Inorg. Chem. **2003**, *42*, 389–397

Reactions of Tris(amino)phosphines with Arylsulfonyl Azides: Product Dependency on Tris(amino)phosphine Structure

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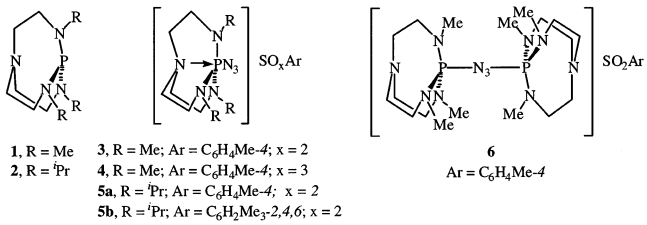
Received August 1, 2002

The Staudinger reaction of $N(CH_2CH_2NR)_3P$ [R = Me (**1**), ^{i}Pr (**2**)] with 1 equiv of $N_3SO_2C_6H_4Me$-4 gave the ionic phosphazides $[\overline{N(CH_2CH_2NR)_3PN_3}][SO_2C_6H_4Me\text{-}4]$ [R = Me (**3**), R = ^{i}Pr (**5a**)], and the same reaction of **2** with $N_3SO_2C_6H_2Me_3$-2,4,6 gave the corresponding aryl sulfinite **5b**. On the other hand, the reaction of **1** with 0.5 equiv of N_3SO_2Ar (Ar = C_6H_4Me-4) furnished the novel ionic phosphazide $\{[N(CH_2CH_2NMe)_3P]_2(\mu\text{-}N_3)\}[SO_2Ar]$ (**6**). Data that shed light on the mechanistic pathway leading to **3** were obtained by low temperature ^{31}P NMR spectroscopy.

A crystal and molecular structure analysis of the phosphazide sulfonate $[\overline{N(CH_2CH_2NMe)_3PN_3}][SO_3C_6H_4Me\text{-}4]$ (**4**), obtained by atmospheric oxidation of **3**, indicated an ionic structure, the cationic part of which is stabilized by a transannular P–N bond. A crystal and molecular structure analysis of **6** also indicated an ionic structure in which the cation features two untransannulated $N(CH_2CH_2NMe)_3P$ cages bridged by an azido group in an $\eta^1{:}\mu{:}\eta^1$ fashion. The reaction of $P(NMe_2)_3$ with N_3SO_2Ar (Ar = C_6H_4Me-4) in a 1:0.5 molar ratio furnished $\{[(Me_2N)_3P]_2(\mu\text{-}N_3)\}[SO_2Ar]$ (**11**) in quantitative yield. On the other hand, the same reaction involving a 1:1 molar ratio of $P(NMe_2)_3$ and N_3SO_2Ar produced a mixture of **11**, $[(Me_2N)_3PN_3][SO_2Ar]$ (**12**), and the iminophosphorane $(Me_2N)_3P{=}NSO_2Ar$ (**10**). In contrast, the bicyclic tris(amino)phosphines $MeC(CH_2NMe)_3P$ (**7**) and $O{=}P(CH_2NMe)_3P$ (**8**) reacted with N_3SO_2Ar (Ar = C_6H_4Me-4) to give the iminophosphorane $MeC(CH_2NMe)_3P{=}NSO_2Ar$ (**14**) (structured by X-ray means) and $O{=}P(CH_2NMe)_3P{=}NSO_2Ar$ (**16**) via the intermediate phosphazides $MeC(CH_2NMe)_3PN_3SO_2Ar$ (**13**) and $O{=}P(CH_2NMe)_3PN_3SO_2Ar$ (**15**), respectively. The variety of products obtained from the reactions of arylsulfonyl azides with proazaphosphatranes (**1** and **2**), acyclic $P(NMe_2)_3$, bicyclic tris(amino)phosphines **7** and **8** are rationalized in terms of steric and basicity variations among the phosphorus reagents.

Introduction

We have been exploring the synthesis and the wide-ranging chemistry of proazaphosphatranes **1**[1] and **2**[2] including reactions of **1** with organic azides RN_3 to form the iminophosphoranes $N(CH_2CH_2NMe)_3P{=}NR'$ (R′ = Ph, CH_2Ph).[3]



1, R = Me
2, R = ^{i}Pr

3, R = Me; Ar = C_6H_4Me-*4*; x = 2
4, R = Me; Ar = C_6H_4Me-*4*; x = 3
5a, R = ^{i}Pr; Ar = C_6H_4Me-*4*; x = *2*
5b, R = ^{i}Pr; Ar = $C_6H_2Me_3$-*2,4,6*; x = 2

6
Ar = C_6H_4Me-*4*

Such iminophosphoranes were shown to act as catalysts in several organic transformations viz., the conversion of aryl isocyanates to isocyanurates[4] and the acylation of alcohols using enolesters.[5] Herein we report the interesting products **3**−**6** obtained in a study of the reactions of **1** and **2** with N_3SO_2R' which was originally aimed at preparing iminophosphoranes of the type $N(CH_2CH_2NR)_3P{=}NR'$ (R = Me, ^{i}Pr; R′ = SO_2Ar, $SiMe_3$). We also compare and contrast our results with those obtained with the bicyclic tris(amino)phosphines **7**[6] and **8**[7] and with the acyclic analogue $P(NMe_2)_3$.

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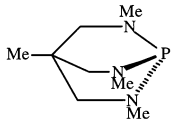
10.1021/ic025920s CCC: $25.00
Published on Web 12/24/2002



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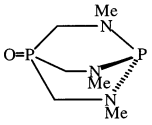

8

Iminophosphoranes prepared by the classical Staudinger reaction involve the combination of a trivalent phosphorus compound with an organic azide. This reaction has been shown to be a two-step process involving the initial electrophilic addition of an azide to a P(III) lone pair followed by dinitrogen elimination from the intermediate phosphazide **A** giving the iminophosphorane **B**.[8]

$$R_3P + N_3R' \rightarrow \underset{\mathbf{A}}{R_3P{=}N{-}N{=}N{-}R'} \rightarrow \underset{\mathbf{B}}{R_3P{=}N{-}R'} + N_2 \quad (1)$$

In numerous instances, the intermediate neutral phosphazide **A** can be isolated,[8] and in a few cases, it has been shown to exist as ionic species **C** that contains the azidophosphonium ion.

$$\underset{\mathbf{C}}{[R_3P{=}N{-}N{=}N]R'}$$

Thus, the unusual ionic salt $[(PhN_3)_2(\mu\text{-}PBu^t_2)][(Me_2N)_2CH]$ was reported to form in the reaction of $Bu^t_2P{-}CH(NMe_2)_2$ with 2 equiv of PhN_3.[9] The novel salt $[Ph_3PN_3C(NH_2)_2]Cl$ was described as a product of the reaction of Ph_3P and $[C(NH_2)_2N_3]Cl$.[10] The ionic compounds $[Ph_3PN_3][SbCl_4]$ and $[(Ph_3P)_2(\mu\text{-}N_3)][SbCl_4]$ were synthesized from PPh_3 and $SbCl_4N_3$ in 1:1 and 1:0.5 molar ratios, respectively.[11] The cationic moieties in these compounds are isostructural with those observed in **3**, **4**, **5a**, **5b**, and **6**, respectively. The reaction of $P(NMe_2)_3$ with Br_2 in the presence of KPF_6 was reported to give $[(Me_2N)_3PBr]PF_6$, which on subsequent reaction with NaN_3 produced $[(Me_2N)_3PN_3]PF_6$.[12] $[(Me_2N)_3PN_3]Cl$ was shown to form in the reaction of $P(NMe_2)_3$, CCl_4, and trimethylsilyl azide.[13] Azidophosphonium salts can also be synthesized by alkylation of neutral phosphazides (**A**) at the terminal nitrogen atom with Et_3OBF_4 in a regiospecific manner.[14] The X-ray structure for one such salt, namely $[(R_2N)_3P{-}N{=}N{-}N(Et)Ar]BF_4$ [$R_2 = -(CH_2)_2O(CH_2)_2-$; Ar = $C_6H_2(NO_2)_3$-2,4,6], has been reported.[14b]

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Experimental Section

All reactions were carried out under argon. Solvents were distilled by standard procedures prior to use,[15] and the following compounds were prepared by published methods: $P(NMeCH_2CH_2)_3N$ (**1**),[3b] $P(NPr^iCH_2CH_2)_3N$ (**2**),[2] $MeC(CH_2NMe)_3P$ (**7**),[6] $O{=}P(CH_2NMe)_3P$ (**8**),[7] 4-toluenesulfonyl azide,[16] 2,4,6-trimethylbenzenesulfonyl azide,[17] and the triamine $MeC(CH_2NMeH)_3$ [18] that was used to prepare **7**. It may be noted that **1** and **2** are available from Aldrich. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected. Electrospray ionization (ESI) and electron impact (EI) ionization mass spectral analyses were performed on a Finnigan TSQ700 triple quadrupole mass spectrometer fitted with a Finnigan ESI interface or Finnigan EI/CI ion source. Elemental analyses were performed in the Instrument Services Laboratory of the Chemistry Department at Iowa State University. It may be noted that the carbon analyses for **3**, **4**, and **6** are somewhat low, but attempts to improve these analyses by further purification were not successful. We have had the same problem with carbon analyses of other phosphorus azide compounds. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian VXR 400 or a VXR 300 NMR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM-200 or a VXR 400 NMR spectrometer using 85% H_3PO_4 as the external standard. X-ray data collections and structure solutions were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using SHELXTL-Plus and SHELXL-93 programs.

Synthesis of $[N(CH_2CH_2NMe)_3PN_3][SO_2C_6Me\text{-}4]$ (3). 4-Toluenesulfonyl azide (1.11 g, 5.62 mmol) was dissolved in acetonitrile (10 mL). To this solution was added dropwise an acetonitrile (20 mL) solution of freshly sublimed **1** (1.11 g, 5.11 mmol). The reaction mixture was allowed to stir for 5 h, and then, solvent was removed under reduced pressure to give a white solid contaminated with a small amount of 4-toluenesulfonyl azide. Diethyl ether (10 mL) was added to the mixture, which was then stirred and filtered. The ether-insoluble colorless material was dried under reduced pressure to give **3** in quantitative yield. Mp 120−121 °C. ^{31}P NMR (CD_3CN): δ −32.2 (s). ^1H NMR (CD_3CN): δ 2.30 (s, $C_6H_4CH_3$-4, 3 H), 2.84 (d, CH_3, $^3J(PH) = 12.8$ Hz, 9 H), 3.13 (m, CH_2N_{ax}, 6 H), 3.20 (m, CH_2N_{eq}, 6 H), 7.26 (m, C_6H_4, 4 H). ^{13}C NMR (CD_3CN): δ 21.19 (s, $C_6H_4CH_3$-4, 1 C), 37.87 (d, CH_3, $^2J(PC) = 3.5$ Hz, 3 C), 46.14 (d, CH_2N_{ax}, $^2J(PC) = 8.30$ Hz, 3 C), 46.41 (d, CH_2N_{eq}, $^3J(PC) = 9.70$ Hz, 3 C), 125.25, 129.23, 138.01, 159.26 (s, C_6H_4, 6 C). ESI-MS (*m*/*z*): 257.9 (cation of **3**), 155.9 (anion of **3**). Anal. Calcd for $C_{16}H_{28}N_7O_2PS{\cdot}H_2O$: C, 44.54; H, 7.01; N, 22.72; S, 7.43. Found: C, 43.92; H, 7.29; N, 22.56; S, 7.48%.

^{31}P NMR Detection of 3′. To a solution of **1** (0.02 mmol) in CD_3CN (0.7 mL) in a 5 mm NMR tube at −30 °C was added excess 4-toluenesulfonyl azide (0.06 mmol). After briefly shaking the NMR tube, five sets of 10 ^{31}P NMR spectral scans were taken at −30 °C at the following time intervals. The first 10 spectra were acquired at 60 s intervals, the second set at 300 s intervals, the third set at 600 s intervals, the fourth at 1200 s intervals, and the fifth at 1800 s intervals. Three hundred seconds were required to acquire each ^{31}P NMR spectrum.

Synthesis of $[N(CH_2CH_2NMe)_3PN_3][SO_3C_6H_4Me\text{-}4]$ (4). Slow diffusion of diethyl ether into an acetonitrile solution of **3** over a

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period of two weeks in the presence of atmospheric oxygen gave **4** in quantitative yield. Mp 135−136 °C. ^{31}P NMR (CD_3CN): δ −32.1 (s). ^{1}H NMR (CD_3CN): δ 2.31 (s, $C_6H_4CH_3$-4, 3 H), 2.83 (d, CH_3, ^3J(PH) = 13.2 Hz, 9 H), 3.11 (m, CH_2N_{ax}, 6 H), 3.19 (m, CH_2N_{eq}, 6 H), 7.35 (m, C_6H_4, 4 H). ^{13}C NMR (CD_3CN): δ 20.30 (s, $C_6H_4CH_3$-4, 1 C), 36.97 (d, CH_3, ^2J(PC) = 3.7 Hz, 3 C), 45.22 (d, CH_2N_{ax}, ^2J(PC) = 8.20 Hz, 3 C), 45.50 (d, CH_2N_{eq}, ^3J(PC) = 9.20 Hz, 3 C), 125.72, 128.28, 138.39, 146.15 (s, C_6H_4, 6 C). ESI-MS (*m*/*z*): 258.1 (cation of **4**), 171.9 (anion of **4**). Anal. Calcd for $C_{16}H_{28}N_7O_3PS$: C, 44.75; H, 6.57; N, 22.83; S, 7.47. Found: C, 44.28; H, 7.00; N, 22.12; S, 7.44%.

Synthesis of [N(CH$_2$CH$_2$N^{i}Pr)$_3$PN$_3$][SO$_2$C$_6$H$_4$Me-4] (5a). Compound **2** (1.34 g, 4.46 mmol) and 900 mg (4.56 mmol) of 4-toluenesulfonyl azide were dissolved in diethyl ether (30 mL) in separate flasks. The ether solution of the azide was added to the ether solution of **2**, which resulted in the immediate formation of a white precipitate. The reaction mixture was stirred for an additional 12 h, and then, the precipitate was filtered off, washed with pentane (5 mL), and dried under reduced pressure to give **5a** in 68% yield (1.50 g, 3.01 mmol). Mp 105−106 °C. ^{31}P NMR: δ −26.4 (CD_3CN), −33.0 (C_6D_6), −30.8 (THF), −26.0 (CD_3OD) all singlets. ^{1}H NMR (CD_3CN): δ 1.16 (d, CH_3, ^3J(HH) = 6.72 Hz, 18 H), 2.37 (s, $C_6H_4CH_3$-4, 3 H), 2.94 (m, CH_2N_{ax}, 6 H), 3.08 (m, CH_2N_{eq}, 6 H), 3.96 (m, C*H*, 3 H), 7.34 (m, C_6H_4, 4 H). ^{13}C NMR (CD_3CN): δ 21.96 (s, $C_6H_4CH_3$-4, 1 C), 22.13 (d, CH_3, ^3J(PC) = 4.27 Hz, 6 C), 37.20 (d, CH_2N_{ax}, ^2J(PC) = 8.81 Hz, 3 C), 49.15 (d, CH_2N_{eq}, ^3J(PC) = 10.14 Hz, 3 C), 50.78 (m, *C*H, 3 C), 128.96, 130.41, 139.94, 143.78 (s, C_6H_4, 6 C). ESI-MS (*m*/*z*): 342 (cation of **5a**), 155 (anion of **5a**). Several attempts to obtain satisfactory elemental analysis values were unsuccessful.

Synthesis of [N(CH$_2$CH$_2$N^{i}Pr)$_3$PN$_3$][SO$_2$C$_6$H$_2$Me$_3$-2,4,6] (5b). This compound was prepared from **2** (1.05 g, 3.48 mmol) and 2,4,6-trimethylbenzenesulfonyl azide (0.792 g, 3.51 mmol) by a procedure analogous to that used for **5a**. Yield: 76% (1.40 g). Mp 149−150 °C. ^{31}P NMR (CD_3CN): δ −21.9 (s). ^{1}H NMR (CD_3CN): δ 1.17 (d, CH_3, ^3J(HH) = 6.72 Hz, 18 H), 2.17 (s, $C_6H_4CH_3$-4, 3 H), 2.54 (s, $C_6H_2(CH_3)_2$-2,6, 6 H), 2.96 (m, CH_2N_{ax}, 6 H), 3.09 (m, CH_2N_{eq}, 6 H), 3.97 (m, C*H*, 3 H), 6.63 (s, C_6H_2, 2 H). ^{13}C NMR (CD_3CN): δ 18.81 (s, $C_6H_2(CH_3)_2$-2,6, 2 C), 21.03 (s, $C_6H_2CH_3$-4, 1 C), 21.73 (d, CH_3, ^3J(PC) = 5.05 Hz, 6 C), 36.79 (d, CH_2N_{ax}, ^2J(PC) = 8.42 Hz, 3 C), 48.63 (d, CH_2N_{eq}, ^3J(PC) = 10.11 Hz, 3 C), 50.42 (s, *C*H, 3 C), 130.38, 131.12, 135.81, 136.92 (s, C_6H_2, 6 C). ESI-MS (*m*/*z*): 342 (cation of **5b**), 184 (anion of **5b**). Several attempts to obtain satisfactory elemental analysis values were unsuccessful.

Synthesis of {[N(CH$_2$CH$_2$NMe)$_3$P]$_2$(μ-N$_3$)}[SO$_2$C$_6$H$_4$Me-4] (6). Freshly sublimed **1** (1.38 g, 6.39 mmol) was dissolved in acetonitrile (10 mL). To this solution was slowly added an acetonitrile (20 mL) solution of 4-toluenesulfonyl azide (0.630 g, 3.18 mmol), and then, the reaction mixture was stirred for 5 h. The solvent was removed under reduced pressure to give an oily material that was further dried under reduced pressure for 12 h to give a foamy solid. The solid was transferred into another flask containing diethyl ether (10 mL), and the mixture was stirred. Diethyl-ether-soluble material was removed by filtration, and the insoluble material was dried under reduced pressure to give **6** in 73% yield (1.47 g). A spectroscopically pure sample was obtained by vapor diffusion of ether or pentane into an acetone solution of **6**. Mp 132−133 °C. ^{31}P NMR (CD_3CN): δ 37.5 (s). ^{1}H NMR (CD_3CN): δ 2.29 (s, $C_6H_4CH_3$-4, 3 H), 2.65 (d, CH_3, ^2J(PH) = 8.4 Hz, 18 H), 2.77 (m, CH_2N_{ax}, 6 H), 2.92 (m, CH_2N_{eq}, 6 H), 7.25 (m, C_6H_4, 4 H). ^{13}C NMR (CD_3CN): δ 21.27 (s, $C_6H_4CH_3$-4, 1 C), 35.65 (s, CH_3, 6 C), 50.25 (s, CH_2N_{ax}, 6 C), 51.69 (s, CH_2N_{eq}, 6 C), 125.32, 129.22, 137.81, 159.78 (s, C_6H_4, 6 C). ESI-MS (*m*/*z*): 474 (cation of **6**), 155 (anion of **6**). Anal. Calcd for $C_{25}H_{49}N_{11}O_2P_2S$: C, 47.68; H, 7.84; N, 24.47; S, 5.09. Found: C, 46.79; H, 8.05; N, 24.56; S, 5.11%.

Synthesis of {[(Me$_2$N)$_3$P]$_2$(μ-N$_3$)}[SO$_2$C$_6$H$_4$Me-4] (11). $P(NMe_2)_3$ (0.340 g, 2.08 mmol) was slowly added to 4-toluenesulfonyl azide (0.210 g, 1.04 mmol) which had been dissolved in acetonitrile (10 mL). The reaction mixture was stirred for 5 h, and then, acetonitrile was removed under reduced pressure to give **11** as an oil in quantitative yield. ^{31}P NMR (C_6D_6): δ 42.0 (s). ^{1}H NMR (CD_3CN): δ 2.30 (s, $C_6H_4CH_3$-4, 3 H), 2.68 (d, CH_3, ^3J(PH) = 9.32 Hz, 36 H), 7.26 (m, C_6H_4, 4 H). ^{13}C NMR (CD_3CN): δ 21.84 (s, $C_6H_4CH_3$-4, 1 C), 37.92 (d, CH_3, ^2J(PC) = 2.66 Hz, 12 C), 128.85, 129.75, 138.38, 160.0 (s, C_6H_4, 6 C). ESI-MS: 368 (cation of **11**), 155 (anion of **11**). Anal. Calcd for $C_{19}H_{43}N_9O_2P_2S\cdot(1/3)\,H_2O$: C, 43.09; H, 8.31; N, 23.80. Found. C, 42.66; H, 8.40; N, 23.16%.

Although the reaction of $P(NMe_2)_3$ with N_3SO_2Ar (Ar = C_6H_4-Me-4) was reported to give $(Me_2N)_3PN_3SO_2Ar$ (**9**) and $(Me_2N)_3P{=}NSO_2Ar$ (**10**),[19] we repeated this reaction on an NMR scale using CD_3CN as the solvent. The CD_3CN (0.5 mL) solution of 4-toluenesulfonyl azide (67.0 mg, 340 μmol) was syringed into a CD_3CN (0.5 mL) solution of $P(NMe_2)_3$ (49.0 mg, 300 μmol), and the mixture was briefly shaken. The NMR (^{31}P, ^{1}H, and ^{13}C) spectroscopic data for the reaction mixture showed three species, namely, $(Me_2N)_3P{=}NSO_2Ar$ (**10**), $(Me_2N)_3P(\mu\text{-}N_3)P(NMe_2)_3]O_2SAr$ (**11**), and $[(Me_2N)_3PN_3]SO_2Ar$ (**12**) (see Results and Discussion section). Proton-coupled ^{31}P NMR and ^{31}P−^{1}H COSY NMR spectra were utilized to assign unambiguously the peak positions for **10**−**12**. ^{31}P NMR (CD_3CN): δ 25.8, 38.7, and 42.5 (singlets for **10**, **12**, and **11**, respectively). ^{1}H NMR (CD_3CN): δ 2.37 (s, $C_6H_4CH_3$-4, 9 H, **10**, **11** and **12**), 2.56 (d, CH_3, ^3J(PH) = 9.32 Hz, 18 H, **10**), 2.69 (d, CH_3, ^3J(PH) = 9.30 Hz, 36 H, **11**), 2.78 (d, CH_3, ^3J(PH) = 11.00 Hz, 18 H, **12**), 7.32 (m, C_6H_4, 12 H, **10**, **11**, **12**). The intensity ratio of **10**:**11**:**12** was 0.86:0.46:1.00. ^{13}C NMR (CD_3CN): δ 21.55 (s, $C_6H_4CH_3$-4, 3 C, **10**, **11**, **12**), 37.11, 37.22, 37.37 (br, CH_3, 24 C, **10**, **11**, **12**), 128.39, 128.52, 128.61, 129.91, 130.01, 130.55, 131.33, 137.24, 139.58, 143.31 (s, C_6H_4, **10**, **11**, **12**). To this reaction mixture was added a solution of 4-toluenesulfonyl azide (53.0 mg, 270 μmmol) in CD_3CN (0.5 mL), and the mixture was briefly shaken. The ^{31}P NMR spectrum of the NMR tube contents showed an increase in the intensity of a peak corresponding to **11** (42.5 ppm) with complete disappearance of the peak corresponding to **12** (38.7 ppm). The intensity of the peak corresponding to **10** (25.8 ppm) remained unaffected. The origin of a new peak at 62.95 ppm remains unclear at this time.

Synthesis of MeC(CH$_2$NMe)$_3$PN$_3$SO$_2$C$_6$H$_4$Me-4 (13). Separate solutions of **7** (305 mg, 1.63 mmol) and 4-toluenesulfonyl azide (340 mg, 1.72 mmol) dissolved in diethyl ether (15 mL) were made. The ether solution of the azide was added to the ether solution of **7** leading to the immediate formation of a white precipitate. The reaction mixture was stirred for an additional 12 h, and then, the precipitate was filtered off, washed with pentane (5 mL), and dried under reduced pressure to give **13** in quantitative yield. Mp 109−110 °C. ^{31}P NMR ($CDCl_3$): δ 34.9 (s). ^{1}H NMR ($CDCl_3$): δ 0.96 (s, $C_{bridgehead}$-CH_3, 3 H), 2.39 (s, $C_6H_4CH_3$-4, 3 H), 2.47 (d, CH_3, ^3J(PH) = 12.0 Hz, 9 H), 3.12 (d, CH_2, ^3J(PH) = 6.04 Hz, 6 H), 7.51 (m, C_6H_4, 4 H). ^{13}C NMR ($CDCl_3$): δ 20.68 (s, $C_{bridgehead}$-CH_3, 1 C), 21.51 (s, $C_6H_4CH_3$-4, 1 C), 36.17 (d, $C_{bridgehead}$, ^3J(PC) = 30.33 Hz, 1 C), 36.74 (d, CH_3, ^2J(PC) = 2.65 Hz, 3 C), 63.03 (d, CH_2, ^2J(PC) = 1.13 Hz, 3 C), 128.51, 129.09, 136.01, and

(19) Martin, G. J.; Sanchez, M.; Marre, M.-R. *Tetrahedron Lett.* **1983**, *24*, 4989−92.

143.26 (s, C_6H_4, 6 C). Anal. Calcd for $C_{15}H_{25}N_6O_2PS$: C, 46.87; H, 6.55; N, 21.86; S, 8.34. Found: C, 46.53; H, 6.95; N, 21.56; S, 8.47%.

A $CDCl_3$ (0.5 mL) solution of 4-toluenesulfonyl azide (25.0 mg, 0.127 mmol) was syringed into an NMR tube containing a $CDCl_3$ (0.5 mL) solution of **7** (52.0 mg, 0.28 mmol). The tube was briefly shaken and kept at room temperature for 12 h. The ^{31}P NMR spectrum indicated the presence of unreacted **7** and formation of $MeC(CH_2NMe)_3P{=}NSO_2C_6H_4Me$-4 (**14**) (see next paragraph).

Synthesis of $MeC(CH_2NMe)_3P{=}NSO_2C_6H_4Me$-4 (14). Compound **13** (0.200 g, 0.520 mmol) was dissolved in dichloromethane (5 mL), and the solution was allowed to stir for 12 h. The solvent was removed under reduced pressure to give **14** as a white solid in quantitative yield. Single crystals were grown by slow diffusion of pentane into a dichloromethane solution of **14** over a period of several days. Mp 148 °C. ^{31}P NMR ($CDCl_3$): δ 16.7 (s). ^1H NMR ($CDCl_3$): δ 0.91 (s, $C_{bridgehead}-CH_3$, 3 H), 2.38 (s, $C_6H_4CH_3$-4, 3 H), 2.71 (d, CH_3, $^3J(PH) = 13.2$ Hz, 9 H), 3.08 (d, CH_2, $^3J(PH) = 6.84$ Hz, 6 H), 7.53 (m, C_6H_4, 4 H). ^{13}C NMR ($CDCl_3$): δ 20.96 (d, $C_{bridgehead}-CH_3$, $^4J(PC) = 1.52$ Hz, 1 C), 21.38 (s, $C_6H_4CH_3$-4, 1 C), 35.20 (d, $C_{bridgehead}$, $^3J(PC) = 31.85$ Hz, 1 C), 37.18 (d, CH_3, $^2J(PC) = 1.51$ Hz, 3 C), 63.14 (s, CH_2, 3 C), 125.64, 128.85, 142.98, and 143.06 (s, C_6H_4, 6 C). EI-MS: 356 (molecular ion). Anal. Calcd for $C_{15}H_{25}N_4O_2PS$: C, 50.55; H, 7.07; N, 15.72; S, 9.00. Found; C, 50.33; H, 7.11; N, 15.60; S, 8.99%.

Preparation of $O{=}P(CH_2NMe)_3P{=}NSO_2C_6H_4Me$-4 (16). Solutions of **8** (87.0 mg, 420 μmol) and 87.0 mg (440 μmol) of 4-toluenesulfonyl azide in CD_3CN (1.0 mL) were created in separate NMR tubes. The CD_3CN solution of *4*-toluenesulfonyl azide was slowly added to the CD_3CN solution of **8**. The ^{31}P NMR spectrum recorded immediately after mixing showed complete disappearance of signals due to **8**, and new peaks appeared at δ 33.0 (d, $C_3P{=}O$, $^3J(PP) = 116.6$ Hz) and 26.19 [d, $(N)_3PN_3$, $^3J(PP) = 116.6$ Hz]. These signals are presumably due to the phosphazide $O{=}P(CH_2NMe)_3PN_3SO_2C_6H_4Me$-4 (**15**). Slow precipitation was noticed after ca. 0.5 h, and so, the reaction mixture was occasionally shaken and monitored by ^{31}P NMR spectroscopy while storing at ambient temperature. The formation of **16** was complete after ca. 3 days. The solid was filtered, washed with diethyl ether, and dried under reduced pressure to give iminophosphorane, **16**, in 61% yield (96.0 mg). Analytically pure material was obtained by vapor diffusion of ether into a chloroform solution of **16**. Mp 263−264 °C. ^{31}P NMR (CD_3CN): δ 3.07 (d, $N_3P{=}N$, $^3J(PP) = 114.6$ Hz), 33.10 (d, $C_3P{=}O$, $^3J(PP) = 114.6$ Hz). ^1H NMR ($CDCl_3/CD_3CN$): δ 2.28 (s, $C_6H_4CH_3$-4, 3 H), 2.75 (dd, CH_3, $^3J(PH) = 4.60$ Hz; $^4J(HH) = 0.95$ Hz, 9 H), 3.48 (dd, CH_2, $^2J(PH) = 9.52$ Hz; $^3J(PH) = 8.32$ Hz, 6 H), 7.39 (m, C_6H_4, 4 H). ^{13}C NMR ($CDCl_3/CD_3CN$): δ 21.02 (s, $C_6H_4CH_3$-4, 1 C), 38.69 (s, CH_3, 3 C), 49.08 (d, NCH_2, $^1J(PC) = 60.28$ Hz, 3 C), 125.17, 128.83, 141.30, and 142.23 (s, C_6H_4, 6 C). ESI-MS: 377 ($\mathbf{16} + H)^+$. Anal. Calcd for $C_{13}H_{22}N_4O_3P_2S$: C, 41.48; H, 5.89; N, 14.89; S, 8.52. Found: C, 41.33; H, 5.94; N, 14.85; S, 8.50%.

The deuterio-acetonitrile-soluble material showed the presence of two compounds by ^{31}P NMR spectroscopy. However, complete characterization of these decomposition products was not carried out. ^{31}P NMR (CD_3CN): δ 30.0, 7.35 [d, $^3J(PP) = 112.31$ Hz, major component], 32.3, 4.00 [d, $^3J(PP) = 112.31$ Hz, minor component].

X-ray Crystallographic Determinations. Crystals of **4** and **14** were selected from oil under ambient conditions whereas a crystal of **6** was selected under ambient conditions. The former crystals were attached to the tip of a glass capillary and were mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam using a video camera. Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with a diffractometer-to-crystal distance of 5.08 cm. The crystal of **6** was mounted directly and was centered in the X-ray beam using a video camera. Crystal evaluation and data collection for this crystal were performed on a Bruker CCD-1000 diffractometer with a diffractometer-to-crystal distance of 5.08 cm. The initial cell constants for crystals of **4** and **6** were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about ω with an exposure time of 20 and 10 s per frame, respectively. For the crystals of **6**, the initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 30 frames at intervals of 0.3° in a 10° range about ω with an exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The final cell constants were calculated from a set of 6697 (**4**), 6528 (**6**), and 4640 (**14**) strong reflections from the actual data collection.

The data were collected using the hemisphere data collection routine, and the data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[20,21] A summary of crystallographic data (including unit cells and refinement data for each of the structure analyses) appears in Table 1.

Results and Discussion

Reactions of Proazaphosphatranes with Arysulfonyl Azides. Reactions of **1** with N_3SO_2Ar (Ar = 4-tolyl) produced **3** in quantitative yield, while **2** with N_3SO_2Ar (Ar = 4-tolyl or mesityl) gave **5a** and **5b** in 68% and 76% yield, respectively (Scheme 1). These compounds are stable to air and moisture for brief periods. However, prolonged exposure to solvents that were not deaerated causes oxidation of the counter anion SO_2Ar^- to SO_3Ar^- as can be seen from the formation of **4** from **3**. Compound **5a** did not lose dinitrogen in toluene even under reflux conditions, and it decomposed into unidentified products upon heating a neat sample at 170 °C. It is interesting to note that the structurally related phosphazide $PhN_3P(NMeCH_2CH_2)_3N$ decomposed to the iminophosphorane $PhN{=}P(NMeCH_2CH_2)_3N$ on prolonged heating.[3b] From our aforementioned observations, we believe compounds **3**, **4**, **5a**, and **5b** are ionic species that are thermally stable owing to the presence of a transannular P—N bond for which evidence will be presented.

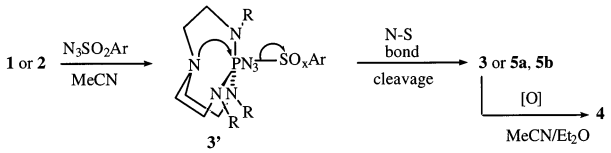
The reaction of **1** with 4-toluenesulfonyl azide was monitored in a low temperature ^{31}P NMR experiment to gain some insight on the nature of the intermediate produced during the formation of **3**. When compound **1** was allowed to react with excess of 4-toluenesulfonyl azide in CD_3CN at −30 °C, two ^{31}P NMR resonances [δ ^{31}P 37.5 (major) and −32.2 (minor)] were observed with no evidence of the resonance corresponding to **1**. The intensity of the resonance at 37.5 ppm decreased over time with a concomitant increase in the intensity of the peak at −32.2 ppm. Upon completion of the reaction, only the −32.2 ppm resonance was observed,

(20) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.
(21) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 1. Crystal Data and Structure Refinement for **4**, **6**, and **14**

empirical formula	$C_{16}H_{29}N_7O_{3.5}PS$ (**4**)	$C_{25}H_{49}N_{11}O_2P_2S$ (**6**)	$C_{15}H_{25}N_4O_2PS$ (**14**)
fw	438.49	629.75	356.42
T	173(2) K	173(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
unit cell dimensions	$a = 10.7246(5)$ Å $b = 13.0474(6)$ Å $c = 15.5374(7)$ Å $\alpha = 73.3363(10)°$ $\beta = 84.5807(10)°$ $\gamma = 85.4542(10)°$	$a = 16.2643(8)$ Å $b = 13.5572(7)$ Å $c = 13.9512(7)$ Å $\beta = 91.7620(10)°$	$a = 12.6710(6)$ Å $b = 10.6922(5)$ Å $c = 13.3279(7)$ Å $\beta = 105.3497(10)°$
V	2070.40(16) Å^3	3074.8(3) Å^3	1741.26(15) Å^3
Z	4	4	4
density (calcd)	1.407 Mg/m^3	1.360 Mg/m^3	1.360 Mg/m^3
abs coeff	0.270 mm^{-1}	0.254 mm^{-1}	0.293 mm^{-1}
F(000)	932	1352	760
cryst size, mm^3	0.50 × 0.50 × 0.10	0.2 × 0.3 × 0.6	0.50 × 0.40 × 0.40
θ range for data collection	1.37−26.37°	1.96−28.27°	2.48−26.37°
index ranges	$-13 \le h \le 13$, $-15 \le k \le 16$, $0 \le l \le 19$	$-21 \le h \le 21$, $-15 \le k \le 17$, $-18 \le l \le 15$	$-15 \le h \le 15$, $0 \le k \le 13$, $0 \le l \le 16$
reflns collected	18192	24643	15353
indep reflns	8043 [*R*(int) = 0.0287]	7150 [*R*(int) = 0.0372]	3562 [*R*(int) = 0.0190]
completeness to $\theta = 26.37°$	99.1%	93.9%	99.9%
abs correction	empirical with DIFABS	empirical	empirical with SADABS
max and min trans	0.9735 and 0.8770	1 and 0.88	0.8920 and 0.8675
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	8043/2/530	7150/0/377	3562/0/213
GOF on F^2	1.061	0.947	1.014
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0420, wR2 = 0.1187	R1 = 0.0435, wR2 = 0.1059	R1 = 0.0381, wR2 = 0.1006
R indices (all data)	R1 = 0.0595, wR2 = 0.1267	R1 = 0.0758, wR2 = 0.1151	R1 = 0.0417, wR2 = 0.1032
largest diff. peak and hole	0.419 and −0.336 e Å^{-3}	1.024 and −0.365 e Å^{-3}	0.350 and −0.487 e Å^{-3}

Scheme 1



the upfield position of which suggests that the final product **3** possesses a five-coordinate transannulated structure. The presence of a transannulated P−N bond in **4** was subsequently confirmed by X-ray means (see below). The reaction between **1** and 4-toluenesulfonyl azide at ambient temperature is complete within 5 min. Only at −30 °C is this process sufficiently slow for ^{31}P NMR monitoring, and from these experiments, it is reasonable to conclude that the ^{31}P resonance at 37.5 ppm represents the structure of the intermediate **3′** in Scheme 1. This ^{31}P NMR chemical shift is comparable to those assigned to $PhN_3P(MeNCH_2CH_2)_3N$ (δ ^{31}P 38.1)[3b] and $(Me_2N)_3PN_3SO_2C_6H_4Me$-4 (**9**, δ ^{31}P 36.2, see later).[19] The downfield position of the ^{31}P NMR resonance for **3′** is also consistent with the absence of a transannular P−N bond in this species. The formation of **3** from **3′** is believed to result from S_N2 transannular attack of the bridgehead nitrogen lone pair on the phosphorus accompanied by subsequent cleavage of the N−S bond (Scheme 1).

The ESI-MS technique has been shown to be a valuable tool for detecting transient intermediates in reactions of phosphines,[22] and the ionic nature of **3**, **4**, **5a**, and **5b** was supported by these spectra. Thus, compounds **3** and **4** showed a peak at $m/z = 258$ for the $[N(CH_2CH_2NMe)_3PN_3]^+$ fragment and at $m/z = 155.9$ and 171.9 for the $[SO_2Ar]^-$ and $[SO_3Ar]^-$ (Ar = C_6H_4Me-4) fragments, respectively. Compounds **5a** and **5b** showed a peak at $m/z = 342$ for the $[N(CH_2CH_2N^iPr)_3PN_3]^+$ fragment and $m/z = 155$ and 184 for the $[SO_2C_6H_4Me\text{-}4]^-$ and $[SO_2C_6H_2Me_3\text{-}2,4,6]^-$ fragments, respectively. The ^{31}P NMR spectra of **3**, **4**, **5a**, and **5b** displayed strongly upfield shifted signals (δ ^{31}P −20 to −32 in CD_3CN) indicating the strong possibility of P−N transannular bonding. Interestingly, **5a** showed a rather solvent dependent ^{31}P NMR chemical shift (δ ^{31}P −26.0 in CD_3OD, −26.4 in CD_3CN, −30.8 in THF, and −33.0 in C_6D_6). ^{1}H and ^{13}C NMR data for the cation of **3** and **4** are very close to those observed for the cation in transannulated $[N(CH_2CH_2NMe)_3PCl][O_2PCl_2]$.[1b] The ^{1}H NMR spectrum for the anion of **3** and **4** exhibited a singlet and a multiplet for C*H*$_3$ and the aryl protons, respectively. Both the ^{1}H and

(22) Wilson, S. R.; Perez, J.; Pasternak, A. J. *Am. Chem. Soc.* **1993**, *115*, 1994−97.

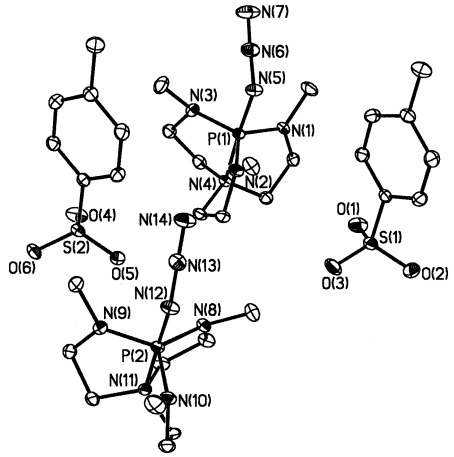


Figure 1. Computer drawing of the molecular structure of **4**. Two molecules per asymmetric unit have been shown, and hydrogen atoms have been omitted for clarity.

Table 2. Pertinent Bond Distances (Å) and Bond Angles (deg) for **4**

molecule 1	molecule 2
P(1)−N(2) 1.662(2)	P(2)−N(9) 1.661(2)
P(1)−N(1) 1.665(2)	P(2)−N(10) 1.672(2)
P(1)−N(3) 1.675(2)	P(2)−N(8) 1.681(2)
P(1)−N(5) 1.767(2)	P(2)−N(12) 1.764(2)
P(1)−N(4) 1.940(2)	P(2)−N(11) 1.945(2)
N(5)−N(6) 1.225(2)	N(12)−N(13) 1.229(2)\
N(6)−N(7) 1.134(3)	N(13)−N(14) 1.138(2)
N(2)−P(1)−N(1) 121.35(9)	N(9)−P(2)−N(10) 119.85(9)
N(2)−P(1)−N(3) 118.97(9)	N(9)−P(2)−N(8) 121.59(9)
N(1)−P(1)−N(3) 118.67(9)	N(10)−P(2)−N(8) 117.50(9)
N(2)−P(1)−N(5) 90.80(8)	N(9)−P(2)−N(12) 95.03(9)
N(1)−P(1)−N(5) 93.49(8)	N(10)−P(2)−N(12) 90.66(8)
N(3)−P(1)−N(5) 95.76(9)	N(8)−P(2)−N(12) 94.51(8)
N(2)−P(1)−N(4) 86.98(8)	N(9)−P(2)−N(11) 85.80(8)
N(1)−P(1)−N(4) 85.68(7)	N(10)−P(2)−N(11) 87.55(8)
N(3)−P(1)−N(4) 87.37(8)	N(8)−P(2)−N(11) 84.40(8)
N(5)−P(1)−N(4) 176.77(8)	N(12)−P(2)−N(11) 178.21(8)
C(3)−N(4)−P(1) 107.4(1)	C(23)−N(10)−P(2) 124.0(2)
C(9)−N(4)−P(1) 106.1(1)	C(19)−N(11)−P(2) 106.5(1)
C(6)−N(4)−P(1) 106.6(1)	C(25)−N(11)−P(2) 105.5(1)
N(6)−N(5)−P(1) 124.3(2)	C(22)−N(11)−P(2) 107.4(1)
N(7)−N(6)−N(5) 173.8(2)	N(13)−N(12)−P(2) 123.2(2)
	N(14)−N(13)−N(12) 173.8(2)

^{13}C NMR data for compounds **5a** and **5b** are also consistent with transannulated structures.

The molecular structure of **4** is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The cation consists of a phosphorus center with a distorted trigonal bipyramidal geometry. The azido group and the axial ring nitrogen N4 (or N11 in molecule 2) occupy apical positions while the ring nitrogens N1, N2, and N3 (or N8, N9, and N10 in molecule 2) occupy equatorial positions. The geometry at N4 (or N11 in molecule 2) is quite tetrahedral, which is consistent with a transannular P—N bond (1.943-(2) Å, the average of this length in molecules 1 and 2). As expected from previous studies of azaphosphatranes, the apical P—N distances are longer than the equatorial P—N bond lengths, and these distances in the phosphatrane cage of **4** are comparable to those found in $[N(CH_2CH_2NMe)_3PCl][PCl_6]$.[1b] The N5—N6 distance in **4** [1.223(2) Å] is closer to a N=N distance (1.17−1.25 Å) while the N6—N7 distance [1.134(3) Å] is closer to an N≡N distance (1.0976 Å).[23] The geometry at N3 in molecule 1 deviates slightly from planarity (angle sum = 351.97°) while those of N1 and N2 are quite planar (angle sums = 358.48° and 359.59°, respectively). However, in molecule 2, N9 maintains a planar geometry (angle sum = 359.87°) while those at N8 and N10 deviate slightly from planarity (angle sums = 353.56° and 353.75°, respectively). The azido fragment is nearly linear in both molecules 1 and 2. The torsion angle involving P1, N5, N6, and N7 in molecule 1 is 5.6°, and in molecule 2, it is −178.5°.

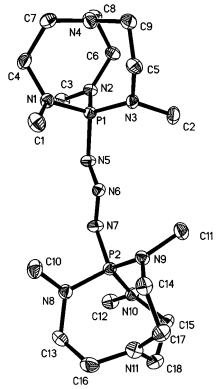
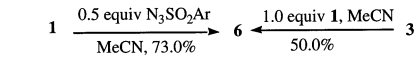


Figure 2. Computer drawing of the molecular structure of **6**. The anionic part is not shown, and hydrogen atoms have been omitted for clarity.

Scheme 2



Compound **3** upon reaction with 1 equiv of **1** gave $\{[N(CH_2CH_2NMe)_3P]_2(\mu\text{-}N_3)\}[SO_2C_6H_4Me\text{-}4]$ (**6**) in 50% yield (Scheme 2). Compound **6** can be prepared in higher yield (73%) by the reaction of **1** with 0.5 equiv of 4-toluenesulfonyl azide (Scheme 2). Compound **6** is a hygroscopic yellow solid, soluble in acetone and acetonitrile, but insoluble in hexanes and diethyl ether. ESI-MS data for **6** indicate that the structure is ionic with peaks at $m/z = 474$ and 155 attributable to $\{[N(CH_2CH_2NMe)_3P]_2(\mu\text{-}N_3)\}^+$ and $[SO_2C_6H_4Me\text{-}4]^-$ fragments, respectively. The ^{31}P NMR spectrum of **6** showed a resonance at 37.5 ppm which is comparable to those observed for $\{[Me_2N)_3P]_2(\mu\text{-}N_3)\}[SO_2C_6H_4Me\text{-}4]$ (**11**, δ ^{31}P 42.0, see later) and the tris-(azidophosphine)cyclohexyl derivative, *cis*-1,3,5-$X_3C_6H_9$−(X = $N_3P(MeNCH_2CH_2)N$, δ ^{31}P 37.1),[24] which was recently reported from our laboratories. Not unexpectedly, δ ^{31}P for **6** is shifted upfield relative to **1** (δ ^{31}P 120.8),[3b] but the substantially positive magnitude of the chemical shift for **6** is consistent with the absence of a transannular P−N bond which was confirmed by X-ray means, as we now discuss.

The molecular structure of **6** is shown in Figure 2, and selected bond lengths and angles are given in Table 3. To our knowledge, this structure represents the first structured example of an azido-bridged-bis-trialkylaminophosphonium salt. The cationic fragment consists of two $N(CH_2CH_2\text{-}NMe)_3P$ units with an azido group bridging the phosphorus atoms in an $\eta^1{:}\mu{:}\eta^1$ fashion. The geometry at the phosphorus

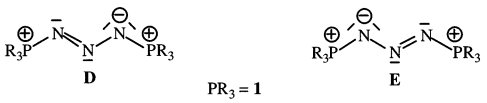
(23) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed; Butterworth and Heinenmann: Oxford, 1998.
(24) Liu, X.; Zhang, G.; Verkade, J. G. *Tetrahedron Lett.* **2001**, *42*, 4449−51.

Table 3. Pertinent Bond Distances (Å) and Bond Angles (deg) for **6**

P(1)−N(2) 1.630(2)	P(2)−N(4) 1.945(2)
P(1)−N(3) 1.635(2)	P(2)−N(10) 1.636(2)
P(1)−N(1) 1.643(2)	P(2)−N(8) 1.638(2)
P(1)−N(5) 1.649(2)	P(2)−N(7) 1.669(2)
P(2)−N(9) 1.631(2)	N(5)−N(6) 1.322(2)
P(1)−N(4) 1.940(2)	N(6)−N(7) 1.298(2)
N(2)−P(1)−N(3) 111.42(9)	C(6)−N(2)−P(1) 121.3(1)
N(2)−P(1)−N(1) 110.64(9)	C(3)−N(2)−P(1) 121.4(1)
N(3)−P(1)−N(1) 110.30(9)	C(2)−N(3)−P(1) 119.6(1)
N(2)−P(1)−N(5) 102.19(8)	C(5)−N(3)−P(1) 122.5(1)
N(3)−P(1)−N(5) 112.68(9)	N(6)−N(5)−P(1) 117.1(1)
N(1)−P(1)−P(5) 109.36(9)	N(7)−N(6)−N(5) 111.5(2)
N(9)−P(2)−N(10) 113.28(9)	N(6)−N(7)−P(2) 117.8(1)
N(9)−P(2)−N(8) 112.16(9)	C(10)−N(8)−P(2) 119.1(1)
N(10)−P(2)−N(8) 111.29(9)	C(13)−N(8)−P(2) 121.3(1)
N(9)−P(2)−N(7) 111.85(9)	C(11)−N(9)−P(2) 120.5(1)
N(10)−P(2)−N(7) 101.68(8)	C(14)−N(9)−P(2) 121.2(1)
N(8)−P(2)−N(7) 105.88(9)	C(15)−N(10)−P(2) 120.9(1)
C(1)−P(1)−N(1) 119.30(1)	C(12)−N(10)−P(2) 120.8(1)

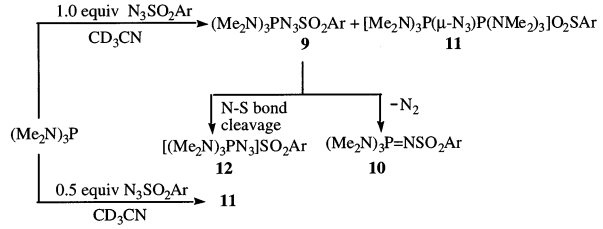
atoms is distorted tetrahedral while the geometries at the bridgehead nitrogens N4 (angle sum = 359.80°) and N11 (angle sum = 358.21°) are nearly planar as is also the case at the remaining ring nitrogens N1 (357.05°), N2 (359.80°), N3 (357.51°), N8 (356.86°), N9 (356.73°), and N10 (356.62°). The average ring P−N distance [1.635(2) Å] is slightly longer than that observed in the R_2N−P moieties in $[(R_2N)_3P{-}N{=}N{-}N(Et)Ar]BF_4$ [$R_2 = -(CH_2)_2O(CH_2)_2-$; Ar = $C_6H_2(NO_2)_3$-2,4,6; av distance = 1.619(1) Å][14b] but shorter than the corresponding distance [1.667(2) and 1.671(2) Å for molecules 1 and 2, respectively] observed in **4**. The P1−N5 distance in **6** of 1.649(2) Å is slightly shorter than the P2−N7 distance [1.669(2) Å]. Interestingly, no transannular P−N bond [P1−N4 = 2.964(2) Å; P2−N11 = 2.835(2) Å] was observed within the cage moieties of **6**.

Because the solution ^{31}P NMR spectrum of **6** exhibited only one peak and the NCH_3 and the NCH_2 fragments from both cages showed identical ^1H and ^{13}C NMR signals, the cage moieties are likely to be in the same untransannulated conformation in solution as they are in the solid state. The PN_3P fragment of **6** adopts a W shape as expected on the basis of its Lewis structure and the bond angles at N5, N6, and N7 [117.1(1), 111.5(2), and 117.8(1)°, respectively]. The P1−N5−N6−N7 and P2−N7−N6−N5 torsion angles are 179.0° and 177.6°, respectively, with a mean plane between these aforementioned torsion angles that suggests near planarity of the PN_3P fragment. The N5−N6 [1.322(2) Å] and N6−N7 [1.298(2) Å] distances are shorter than a N−N single bond (1.43−1.75 Å) but longer than a N=N double bond (1.17−1.25 Å).[23] Because the P1−N5 and P2−N7 distances involving the exocyclic nitrogens are within experimental error of their respective P−N bond distances involving the endocyclic nitrogens, and as just noted the N−N distances in the azido moiety are somewhat shorter than N−N single bond, the resonance structures shown in **D** and **E** would appear to be the major contributors. These resonance



structures are consistent with the bond lengths in the PN_3P framework and also with the aforementioned PNN bond angles which are indicative of sp^2 bonding at the PN nitrogens. The 111.5(2)° bond angle at the central nitrogen seems somewhat unexpectedly narrow, however.

Scheme 3

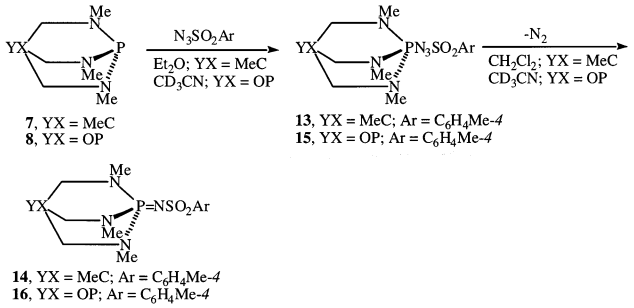


Reactions of $P(NMe_2)_3$with 4-Toluenesulfonyl Azide. In the previous section, we proposed that compound **3** could be formed from **3′** by cleavage of an N−S bond assisted by the formation of a transannular P−N bond which stabilizes the N_3 fragment in **3**. If this hypothesis is correct, then the acyclic analogue of **1**, $P(NMe_2)_3$, upon reaction with a stoichiometric amount of N_3SO_2Ar (Ar = C_6H_4Me-4), could be expected to give the covalent phosphazide $(Me_2N)_3PN_3$-SO_2Ar (**9**, δ ^{31}P 36.2) which would lose N_2 to give the iminophosphorane $(Me_2N)_3P{=}NSO_2Ar$ (**10**, δ ^{31}P 25.3) as was reported by others.[19] However, when we reacted $P(NMe_2)_3$ with 1 equiv of 4-toluenesulfonyl azide, we obtained an oil whose ^{31}P NMR spectrum showed three singlets (δ ^{31}P 42.5, 38.7, and 25.8) which we assign to $\{[(Me_2N)_3P]_2(\mu\text{-}N_3)\}[SO_2Ar]$ (**11**), $[(Me_2N)_3PN_3][SO_2Ar]$ (**12**), and $(Me_2N)_3P{=}NSO_2Ar$ (**10**), respectively (Scheme 3). The assignments of these resonances are based on proton-coupled ^{31}P and $^{31}P-^1H$ COSY NMR measurements, as well as on their reactivity with added $P(NMe_2)_3$. Thus, when another equivalent of $P(NMe_2)_3$ was added to the reaction mixture containing **10**, **11**, and **12**, the intensity of the resonance corresponding to **11** increased, the intensity of the peak assigned to **12** decreased, and the intensity of the resonance corresponding to **10** remained unaffected. Thus, it can be concluded that **11** and the intermediate **9** were formed initially, although the latter compound was not detected. Compound **11** was independently prepared in quantitative yield by reacting $P(NMe_2)_3$ with 0.5 equiv of 4-toluenesulfonyl azide (Scheme 3).

It may be noted that the ^{31}P chemical shift of **12** (δ ^{31}P 38.7) is comparable to that observed for $[(Me_2N)_3PN_3]Cl$ (δ ^{31}P 37.8)[13] but is much further downfield relative to **3** (δ ^{31}P −32.2). This large difference is clearly due to the absence of an opportunity for transannulunar P−N bonding in **12**. Compound **11** is a hygroscopic yellow oil whose ESI-mass spectrum featured peaks at m/z = 368 and 155 for the $\{[(Me_2N)_3P]_2(\mu\text{-}N_3)\}^+$ and $[SO_2C_6H_4Me\text{-}4]^-$ fragments, respectively.

Reactions of $YX(CH_2NMe)_3P$ with 4-Toluenesulfonyl Azide. It is apparent that for tris(amino)phosphines, the formation of a transannular P−N bond is not a requirement for stabilizing an azidophosphonium ion. We therefore suspected that the basicities of untransannulated **1** and **2**, and of acyclic $P(NMe_2)_3$, are sufficiently similar to permit N−S bond cleavage in **3′** and **9** to give **3** and **12**, respectively. Hence, we decided to react 4-toluenesulfonyl azide with tris-

Scheme 4



7, YX = MeC
8, YX = OP

13, YX = MeC; Ar = C_6H_4Me-*4*
15, YX = OP; Ar = C_6H_4Me-*4*

14, YX = MeC; Ar = C_6H_4Me-*4*
16, YX = OP; Ar = C_6H_4Me-*4*

(amino)phosphines **7** and **8** in Scheme 4 which have no possibility for transannular bonding, possess a bicyclic structure akin to **1** and **2**, and, yet, contain less basic tricoordinate phosphorus sites.[25] Reaction of **7** with 4-toluenesulfonyl azide in diethyl either instantly gave the covalent intermediate phosphazide $MeC(CH_2NMe)_3PN_3SO_2C_6H_4Me$-4 (**13**) as a white solid in quantitative yield (Scheme 4). A CH_2Cl_2 solution of **13** upon stirring at ambient temperature for 12 h gave iminophosphorane **14** in quantitative yield. Phosphazide **13** is soluble in $CHCl_3$ and CH_2Cl_2, but it is insoluble in ether and pentane and decomposed into unidentified species upon storing in an CH_3CN solution. Bicyclic aminophosphine **8** reacted within 30 min of mixing with 1 equiv of 4-toluenesulfonyl azide in CD_3CN to give the covalent intermediate phosphazide **15** as detected by ^{31}P NMR spectroscopy (see below). Phosphazide **15** was transformed to the corresponding iminophosphorane **16** in 69% yield after 3 days in CD_3CN, from which **16** precipitated (Scheme 4). The more sluggish rate of decomposition of **15** to its corresponding iminophosphorane **16** compared with that of **13** to **14** may be attributed to the lower basicity of the bicyclic phosphorus moiety in **15** as a consequence of the presence of the OP group which is expected to be more electron withdrawing than the MeC group in **13**. Compound **16** is a colorless crystalline material, soluble in $CHCl_3$ and CH_2Cl_2 but insoluble in CD_3CN. Attempts to synthesize $[(R_3P)_2(\mu\text{-}N_3)][SO_2C_6H_4Me\text{-}4]$ (R_3P = **7** or **8**), a structural analogue of **6** and **11**, were not successful. For example, compound **7** upon reaction with 0.5 equiv of 4-toluenesulfonyl azide in diethyl ether gave **13** in 50% yield with unreacted **7** remaining in solution. Compound **8** upon reaction with 0.5 equiv of 4-toluenesulfonyl azide in CD_3CN produced a complex mixture.

The ESI-mass spectrum of **13** showed peaks at $m/z = 357$ and 356 corresponding to the iminophosphorane (**14** + H and **14**) indicating a rapid decomposition of **13** to **14** under mass spectral conditions. Compound **16** showed a peak at $m/z = 377$ corresponding to $(\mathbf{16} + H)^+$. The ^{31}P NMR spectrum of **13** showed a singlet at 34.87 ppm which is comparable to that observed for $MeC(CH_2NMe)_3PN_3Ph$ (δ ^{31}P 33.7).[25] On the other hand, compound **15** showed a doublet at 26.19 ppm for the $(\rangle N)_3PN_3$ moiety due to coupling with the $O{=}PC_3$ phosphorus. The ^{31}P NMR chemical shift for **14** (δ ^{31}P 16.7) compares well with that reported for the iminophosphorane $MeC(CH_2NMe)_3P{=}NPh$ (δ ^{31}P 11.5).[25]

(25) Kroshefsky, R. D.; Verkade, J. G. *Inorg. Chem.* **1975**, *14*, 3090−95.

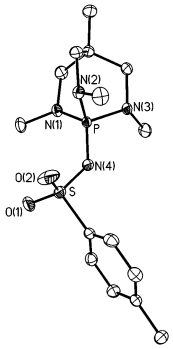


Figure 3. Computer drawing of the molecular structure of **14**. Hydrogen atoms have been omitted for clarity.

Table 4. Pertinent Bond Distances (Å) and Bond Angles (deg) for **14**

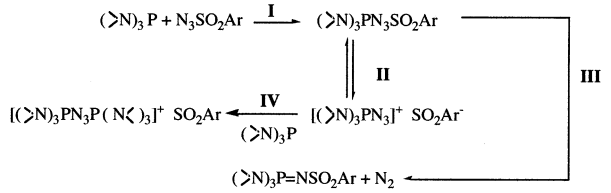
P−N(4)	1.570(1)	P−N(3)	1.651(1)
P−N(1)	1.640(1)	C(1)−N(1)−P	124.4(1)
P−N(2)	1.645(1)	C(2)−N(1)−P	112.9(1)
N(4)−P−N(1)	115.62(8)	C(3)−N(2)−P	120.0(1)
N(4)−P−N(2)	116.71(8)	C(4)−N(2)−P	111.3(1)
N(1)−P−N(2)	105.10(7)	C(5)−N(3)−P	120.9(1)
N(4)−P−N(3)	109.90(8)	C(6)−N(3)−P	110.8(1)
N(1)−P−N(3)	104.63(7)	P−N(4)−S	131.6(1)
N(2)−P−N(3)	103.58(7)		

Compounds **15** and **16** showed large $^3J(PP)$ spin−spin couplings of 116.6 and 114.6 Hz, respectively, due to the coupling with the P═O phosphorus. These values are much higher than that observed for **8** [$^3J(PP) = 14.03$ Hz].[7] Interestingly, the $^3J(PC)$ couplings involving the bridgehead carbon of **13** and **14** are 30.33 and 31.85 Hz, respectively. A similarly large $^3J(PC)$ value was also observed for structurally related compounds of the type $MeC(CH_2NMe_3)_3$-PX [X = lone pair (25.9 Hz), X = O (30.8 Hz), S (25.4 Hz), and Se (24.4 Hz)][26] and also for the tris(iminophosphine)cyclohexyl derivative, *cis*-1,3,5-$C_9H_9X_3$ [X = N═$P(NMeCH_2)_3CMe$; $^3J(PC) = 26.97$ Hz].[27] These substantial $^3J(PC)$ couplings observed for **13** and **14** and the $^3J(PP)$ couplings observed for **15** and **16** can be associated with their bicyclic structures which provide three through-bond coupling pathways for the bridgehead atoms.

The molecular structure of **14** is shown in Figure 3, and selected bond lengths and angles are given in Table 4. The geometry at the phosphorus atom is distorted tetrahedral with NPN angles varying from 103.58(7)° to 116.71(8)°. The average P−N distance involving the cage nitrogens [1.645(1) Å] is comparable to that observed in $(Me_2N)_3P{=}NH$ (av P−N = 1.666(1) Å)[28] but is significantly longer than that observed in $MeC(CH_2NMe_3)_2P{=}O$ (av P−N = 1.590(8) Å).[29] The exocyclic P−N4 distance in **14** [1.570(1) Å] is also comparable with that observed for the P═N link in $(Me_2N)_3P{=}NH$ [P−N = 1.557(1) Å].[28] The degree of deviation from planarity for the cage nitrogens in **14** is perhaps somewhat more pronounced (angle sums around N1,

(26) Kroshefsky, R. D.; Verkade, J. G. *Phosphorus Sulfur Relat. Elem.* **1979**, *6*, 397−403.
(27) Liu, X.; Thirupathi, N.; Zhang, G.; Guzei, I. A.; Verkade, J. G. To be published.
(28) Mitzel, N. W.; Lustig, C. *J. Chem. Soc., Dalton Trans.* **1999**, 3177−83.
(29) Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 133−41.

Scheme 5



N2, N3 = 352.3°, 345.4°, and 346.0°, respectively) compared with those observed in $(Me_2N)_3P{=}NH$ (angle sums around Me_2N nitrogens = 343.5, 358.3, 357.0°)[28] and in $MeC(CH_2NMe)_3P{=}O$ (angle sums around nitrogens = 358.4, 355.4, and 357.4°).[29]

Conclusions. In their reactions with arylsufonyl azides, proazaphosphatranes **1** and **2** as well as the acyclic analogue $P(NMe_2)_3$ are sufficiently basic to promote N−S bond cleavage in the neutral arylsulfonyl azide Staudinger intermediate to permit azidophosphonium ion formation as depicted in Scheme 5 via paths I and II. In the case of the proazaphosphatranes, however, the azidophosphonium cation is stabilized by transannular bonding in the cage (confirmed by a molecular structure determination) whereas the analogous acyclic azidophosphonium cation formed from $(Me_2N)_3P$ is not. Hence, the acyclic arylsulfonyl azide intermediate has the additional option of decomposing to the corresponding acyclic iminophosphorane represented in pathway III in Scheme 5 via equilibrium II. Azidophosphonium cations formed from proazaphosphatranes **1**, **2**, and $(Me_2N)_3P$ can also be stabilized as azido-bis-phosphonium cations upon reaction with an additional molecule of tris(amino)phosphine (path IV in Scheme 5). In this transformation, the azidoproazaphosphatrane cations lose their transannulated configuration owing to the presence of a second phosphorus to which the positive charge can be delocalized.

The bicylic tris(amino)phosphines represented by **7** and **8** are less basic than either proazaphosphatranes **1** and **2** or $(Me_2N)_3P$, although they are not significantly less sterically hindered. Their decreased basicity stems from constraints in the cage framework which cause a decrease in the PNC angles upon bond formation of the phosphorus with a Lewis acid resulting in rehybridization of the N from sp^2 to sp^3.[30] Because of this decreased basicity, the corresponding neutral Staudinger intermediates formed from **7** and **8** in path I of Scheme 5 are less prone to form the corresponding azidophosphonium salts via equilibrium pathway II. Compounds **7** and **8** are apparently sufficiently sterically hindered, however, that their corresponding neutral Staudinger intermediates are somewhat stabilized with respect to N_2 elimination. (Steric stabilization to N_2 elimination of such azido intermediates formed from trialkyl phosphines has been noted by others.[8]) However, **7** and **8** are not sufficiently basic to completely complement steric hindrance in stabilizing these neutral intermediates to N_2 elimination. (Thus, in addition to steric bulk, increased phosphine basicity has also been noted to stabilize such intermediates to N_2 elimination.[8]) The lower basicity of **8** compared with **7** (owing to the electron withdrawing nature power of the O=P group in **6**) may be responsible for the substantially slower decomposition rate of the neutral intermediate for **8** formed in path I of Scheme 5. The lower basicity of both **7** and **8** compared with **1**, **2**, and $(Me_2N)_3P$ is in all likelihood also responsible for our failure to stabilize the cation formed via path IV, indicating that equilibrium II in Scheme 5 lies strongly in favor of the neutral intermediate in the cases of **7** and **8**.

The leaving group properties of the arylsulfonyl group in our study affords an alternate decomposition pathway from the usual N_2 elimination route observed with Staudinger intermediates. Thus, a sufficiently basic phosphine [tris(amino)phosphines in our work], in the presence of an azide reagent, allowed observation for only the second time (see Introduction) the formation of an azidophosphonium and an azido-bis-phosphonium salt. Noteworthy is the recent report by others[31] that the reaction of alkylsulfonyl azides with arylphosphines readily leads to the corresponding iminophosphine, rather than affording stable intermediate neutral or cationic azido phosphines.

Acknowledgment. The authors are grateful to the National Science Foundation and the donors of the Petroleum Research Fund administered by the American Chemical Society for grant support of this work and to Dr. Ilya Guzei for solving two of the structures by X-ray means.

Supporting Information Available: Additional crystallographic data including atomic coordinates, bond angles and lengths, anisotropic displacement parameters and hydrogen coordinates (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC025920S

(30) The rehybridization of the nitrogens from sp^2 toward sp^3 (note the av PNC bond angle in **14** is 347.9°) causes the nitrogen lone pairs in **7** and **8** to adopt more sp^3 character which reduces their ability to augment electron density on the phosphorus inductively. (a) Vande Griend, L. G.; Verkade, J. G.; Pennings, J. F. M.; Buck, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 2459−63. (b) Verkade, J. G. *Bioinorg. Chem.* **1974**, *3*, 165−182. (c) Clarke, M. L.; Holliday, G. L.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1093−1103.

(31) Andersen, N. G.; Ramsden, P. D.; Che, D.; Parvez, M.; Keavy, B. A. *J. Org. Chem.* **2001**, *66*, 7478−86.