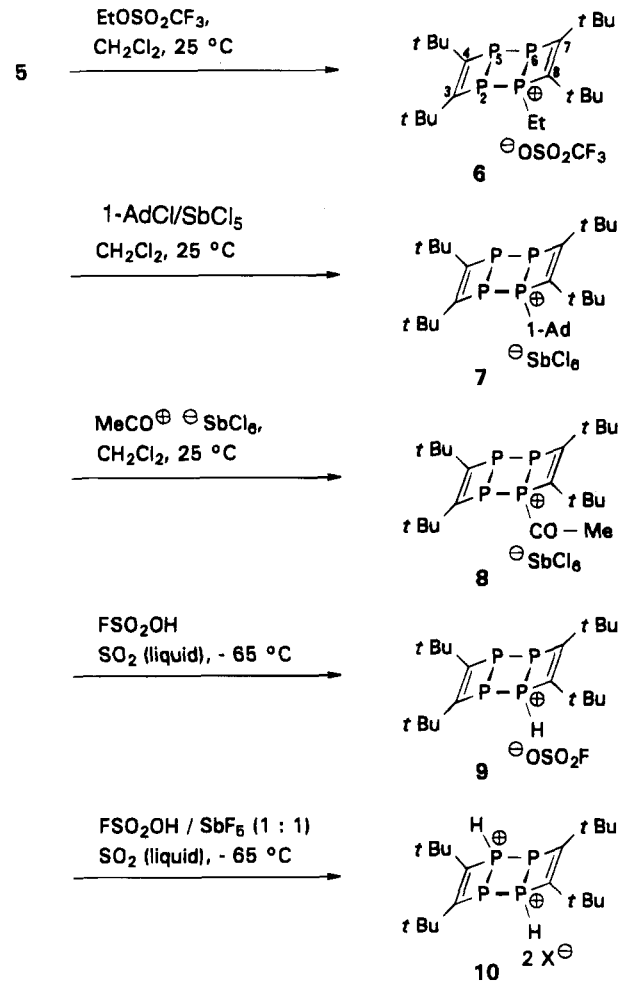
Scheme 2. Reaction of 5 with Super Electrophiles and Superacids



The ^{31}P NMR spectrum of **6** is displayed in Figure 1. It shows four sets of resonances (1P each) for the tricyclooctadiene framework as doublets of doublets of doublets, the most downfield of which at 12.0 ppm is assigned to P^+ (Table 1) (the spectrum also contains two minor singlet absorptions for Ph_3PO at 28.3 ppm (not shown) from oxidation of Ph_3P impurity, its P-ethylated triflate at 6.41 ppm, and unreacted **5**).

The stereochemical dependence of P,P one-bond spin–spin coupling and the influence of the phosphorus lone pair spatial relationship on P,P coupling have been previously discussed.[10,5] The dependence of P,P coupling on the dihedral angle in P_2H_4 has been probed by theory: For a 0° dihedral angle (eclipsed conformation) the P,P coupling is 283 Hz, whereas for a 180° dihedral angle (anti) the coupling is 11 Hz.[10b]

Analysis of the one-bond P,P coupling constants for **6** shows the following trend P-1/P-6 > P-2/P-5 > P-1/P-2. This trend is analogous to those of the 1-oxo-**11** and 1-thioxo derivative **12** and the tosylimino derivative **13** (see Chart 1 and later discussion).

There are four sp^2-hybridized carbon resonances in the ^{13}C NMR spectrum of **6**, all appearing as multiplets due to phosphorus coupling, and four tBu groups.

For the P^+Et group, two multiplets are seen in the ^1H NMR spectrum (at 2.95 and 2.49 ppm). Interestingly, the two-bond P,C is larger than the one-bond P,C coupling in the ^{13}C NMR for the P^+Et group. Thus the Et(Me) is a 4.2 Hz doublet but the Et(CH_2) appears as a singlet.

The phosphonium triflate **6** appears indefinitely stable when refrigerated (^{31}P NMR). A FAB mass spectrum of **6** could be obtained (using sulfolane as matrix). It displayed an intense m/z 429 peak for the cation and fragment ions at m/z 169 (base peak) and 291.

Chemoselective P-adamantylation of **5** with 1-AdCl/$SbCl_5$ complex could not be achieved (Scheme 2). The desired **7** was obtained in ca. 30% yield in a mixture (estimated from ^{31}P NMR).

Phosphonium Ion of Acylation (Scheme 2). The overnight reaction (ca. 15 h) of **5** with 1 equivalent of $MeCO^+$ $SbCl_6^-$ salt changed the colorless solution to brown. The ^{31}P NMR spectrum of the reaction mixture clearly shows the formation of P-acylated salt **8** in ca. 75% yield (with Ph_3PO and Ph_3P^+COMe as byproducts).

Phosphonium salt **8** exhibits four sets of phosphorus resonances as doublets of doublets of doublets, the most downfield of which is at 66.4 ppm assigned to P^+ (Table 1). Analysis of the P,P coupling constants (Chart 1) shows that for **8** the P-2/P-5 coupling is larger than P-1/P-6 coupling. A similar situation is observed for **13** (see later). There are four different sp^2-hybridized carbons in the ^{13}C NMR (between 160–170 ppm), in addition to four tBu(C) and three tBu(Me) resonances. The acetyl carbonyl group appears as a pseudotriplet at 162.2 ppm with its methyl at 22.2 ppm. The acetyl(Me) gives rise to a 0.7 Hz doublet in the ^1H NMR at 2.61 ppm.

The P-acylated salt was also found to be indefinitely stable when kept in a freezer (^{31}P NMR); attempts to observe the intact cation by FABMS were unsuccessful.

Phosphonium Ions of Protonation (Scheme 2 and Chart 1). Addition of a cold solution of FSO_3H/SO_2 to **5** in SO_2 at −78 °C gave an orange-yellow solution whose ^{31}P NMR spectrum (recorded at −80 °C) gave two broad resonances at −38.6 and −39.6 ppm (doublet?). On raising temperature to −65 °C these resonances slowly disappear (within minutes) and are replaced by four well resolved resonances (1P each) for the P-protonated monocation **9** (Table 1) (minor amounts of Ph_3PH^+ are also formed by protonation of Ph_3P byproduct). The most deshielded phosphorus resonances for **9** is at 55.3 ppm assigned to PH^+. Analysis of the P,P coupling for the monophosphonium ion of protonation shows a dramatic increase in P-1,P-6 coupling (406.3 Hz). The P-2/P-5 coupling is now only slightly larger than P-1/P-2 coupling.

The expected four sp^2-hybridized carbon resonances appear between 179–154 ppm. There are two tBu groups in the ^{13}C NMR spectrum. The P^+H can not be seen in the ^1H NMR spectrum.

Compound **5** reacts instantly with $FSO_3H{\cdot}SbF_5$(1:1)/SO_2 at dry ice/acetone temperature to give a yellow-orange solution which slowly polymerizes in the NMR tube. The ^{31}P NMR spectrum of the sample recorded immediately exhibits two phosphorus resonances at −7.0 and −38.9 (2P each). These resonances form an AA'BB' spin system whose appearance is identical with that of the bis(tosylimino)derivative **14** reported below. On this basis these are assigned to the diprotonated dication **10** (40% of the reaction mixture). In addition to these resonances, the ^{31}P NMR shows Ph_3PH^+ (at 10.3 ppm), and a broad featureless envelope between (−45 to −55 ppm). Because of competing polymerization it was not

(10) (a) Allbrand, J. P.; Gagnaire, D.; Robert, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 6498. (b) Allbrand, J. P.; Faucher, H.; Gagnaire, D. *Chem. Phys. Lett.* **1976**, *38*, 521.

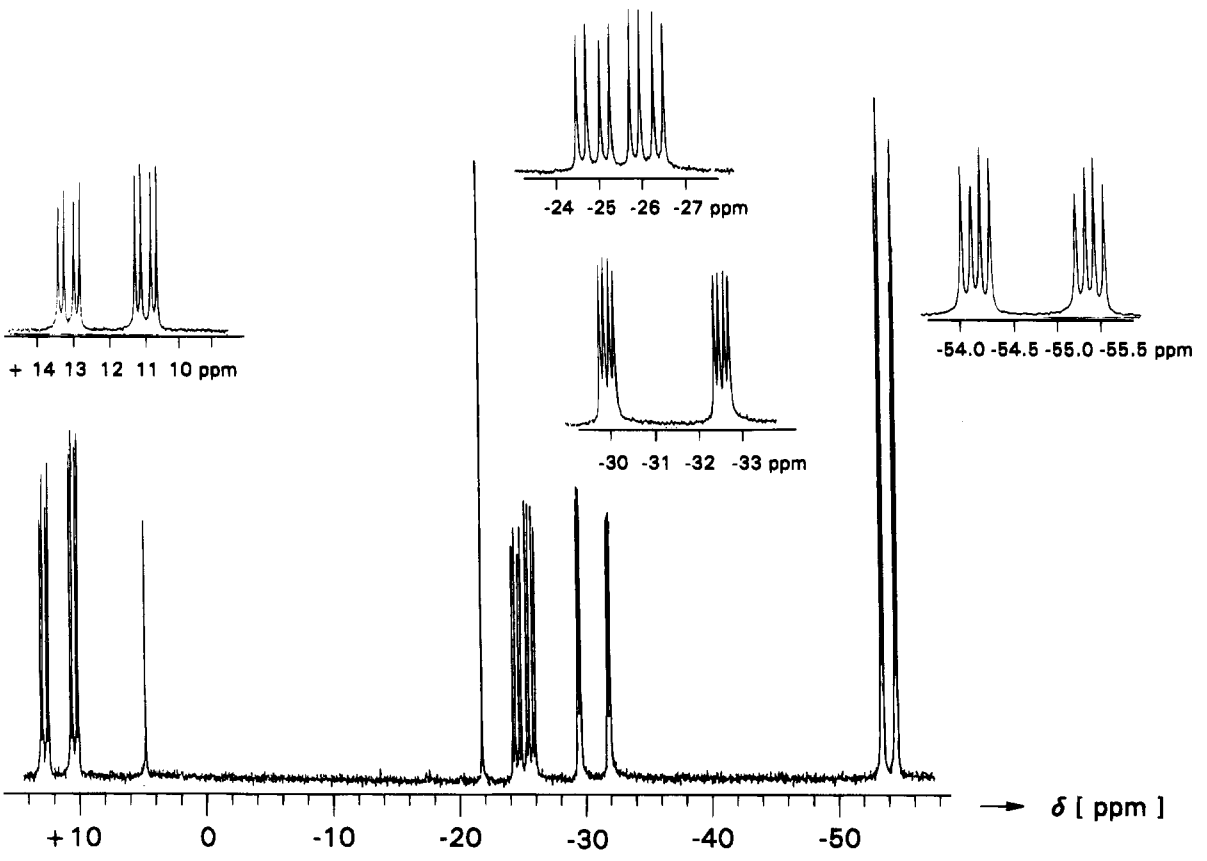


Figure 1. ^{31}P NMR spectrum of **6** in $CDCl_3$.

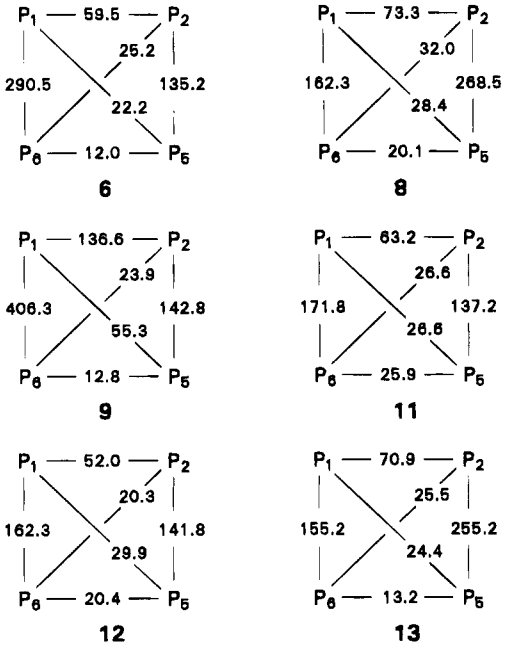
Table 1. Multinuclear NMR Data for the Phosphonium Ions of 5

phosphonium ion	^{31}P NMR	^{13}C NMR	^{1}H NMR
6	+12.0 (ddd; P-1), −25.4 (ddd; P-2), −30.9 (ddd; P-6), −54.8 (ddd; P-5)	179.3 (m), 176.2 (m), 164.8 (m), 154.7 (m), 40.5 (m), 40.3 (m), 39.3 (d, $^{2}J_{PC}$ = 7.2 Hz), 38.8 (d, $^{2}J_{PC}$ = 5.7 Hz), 31.3 (d; 6.0 Hz; 1 tBu (Me)), 30.2-31.0 (m; 3 tBu (Me)), 24.9 (s; $P^{+}CH_2$), 7.7 (d; $^{2}J_{PC}$ = 4.2 Hz, PCH_2CH_3)	2.95 (m; $P^{+}CH_2CH_3$), 2.49 (m; P^{+}-CH_2CH_3), 1.39 (s, 9H), 1.37 (s, 9H), 1.33 (s, 9H), 1.31 (s, 9H)
7	+17.5 (ddd; P-1), −27.0 (ddd; P-2), −48.0 (ddd; P-6), −53.0 (ddd; P-5)		
8	66.4 (ddd; P-1), 23.9 (ddd; P-2), 8.5 (ddd; P-5), −88.7 (ddd; P-6)	169.9 (m), 166.8 (m), 164.4 (m), 162.2 (pseudo-t, $P^{+}COMe$, J_{PC} = 6.6 Hz), 160.2 (m) 39.0 (d; $^{2}J_{PC}$ = 6.8 Hz), 38.5 (s), 38.1 (pseudo-t, J_{PC} = 12.0 Hz), 37.6 (pseudo-t, J_{PC} = 72 Hz), 31.6 (d; $^{3}J_{PC}$ = 3.0 Hz), 31.2 (d; $^{3}J_{P,C}$ = 6.1 Hz),30.7 (s; 2tBu(Me)), 22.2 (s, $P^{+}COMe$)	2.61 (d, 3H; $P^{+}COCH_3$; $^{3}J_{P,H}$ = 0.7 Hz), 1.44 (s, 9H), 1.36 (s, 9H), 1.34 (s, 18H)
9	55.3 (ddd; P-1), 37.3 (dpt; P-2), −9.8 (ddd; P-6), −63.1 (ddd; P-5)	179.2 (m), 177.1 (m), 162.9 (m), 154.1 (m), 41.3 (dd; 11.8 Hz, 4.3 Hz) 40.6 (d; 14.1 Hz); 40.2 (d; 14.7 Hz) 39.2 (d; 9.2 Hz). } CMe_3 30.4 (d; 5.9 Hz; 1 tBu), 30.0 (s; 3 tBu) } CMe_3	1.42 (s, 9H), 1.36 (s, 18H), 1.25 (s, 9H)
10	−7.0 (m, 2 $P^{+}H$), −38.9 (m, 2 P)		

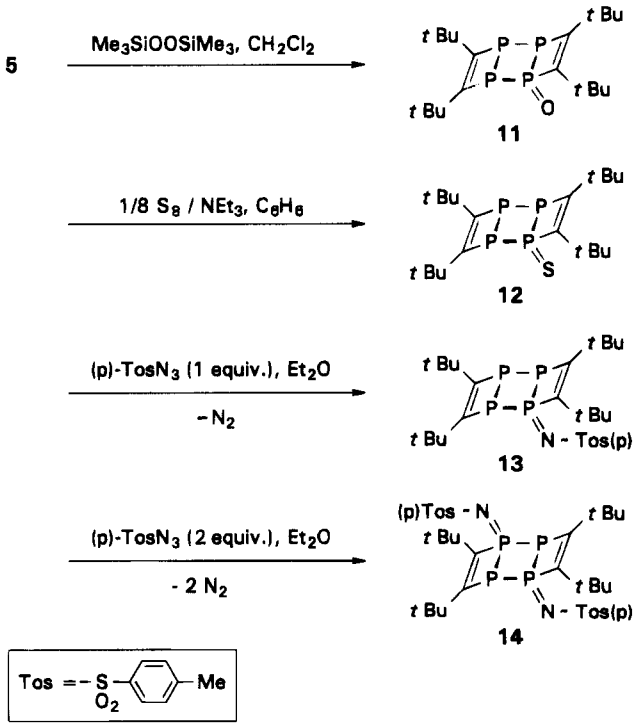
feasible to determine if the broad resonances will disappear on raising temperature.

P-Functionalization of 5 by Controlled Oxidation (Scheme 3). (a) P-Oxygenation (→ 11). Addition of bis(trimethylsilyl) peroxide (1 equiv) to **5** in methylene chloride solvent initially at dry ice/acetone temperature followed by stirring for 48 h at room temperature gave a 90% yield of the monoxo derivative **11** (white crystals) whose ^{31}P NMR spectrum exhibited four distinct phosphorus resonances (1P each) with the oxygen-bearing phosphorus being most deshielded, appearing as a doublet of doublet at 75.3 ppm. Out of the three remaining P centers P2 is most deshielded, appearing as a doublet of pseudotriplet at 12.0 ppm. The largest one-bond P,P coupling is observed for P1/P6 (Chart 1). In the ^{13}C NMR spectrum, there are four sp^2-hybridized carbon resonances appearing as multiplets between 167−162 ppm, four tBu(Me) resonances (all doublets), and four tBu(C)

Chart 1. P–P Coupling Constants for the Phosphonium Cations 6, 8, 9 and the Monofunctionalized Tetraphosphatricyclooctadienes 11–13



Scheme 3. Synthesis of the Monoxo 11, Thioxo 12, Mono-*p*-Tosylimino 13, and 1,5-Bis(*p*-tosylimino) 14 Derivatives of 5



signals, one of which is a doublet of doublet due to one and two bond P,C coupling, and the rest appear as doublets (only one-bond P,C coupling) (see Experimental Section for details).

(b) P-Sulfuration of 5 (→ 12). The utility of sulfur/triethylamine reagent for synthesis of thioxo-derivatives of tetraphosphacubane was previously demonstrated.[3,11,12] In the present study, the room temperature reaction of **5** with S_8/Et_3N (1 equiv) in benzene solvent gave a 70% isolated yield of the monothioxo derivative **12** as a bright yellow powder. Its ^{31}P NMR spectrum exhibited four phosphorus resonances, all as doublet of doublets except for the most upfield resonance (P6) which was a doublet of pseudotriplet. Examination of the one-bond and two-bond P,P couplings show very similar trends in comparison with **11**. In the ^{13}C NMR, the alkene carbons appear as four small low field multiplets between 169–161 ppm. There are four distinct tBu groups all of which show P,C coupling. Thus a two-bond P,C coupling of ca. 14 Hz and a three-bond P,C coupling of ca. 4 Hz are observed (Experimental Section).

(c) *p*-Tosylimino Derivatives 13 and 14 by Staudinger Reaction with *p*-Tosyl Azide. It was shown previously[3,12] that *p*-tosyl azide reacts with tetraphosphacubane **4** to produce a phosphatriazine derivative (the Staudinger product), which loses dinitrogen at elevated temperatures. Double Staudinger reaction could be effected with 1,4-diazidobenzene to give the phenylene-bridged bis(iminophosphorane) derivative of **4**.[3,11,12] With the less reactive alkyl azides, the reaction had to be carried out at elevated temperatures. Under these conditions, *in situ* loss of dinitrogen from the Staudinger product occurred leading to the iminoderivative.

In the present study we find that the phosphatriazine derivative of **5** cannot be isolated in a room temperature reaction with *p*-tosyl azide. Initial addition of 1 equiv of *p*-tosyl azide in ether solvent to **5** in ether and slow warming to room temperature produced the monotosylimino derivative **13** in 85% isolated yield. A similar reaction using 2 equiv of *p*-tosyl azide gave a 60% isolated yield of the 1,5-bis(tosylimino) derivative **14**. The appearance of the ^{31}P NMR spectrum of **13** is very similar to those of **8** and **6**, showing four doublet of doublet of doublet absorptions (1P each). Analysis of the P,P coupling pattern (Chart 1) shows it to be very close to that of the acylated phosphonium cation **8** where the P-2/P-5 coupling is significantly larger than P-1/P-6 coupling.

The ^{31}P NMR spectrum of the bis(tosylimino) derivative **14** consists of two multiplets at 26.6 and −9.1 ppm having characteristic appearance of a AA'BB' spin system, where P-2/P-6 are the AA' and P-1/P-5 are the BB' components. The alkene carbons give rise to two multiplets in the ^{13}C NMR spectrum and there are also two tBu groups; only the tBu(C) resonances show phosphorus coupling (Experimental Section).

Concluding Remarks. We have prepared several derivatives of the novel phosphaalkyne tetramer **5**. The phosphonium salts were prepared by P-alkylation and P-acylation, whereas acidic phosphonium mono- and dications were generated by low temperature protonation in superacid media.

The ^{31}P NMR chemical shift of the phosphonium ions and the ^{13}C NMR of the sp^2-hybridized carbons appear normal. The phosphorus shifts in the phosphonium cations are in range for alkylated or (protonated) phosphines.

Controlled monooxygenation and monosulfuration of **5** have been achieved. The Staudinger reaction allows the mono-*p*-tosylimino and 1,5-bis(*p*-tosylimino) derivatives to be selectively synthesized.

Our studies point to a marked difference in the nature of the P–C bond between the two isomeric phos-

(11) Regitz, M. *Bull. Soc. Chim. Belg.* **1992**, *101*, 359.
(12) Birkel, M. Ph.D. Thesis, University of Kaiserslautern, 1992.

phaalkyne tetramers **4** and **5**. The extreme positions of the cage ^{13}C and ^{31}P resonances observed in **4** and its phosphonium cations[7,8] are no longer seen in **5** and its derivatives. Interestingly, the extreme NMR positions of the cage P/C in **4** diminishes with higher degree of functionalization.[3] Our studies should facilitate further synthetic elaboration of **5**.

Experimental Section

Compound **5** was prepared according to Regitz and coworkers as outlined in Scheme 1.[4] Complete removal of Ph_3P byproduct by repeated sublimation could not be achieved.

EtOTf (Aldrich) was distilled under dry nitrogen prior to use. $MeCO^+$ $SbCl_6^-$ and 1-AdCl/$SbCl_5$ salts were prepared according to Olah et al.[13,14]

FSO_3H (Allied) and SbF_5 (Aldrich) were distilled in an all glass distillation unit under a fast flow of dry nitrogen or argon. Magic acid was freshly prepared as previously described.[7] SO_2 (anhydrous Linde) was used without further purification.

The room temperature reactions were usually carried out in Schlenk pressure tubes under argon.

A GE GN-300 MHz NMR instrument was used to record the NMR data for the phosphonium ions, whereas a Bruker AMX 400 MHz instrument was used for analysis of other products.

Ethylation of 5 (→ 6). Compound **5** (96 mg, 0.24 mmol) was charged into a Schlenk pressure tube under argon and dissolved in dry CH_2Cl_2 (15 mL). Ethyl triflate (43 mg, 0.24 mmol; 0.031 mL) was added directly under argon at rt with efficient magnetic stirring.

The tube was sealed and left to stir at room temperature overnight. The solvent was removed under vacuum, and the colorless residue was washed with hexane. The hexane phase was removed, and the residue was dried under vacuum and dissolved in $CDCl_3$ for NMR analysis. The ^{31}P NMR examination of the hexane wash showed that in most cases only trace amounts of **5** had remained unreacted. The yields were estimated by ^{31}P NMR.

Adamantylation of 5 (→ 7). The substrate (70 mg, 0.175 mmol) was charged into a Schlenk tube under argon and dissolved in methylene chloride (ca. 20 mL). The AdCl–$SbCl_5$ complex (94 mg, 0.2 mmol) was added directly under argon with stirring, and the tube was sealed. The resulting colorless solution was allowed to stir at room temperature for 4 days. Removal of solvent under vacuum gave a viscous oil whose ^{31}P NMR spectrum (Table 1) indicated the formation of **7** (ca. 30% based on integrals) in a complex mixture (with ^{31}P NMR resonances between −90 and +80 ppm). Due to low yield of phosphonium salt **7** purification was not attempted.

Acylation of 5 (→ 8). The substrate (105 mg, 0.262 mmol) was charged into a Schlenk pressure tube under argon and dissolved in methylene chloride (10 mL). The acylating agent (99 mg, 0.262 mmol) was added directly with efficient stirring under argon, whereupon the colorless solution slowly turned brown. The isolation/purification procedure was similar to alkylations.

Characterization of the generated phosphonium ions was by multinuclear NMR (Table 1). In addition, for **6** a FABMS analysis was realized (see Discussion) and for **8** a microanalysis could be obtained after the following purification procedure: The crude product was dissolved in dry chloroform and filtered through celite. The solvent was removed under vacuum, and the residue was dissolved in dry toluene (suspension) and cooled (−20 °C). The solvent was removed via a pipette and the colorless residue washed with hexane and pentane and dried (6 h/10^{-3} mbar). Anal. Calcd for $C_{22}H_{39}OP_4Cl_6Sb$: C, 33.97; H, 5.05. Found: C, 34.7; H, 4.7.

Stable Ion Studies. The procedure for stable ion generation at low temperature was analogous to those already described.[7,8]

Typically, to a slurry of **5** (109 mg, 0.273 mmol) in SO_2 (ca. 1 mL) charged into a 10 mm NMR tube was added a clear solution of either FSO_3H (ca. 1 mL) diluted in SO_2 (ca. 1 mL) or $FSO_3H.SbF_5$ (1:1) "magic acid"/SO_2 (ca. 1 mL each), at dry ice/acetone temperature with vigorous stirring. In both cases yellow-orange solutions were formed on contact. Cold aliquots were transferred directly into 5 mm NMR tubes for immediate NMR studies.

Preparation of 1-Oxo-tetra-*tert*-butyl-1,5-tetraphosphatricyclo[4.2.0.0^{2,5}]octadiene (11). To a solution of **5** (200 mg, 0.5 mmol) in 10 mL of methylene chloride cooled to dry ice/acetone temperature was added a solution of bis(trimethylsilyl) peroxide (90 mg, 0.5 mmol) in the same solvent. The mixture was warmed to rt overnight. After two days stirring, all volatile components were removed under vacuum, the residue was dissolved in dry ether and crystallized at −78 °C (white crystals). Yield: 190 mg (90%). ^{31}P NMR ($CDCl_3$) δ (P1) 75.3 (ddd), (P2) 16.0 (ddd), (P5) 12.0 (dpt), (P6) −105.8 (dpt); ^{13}C NMR ($CDCl_3$) δ 167.3 (m), 167.0 (m), 165.4 (m), 162.2 (m), 39.4 (s), 39.2 (d, $^2J_{PC}$ = 7.6 Hz), 38.0 (d, $^2J_{PC}$ = 12.3), 37.2 (dd, $^2J_{PC}$ = 20.5 Hz, $^3J_{PC}$ = 14.5 Hz), 31.9 (d, $^3J_{PC}$ = 6.9 Hz), 31.7 (d, $^3J_{PC}$ = 4.8 Hz), 31.4 (s), 30.7 (d, $^3J_{PC}$ = 7.8 Hz); ^1H NMR ($CDCl_3$) δ 1.43 (s, 9H), 1.34 (s,9H), 1.33 (s, 9H), 1.32 (s, 9H); MS (70 eV), *m/z* 416 (16.2%, M^+), 278 (70.0%, $M^+ - C_{10}H_{18}$), 231 (41.5%, $M^+ - C_{10}H_{18}PO$), 200 (15.9%, $[(tBuCP)_2]^+$), 185 (9.5%, $[C_{10}H_{18}PO]^+$), 169 (66.8%, $[C_{10}H_{18}P]^+$).

Preparation of Tetra-*tert*-butyl-1-thioxo-1,5-tetraphosphatricyclo[4.2.0.0^{2,5}]octadiene (12). To a solution of **5** (200 mg, 0.5 mmol) in 10 mL of benzene was added sulfur (16 mg, 0.5 mmol) and triethylamine (0.1 mL). After three days stirring at room temperature, the solvent was removed under vacuum and the residue dissolved in pentane/ether (10:1). The product was purified by flash chromatography (silica gel) and crystallized at −78 °C to give a bright yellow powder. Yield: 150 mg (70%). ^{31}P NMR ($CDCl_3$) δ (P1) 32.8 (ddd), (P2) 21.6 (ddd), (P5) 17.5 (ddd), (P6) −85.7 (dpt); ^{13}C NMR ($CDCl_3$) δ 169.0 (m), 166.9 (m), 164.6 (m), 161.4 (m), 39.7 (d, $^2J_{PC}$ = 7.6 Hz), 38.8 (dd, $^2J_{PC}$ = 12.9 Hz, $^3J_{PC}$ = 3.1 Hz), 38.4 (dd, $^2J_{PC}$ = 13.9 Hz, $^3J_{PC}$ = 3.8 Hz), 36.9 (m), 31.1 (d, $^3J_{PC}$ = 7.4 Hz), 30.7 (d, $^3J_{PC}$ = 6.1 Hz), 30.4 (s), 30.3 (d, $^3J_{PC}$ = 9.9 Hz); ^1H NMR ($CDCl_3$) δ 1.50 (s,9H), 1.33 (s,9H), 1.31 (s,9H), 1.30 (s, 9H); IR (KBr) ν 2962 (s), 1460 (m), 1392 (m), 1362 (m), 1262 (s), 1098 (vs), 1024 (vs), 800 (vs); MS (70 eV) *m/z* 432 (28.6%, M^+), 400 (4.5%, $M^+ - S$), 294 (14.1%) $M^+ - C_{10}H_{18}$), 231 (96.7%), $M^+ - C_{10}H_{18}$ PS), 201 (2.8%, $[C_{10}H_{18}PS]^+$), 200 (6.6%), $[(tBuCP)_2]^+$, 169 (100%, $[C_{10}H_{18}P]^+$).

Synthesis of Tetra-*tert*-butyl-1-(*p*-tosylimino)-1,5-tetraphosphatricyclo[4.2.0.0^{2,5}]octadiene (13). To a solution of **5** (200 mg, 0.5 mmol) in ether (10 mL) was added a solution of *p*-tosyl azide (100 mg, 0.5 mol) in 2 mL of ether at 0 °C. The mixture was brought to rt while stirring. After 30 min, the solvent was removed under vacuum. The residue was washed with pentane and the product crystallized from methylene chloride/ether (1:5) at −78 °C to give **13** as a colorless solid (mp = 171 °C). Yield: 240 mg (85%). ^{31}P NMR ($CDCl_3$) δ (P1) 35.6 (ddd), (P2) −7.0 (ddd), (P5) −17.3 (ddd), (P6) −79.3 (ddd); ^{13}C NMR ($CDCl_3$) δ 170.5 (m), 167.8 (m), 165.5 (m), 160.3 (m), (*m*-Ph) 142.0 (s), (*o*-Ph) 140.6 (s), (*p*-Ph) 128.3 (s), (*ipso*-Ph) 125.4 (s), 39.1 (d, $^2J_{PC}$ = 13.5 Hz), 38.8 (d, $^2J_{PC}$ = 15.3 Hz), 37.8 (d, $^2J_{PC}$ = 6.5 Hz), 37.5 (d, $^2J_{PC}$ = 12.0 Hz), 31.2 (s), 30.6 (s), 30.3 (s), 30.2 (s), ($PhCH_3$) 20.8 (s); ^1H NMR ($CDCl_3$) δ (*o*-Ph) 7.69 (d, 2H), (*m*-Ph) 7.04 (d; $^3J_{H,H}$ = 7.5 Hz), ($PhCH_3$) 2.22 (s, 3H), 1.40 (s, 9H), 1.26 (s, 9H), 1.18 (s, 9H), 1.08 (s, 9H); IR (KBr) ν 2956 (s), 1468 (s), 1394 (s), 1295 (s), 1182 (vs), 1127 (vs), 1094 (s); MS (70 eV) *m/z* 569 (6.7%, M^+), 431 (3.0%, $M^+ - C_{10}H_{18}$), 400 (2.4% M^+ − TosN), 293 14.3%, $[C_{10}H_{18}P_4]^+$, 169 (100%, $[C_{10}H_{18}P]^+$. Anal. Calcd for $C_{27}H_{44}NO_2P_4S$: C, 56.93; H, 7.61; N, 2.46. Found: C, 56.7; H, 7.5; N, 2.4.

(13) Olah, G. A.; Svoboda, J. J.; Ku, A. J. *Synthesis* **1973**, 492.

(14) (a) Olah, G. A.; Lin, H. C.; Germain, A. *Synthesis* **1974**, 895. (b) Preparation of carbocation salt 1-Ad^+ SbF_6^- from adamantyl fluoride–SbF_5 has been described in ref 14a. We used the same procedure with some modification for reaction of 1-AdCl with $SbCl_5$ and thought we had obtained 1-Ad^+ $SbCl_6^-$, which we subsequently used for adamantylation reactions (see ref 8). We have since learned that 1-AdCl is not fully ionized with $SbCl_5$; chloroadamantane–$SbCl_5$ complex is formed. We are grateful to one of the reviewers of this paper for pointing this out.

Synthesis of Tetra-*tert*-butyl-1,5-bis(p-tosylimino)-1,5-tetraphosphatricyclo[4.2.0.0^{2,5}]octadiene (14). To a solution of **5** (200 mg, 0.5 mmol) in methylene chloride (10 mL) was added a solution of p-tosylazide (200 mg, 1.0 mmol) in methylene chloride (4 mL) in a Schlenk pressure tube at 0 °C.

The reaction mixture was slowly heated at 90 °C for 3 h followed by stirring at rt for 24 h. The solvent was removed under vacuum and the residue washed with pentane. The product was crystallized from methylene chloride/ether (1:1) at −78 °C. mp = 180 °C. ^{31}P NMR ($CDCl_3$) δ (P1/P5) 26.6 (m), (P2/P6) −9.1 (m); ^{13}C NMR ($CDCl_3$) δ 172.5 (m), 160.4 (m), (*m*-Ph) 142.5 (s), (*o*-Ph) 142.0 (s), (*p*-Ph) 129.6 (s), (*ipso*-Ph) 126.1 (s), 39.6 (m), 38.7 (m), 32.1 (s), 30.9 (s), 21.4 (s); ^{1}H NMR ($CDCl_3$) δ (*o*-Ph) 7.63 (d, 4H), (*m*-Ph) 7.24 (d, 4H, $^3J_{H,H}$ = 8.1 Hz), (CH_3Ph) 2.39 (s, 6H), (tBu) 1.43 (s, 18H), (tBu) 1.25 (s, 18H); IR (KBr): ν 3224 (m), 2965 (s), 2870 (m), 1596 (m), 1472 (m), 1364 (m), 1306 (s), 1150 (vs), 1110 (vs), 1084 (vs), 746 (s); MS (70 eV) *m*/*z* 617 (1.2%, $M^+ - C_7H_7O_2$), 602 (1.0% $M^+ - C_{10}H_{18}$), 585 (4.7%, M^+ − tosyl), 480 (1.3%, $M^+ - C_{10}H_{18}$-$C_7H_7O_2$), 448 (9.2%, $M^+ - C_{10}H_{18}$-tosyl), 400 (3.2%, M^+ − 2 tosylN), 169 (100%, $[tosylN]^+$), 155 (40.4%, $[tosyl]^+$, 91 (94%, $[C_7H_7]^+$. Anal. Calcd for $C_{34}H_{51}N_2O_4P_4S_2$: C, 55.20; H, 6.82; N, 3.79. Found: C, 54.2; H, 6.7; N, 3.9.

Acknowledgment. We thank NATO for partial support and the Ohio academic challenge program for the purchasing funds for the GE GN-300 NMR. We are also grateful to the Fonds der Chemischen Industrie and the Volkswagen-Stiftung for financial support.

JO942090U