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Skeletally Stabilized Triphosphazanes: New Classes of Linear Phosphazanes

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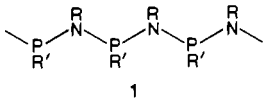
Reaction of 1,2-$(NH_2)_2C_6H_4$ with $(Et_2N)_3P$ produces the linear triphosphazane $C_6H_4N_2[P(NEt_2)_2]_2PNEt_2$ (**6**), in which the phosphorus–nitrogen skeleton is stabilized by incorporation into a 1,3,2-diazaphosphole unit. ^{31}P NMR spectral evidence has been obtained for mono- and diphosphorus intermediates $C_6H_4(NH)_2PNEt_2$ (**7**) and $C_6H_4N(NH)(PNEt_2)P(NEt_2)_2$ (**8**). Reaction of **6** with S_8 yields $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**9**) followed by $C_6H_4N_2[P(S)(NEt_2)_2]_2P(S)NEt_2$ (**10**), in a highly regioselective oxidation of exo phosphorus atoms. Hydrolysis of **6** occurs exclusively at the central phosphorus atom to form phosphine oxide $C_6H_4N_2[P(NEt_2)_2]_2P(O)H$ (**11**). **9** with gaseous HCl yields the monochloride $C_6H_4N_2[P(S)(NEt_2)_2]_2PCl$ (**12**). Reactions of **12** with Et_2NH, H_2O, NH_3, and Me_3SiN_3 yield **6** and the new compounds $C_6H_4N_2[P(S)(NEt_2)_2]_2P(O)H$ (**13**), $C_6H_4N_2[P(S)(NEt_2)_2]_2PNH_2$ (**14**), and $C_6H_4N_2[P(S)(NEt_2)_2]_2PN_3$ (**15**), respectively. **6** and **9**–**15** have been characterized by spectral (^1H and ^{31}P NMR, IR, and MS) data. In addition, **9** has been characterized by single-crystal X-ray diffraction: orthorhombic, *Pbca*, $a = 14.652$ (5) Å, $b = 18.911$ (9) Å, $c = 24.324$ (9) Å, $V = 6739$ (4) Å^3, $Z = 8$, $R = 0.060$, $R_w = 0.075$. The P=S bonds of the bulky $P(S)(NEt_2)_2$ units are oriented approximately trans relative to the electron pair of the inner phosphorus atom P(2), creating a hindered molecular cleft at that phosphorus atom. The reactivity data for **6**, **9**, and **12** confirm the hindered, highly selective character of the central phosphorus site.

Introduction

Reactions between difunctional nitrogen (>NR) and phosphorus (>PR′) compounds that have the potential to form linear P(III) phosphazanes (**1**) instead generally yield cyclic products



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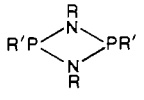

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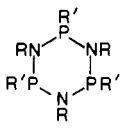
containing four- (**2**), six- (**3**), or eight-membered rings (**4**).



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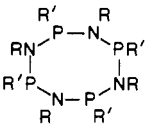

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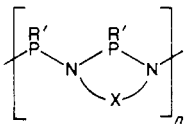

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Four-membered rings are favored with large substituents (R = alkyl, aryl; R′ = alkyl NR_2, OR, halogen),[1-11] whereas six-[12-15] and eight-membered[16-18] rings result when the R and R′ groups (e.g. R = Me, Et; R′ = Me) are small. This tendency toward ring formation, at least in part to minimize intragroup R and R′ repulsions along the P–N skeleton,[2,8] has frustrated attempts to synthesize phosphazanes of significant chain extension and the formation of linear phosphazane polymers. Only the linear triphosphazane $PhP[N(R)PPh_2]_2$ (R = Me, Et) has been characterized;[19,20] however, since the phosphorus atoms were phenyl substituted, the molecule had limited useful functionality.[20,21] This absence of linear P(III) phosphazanes is in contrast to the situation with P(V) phosphazanes, where linear molecules are formed readily.[1,21-25] Since linear P(III) phosphazanes are largely unknown, their general reactivity and structural properties remain unexplored.

In order to synthesize tractable series of linear P(III) phosphazane oligomers and/or polymers, it is necessary to stabilize the linear skeleton relative to small rings both during the P–N bond formation process and after phosphazane oligomer/polymer formation. Further, it is desirable to stabilize the phosphazane without sacrificing its functionality/reactivity, as can happen when systems are stabilized by sterically bulky substituents or by metal coordination. One approach is to design skeleton systems that cannot form small rings because of built in structural constraints and will prefer formation of linear products. This skeletal stabilization might be achieved by connecting adjacent nitrogen atoms (**5**; X = connecting group), such that condensation intermediates must oligomerize linearly. We have now undertaken studies of such phosphazanes, and our work is reported herein. A preliminary report of this work has been published.[26]

Experimental Section

Apparatus and Materials. Phosphorus-31 NMR spectra were recorded with JEOL FX-90Q and Bruker WM-250 spectrometers at 36.5 and 101.2 MHz, respectively. ^1H NMR spectra were obtained on a JEOL FX-90Q spectrometer at 90 MHz. ^{31}P and ^1H NMR chemical shifts downfield from 85% H_3PO_4 (external) and $(CH_3)_4Si$ (internal) are reported as positive (+δ). IR spectra (4000–400 cm^{-1}) were obtained by using a Beckman 4250 grating spectrometer. Mass spectra were obtained at 70 eV with a Varian MAT-CH5 or VG Analytical 7070 EQ-HF spectrometer. Mass spectral data refer to the major peak of the re-

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spective envelope. X-ray diffraction data were collected on a Nicolet P3/F automated diffractometer equipped with a graphite monochromator and low-temperature attachment. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, CO. All manipulations were carried out by using standard vacuum-line, glovebag, or Schlenk techniques under dry N_2.[27] UV photolyses (2537–3500 Å) were carried out in quartz reaction vessels using a Rayonet reactor.

1,2-$(NH_2)_2C_6H_4$ (Aldrich) was recrystallized repeatedly from toluene. $P(NR_2)_3$ (R = Me, Et, *i*-Pr) were synthesized by standard procedures.[28] PCl_3 (Mallinckrodt), Et_3N (Baker), Me_2NH (Fluka), Et_2NH (Aldrich), and *i*-Pr_2NH (Aldrich) were distilled from CaH_2. Gaseous HCl (Matheson) and NH_3 (Matheson) were used directly. Elemental sulfur (EM Scientific), silica gel (Fisher), and Me_3SiN_3 (Aldrich) were used as obtained. Toluene (over Na/Pb alloy) and CH_2Cl_2 (over P_4O_{10}) were distilled before use.

Reaction of 1,2-$(NH_2)_2C_6H_4$ with $(R_2N)_3P$. (A) R = Et [Product $C_6H_4N_2[P(NEt_2)_2]_2PNEt_2$ (6)]. 1,2-$(NH_2)_2C_6H_4$ (0.043 mol) and $(Et_2N)_3P$ (0.22 mol) were allowed to react at 80 °C. After 6 h, excess $(Et_2N)_3P$ was removed in vacuo. The resulting product was dissolved in CH_2Cl_2 and passed through a 5-cm silica gel column. Pure $C_6H_4N_2[P(NEt_2)_2]_2PNEt_2$ (**6**) was obtained as an oil nearly quantitatively (>95%) after solvent removal. $^{31}P\{^1H\}$ NMR (C_6D_6): AX_2,[29] δ 106.5 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 43.5 Hz], 100.5 [t, area 1, P(2)]. ^1H NMR: δ 7.1–6.9 [complex multiplet, area 2, Ph], 6.8–6.6 [complex multiplet, area 2, Ph], 3.1–2.7 [complex, area 20, CH_2], 1.3–0.8 [complex, area 30, CH_3]. IR (NaCl): 2973 (vs), 2939 (m), 2868 (m), 1572 (w), 1479 (vs), 1467 (m), 1367 (s), 1347 (w), 1295 (w), 1246 (vs), 1200 (vs), 1188 (vs), 1111 (w), 1057 (w), 1018 (vs, br), 921 (vs), 904 (vs), 895 (m, sh), 860 (w), 792 (w), 730 (m), 681 (m) cm^{-1}. MS (parent and five most intense envelopes) [*m/e* (relative intensity)]: 557 (36, M^+), 485 (39), 382 (12), 310 (41), 247 (100), 238 (62). Anal. Calcd for $C_{26}H_{54}N_7P_3$: C, 56.00; H, 9.76; N, 17.58; P, 16.66. Found: C, 55.90; H, 9.57; N, 17.40; P, 16.77. **6** is soluble in toluene and benzene.

^{31}P NMR spectra taken during the course of the 1,2-$(NH_2)_2C_6H_4$/$(Et_2N)_3P$ reaction show intermediate products at δ 89.4 (s) (**7**) and δ 94.6 and 105.5 (**8**; 1:1 doublets, J = 40.3 Hz) that disappear with the appearance of **6**.

(B) R = Me. $(Me_2N)_3P$ and 1,2-$(NH_2)_2C_6H_4$ heated together in 4:1–10:1 mole ratios for 2–3 days at 100 °C yielded a complex ^{31}P NMR spectrum consisting of 15 peaks in the range δ 111–103. Products were not isolated or characterized.

(C) R = *i*-Pr. *i*-$Pr_2N)_3P$ and 1,2-$(NH_2)_2C_6H_4$ showed no reaction, even after 11 days at 110 °C.

Reaction of 1,3-$(NH_2)_2C_6H_4$ with $(Et_2N)_3P$. $(Et_2N)_3P$ and 1,3-$(NH_2)_2C_6H_4$ heated together in 20:1–6:1 mole ratios, both neat and in toluene solvent, yielded only white intractable products.

Reaction of 6 with S_8. $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (9) and $C_6H_4N_2[P(S)(NEt_2)_2]_2P(S)NEt_2$ (10). To **6** (0.027 mol) in 150 mL of toluene was added S_8 (0.007 mol). After 6 h at 25 °C, **9** crystallized from the reaction solution. Recrystallization from toluene yielded pure **9** (mp 115–118 °C). $^{31}P\{^1H\}$ NMR (C_6D_6): AX_2,[29] δ 65.1 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 63.9 Hz], 98.3 [t, area 1, P(2)]. ^1H NMR: δ 8.0–7.8 [complex multiplet, area 2, Ph *o*-H], 7.0–6.8 [d of d, area 2, Ph *m*-H, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.4 Hz], 3.6–2.7 [complex, area 20, CH_2], 1.2–0.9 [complex, area 30, CH_3]. IR (KBr): 2980 (s), 2941 (s), 2878 (s), 1584 (w), 1483 (s), 1460 (m, sh), 1382 (s), 1351 (m), 1333 (m), 1296 (w), 1251 (vs), 1203 (vs), 1200 (vs), 1172 (vs), 1113 (m), 1102 (m), 1081 (w), 1161 (m), 1028 (vs, br), 951 (vs, br), 887 (s), 865 (m), 844 (m), 799 (s), 741 (s), 710 (vs), 692 (m), 675 (w), 606 (m, P=S), 517 (m), 480 (m), 472 (m), 430 (w) cm^{-1}. MS (parent and five most intense envelopes) [*m/e* (relative intensity)]: 621 (13, M^+) 549 (17), 414 (1), 342 (2), 279 (2), 207 (100). Anal. Calcd for $C_{26}H_{54}N_7P_3S_2$: C, 50.22; H, 8.75; N, 15.77; P, 14.94. Found: C, 50.36; H, 8.68; N, 15.75; P, 14.99. **9** is soluble in benzene, toluene, and CS_2.

A solution of **9** (8.1 mmol) and S_8 (3.0 mmol) in toluene was heated at reflux for 3 days. Upon solvent removal, crystalline **10** formed (mp 145–146 °C; 90% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 64.7 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 19.5 Hz], 68.4 ppm [t, area 1, P(2)]. ^1H NMR (C_6D_6): δ 8.2–8.1 [complex multiplet, area 2, Ph *o*-H], 6.9–6.8 [d of d, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.3 Hz, area 2, Ph *m*-H], 3.9–2.8 [complex, area 20, CH_2], 1.2–0.9 [complex, area 30, CH_3]. MS (parent and three most intense ions above *m/e* 200) [*m/e* (relative intensity)]: 653 (100, M^+), 581 (7), 549 (9), 447 (39). IR (KBr): 2975 (s), 2930 (s), 2875 (s), 1585 (w), 1483 (s), 1455 (m), 1380 (m), 1358 (w), 1327 (w), 1296 (w), 1240 (s), 1200 (s), 1165 (vs), 1120 (s), 1020 (vs), 940 (vs), 920 (vs), 900 (vs), 860 (s), 795 (vs), 745 (s), 725 (s), 712 (vs), 668 (m), 617 (m, P=S), 514 (m), 458 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{54}N_7P_3S_3$: C, 47.76; H, 8.32; N, 14.99; P, 14.21. Found: C, 47.29; H, 8.30; N, 14.10; P, 13.46.

Reaction of 6 with H_2O. $C_6H_4N_2[P(NEt_2)_2]_2P(O)H$ (11). **1** (11 mmol) in 50 mL of CH_2Cl_2 was combined with H_2O (14 mmol). After 10 h, **11** formed as an oil in ca. 80% yield (by ^{31}P NMR spectroscopy). Because of its thermal instability, **11** could not be isolated in >80% purity. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 111.9 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 18.3 Hz], 10.2 [t, area 1, P(2)]. ^{31}P NMR (^1H undecoupled): $^1J_{PH}$ = 670 Hz. ^1H NMR (C_6D_6): δ 8.32 [d, area 1, P–H, $^1J_{PH}$ = 670 Hz], 7.51–6.82 [complex multiplet, area 4, Ph], 3.64–2.48 [complex, area 16, CH_2], 1.14–0.83 [complex, area 24, CH_3]. IR (NaCl): 2970 (vs), 2936 (vs), 2866 (s), 2418 (w, P–H), 1595 (w), 1485 (vs), 1461 (m), 1380 (s), 1346 (m), 1299 (w), 1240 (vs), 1210 (s), 1195 (vs), 1114 (s), 1061 (m), 1025 (vs), 956 (vs), 932 (vs), 915 (s), 798 (m), 747 (m), 676 (m) cm^{-1}. MS (parent and four most intense envelopes) [*m/e* (relative intensity)]: 502 (40, M^+), 429 (8), 310 (85), 238 (53), 175 (100). **11** is soluble in benzene, toluene, and CS_2.

Neat **11** decomposed to give a single ^{31}P NMR resonance at δ 19.7 ($^1J_{PH}$ = 570 Hz) assigned to $(Et_2N)_2P(O)H$. As this resonance appears, **11** disappears and broad resonances appear in the base line between δ 110 and 90.

Reaction of 6 with CS_2. **6** was allowed to stand for 3 days in CS_2 at 22 °C. ^{31}P NMR spectral analysis showed a minor (less than 5% total P) peak at δ 22, but the bulk of the sample was unreacted **6**.

Reaction of 9 with HCl. $C_6H_4N_2[P(S)(NEt_2)_2]_2PCl$ (12). Gaseous HCl (13.5 mmol) was added to **9** (6.7 mmol) in 60 mL of toluene at −196 °C, and the mixture was allowed to warm to 25 °C. After filtration to remove Et_2NH_2Cl, evaporation of the supernatent solution yielded **12** quantiatively. Recrystallization from toluene gave pure **12** (mp 133–136 °C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 64.5 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 66.7 Hz], 143.9 [t, area 1, P(2)]. ^1H NMR (C_6D_6): δ 7.6–7.7 [complex multiplet, area 2, Ph *o*-H], 7.0–6.9 [d of d, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.4 Hz, area 2, Ph *m*-H], 3.3–2.9 [complex, area 16, CH_2], 1.13 [t, area 12, CH_3, $^3J_{HCCH}$ = 7.01 Hz], 0.93 [t, area 12, CH_3, $^3J_{HCCH}$ = 7.01 Hz]. IR (KBr): 2978 (vs), 2935 (s), 2872 (m), 1592 (w), 1483 (vs), 1463 (m), 1382 (s), 1330 (w), 1298 (w), 1249 (vs), 1205 (vs), 1165 (vs), 1118 (s), 1062 (m), 1020 (vs, br), 955 (vs, br), 918 (vs), 795 (m), 780 (w), 743 (s), 718 (vs), 691 (w), 678 (w), 604 (w, P=S), 518 (m), 472 (m) cm^{-1}. MS (parent and four most intense envelopes) [*m/e* (relative intensity)]: 584 (40, M^+), 549 (10), 342 (55), 207 (100), 175 (64). Anal. Calcd for $C_{26}H_{54}N_6P_3S_2Cl$: C, 45.17; H, 7.53; N, 14.37; P, 15.91. Found: C, 45.46; H, 7.82; N, 14.31; P, 15.65. **12** is soluble in toluene.

12 can be obtained by bubbling gaseous HCl (excess) directly into **9** in toluene at 25 °C. No decomposition was seen by ^{31}P NMR spectroscopy, even with large excesses of HCl.

Addition of excess Et_2NH to **12** in toluene yields a product whose ^{31}P NMR spectrum was identical with that of **9**. Four successive repetitive additions of gaseous HCl followed by Et_2NH, while the reactions were monitored by ^{31}P NMR spectroscopy, showed relatively little decomposition (<5%) of **9** or **12**.

Reaction of 12 with H_2O. $C_6H_4N_2[P(S)(NEt_2)_2]_2P(O)H$ (13). **12** (3.8 mmol) in 40 mL of CH_2Cl_2 was combined with H_2O (3.8 mmol). After 5 h, removal of solvent in vacuo gave **13** (mp 110–114 °C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 63.8 [d, area, 2, P(1) and P(3), $^2J_{PP}$ = 10.7 Hz], 4.5 [t, area 1, P(2)]. ^{31}P NMR (^1H undecoupled): $^1J_{PH}$ = 708 Hz. ^1H NMR (C_6D_6): δ 8.35 [d of t, area 1, P–H, $^1J_{PH}$ = 708 Hz, $^3J_{PH}$ = 1.45 Hz], 8.0–7.9 [complex multiplet, area 2, Ph *o*-H], 7.1–6.8 [d of d, area 2, Ph *m*-H, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 3.4 Hz], 3.8–2.8 [complex, area 20, CH_2], 1.06 [t, area 12, CH_3, $^3J_{HCCH}$ = 7.01 Hz], 0.89 [t, area 12, CH_3, $^3J_{HCCH}$ = 7.01 Hz]. IR (KBr): 2970 (s), 2930 (m), 2878 (m), 2470 (w, P–H), 1590 (w), 1485 (vs), 1462 (m), 1380 (s), 1332 (m), 1296 (w), 1248 (vs), 1205 (vs), 1170 (vs), 1155 (vs), 1120 (vs), 1055 (m), 1030 (vs), 1015 (vs), 990 (m), 955 (vs), 920 (vs), 796 (s), 779 (m), 752 (vs), 718 (vs), 694 (m), 675 (m), 606 (m, P=S), 511 (m), 470 (s), 440 (m), 428 (m) cm^{-1}. MS (parent and four most intense envelopes) [*m/e* (relative intensity)]: 566 (11, M^+), 343 (10), 207 (100), 175 (35), 72 (48). Anal. Calcd for $C_{22}H_{45}N_6OP_3S_2$: C, 46.63; H, 8.00; N, 14.83; P, 16.40. Found: C, 44.81; H, 7.90; N, 13.70; P, 15.73. **13** is soluble in CH_2Cl_2.

Reaction of 12 with NH_3. $C_6H_4N_2[P(S)(NEt_2)_2]_2PNH_2$ (14). Gaseous NH_3 (excess) was bubbled into **12** (1.9 mmol) in toluene. After filtration of NH_4Cl, solvent was removed in vacuo. **14** could not be obtained completely pure by either crystallization or chromatographic techniques. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65.1 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 59.8 Hz], 94.1 [t, area 1, P(2)]. ^{31}P NMR (C_6D_6): δ 92.0 [t of t, $^2J_{PH}$ = 13.7 Hz], 63.1 [d of t, $^4J_{PH}$ = 10.7 Hz]. MS (parent and four most intense envelopes) [*m/e* (relative intensity)]: 565 (25, M^+), 549 (5), 447 (9), 342 (14), 207 (100).

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Table I. Crystal Data and Refinement Details for $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**9**)

formula	$C_{26}H_{54}N_7P_3S_2$
fw	621.81
space group	orthorhombic, *Pbca*
cryst dimens, mm	0.30 × 0.20 × 0.15
a, *b*, *c*, Å	14.652 (5), 18.911 (9), 24.324 (9)
V, Å^3; *Z*; d_{calc}, g cm^{-3}	6739 (4); 8; 1.23
F(000)	2687
μ, cm^{-1}	3.20
data collcd	$+h,+k,+l$
radiation (λ, Å)	Mo Kα (0.71069)
monochromator angle, deg	12.2
temp, K	193
scan technique	Wycoff ω scan
2θ scan range, deg	3.0–45.0
scan speed, deg min^{-1}	3.91–29.30
scan range, deg	1.0
check reflections	(1,3,6), (6,1,1)
frequency	every 98 measurements
variation	random
no. of reflcns measd	5029
no. of unique reflcns	4413
no. of obsd reflcns	2754
criterion	$F > 6\sigma(F)$
programs	SHELXTL
R, R_w	0.060, 0.075
w	$1/(\sigma(F)^2 + 0.0012F^2)$
no. of params	345
ratio of observns to params	7.98
GOF	1.76

12 (9.6 mmol), **14** (9.0 mmol), and Et_3N (40 mmol) were dissolved in 5 mL of toluene, and the solution was heated to 110 °C. After 3 days, ^{31}P NMR spectral analysis showed only unreacted starting materials.

Reaction of 12 with Me_3SiN_3. $C_6H_4N_2[P(S)(NEt_2)_2]_2PN_3$ (15). Me_3SiN_3 (1.9 mmol) was added to **12** (1.8 mmol) in 30 mL of toluene. After 4 h, the solution was evaporated in vacuo. **15** was obtained in >90% yield and recrystallized from toluene as a waxy solid (mp 71–74 °C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65.8 [d, area 2, P(1) and P(3), $^2J_{PP}$ = 70.8 Hz], 121.4 [t, area 1, P(2). ^1H NMR (C_6D_6): δ 7.69–7.57 [complex multiplet, area 2, Ph *o*-H], 6.96–6.86 [d of d, area 2, Ph *m*-H, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.4 Hz], 3.40–2.93 [complex multiplet, area 16, CH_2], 1.02 [t, area 12, CH_3, $^3J_{HCCH}$ = 7.01 Hz], 0.92 [t, area 12, CH_3, $^3J_{HCCH}$ = 7.01 Hz]. IR (KBr): 2970 (vs), 2930 (s), 2868 (m), 2190 (vs, P–N_3), 1587 (w), 1481 (s), 1460 (m), 1382 (s), 1350 (w), 1330 (w), 1296 (w), 1249 (vs), 1200 (vs), 1164 (vs), 1115 (s), 1060 (m), 1014 (vs), 945 (vs, br), 891 (s), 853 (w), 790 (s), 748 (s), 713 (vs), 690 (m), 673 (m), 600 (m, P=S), 503 (m), 458 (s), 403 (w) cm^{-1}. MS (parent and four most intense envelopes) [*m*/*e* (relative intensity)]: 591 (20, M^+), 563 (60), 549 (100), 342 (30), 207 (90). Anal. Calcd for $C_{22}H_{44}N_9P_3S_2$: C, 44.66; H, 7.49; N, 21.30; P, 15.70. Found: C, 44.80; H, 7.56; N, 18.67; P, 15.40. **10** is soluble in toluene.

15 showed no decomposition in 3 weeks at 25 °C, as a neat solid or in solution (toluene or CH_2Cl_2). Thermolysis at 95 °C for 48 h in toluene yields ^{31}P NMR spectral resonances for **15** along with a complex set of peaks centered at δ 64.2. UV photolysis of **15** for 12 h in toluene at 25 °C results in a ^{31}P NMR spectrum where **15** is no longer seen and the main feature is a complex set of peaks centered at δ 64.5.

*Note: Although **15** has been handled without problems, extreme caution must be used when azides are used.*

X-ray Crystal Structure of 9. Crystallographic data for **9** (crystallized from toluene) were collected at −80 °C by Dr. C. Campana at Nicolet Inc. Details of the X-ray diffraction experiment are reported in Table I. Positional parameters are given in Table II. A structure analysis performed at 23 °C showed significant disorder in the ethyl groups. Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with 2θ in the range 20–25°. The structure was solved by direct methods and refined by block-cascade least-squares calculations treating non-hydrogen atoms anisotropically. Atom scattering factors were those used for neutral atoms.[30] Hydrogen atoms were refined as fixed groups. Calculations were carried out by using programs in the SHELXTL package.[31]

(30) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.
(31) Sheldrick, G. M. "SHELXTL, A Program for Crystal Structure Determination, Version 4.1"; Nicolet Analytical Instruments: Madison, WI, 1983.

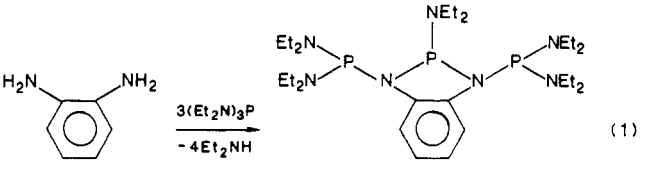
Table II. Positional (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**9**)

	x	*y*	*z*	U^a
S(1)	−1787 (1)	1083 (1)	−307 (1)	45 (1)
S(2)	47 (1)	894 (1)	2836 (1)	38 (1)
P(1)	−2452 (1)	1015 (1)	382 (1)	30 (1)
P(2)	−1547 (1)	439 (1)	1388 (1)	26 (1)
P(3)	−1195 (1)	884 (1)	2560 (1)	29 (1)
N(1)	−1815 (3)	1138 (2)	947 (2)	28 (2)
N(2)	−1299 (3)	1080 (2)	1895 (2)	28 (2)
N(3)	−3254 (3)	1621 (3)	447 (2)	34 (2)
N(4)	−2905 (3)	225 (2)	474 (2)	33 (2)
N(5)	−576 (4)	141 (3)	1150 (3)	50 (2)
N(6)	−1664 (3)	90 (2)	2594 (2)	28 (2)
N(7)	−1838 (3)	1490 (3)	2850 (2)	34 (2)
C(1)	−1409 (4)	1791 (3)	1114 (2)	26 (2)
C(2)	−1120 (4)	1755 (3)	1655 (3)	31 (2)
C(3)	−687 (4)	2331 (3)	1905 (3)	40 (2)
C(4)	−581 (5)	2937 (3)	1592 (3)	46 (3)
C(5)	−874 (4)	2974 (3)	1054 (3)	39 (3)
C(6)	−1299 (4)	2398 (3)	805 (3)	35 (2)
C(31)	−3844 (5)	1756 (4)	−40 (3)	47 (3)
C(32)	−3567 (6)	2400 (4)	−371 (3)	69 (3)
C(33)	−3626 (5)	1854 (3)	976 (3)	42 (2)
C(34)	−3759 (5)	2650 (3)	1020 (3)	60 (3)
C(41)	−3585 (4)	113 (3)	911 (3)	33 (2)
C(42)	−4577 (4)	126 (4)	710 (3)	42 (2)
C(43)	−2499 (5)	−443 (4)	238 (3)	63 (3)
C(44)	−3076 (6)	−790 (4)	−156 (3)	65 (3)
C(51)	156 (7)	565 (5)	751 (4)	101 (5)
C(52)	710 (8)	787 (5)	1138 (4)	106 (5)
C(53)	−406 (4)	−614 (3)	1168 (3)	37 (2)
C(54)	307 (5)	−837 (3)	1580 (3)	46 (3)
C(61)	−2668 (4)	36 (3)	2526 (3)	38 (2)
C(62)	−2991 (5)	−673 (3)	2300 (3)	46 (3)
C(63)	−1228 (4)	−512 (3)	2877 (3)	34 (2)
C(64)	−1598 (5)	−652 (4)	3454 (3)	49 (3)
C(71)	−2718 (5)	1739 (4)	2617 (3)	62 (3)
C(72)	−2941 (6)	2472 (4)	2694 (4)	95 (4)
C(73)	−1761 (5)	1567 (4)	3454 (3)	50 (3)
C(74)	−1249 (5)	2216 (4)	3622 (4)	68 (3)

^{a}Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Transamination reactions between 1,2-$(NH_2)_2C_6H_4$ and tris(amino)phosphines [$(R_2N)_3P$, R = Me, Et, *i*-Pr] as routes to new linear phosphazanes have been investigated. Product formation in these reactions depends on the alkyl group of the tris(amino)phosphine and on the reactant ratio. Reaction of 1,2-$(NH_2)_2C_6H_4$ and excess neat $(Et_2N)_3P$ at 80 °C results in elimination of Et_2NH and the quantitative formation of the triphosphazane $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**6**) as



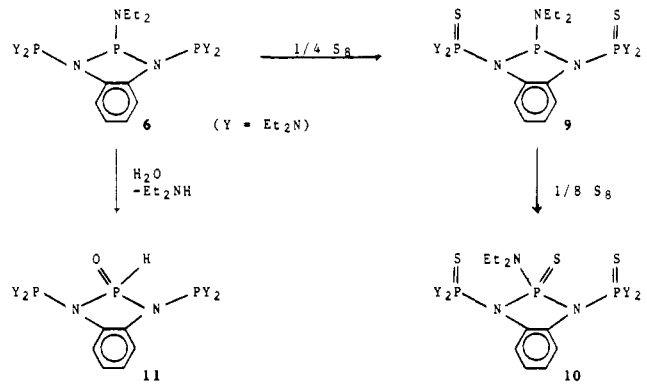
(1)

6

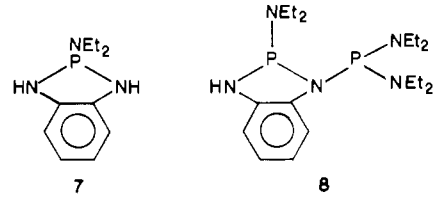
Additional heating of **6** with excess $(Et_2N)_3P$ produces no further reaction. The triphosphorus product **6** is obtained only with excess $P(NEt_2)_3$. In contrast, reactions between 1,2-$(NH_2)_2C_6H_4$ and excess $(Me_2N)_3P$ or $(i\text{-}Pr_2N)_3P$ did not produce products analogous to **6**. From the 1,2-$(NH_2)_2C_6H_4$/$(Me_2N)_3P$ reaction, a complex mixture formed from which no characterizable products could be isolated; whereas from 1,2-$(NH)_2C_6H_4$ with $(i\text{-}Pr_2N)_3P$, no reaction was evident even after heating at 110 °C for 48 h.

At lower $(Et_2N)_3P$:1,2-$(NH_2)_2C_6H_4$ reactant ratios (e.g. ≤2:1), a more complex mixture of products arises which contains species that are reaction intermediates in the formation of **6**. ^{31}P NMR spectral analysis of the reaction mixture as a function of time shows initial formation of a species that exhibits a singlet at δ 89.4 (**7**)

Scheme I

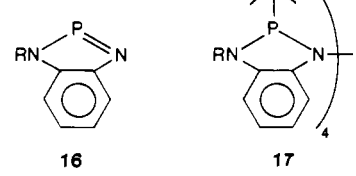


followed by a species (**8**) exhibiting a pair of coupled, equal-area doublets at δ 94.6 and 105.5 ($^2J_{PNP}$ = 40.3 Hz). So far, attempts to isolate **7** and **8** have been unsuccessful owing to their thermal instability, sensitivity to hydrolysis, and instability in the absence of Et_2NH. However, on the basis of the comparison of their ^{31}P NMR spectral properties with those of **6**, known diazaphospholes,[18,32] and other aminophosphines,[1-22] **7** and **8** are tentatively



characterized as the one- and two-phosphorus reaction intermediates. The $^2J_{PNP}$ observed in **8** is consistent with those reported for other P(III) bis(phosphino)amines.[2,4,15,33,34] Attempts at isolation and complete characterization of **7** and **8** continue.

From reactions of *N*-alkyl (or aryl) 1,2-diaminobenzenes with $(Me_2N)_3P$ in approximate 1:1 ratios under conditions where Me_2NH was continuously removed,[17,18] the cyclotetramer **17** was



obtained. At high temperature (110 °C), ^{31}P NMR spectral evidence for its existence in equilibrim with **16** was observed. No evidence was obtained for analogous species under the conditions employed in our work. Apparently, formation of species analogous to **16** or **17** is repressed by the presence of the R_2NH in the reaction mixture. It seems likely that phosphinimine (**16**) formation is preceded by formation of the (dialkylamino)diazaphosphole analogues of **7**, which subsequently are converted to the phosphinimines by Et_2NH elimination at elevated temperatures.

Compound **6** is isolated as a nondistillable viscous oil that is moderately stable to atmospheric moisture and oxygen. Repeated attempts to crystallize **6** were unsuccessful. Characterization of **6** depends on spectral data and depends indirectly upon an X-ray single-crystal study of its disulfide derivative. **6** reacts with elemental sulfur to form stepwise, and highly regioselectively, both a disulfide and a trisulfide (Scheme I). **6** with S_8 in toluene at

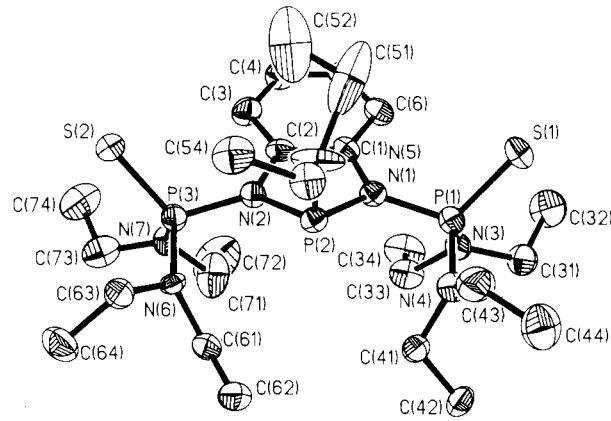


Figure 1. Structure and numbering scheme for $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**9**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

25 °C yields the disulfide **9**, a compound in which oxidation has occurred exclusively at the exo phosphorus atoms. Examination of the ^{31}P NMR spectrum of the reaction mixture showed no evidence for product oxidized at the central phosphorus or for other competing side reactions. Under forcing conditions (100 °C for 3 days) oxidation of the central phosphorus occurs also and the completely oxidized trisulfide **10** is obtained. In the latter case, some decomposition to so far uncharacterized products is noted.

Spectral data (MS and NMR) provide basic characterization for **6**, **9**, and **10**. All compounds exhibit mass spectral parent ions that confirm their molecular weights. **6** shows strong fragment ions at *m/e* 485 and 382, from the loss of Et_2N and $(Et_2N)_2P$ units. **9** and **10** show analogous strong ions arising from the loss of Et_2N and $(Et_2N)_2PS$ moieties. The ^{31}P NMR spectra of **6**, **9**, and **10** display distinct AX_2 (or AB_2 for **10**) patterns[29] of coupled doublets and triplets (**6**, δ 106.5 and 100.5; **9**, δ 98.3 and 65.1; **10**, δ 64.7 and 68.4) consistent with molecules containing, on average, symmetrically oriented triphosphazane units in solution. Resonances for **6** are in the region expected for tris(amino)-substituted phosphines[1-11] and are consistent with what has been reported for other diazaphosphole phosphorus atoms.[32] In **9**, the doublet resonance due to the exo phosphorus is shifted upfield as expected in a sulfur-oxidized aminophosphine.[35] In **10**, both ^{31}P NMR spectral resonances are shifted upfield to the four-coordinate P(V) region; however, because the chemical shift difference (δ 64.7 and 68.4) is small relative to $^2J_{PNP}$ (19.5 Hz), the spectrum is a second-order AB_2 type.[29] The $^2J_{PNP}$ coupling constant of 43.5 Hz at 25 °C for **6** is relatively small. $^2J_{PNP}$ values for *trans*-P–N–P diphosphazane conformations are known to be relatively small, 18–25 Hz, whereas for cis conformations they are larger, typically >200 Hz.[34] Thus, **6** appears to be predominantly in a trans–trans conformation. The $^2J_{PNP}$ of **9** and **10** of 63.9 and 19.5 Hz are in the ranges expected for λ_3–λ_4 and λ_4–λ_4 compounds;[36] however, there is not enough comparison data available to allow detailed correlation of these data with structure.

Structural characterization of **9** is further substantiated by a single-crystal X-ray analysis. The structure is shown in Figure 1. The molecule is a substituted linear triphosphazane in which the two skeletal nitrogen atoms, N(1) and N(2), are incorporated into a 1,3,2-diazaphosphole ring and in which the C_6H_4 unit serves to skeletally stabilize the linear P_3N_2 unit. The *o*-phenylene ring and attached N atoms [N(1) and N(2)] are in a plane; however, the central phosphorus atom P(2) is out of this plane. The dihedral angle between the $C_6H_4N_2$ and N(1),P(2),N(3) planes is 21.4°. Phosphorus atom P(2) is displaced 0.46 Å above and atoms P(1) and P(3) are displaced 0.28 Å below the $C_6H_4N_2$ plane. The sulfur atoms on P(1) and P(3) are directed approximately trans relative

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(33) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1974**, 1674.
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(35) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Topics in Phosphorus Chemistry*; Interscience: New York, 1963; Vol. 5.
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Table III. Selected Molecular Parameters for $C_6H_4N_2[P(S)(NEt_2)_2]_2PNEt_2$ (**9**)

	(a) Bond Distances (Å)		
S(1)–P(1)	1.940 (2)	S(2)–P(3)	1.936 (2)
P(1)–N(1)	1.672 (5)	P(1)–N(3)	1.645 (5)
P(1)–N(4)	1.647 (5)	P(2)–N(1)	1.744 (5)
P(2)–N(2)	1.762 (5)	P(2)–N(5)	1.633 (6)
P(3)–N(2)	1.664 (5)	P(3)–N(6)	1.649 (5)
P(3)–N(7)	1.639 (5)	N(1)–C(1)	1.427 (7)
N(2)–C(2)	1.426 (7)	C(1)–C(2)	1.382 (9)
C(1)–C(6)	1.379 (8)	C(2)–C(3)	1.396 (9)
C(3)–C(4)	1.381 (9)	C(4)–C(5)	1.377 (10)
C(5)–C(6)	1.391 (9)		
	(b) Bond Angles (deg)		
S(1)–P(1)–N(1)	114.8 (2)	S(1)–P(1)–N(3)	113.2 (2)
N(1)–P(1)–N(3)	102.9 (2)	S(1)–P(1)–N(4)	112.2 (2)
N(1)–P(1)–N(4)	103.8 (2)	N(3)–P(1)–N(4)	109.2 (2)
N(1)–P(2)–N(4)	87.5 (2)	N(1)–P(2)–N(5)	103.8 (3)
N(2)–P(2)–N(5)	107.8 (2)	S(2)–P(3)–N(2)	114.7 (2)
S(2)–P(3)–N(6)	112.4 (2)	N(2)–P(3)–N(6)	102.2 (2)
S(2)–P(3)–N(7)	112.5 (2)	N(2)–P(3)–N(7)	102.1 (2)
N(6)–P(3)–N(7)	112.0 (3)	P(1)–N(1)–N(2)	121.6 (3)
P(1)–N(1)–C(1)	125.8 (4)	P(2)–N(1)–C(1)	112.6 (4)
P(2)–N(2)–P(3)	123.0 (3)	P(2)–N(2)–C(2)	111.5 (4)
P(3)–N(2)–C(2)	125.3 (4)	P(1)–N(3)–C(31)	117.2 (4)
P(1)–N(3)–C(33)	123.9 (4)	P(1)–N(4)–C(43)	123.2 (4)
P(1)–N(4)–C(41)	120.0 (4)	P(2)–N(5)–C(51)	127.2 (5)
P(2)–N(5)–C(53)	118.6 (4)	P(3)–P(6)–N(63)	123.0 (4)
P(3)–N(6)–C(61)	118.0 (4)	P(3)–N(7)–C(71)	123.7 (4)
P(3)–N(7)–C(73)	116.8 (4)	N(1)–C(1)–C(6)	127.7 (5)
N(1)–C(1)–C(2)	110.9 (5)	N(2)–C(2)–C(1)	112.0 (5)
C(2)–C(1)–C(6)	121.5 (5)	C(1)–C(2)–C(3)	120.9 (6)
N(2)–C(2)–C(3)	127.1 (6)	C(3)–C(4)–C(5)	121.9 (6)
C(2)–C(3)–C(4)	117.2 (6)	C(1)–C(6)–C(5)	117.7 (6)
C(4)–C(5)–C(6)	120.7 (6)		

to the lone-pair electrons on P(2), giving **9** a trans–trans configuration in the solid state. An approximate symmetry plane passes through and is perpendicular to P(2) and bisects the *o*-phenylene ring. **9** has approximate C_s point group symmetry. Of special interest, the two $(Et_2N)_2P(S)$ units define a "cleft" at the front of the molecule around phosphorus P(2) into which sterically restricted and/or highly selective reaction chemistry occurs.

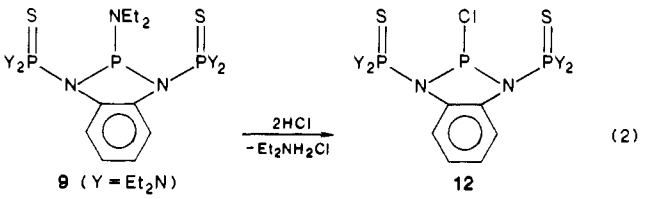
Bond distances and angles in **9** are given in Table III. In general, molecular parameters deviate little from values reported previously for aminophosphines. The P–N bond distances in the diazaphosphole C_2N_2P ring (mean 1.757 Å) are significantly longer than the exo ring bonds (mean 1.671 Å), although both are within the range of previously observed P–N bond distances.[1-4,23,37] The ∠N(1)–P(2)–N(2) is 87.7°, small but consistent with that seen in Malavaud's diazaphosphole **17**[18] and in diazadiphosphetidine rings.[4,8] Although the fit of the diazaphosphole ring to the arene ring is quite good, it is not perfect as seen by the fact that the mean internal ring angles around C(1) and C(2), ∠C(1)–C(2)–N(2) and ∠C(2)–C(1)–N(1), are 111.5°, less than the ideal angle of 120°. Some strain might exist in the diazaphosphole ring, although usually high chemical reactivity of the ring P–N bonds as a result of such strain is not apparent.

The highly selective sulfur oxidation of exo phosphorus atoms in **6** indicates there is a significant difference in reactivity toward electrophilic attack between the exo and endo sites. Similar preferential S_8 oxidation of the triphosphazane $Ph[N(R)PPh_2]_2$ (R = Me, Et) to $Ph[(R)P(S)Ph_2]_2$[20] occurs; however, the regioselectivity is less than that in **6**. In the latter case, reaction selectivity was ascribed to a steric effect on the incoming partially uncyclized S_8 units and not to an electronic effect. Since crowding of groups around the central phosphorus in **6** seems greater than that around the central phosphorus in $Ph[N(R)PPh_2]_2$, steric control seems substantiated.

In contrast to the reactivity pattern **6** exhibits toward S_8, **6** with H_2O undergoes reaction initially and selectively at P(2) to form phosphine oxide **11**. Only traces of other products are seen. **11** is obtained as an unstable oil. Although it could not be obtained completely pure, it was characterized by spectral data and comparison of these data with those for other P(V) diazaphospholes.[32b,38] The $^{31}P\{^1H\}$ NMR spectrum exhibits the characteristic AX_2 pattern at δ 111.9 and 10.2 expected for molecules containing two equivalent trigonal phosphorus atoms and a single four-coordinate >P(O)H center. The phosphine oxide resonance is shown unambiguously in the ^1H-coupled ^{31}P NMR spectrum as a widely spaced doublet (J = 670 Hz) due to P–H coupling and by the IR P–H (2418 cm^{-1}) absorption.[39] **11** decomposes slowly at 25 °C. The only thermal decomposition product identified so far is $(Et_2N)_2P(O)H$, which could form as a result of intramolecular oxygen atom transfer to an exo $P(NEt_2)_2$ group of **11**, followed by elimination of the $(Et_2N)_2P(O)H$ molecule. Also, the mass spectrum (EI^+) of **11** shows a major peak (85% base) at m/e 310 attributable to $(Et_2N)_2P(O)H^+$, an ion unit which is easily eliminated either in the spectrometer source prior to ionization or during the fragmentation process.

The reactivity of **6** toward H_2O suggests that P(2) is more subject to nucleophilic attack, i.e. more electrophilic, than P(1) and P(3), even though the P(2) center is more sterically encumbered. This enhanced electrophilicity correlates with the reduced nucleophilicity at P(2) seen in reactions of **6** with S_8. The formation of $(Et_2N)_2P(O)H$, possibly from an intermediate in which oxygen atom transfer from P(2) to P(1,3) has occurred, is also consistent with P(2) being less electrophilic than P(1,3).

Disulfide **9** reacts cleanly and regioselectively with anhydrous HCl to form the chloride derivative **21** (eq 2). **2** is a potentially



9 (Y = Et_2N) **12** (2)

valuable reagent for further work. The reaction of **9** with HCl exclusively at the P(2)–NEt_2 bond is remarkable. Even with 10-fold excess HCl at 25 °C, no significant cleavage of other P–N bonds in the system is observed. It is not surprising that the endo P–N bonds that involve bonds to oxidized phosphorus centers [P(1,3)] will withstand HCl cleavage;[40] however, it is surprising that the ring diazaphosphole P(III)–N bonds are untouched. Whether this ring stability is due to steric or electronic effects is unclear. However, since HCl is a relatively small reactant, it is unlikely the effect is largely steric in origin.

Compound **12** is a convenient precursor for P(2)-site derivatization of the triphosphazane disulfide skeletally stabilized molecules. Its reactions also provide insight into the nature of the reactive "cleft" in the molecules; hence, reactions with selected amines, Me_3SiN_3, and H_2O were examined (Scheme II). **12** is converted to **13** (the disulfide of **11**) by reaction with H_2O. **13**, unlike **11**, is a stable compound at room temperature. Although good elemental analytical data were not obtained because all samples appeared to contain a trace of H_2O that was not possible to remove completely, spectral data allow characterization of **13**. The ^{31}P NMR spectrum of **13** is an AX_2 pattern at δ 63.8 and 10.7 ($^1J_{PH}$ = 708 Hz), and characteristic P(O)H IR absorptions are seen.[32b]

Ammonia reacts smoothly with **12** to yield the aminated product **14**. **12** is also converted back to **9** by reaction with Et_2NH. Surprisingly, the repeated transformation of **9** to **12** and **12** to **9** by sequential additions of HCl to **9** and Et_2NH to **12** occurs with almost no decomposition of the triphosphazane systems. The

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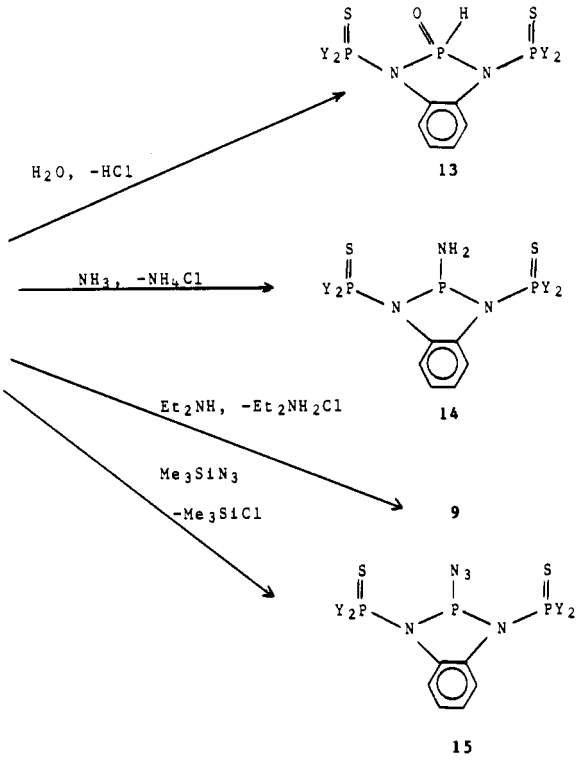
Scheme II



attempted amination of **12** with *i*-Pr_2NH or excess **14**, however, gave no products; **12** appears unreactive to these bulky amines. These results suggest the cleft around the P–Cl bond unit is small enough to be selective toward amines, with the Et_2N unit being the approximate upper limit in size.

Trimethylsilyl azide (Me_3SiN_3) reacts with **12** to form the phosphine azide **15**, even though the Me_3SiN_3 molecule is large. **15** is indefinitely stable as a solid or in solution. An intense IR absorption at 2190 cm^{-1}, characteristic of a P–N_3 group is seen,[41,42] along with a ^{31}P NMR spectrum that is consistent with the assigned structure. Thermolysis and UV photolysis of **15** both give similar results, producing product mixtures that exhibit complex ^{31}P NMR spectra consisting of several peaks centered around δ 64.5. **15** appears to be more thermally stable than most previously reported P(III) phosphine azides,[42] but apparently less stable than the recently reported (*i*-$Pr_2N)_2PN_3$.[43,44] Although the product spectra have not been assigned, no resonance(s) corresponding to either di- or tricyclophosphazenes appear.[41,42] This is interesting, since other phosphine azides, including (*i*-$Pr_2N)_2PN_3$, decompose thermally to dimeric or trimeric cyclophosphazenes.[42-44]

The physical size of the cleft in the triphosphazane **6** and the triphosphazane disulfides **9** and **12** is defined to some degree by the derivatization reactions studied. Whereas small nucleophilic molecules such as H_2O, NH_3, and Et_2NH react easily with the P–Cl bond, larger groups do not due to steric constraints. The inability of either *i*-Pr_2NH or **14** to react with the P–Cl bond of **12** sets an upper limit on the accessibility of reagents to P(2). In a similar way, the failure of **15** to form cyclophosphazene oligomer products from the thermolysis/photolysis reactions can be ascribed to the overwhelming steric hinderance that must be overcome for such reactions to occur. It seems likely that Me_3SiN_3 can react with **12**, because reaction occurs via a front-side four-center elimination process,[44] in which steric effects are less important, and consequently is mechanistically different from reactions of **12** with H_2O or amines.

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Supplementary Material Available: Listings of the crystal structure determination and crystal structure data, hydrogen positional and thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and least-squares planes, deviations, and dihedral angles (10 pages); a listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Reactions of Nitriles with Polyhedral Borane Anions. Reductive-Cyclocondensation and Carbon-Insertion Reactions: Syntheses of *hypho*-5-CH_3-5,11,7,14-$CNS_2B_7H_9$ and *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$

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The reactions of the polyhedral borane anions *arachno*-$S_2B_7H_8^-$ and *arachno*-$C_2B_7H_{12}^-$ with acetonitrile have been explored and found to result in reduction of the nitrile and either the incorporation of a CN unit into the cage framework or a one-carbon insertion accompanied by deamination. Thus, the reaction of the *arachno*-$S_2B_7H_8^-$ anion with acetonitrile under reflux conditions was found to yield the *hypho*-$CH_3CNS_2B_7H_8^-$ anion I, which upon protonation gave the corresponding neutral, air-stable cluster *hypho*-5-CH_3-5,11,7,14-$CNS_2B_7H_9$ (II) in excellent yield. In contrast, the isoelectronic carborane anion *arachno*-$C_2B_7H_{12}^-$ reacted with acetonitrile under reflux conditions to give a one-carbon insertion forming the tricarbon carborane anion *nido*-$CH_3C_3B_7H_9^-$ (III). Acidification of III then gave *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$ (IV) in good yield. A single-crystal X-ray study of II confirmed that the compound has four different main-group cage substituents (boron, sulfur, carbon, and nitrogen) and demonstrated that it adopts a unique hypho-cage geometry that can be derived from a bicapped hexagonal square antiprism by removing three vertices. The structure thus has two puckered six-membered and one planar five-membered open face. Crystal data for II: space group $C2/c$, $Z = 8$, $a = 19.889$ (9) Å, $b = 8.999$ (2) Å, $c = 11.718$ (2) Å, $\beta = 105.00$ (3)°. The structure was refined by full-matrix least squares to final $R = 0.052$ and $R_w = 0.063$ for the 998 unique reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reactions of isocyanides with a number of neutral boron hydrides have previously been explored and shown in several cases to result in one-carbon-insertion products:[1-3]

$$RN{\equiv}C + B_{10}H_{14} \rightarrow \textit{nido}\text{-7-}(RNH_2)CB_{10}H_{12}^1 \quad (1)$$

$$RN{\equiv}C + 6\text{-}SB_9H_{11} \rightarrow \textit{nido}\text{-8-}RNH_2\text{-8,7-}CSB_9H_9^2 \quad (2)$$

The reactions of nitriles with boron hydrides have also been

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