resonances, along with signals due to the original compound. If complexes **1** and **3** are heated in vacuum at 200 °C, $CH_3CN$ and $H_2$ are evolved (eq 2). Nujol IR spectra of the resulting solids

$$(CH_3CN)_xLn[BH_4]_2 \xrightarrow[-CH_3CN,\ -H_2]{200\ ^\circ C,\ vacuum} \text{“}LnB_2\text{”} \qquad (2)$$

$$Ln = Eu, Yb$$

reveal no B-H or ligand stretches, indicating they contain only Ln and B. These solids represent an intimate mixture of elemental lanthanide and boron in a precise 1:2 ratio, an ideal starting point for producing a metal boride. To investigate this further, dry solids from complexes **1** and **3** solids were heated in a quartz tube maintained at $10^{-5}$ Torr to a maximum of 1000 °C over the period of 1 h (eqs 3 and 4). At 100 °C coordinated solvent is evolved,

$$(CH_3CN)_xYb[BH_4]_2 \xrightarrow[-CH_3CN,\ -H_2,\ -Yb]{1000\ ^\circ C,\ vacuum} YbB_4 \qquad (3)$$

$$(CH_3CN)_xEu[BH_4]_2 \xrightarrow[-CH_3CN,\ -H_2,\ -Eu]{7000\ ^\circ C,\ vac} EuB_6 \qquad (4)$$

and hydrogen evolution is observed above 150 °C. Above 450 °C, lanthanide metal was observed to sublime out of both compounds. The resulting materials were shiny gray solids with a metallic luster. Powder X-ray data revealed they were single-phase crystalline $YbB_4$ and $EuB_6$ from complexes **1** and **3**, respectively.[24]

The formation of $EuB_6$ was not surprising, since the binary phase diagram for these elements indicates that the hexaboride is the only stable boride phase.[22] The formation of $YbB_4$ was unusual, however, since a stable $YbB_2$ phase is known but none was formed.[23] There are also stable $YbB_6$ and $YbB_{12}$ phases known, but none of the more boron-rich species were formed either. Obviously, under the reaction conditions the metal-rich boride is unstable, losing metal to give the observed tetraboride. An X-ray powder pattern of $EuB_6$ prepared at 700 °C shows that it is not yet fully crystalline but still identifiable as $EuB_6$. The X-ray powder pattern of $YbB_4$ prepared at 1000 °C shows that it is fully crystalline. There was a slight contaminant of $Yb_2O_3$ in the $YbB_4$, presumably from the quartz tube. Washing the boride with dilute HCl completely removed the oxide impurity, confirmed by the absence of oxide peaks in powder X-ray patterns of the washed material.

## Conclusions

Borohydride complexes of Eu(II) and Yb(II) can be synthesized by using $C_5H_5N$ and $CH_3CN$ as solvents. The amines ligate the lanthanide ions, and isolable coordination complexes are formed. The borohydride complexes are unstable as solids, particularly the $CH_3CN$ complexes, which are easily decomposed to form single crystalline phase europium and ytterbium borides.

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**Supplementary Material Available:** Listings of crystal data, anisotropic thermal parameters, bond distances, and bond angles (5 pages); listings of calculated and observed structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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# New Classes of Skeletally Stabilized Tri- and Tetraphosphazanes

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Reactions of 1,2,4,5-$(NH_2)_4C_6H_2$ with $(Et_2N)_3P$ and 1,2,3-$(NH_2)_3C_6H_3$ with $(Me_2N)_3P$ yield the new bis(triphosphazane) $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (**4**) and tetraphosphazane $C_6H_3N_3[P(NMe_2)_2]_2(PNMe_2)_2$ (**6**), respectively. **4** with sulfur is oxidized at the exo phosphorus atoms to a tetrasulfide $C_6H_2\{N_2[P(S)(NEt_2)_2]_2PNEt_2\}_2$ (**5**). **6** reacts with elemental selenium to form stepwise diselenide $C_6H_3N_3[P(Se)(NMe_2)_2]_2(PNMe_2)_2$ (**7**) and tetraselenide $C_6H_3N_3[P(Se)(NMe_2)_2]_2[P(Se)NMe_2]_2$ (**8**). **6** with elemental sulfur yields directly the tetrasulfide $C_6H_3N_3[P(S)(NMe_2)_2]_2[P(S)NMe_2]_2$ (**10**). **7** reacts smoothly with anhydrous HCl to yield the dichloride $C_6H_3N_3[P(Se)(NMe_2)_2]_2(PCl)_2$ (**9**); in contrast, **4**–**6** with HCl undergo extensive cleavage with skeletal unit destruction. **4**–**10** have been characterized by spectral ($^1H$ and $^{31}P$ NMR, MS, and IR) data. **4**, **8**, and **10** have also been characterized in the solid by single-crystal X-ray diffraction. Crystal data for **4**: monoclinic, $P2_1/c$, $a = 12.573$ (3) Å, $b = 16.976$ (3) Å, $c = 15.455$ (3) Å, $\beta = 111.55$ (2)°, $V = 3068(5)$ Å$^3$, $Z = 2$, $d_{calc} = 1.12$ g cm$^{-3}$, $R = 0.055$, and $R_w = 0.085$. Crystal data for **8**: orthorhombic, *Pbca*, $a = 14.858$ (3) Å, $b = 21.626$ (6) Å, $c = 22.327$ (7) Å, $V = 7174$ (3) Å$^3$, $Z = 8$, $d_{calc} = 1.68$ g cm$^{-3}$, $R = 0.060$, and $R_w = 0.076$. Crystal data for **10**: orthorhombic, *Pbca*, $a = 14.706$ (3) Å, $b = 21.610$ (5) Å, $c = 22.000$ (5) Å, $V = 6991$ (3) Å$^3$, $Z = 8$, $d_{calc} = 1.20$ g cm$^{-3}$, $R = 0.049$, and $R_w = 0.050$. **6** contains the longest linear extension of a P(III) phosphazane system so far achieved, the result of skeletal stabilization of the phosphazane system. **4** contains a near-planar $P_2N_4C_6$ atom core with two 1,3,2-diazaphosphole rings incorporated at the 1,2- and 4,5-positions of a benzene ring. **8** and **10** contain a planar $P_2N_3C_6$ atom core consisting of two fused 1,3,2-diazaphosphole rings attached at the 1,2,3-positions of a benzene ring. Structural features of **4** and **5** and the **6**–**10** series are compared and discussed.

## Introduction

The location of *o*-phenylene groups between adjacent nitrogen atoms of a phosphazane skeleton in order to achieve skeletal stabilization (**1**) has been used for synthesis of a variety of new phosphorus(III) phosphazane oligomers[2-6] and polymers.[5-7] With

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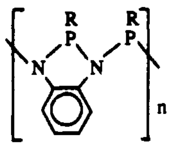
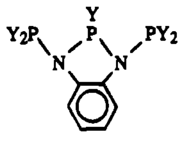


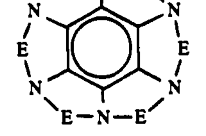
**1**



**2** (Y = $Et_2N$)

this technique, phosphazanes containing phosphorus–nitrogen skeletal systems with degrees of extension higher than observed previously[7-9] have been made; e.g., the stabilized triphosphazane **2** is formed from the transamination reaction of 1,2-$(NH_2)_2C_6H_4$ with $P(NEt_2)_3$.[2,3]

Triphosphazane **2** is interesting not only because of its degree of skeletal extension, conformational properties, and chemical reactivity[2,3] but also because of the ease with which it formed and the surprisingly good fit that exists between the arene ring and the triphosphazane part of the molecule. In fact, these latter observations raise the question as to what degree more extended phosphazane construction around a benzene ring could be developed to form higher-order stabilized phosphazanes. Ultimately, could cyclohexaphosphazane formation around a benzene ring be achieved, creating molecule **3** (E = P–X), which would have concentric cyclophosphazane and six-$\pi$-electron arene rings? Such a molecule and/or its derivatives could have novel electronic and magnetic properties like those reported recently for the analogue octadecahydrohexaazacoronene, **3**(E = $CH_2CH_2$).[10,11]



**3**

In order to extend our understanding of the scope and limitations of skeletally stabilized phosphazane formation reactions, we have now studied the $P(NR_2)_3$ transamination of two higher amines, 1,2,4,5-$(NH_2)_4C_6H_2$ and 1,2,3-$(NH_2)_3C_6H_3$. From these, two new tri- and tetraphosphazanes have been obtained. Preliminary reports of our studies have appeared earlier;[12] complete details of the work appear below.

## 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 instrument at 90 MHz. $^{31}P\{^1H\}$ and $^1H$ NMR chemical shifts downfield from external 85% $H_3PO_4$ and $(CH_3)_4Si$, respectively, are reported as positive (+$\delta$). $^{31}P$ NMR spectral simulations were carried out by using the PANIC program on the ASPECT computer. IR spectra (4000–400 $cm^{-1}$) were obtained by using a Beckman 4250 grating spectrometer. Mass spectra were obtained at 70 eV with Varian MAT-CH5 or VG Analytical 7070 EQ-HF spectrometer. Mass spectral data refer to the major peak of the respective envelope. X-ray diffraction data were collected on a Siemens P3/F automated diffractometer (Mo K$\alpha$, $\lambda$ = 0.71073 Å) equipped with a graphite monochromator and low-temperature attachment. Elemental analyses were performed by Huffman Laboratories, Inc., Wheatridge, CO. All manipulations were carried out with standard glovebag, Schlenk, or vacuum-line techniques.[13] UV photolyses with a Rayonet reactor (2537–3500 Å) were carried out in quartz reaction vessels.

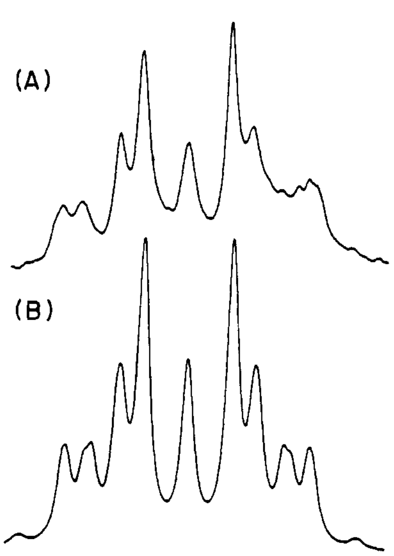


Figure 1. $^{31}P$ NMR spectra (101.2 MHz) of **6**: (A) observed at 27 °C; (B) simulated by using the PANIC program.

Flash chromatography was carried out according to the method of Still et al.[14] A 450-mL column was packed with 12–15 cm of silica gel (230–400 mesh). Compounds were eluted at 5 cm/min with the necessary solvent mixture under $N_2$ pressure.

The $P(NEt_2)_3$ and $P(NMe_2)_3$ were prepared and purified as described previously.[15] 1,2,4,5-$(NH_2)_4C_6H_2{\cdot}4HCl$ (Aldrich) was used as obtained. 1,2,3-$(NH_2)_3C_6H_3$ was prepared by catalytic hydrogenation[16] of 2,6-dinitroaniline (Aldrich). Elemental sulfur and selenium (Fischer) and gaseous HCl (Matheson) were used as obtained. Toluene (over Na/Pb alloy) and $CH_2Cl_2$ (over $P_4O_{10}$) were distilled before use.

**$C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (4).** 1,2,4,5-$(NH_2)_4C_6H_2{\cdot}4HCl$ (0.035 mol) and $(Et_2N)_3P$ (0.21 mol) in toluene (50 mL) were heated to 80 °C for 2 days. $Et_2NH_2Cl$ was removed by filtration. Toluene and $(Et_2N)_3P$ were removed in vacuo. Recrystallization from toluene yielded pure **4** (mp = 170–173 °C; 60% yield). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 108.3 [d, area 2, $^2J_{PP}$ = 54.7 Hz; P(1,4), P(3,6)], 105.4 [t, area 1; P(2,5)]. $^1H$ NMR ($C_6D_6$): $\delta$ 7.55 [s, area 2; arene H], 3.25 [compl mult, area 40; $CH_2$], 1.12 [compl mult, area 60; $CH_3$]. MS (EI$^+$) M$^+$, *m/e*: 1037, [$C_{46}H_{102}N_{14}P_6^+$]. IR (KBr, $cm^{-1}$): 2965 (vs), 2930 (vs), 2864 (vs), 2852 (vs), 2484 (w), 2400 (w), 1504 (m), 1475 (vs), 1418 (w), 1372 (vs), 1342 (m), 1324 (m), 1295 (m), 1219 (s), 1187 (s, br), 1101 (m), 1053 (m), 1011 (s), 955 (vs), 905 (vs, br), 822 (m), 795 (s), 785 (s), 688 (w), 668 (s), 648 (m), 615 (m), 551 (m), 484 (m), 462 (m), 417 (m), 355 (w). Anal. Calcd for $C_{46}H_{102}N_{14}P_6$: C, 53.28; H, 9.85; N, 18.92; P, 17.95. Found: C, 52.09; H, 9.79; N, 18.70; P, 16.87. **4** is soluble in $CH_2Cl_2$, benzene, and toluene.

Alternatively, butyllithium (1.6 mmol) in hexane was added slowly at −78 °C to 1,2,4,5-$(NH_2)_4C_6H_2{\cdot}4HCl$ (0.4 mmol) in tetrahydrofuran (25 mL) in a container shielded from ambient light by aluminum foil wrapping. The mixture was warmed slowly to 25 °C. The solution was filtered and the THF was removed in vacuo leaving mainly 1,2,4,5-$(NH_2)_4C_6H_2$. $P(NEt_2)_3$ (0.025 mmol) and toluene (20 mL) were added and the mixture was heated to 70 °C. After 20 h, the solution was filtered and toluene and $Et_2NH$ were removed in vacuo. Repeated recrystallization from toluene gave **4** (45% yield).

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**$C_6H_2\{N_2[P(S)(NEt_2)_2]_2PNEt_2\}_2$ (5).** Sulfur ($S_8$; 2.5 mol) was added to a solution of **4** (5 mmol) in toluene (50 mL) and allowed to react at 25 °C for 6 h. Removal of solvent in vacuo followed by recrystallization from toluene yielded pure **5** (>90% yield; mp = 207–211 °C). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 63.1 [d, area 2, $^2J_{PP}$ = 65.5 Hz; P(1,3)], 100.9 [t, area 1; P(2)]. $^1H$ NMR ($C_6D_6$): $\delta$ 8.09 [s, area 2; arene H], 3.6–2.9 [compl mult, area 40; $CH_2$], 1.14 [t, area 60, $^3J_{HH}$ = 7.01 Hz; $CH_3$]. **5** failed to give a parent ion in the $EI^+$ or FAB mass spectrum. IR (KBr, $cm^{-1}$): 3000 (vs), 2960 (vs), 2885 (s), 1489 (vs), 1393 (vs), 1364 (m), 1310 (w), 1278 (w), 1214 (vs), 1198 (vs), 1185 (vs), 1113 (m), 1072 (m), 1035 (vs), 1005 (s), 939 (vs, br), 873 (m), 834 (m), 808 (s), 722 (vs), 703 (s), 678 (m), 643 (s), 604 [(w), P=S], 540 (w), 495 (m). Anal. Calcd for $C_{46}H_{102}N_{14}P_6S_4$: C, 47.42; H, 8.76; N, 16.84; P, 15.98. Found: C, 46.55; H, 7.82; N, 16.35; P, 15.06.

Reaction of **5** with excess $S_8$ in toluene at 100 °C slowly yielded further oxidation products; however, attempts to isolate these from the reaction mixtures failed.

**Reaction 5 with HCl.** Addition of gaseous HCl to solutions of **5** in toluene at temperatures ranging from −78 to +25 °C gave complex $^{31}P\{^1H\}$ NMR spectral patterns. $^{31}P$ NMR spectra typically revealed two $AX_2$ patterns; a major triplet at $\delta$ 149 and doublet at $\delta$ 64.3 ($^2J_{PP}$ = 63.2 Hz) and a minor triplet at $\delta$ 146.2 and doublet at $\delta$ 64.7 ($^2J_{PP}$ = 58.0 Hz). No products were isolated from the reaction mixture.

**$C_6H_3N_3[P(NMe_2)_2]_2(PNMe_2)_2$ (6).** 1,2,3-$(NH_2)_3C_6H_3$ (8.1 mmol) and $(Me_2N)_3P$ (49 mmol) were fluxed for 36 h. After removal of excess $(Me_2N)_3P$ by vacuum distillation, **6** was obtained as a viscous oil. When the oil was left standing at ambient temperature for several weeks, **6** crystallized from the reaction mixture (mp = 63–66 °C). $^{31}P\{^1H\}$ NMR ($C_6D_6$) (NMR parameters determined by spectral simulation; see Figure 1): AA′BB′ pattern;[17] $\delta$ 110.6 [area 2, $^2J_{P(1)P(2)}$ = 66.4 Hz, $^2J_{P(2)P(3)}$ = 70.4 Hz, $^6J_{P(1)P(4)}$ = 0.7 Hz, $^4J_{P(1)P(3)}$ = 0.9 Hz; P(1)P(4)] and 109.2 [area 2; P(2)P(3)]. $^1H$ NMR ($C_6D_6$): $\delta$ 6.78 [compl mult, area 3; arene H], 2.59 [d, area 24; $CH_3$, exo], 2.40 [d, area 12; $CH_3$, ring]. MS ($EI^+$, $M^+$, *m/e*: 505, [$C_{18}H_{39}N_9P_4^+$]. IR (KBr, $cm^{-1}$): 2962 (m), 2868 (w), 2825 (s), 2792 (s), 1643 (m), 1480 (s), 1460 (s), 1405 (w), 1355 (w), 1306 (s), 1270 (s), 1242 (m), 1193 (s), 1156 (m), 1137 (w), 1090 (s), 1060 (m), 1038 (m), 964 (vs), 952 (vs), 933 (vs), 905 (s), 816 (s), 751 (m), 718 (m), 692 (m), 655 (s), 545 (m, sh), 535 (m, sh), 522 (m), 484 (m), 407 (w). Anal. Calcd for $C_{18}H_{39}N_9P_4$: C, 42.77; H, 7.78; N, 24.94; P, 24.51. Found: C, 43.16; H, 7.74; N, 23.90; P, 24.60. **6** is soluble in $CH_2Cl_2$, benzene, and toluene.

$(Me_2N)_3P$ and 1,2,3-$(NH_2)_3C_6H_3$ in mole ratios between 1.0:1.0 and 4.0:1.0 were heated to 110 °C while being monitored by $^{31}P$ NMR spectroscopy. Complex spectra arose preceding formation of **6**; however, these could not be interpreted, and intermediate reaction products were not separated.

1,2,3-$(NH_2)_3C_6H_3$ (20 mmol) and $(Et_2N)_3P$ (180 mmol) were heated to 110 °C for 3 days. $^{31}P$ NMR spectra of the reaction mixture showed only starting material and a minor, unassigned resonance at $\delta$ 108. No products were isolated from the reaction mixture.

**$C_6H_3N_3[P(Se)(NMe_2)_2]_2(PNMe_2)_2$ (7).** Selenium (4.0 mmol) and **6** (2.0 mmol) were stirred in $CH_2Cl_2$ (25 mL) at 25 °C. After 24 h, removal of solvent and recrystallization from toluene yielded pure **7** (mp = 92–94 °C). $^{31}P\{^1H\}$ NMR ($C_6D_6$) (NMR parameters determined by spectral simulation): AA′XX′ pattern;[17] $\delta$ 120.6 [area 2, P(2)P(3); $^2J_{P(1)P(2)}$ = 70.7 Hz, $^2J_{P(2)P(3)}$ = 82.0 Hz, $^4J_{P(1)P(3)}$ = −2.2 Hz] and 75.0 [area 2; P(1)P(4)]. $^1H$ NMR ($C_6D_6$): $\delta$ 6.98–6.77 [compl broad mult, area 3; arene H], 2.52 [compl mult, area 36; $CH_3$]. IR (KBr, $cm^{-1}$): 2936 (s), 2890 (s), 2848 (m), 2808 (m), 1636 (w), 1478 (s), 1464 (s), 1408 (w), 1347 (w), 1306 (m), 1285 (m), 1184 (m), 1164 (s), 1090 (vs), 1062 (m), 978 (m), 912 (m), 805 (m), 758 (w), 730 (m), 712 (m), 680 (m), 530 (s). **7** failed to give a parent ion in the mass spectrum. Anal. Calcd for $C_{18}H_{39}N_9P_4Se_2$: C, 32.59; H, 5.92; N, 19.00; P, 18.68. Found: C, 31.60; H, 5.69; N, 18.17; P, 18.37. **7** is soluble in $CH_2Cl_2$, benzene, and toluene.

**$C_6H_3N_3[P(Se)(NMe_2)_2]_2[P(Se)NMe_2]_2$ (8).** **6** (1.4 mmol) and Se (5.7 mmol) were refluxed in $CH_2Cl_2$ (25 mL) for 3 days. Recrystallization of reaction products from $CH_2Cl_2$ yielded pure **8** (mp = 255–258 °C). $^{31}P\{^1H\}$ NMR ($C_6D_6$) (NMR parameters determined by simulation): AA′XX′ pattern;[17] $\delta$ 59.0 [area 2, P(2)P(3); $^2J_{P(1)P(2)}$ = 15.5 Hz, $^2J_{P(2)P(3)}$ = 11.0 Hz, $^4J_{P(1)P(3)}$ = −2.1 Hz] and 52.1 [area 2; P(1)P(4)]. $^1H$ NMR ($C_6D_6$): $\delta$ 7.08–6.89 [compl mult, area 3; arene H], 2.50–2.11 [compl mult, area 24; $CH_3$]. **8** failed to give a parent ion in $EI^+$ or FAB mass spectrum. IR (KBr, $cm^{-1}$): 3044 (m), 3004 (m), 2910 (vs, br), 2842 (s), 2818 (s), 2460 (w, br), 1663 (m), 1422 (vs, br), 1408 (w), 1350 (w), 1315 (s), 1288 (vs), 1163 (vs, br), 1084 (vs), 1063 (vs, br), 1047 (s), 978 (vs, br), 959 (vs), 920 (vs), 857 (vs), 722 (vs), 680 (s), 646 (w), 618 (w), 557 (s), 508 (s), 440 (m). Anal. Calcd for $C_{18}H_{39}N_9P_4Se_4\cdot CH_2Cl_2$: C, 25.18; H, 4.56; N, 13.91; P, 13.67. Found: C, 25.16; H, 4.80; N, 11.05; P, 13.10. **8** is soluble in $CH_2Cl_2$, benzene, and toluene.

**Table I.** Crystallographic Data for $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (4)

| | | | |
|---|---|---|---|
| formula | $C_{46}H_{102}N_{14}P_6$ | *Z* | 2 |
| fw | 1037.44 | $d_{calc}$, g/cm$^3$ | 1.12 |
| space group | $P2_1/c$ | $d_{obs}$, g/cm$^3$ | 1.10 |
| *a*, Å | 12.573 (3) | radiation (λ, Å) | Mo K$\alpha$ (0.71073) |
| *b*, Å | 16.976 (3) | temp, K | 173 |
| *c*, Å | 15.455 (3) | transm factors | 0.792, 0.638 |
| $\beta$, deg | 111.55 (2) | $\mu$, cm$^{-1}$ | 2.11 |
| *V*, Å$^3$ | 3068 (5) | *R* | 0.055 |
| *F*(000) | 1132 | $R_w$ | 0.085 |

**Table II.** Crystallographic Data for $C_6H_3N_3[P(Se)(NMe_2)_2]_2[P(Se)NMe_2]_2$ (8) and $C_6H_3N_3[P(S)(NMe_2)_2]_2[P(S)NMe_2]_2$ (10)

| | **8** | **10** |
|---|---|---|
| formula | $C_{18}H_{39}N_9P_4Se_4\cdot CH_2Cl_2$ | $C_{18}H_{39}N_9P_4S_4\cdot CH_2Cl_2$ |
| fw | 906.24 | 633.72 |
| space group | *Pbca* | *Pbca* |
| *a*, Å | 14.858 (3) | 14.706 (3) |
| *b*, Å | 21.626 (6) | 21.610 (5) |
| *c*, Å | 22.327 (7) | 22.000 (5) |
| *V*, Å$^3$ | 7174 (3) | 6991 (3) |
| *Z* | 8 | 8 |
| $d_{calc}$, g/cm$^3$ | 1.68 | 1.365 |
| *F*(000) | 3584 | 3008 |
| $\mu$, cm$^{-1}$ | 40.4 | 6.22 |
| radiation (λ, Å) | Mo K$\alpha$ (0.71073) | Mo K$\alpha$ (0.71073) |
| temp, K | 294–296 | 294–296 |
| *R* | 0.066 | 0.049 |
| $R_w$ | 0.076 | 0.059 |

**$C_6H_3N_3[P(Se)(NMe_2)_2]_2(PCl_2)_2$ (9).** **7** (2.2 mmol) in toluene (25 mL), was cooled to −196 °C and gaseous HCl (8.8 mmol) was added. **9** formed upon slow warming (3–5 h) of the mixture to room temperature. Reactions could be monitored by $^{31}P$ NMR spectral analysis. **9** was obtained by recrystallization from $CH_2Cl_2$ (mp = 125 °C dec). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 147.8 [d, area 2, $^2J_{PP}$ = 71.3 Hz; P(2)P(3)], 65.6 [d, area 2; P(1)P(4)]. $^1H$ NMR ($C_6D_6$): $\delta$ 7.08–6.89 [compl mult, area 3; arene H], 2.50–2.11 [compl mult, area 24; $CH_3$]. **9** failed to give a parent ion in the $EI^+$ and FAB mass spectra. IR (KBr, $cm^{-1}$): 2962 (s), 2764 (s, br), 1636 (w), 1464 (m), 1388 (m), 1285 (m, sh), 1260 (s), 1174 (m), 1084 (m), 1010 (m), 975 (s, br), 875 (m), 800 (m), 720 (m), 692 (m), 520 (m), 400 (m, br). Anal. Calcd for $C_{14}H_{27}N_7P_4Cl_2Se_2\cdot CH_2Cl_2$: C, 24.64; H, 4.00; N, 13.41; P, 16.95. Found: C, 27.55; H, 4.73; N, 13.83; P, 17.27.

**$C_6H_3N_3[P(S)(NMe_2)_2]_2[P(S)NMe_2]_2$ (10).** Elemental sulfur (1.0 mmol) and **6** (2.0 mmol) in toluene (25 mL) were allowed to react at 25 °C for 24 h. Recrystallization from toluene yielded **10** (mp = 225 °C dec). $^{31}P\{^1H\}$ NMR ($C_6D_6$) (NMR parameters determined by simulation): AA′BB′ pattern;[17] $\delta$ 60.6 [area 2, P(2)P(3); $^2J_{P(1)P(2)}$ = 18.2 Hz, $^2J_{P(2)P(3)}$ = 11.0 Hz, $^6J_{P(1)P(4)}$ = 0.2 Hz, $^4J_{P(1)P(3)}$ = −2.1 Hz] and 60.1 [area 2; P(1)P(4)]. $^1H$ NMR ($C_6D_6$): $\delta$ 6.82 [compl mult, area 3; arene H], 2.85 [compl mult, area 24; $CH_3$, exo], 2.74 [compl mult, area 12; $CH_3$, ring]. MS (FAB, matrix of glycerol and $CH_2Cl_2$, $M^+$, *m/e*): 634, [$C_{18}H_{39}N_9P_4S_4^+$]. IR (KBr, $cm^{-1}$): 2924 (s), 2852 (m), 2808 (m), 1658 (m), 1468 (s, br), 1406 (w), 1375 (w), 1338 (m, sh), 1314 (m), 1290 (m), 1262 (m), 1178 (m, br), 1088 (vs, br), 984 (vs), 920 (s), 864 (m), 800 (m), 755 (s), 738 (s), 706 (m), 621 [(m), P=S], 593 [(m), P=S], 507 (m), 458 (m). Anal. Calcd for $C_{18}H_{39}N_9P_4S_4$: C, 34.12; H, 6.20; N, 19.89; P, 19.55. Found: C, 37.72; H, 6.20; N, 15.05; P, 16.54. **10** in soluble in $CH_2Cl_2$, benzene, and toluene.

Attempts to isolate partial oxidation products, i.e., mono-, di-, or trisulfides, from reactions conducted for shorter times were unsuccessful.

**X-ray Analyses. (A) $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (4).** Yellow parallelepipeds of **4**, obtained by crystallization from toluene, were mounted on glass fibers and analyzed at 173 K. Cell dimensions and crystal symmetry were determined on the diffractometer. Crystal data are given in Table I. Hydrogen atoms were included in fixed idealized positions. Complete details of the experimental conditions and results of the refinement are given in the supplementary material. Positional parameters are given in Table III; bond distances and angles are given in Tables VI and VII.

**(B) $C_6H_3N_3[P(Se)(NMe_2)_2]_2[P(Se)NMe_2]_2\cdot CH_2Cl_2$ (8).** Clear pale yellow parallelpiped crystals of **8** were obtained by recrystallization from $CH_2Cl_2$. A crystal suitable for X-ray diffraction analysis was selected, mounted on a glass fiber, and coated with epoxy. In spite of these

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[17] Abraham, R. J. *The Analysis of High Resolution NMR Spectra*; Elsevier: New York, 1971.

**Table III.** Positional (×10⁴) and Isotropic Displacement Parameters (Å × 10³) for $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (4)

| atom[a] | *x/a* | *y/b* | *z/c* | $U_{eq}$[b] |
|---|---|---|---|---|
| P(1) | 1794 (1) | 5701 (1) | 4580 (1) | 44 (1) |
| P(2) | 2257 (1) | 4909 (1) | 2956 (1) | 40 (1) |
| P(3) | 4240 (1) | 4468 (1) | 2313 (1) | 49 (1) |
| N(1) | 2691 (2) | 5345 (2) | 4052 (2) | 39 (1) |
| N(2) | 3686 (2) | 4808 (2) | 3113 (2) | 39 (1) |
| N(3) | 2405 (3) | 6579 (2) | 4942 (2) | 54 (1) |
| N(4) | 597 (3) | 5811 (2) | 3614 (2) | 47 (1) |
| N(5) | 1811 (3) | 4008 (2) | 3094 (2) | 49 (1) |
| N(6) | 5109 (4) | 5227 (3) | 2336 (3) | 83 (2) |
| N(7) | 3057 (3) | 4492 (2) | 1344 (2) | 50 (1) |
| C(1) | 3856 (3) | 5192 (2) | 4598 (2) | 37 (1) |
| C(2) | 4440 (3) | 4890 (2) | 4059 (2) | 37 (1) |
| C(3) | 5589 (3) | 4691 (2) | 4447 (2) | 38 (1) |
| C(31) | 2908 (5) | 7082 (3) | 4454 (4) | 90 (3) |
| C(32)* | 4064 (5) | 7393 (4) | 4964 (5) | 78 (3) |
| C(3D)* | 2817 (20) | 7813 (11) | 4270 (14) | 138 (12) |
| C(33) | 2432 (5) | 6847 (3) | 5853 (4) | 97 (3) |
| C(34) | 1839 (7) | 7561 (4) | 5893 (7) | 175 (6) |
| C(41) | 507 (4) | 6413 (3) | 2904 (3) | 57 (2) |
| C(42) | −373 (4) | 6219 (3) | 1955 (3) | 77 (2) |
| C(43) | −463 (3) | 5638 (3) | 3772 (3) | 60 (2) |
| C(44) | −921 (4) | 6311 (3) | 4171 (4) | 92 (3) |
| C(51) | 722 (3) | 3729 (3) | 2422 (3) | 61 (2) |
| C(52) | −209 (4) | 3647 (3) | 2801 (4) | 98 (3) |
| C(53) | 2425 (4) | 3456 (2) | 3835 (3) | 61 (2) |
| C(54) | 2977 (4) | 2779 (3) | 3526 (4) | 80 (2) |
| C(61) | 4832 (6) | 6071 (4) | 2419 (4) | 119 (3) |
| C(62) | 5733 (7) | 6527 (4) | 3168 (4) | 158 (4) |
| C(63) | 6224 (5) | 4974 (5) | 2222 (4) | 139 (4) |
| C(64) | 6218 (8) | 5141 (7) | 1303 (6) | 234 (8) |
| C(71) | 2526 (5) | 5250 (3) | 891 (3) | 81 (2) |
| C(72)* | 1353 (5) | 5224 (4) | 323 (4) | 73 (3) |
| C(7D)* | 2350 (19) | 5486 (10) | 42 (11) | 96 (10) |
| C(73) | 2972 (4) | 3832 (3) | 673 (3) | 75 (2) |
| C(74) | 2091 (5) | 3277 (3) | 668 (4) | 99 (3) |

[a] Atoms have occupancies of 1.0 except as marked with an asterisk above: C(32), 0.6689; C(3D), 0.3311; C(72), 0.6890; and C(7D), 0.3110. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

precautions, the crystal lost $CH_2Cl_2$ during data collection. Crystal data are given in Table II. Because of this decomposition and because of the isotropic shape of the crystal, no absorption correction was applied. Hydrogen atoms were not included in the final model for the compound. Complete details of the experimental conditions and results of the refinement are given in the supplementary material. Positional parameters are given in Table IV; bond distances and angles are given in Tables VIII and IX.

**(C) $C_6H_3N_3[P(S)(NMe_2)_2]_2[P(S)NMe_2]_2{\cdot}CH_2Cl_2$ (10).** Crystals of **10**, obtained by recrystallization from $CH_2Cl_2$, were mounted on glass fibers and coated with epoxy resin. Initially, the cell was determined to be orthorhombic, *Pnca*, *a* = 14.7421 (4) Å, *b* = 10.806 (6) Å, and *c* = 22.020 (13) Å. This cell resulted in a disordered model with the $C_6H_3N_3P_4$ moiety positioned on a crystallographic mirror plane, and sulfur atoms and $NMe_2$ groups disordered above and below the plane. Least-squares calculations using this model converged with $R = 0.039$, $R_w = 0.049$ for 1409 observed reflections and 271 variables. A comparison of the cell dimensions given above with those of **8** showed that if *b* were doubled the resulting cell would be isomorphous with **8**. Reexamination of **10** showed that the double cell was correct although the average intensity of that *l*-odd reflections was only 7% of the *k*-even reflections. Results presented in this paper are for a model based on the doubled cell. As with **8**, decomposition of the crystals occurred as a result of the loss of $CH_2Cl_2$. The data were corrected for this decline and for absorption. Crystal data are given in Table II. Hydrogen atoms were included in fixed idealized positions. Complete details of the experimental conditions and results of the refinement are given in the supplementary material. Positional parameters are given in Table V; bond distances and angles are given in Tables VIII and IX.

## Results and Discussion

Transamination reactions between 1,2,4,5-$(NH_2)_4C_6H_2$ [or 1,2,4,5-$(NH_2)_4C_6H_2{\cdot}4HCl$] and $(Et_2N)_3P$ or 1,2,3-$(NH_2)_3C_6H_3$ and $(Me_2N)_3P$ yield the new bis(triphosphazane) **4** (Scheme I) and tetraphosphazane **7** (Scheme II), respectively. The free amines, 1,2,4,5-$(NH_2)_4C_6H_2$ and 1,2,3-$(NH_2)_3C_6H_3$ react cleanly with neat liquid excess $(Et_2N)_3P$ and $(Me_2N)_3P$ at the refflux temperatures of the reaction mixtures. Solvent and/or liberated dialkylamine are removed periodically in vacuo to shift the transamination equilibria toward the tri- and tetraphosphazane products. Alternatively, reaction of 1,2,4,5-$(NH_2)_4C_6H_2{\cdot}4HCl$ with $(Et_2N)_3P$ occurs smoothly during 2 days in toluene at 80 °C. The amine hydrochloride offers the advantage of being more oxidatively stable and therefore easier to handle. Both **4** and **6** are surprisingly oxidatively and thermally stable. After 2 weeks

**Table IV.** Positional (×10⁴) and Isotropic Thermal Parameters (Å × 10³) for $C_6H_3N_3[P(Se)(NMe_2)_2]_2[P(Se)NMe_2]_2$ (8)

| atom[a] | *x/a* | *y/b* | *z/c* | *U*[b] |
|---|---|---|---|---|
| Se(1) | 3714 (2) | 750 (2) | −1106 (2) | 68 (2)* |
| Se(2) | 1362 (3) | −219 (2) | 834 (2) | 86 (2)* |
| Se(3) | 3459 (3) | 824 (2) | 2330 (2) | 76 (2)* |
| Se(4) | 1141 (2) | 3067 (2) | 1997 (2) | 68 (2)* |
| P(1) | 2509 (7) | 502 (4) | −685 (4) | 55 (4)* |
| P(2) | 2446 (7) | 358 (4) | 675 (4) | 51 (4)* |
| P(3) | 2421 (6) | 1197 (4) | 1839 (4) | 50 (4)* |
| P(4) | 2338 (6) | 2584 (4) | 2157 (4) | 53 (4)* |
| N(1) | 2474 (14) | 794 (10) | 22 (9) | 38 (7) |
| N(2) | 2434 (14) | 1001 (10) | 1102 (10) | 35 (6) |
| N(3) | 2439 (14) | 1984 (10) | 1660 (9) | 31 (6) |
| N(4) | 1595 (17) | 824 (13) | −984 (13) | 78 (9) |
| N(5) | 2399 (19) | −262 (12) | −633 (12) | 72 (8) |
| N(6) | 3429 (15) | 37 (11) | 731 (11) | 55 (8) |
| N(7) | 1390 (16) | 1052 (12) | 2114 (11) | 75 (9) |
| N(8) | 3249 (17) | 2994 (13) | 2024 (12) | 73 (9) |
| N(9) | 2412 (16) | 2291 (12) | 2833 (10) | 70 (9) |
| C(1) | 2489 (19) | 1436 (13) | 142 (12) | 43 (9) |
| C(2) | 2442 (19) | 1527 (13) | 759 (12) | 36 (8) |
| C(3) | 2477 (18) | 2083 (14) | 1021 (13) | 42 (9) |
| C(4) | 2530 (18) | 2641 (13) | 687 (13) | 37 (8) |
| C(5) | 2522 (21) | 2553 (16) | 51 (14) | 65 (10) |
| C(6) | 2523 (20) | 1974 (17) | −224 (13) | 63 (11) |
| C(41) | 1535 (26) | 808 (19) | −1660 (18) | 113 (14) |
| C(42) | 787 (23) | 1003 (16) | −659 (16) | 87 (12) |
| C(51) | 3173 (24) | −675 (18) | −561 (17) | 97 (13) |
| C(52) | 1472 (25) | −540 (17) | −741 (16) | 101 (14) |
| C(61) | 3634 (23) | −561 (16) | 1051 (16) | 82 (12) |
| C(62) | 4257 (19) | 418 (13) | 673 (13) | 44 (9) |
| C(71) | 1201 (22) | 539 (15) | 2572 (16) | 71 (11) |
| C(72) | 625 (19) | 1292 (15) | 1775 (14) | 67 (11) |
| C(81) | 3323 (22) | 3647 (16) | 2175 (14) | 84 (12) |
| C(82) | 4137 (21) | 2687 (15) | 1777 (14) | 71 (12) |
| C(91) | 3264 (21) | 2289 (14) | 3182 (14) | 64 (11) |
| C(92) | 1570 (21) | 2119 (16) | 3172 (15) | 77 (12) |
| Cl(1) | −215 (7) | 2063 (6) | 455 (5) | 130 (6)* |
| Cl(2) | 199 (7) | 3039 (5) | −365 (5) | 129 (6)* |
| C(10) | 77 (28) | 2863 (17) | 396 (17) | 117 (21)* |

[a] All atoms have occupancies of 1.0. [b] For atoms with values marked with an asterisk, the equivalent *U* is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Scheme I**

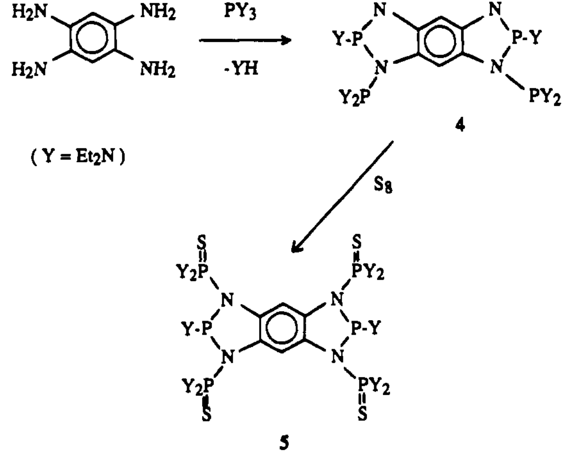


**Table V.** Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å × 10$^3$) for $C_6H_3N_3[PS(NMe_2)_2]_2[P(S)NMe_2]_2$ (**10**)

| atom[a] | *x/a* | *y/b* | *z/c* | $U_{eq}$[b] |
|---|---|---|---|---|
| S(1) | 3607 (1) | 687 (1) | −1053 (1) | 66 (1) |
| S(2) | 1425 (2) | −180 (1) | 906 (1) | 78 (1) |
| S(3) | 3421 (1) | 883 (1) | 2368 (1) | 69 (1) |
| S(4) | 1258 (1) | 3061 (1) | 2039 (1) | 61 (1) |
| P(1) | 2488 (1) | 469 (1) | −645 (1) | 48 (1) |
| P(2) | 2434 (1) | 350 (1) | 739 (1) | 45 (1) |
| P(3) | 2440 (1) | 1220 (1) | 1903 (1) | 42 (1) |
| P(4) | 2367 (1) | 2610 (1) | 2190 (1) | 46 (1) |
| N(1) | 2439 (4) | 763 (2) | 70 (2) | 43 (2) |
| N(2) | 2444 (3) | 1013 (2) | 1160 (2) | 40 (2) |
| N(3) | 2477 (3) | 1998 (2) | 1711 (2) | 40 (2) |
| N(4) | 1571 (4) | 764 (3) | −946 (3) | 60 (2) |
| N(5) | 2345 (4) | −278 (3) | −569 (3) | 67 (2) |
| N(6) | 3418 (4) | 19 (2) | 791 (3) | 54 (2) |
| N(7) | 1440 (4) | 1089 (3) | 2187 (3) | 54 (2) |
| N(8) | 3301 (4) | 2984 (3) | 2050 (3) | 62 (2) |
| N(9) | 2422 (4) | 2325 (3) | 2877 (2) | 58 (2) |
| C(1) | 2490 (4) | 1419 (3) | 175 (3) | 36 (2) |
| C(2) | 2480 (4) | 1527 (3) | 782 (3) | 38 (2) |
| C(3) | 2492 (4) | 2085 (3) | 1058 (3) | 40 (2) |
| C(4) | 2530 (4) | 2598 (3) | 697 (3) | 48 (2) |
| C(5) | 2539 (4) | 2511 (3) | 68 (3) | 51 (2) |
| C(6) | 2519 (4) | 1927 (3) | −199 (3) | 46 (2) |
| C(41) | 1466 (7) | 763 (5) | −1609 (4) | 116 (5) |
| C(42) | 768 (5) | 961 (4) | −628 (4) | 94 (4) |
| C(51) | 3112 (7) | −703 (4) | −517 (4) | 99 (4) |
| C(52) | 1468 (7) | −585 (4) | −644 (4) | 100 (4) |
| C(61) | 3583 (6) | −556 (3) | 1136 (4) | 87 (4) |
| C(62) | 4241 (4) | 396 (4) | 720 (4) | 69 (3) |
| C(71) | 1271 (7) | 604 (4) | 2626 (4) | 94 (4) |
| C(72) | 641 (4) | 1290 (4) | 1851 (4) | 73 (3) |
| C(81) | 3380 (6) | 3633 (4) | 2236 (4) | 88 (4) |
| C(82) | 4154 (5) | 2720 (4) | 1838 (4) | 90 (4) |
| C(91) | 3287 (5) | 2290 (4) | 3217 (4) | 83 (4) |
| C(92) | 1614 (5) | 2192 (4) | 3236 (3) | 82 (4) |
| Cl(1) | −164 (2) | 2086 (1) | 492 (1) | 106 (1) |
| Cl(2) | 190 (2) | 3070 (1) | −350 (1) | 121 (1) |
| C(10) | 39 (6) | 2866 (4) | 415 (4) | 95 (4) |

[a] All atoms have occupancies of 1.0. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table VI.** Bond Distances (Å) for $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (**4**)

| | | | |
|---|---|---|---|
| P(1)–N(1) | 1.725 (4) | P(1)–N(3) | 1.677 (3) |
| P(1)–N(4) | 1.696 (3) | P(2)–N(1) | 1.742 (3) |
| P(2)–N(2) | 1.731 (3) | P(2)–N(5) | 1.669 (3) |
| P(3)–N(2) | 1.727 (4) | P(3)–N(6) | 1.681 (5) |
| P(3)–N(7) | 1.680 (3) | N(1)–C(1) | 1.421 (4) |
| N(2)–C(2) | 1.428 (4) | N(3)–C(31) | 1.431 (7) |
| N(3)–C(33) | 1.467 (7) | N(4)–C(41) | 1.473 (5) |
| N(4)–C(43) | 1.471 (6) | N(5)–C(51) | 1.460 (4) |
| N(5)–C(53) | 1.461 (5) | N(6)–C(61) | 1.492 (8) |
| N(6)–C(63) | 1.538 (9) | N(7)–C(71) | 1.499 (5) |
| N(7)–C(73) | 1.504 (6) | C(1)–C(2) | 1.395 (6) |
| C(1)–C(3′)[a] | 1.395 (5) | C(2)–C(3) | 1.387 (5) |

[a] Atom C(3′) is symmetry related to C(3) by the following operation: 1.0 − *x*, 1.0 − *y*, 1.0 − *z*.

in air, no decomposition was seen in the $^{31}$P NMR spectral samples; prolonged exposure of **4** to air caused discoloration but no obvious decomposition. In $CH_2Cl_2$ solution, **4** in air turned red slowly; however, decomposition product concentrations were too low to detect by either $^{31}$P or $^1$H NMR spectroscopy.

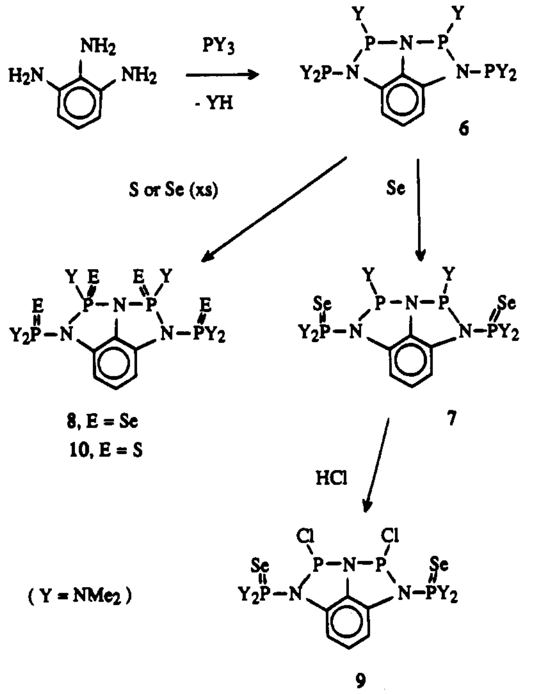
The observed reactions appear to be analogous to those reported earlier between $(Et_2N)_3P$ and 1,2-$(NH_2)_2C_6H_4$, which yield the triphosphazane $C_6H_4N_2[P(NEt_2)_2]_2PNEt_2$ (**2**).[2,3] Like the $(Et_2N)_3P$/1,2-$(NH_2)_2C_6H_4$ reactions, these transaminations also depend substantially on the nature of the alkyl group of the tris(amino)phosphine. 1,2,4,5-$(NH_2)_4C_6H_2$ [or 1,2,4,5-$(NH_2)_4C_6H_2$·4HCl] reacts with $(Me_2N)_3P$ to form transamination products, but the reaction mixtures are complex and it was not possible to determine unambiguously if a product analogous to **4** had formed. Similarly, even though 1,2,3-$(NH_2)_3C_6H_3$ reacts cleanly with $(Me_2N)_3P$, no reaction with $(Et_2N)_3P$ is observed over 3 days at 110 °C. It is presumed that the much lower reactivity results because $(Et_2N)_3P$ is more sterically bulky than $(Me_2N)_3P$ and as a result is less able to react with the more crowded 1,2,3-amine-substituted arene system.

**Table VII.** Bond Angles (deg) for $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (4)

| | | | |
|---|---|---|---|
| N(1)–P(1)–N(3) | 99.9 (2) | N(1)–P(1)–N(4) | 98.3 (2) |
| N(3)–P(1)–N(4) | 110.2 (2) | N(1)–P(2)–N(2) | 88.1 (1) |
| N(1)–P(2)–N(5) | 105.4 (2) | N(2)–P(2)–N(5) | 105.8 (2) |
| N(2)–P(3)–N(6) | 99.1 (2) | N(2)–P(3)–N(7) | 99.9 (2) |
| N(6)–P(3)–N(7) | 110.9 (2) | P(1)–N(1)–P(2) | 125.6 (2) |
| P(1)–N(1)–C(1) | 119.5 (2) | P(2)–N(1)–C(1) | 112.8 (3) |
| P(2)–N(2)–P(3) | 127.1 (2) | P(2)–N(2)–C(2) | 113.5 (3) |
| P(3)–N(2)–C(2) | 118.4 (2) | P(1)–N(3)–C(31) | 126.2 (3) |
| P(1)–N(3)–C(33) | 116.3 (3) | C(31)–N(3)–C(33) | 117.5 (4) |
| P(1)–N(4)–C(41) | 122.2 (3) | P(1)–N(4)–C(43) | 113.4 (3) |
| C(41)–N(4)–C(43) | 115.8 (3) | P(2)–N(5)–C(51) | 118.5 (3) |
| P(2)–N(5)–C(53) | 125.6 (2) | C(51)–N(5)–C(53) | 115.9 (3) |
| P(3)–N(6)–C(61) | 124.6 (4) | P(3)–N(6)–C(63) | 113.4 (5) |
| C(61)–N(6)–C(63) | 122.0 (6) | P(3)–N(7)–C(71) | 122.3 (3) |
| P(3)–N(7)–C(73) | 114.3 (3) | C(71)–N(7)–C(73) | 114.3 (3) |
| N(1)–C(1)–C(2) | 111.5 (3) | N(1)–C(1)–C(3′) | 127.5 (4) |
| C(2)–C(1)–C(3′)[g] | 121.03 (3) | N(2)–C(2)–C(1) | 110.5 (3) |
| N(2)–C(2)–C(3) | 127.8 (4) | C(1)–C(2)–C(3) | 121.7 (3) |
| C(2)–C(3)–C(1′) | 117.3 (4) | | |

[a] Atoms C(1′) and C(3′) are symmetry related atoms generated from C(1) and C(3) by the following operation: 1.0 − *x*, 1.0 − *y*, 1.0 − *z*.

**Scheme II**



Spectral data ($^1$H and $^{31}$P NMR, IR, MS) provide basic characterization for **4** and **6**. Mass spectral parent ions occur at *m/e* 1037 and 505 for **4** and **6**, respectively, and major fragment ions appear consistent with those expected[18] by the loss of $R_2N$ and $(R_2N)_2P$ moieties. The $^{31}$P NMR spectrum of **4** exhibits a distinct, coupled, doublet and triplet $AX_2$ pattern[17] at δ 108.3 and 105.4, at chemical shifts agreeing closely with those observed earlier for **2**.[2] Both resonances are in the region expected for phosphadiazole[19-21] and tris(amino)phosphine[20,22-24] phosphorus

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**Table VIII.** Selected Bond Distances (Å) for $C_6H_3N_3[PSe)(NMe_2)_2]_2[P(Se)NMe_2]_2$ (**8**) and $C_6H_3N_3[P(S)(NMe_2)_2]_2[P(S)NMe_2]_2{\cdot}CH_2Cl_2$ (**10**)

| | **8** (E = Se) | **10** (E = S) | | **8** (E = Se) | **10** (E = S) |
|---|---|---|---|---|---|
| P(1)–N(1) | 1.70 (2) | 1.696 (5) | P(4)–N(8) | 1.64 (3) | 1.623 (6) |
| P(1)–N(4) | 1.66 (3) | 1.633 (6) | P(4)–N(9) | 1.64 (2) | 1.634 (6) |
| P(1)–N(5) | 1.66 (3) | 1.636 (6) | P(4)–E(4) | 2.09 (1) | 1.928 (3) |
| P(1)–E(1) | 2.09 (1) | 1.933 (3) | N(1)–C(1) | 1.41 (4) | 1.438 (7) |
| P(2)–N(1) | 1.73 (2) | 1.722 (5) | N(2)–C(2) | 1.37 (4) | 1.390 (7) |
| P(2)–N(2) | 1.68 (2) | 1.707 (5) | N(3)–C(3) | 1.44 (3) | 1.448 (7) |
| P(2)–N(6) | 1.62 (3) | 1.618 (6) | C(1)–C(2) | 1.39 (4) | 1.355 (8) |
| P(2)–E(2) | 2.06 (1) | 1.910 (3) | C(1)–C(6) | 1.42 (4) | 1.373 (8) |
| P(3)–N(2) | 1.69 (2) | 1.695 (5) | C(2)–C(3) | 1.34 (4) | 1.351 (8) |
| P(3)–N(3) | 1.75 (2) | 1.734 (5) | C(3)–C(4) | 1.42 (4) | 1.364 (9) |
| P(3)–N(7) | 1.67 (3) | 1.623 (6) | C(4)–C(5) | 1.43 (4) | 1.397 (9) |
| P(3)–E(3) | 2.05 (1) | 1.912 (3) | C(5)–C(6) | 1.39 (5) | 1.392 (9) |
| P(4)–N(3) | 1.71 (2) | 1.699 (5) | | | |

**Table IX.** Selected Bond Angles (deg) for $C_6H_3N_3[P(Se)(NMe_2)_2]_2[P(Se)NMe_2]_2$ (**8**) and $C_6H_3N_3[P(S)(NMe_2)_2]_2[P(S)NMe_2]_2{\cdot}CH_2Cl_2$ (**10**)

| | **8** (E = Se) | **10** (E = S) | | **8** (E = Se) | **10** (E = S) |
|---|---|---|---|---|---|
| E(1)–P(1)–N(1) | 110.4 (8) | 112.0 (2) | N(8)–P(4)–N(9) | 108.6 (13) | 108.8 (3) |
| E(1)–P(1)–N(4) | 114.2 (10) | 114.8 (2) | P(1)–N(1)–C(1) | 122.7 (18) | 121.1 (4) |
| E(1)–P(1)–N(5) | 111.7 (11) | 113.4 (2) | P(1)–N(1)–P(2) | 125.2 (13) | 126.7 (3) |
| N(1)–P(1)–N(4) | 101.0 (13) | 101.3 (3) | P(2)–N(1)–C(1) | 112.1 (17) | 111.9 (4) |
| N(1)–P(1)–N(5) | 107.6 (12) | 105.6 (3) | P(2)–N(2)–P(3) | 138.8 (4) | 138.2 (3) |
| N(4)–P(1)–N(5) | 111.2 (14) | 108.7 (3) | P(3)–N(2)–C(2) | 109.5 (18) | 111.5 (4) |
| E(2)–P(2)–N(1) | 119.4 (8) | 118.7 (2) | P(2)–N(2)–C(2) | 111.7 (18) | 110.3 (4) |
| E(2)–P(2)–N(2) | 113.1 (9) | 113.9 (2) | P(3)–N(3)–C(3) | 111.8 (18) | 111.7 (4) |
| E(2)–P(2)–N(6) | 115.4 (10) | 114.6 (2) | P(3)–N(3)–P(4) | 126.1 (12) | 126.9 (3) |
| N(1)–P(2)–N(2) | 91.4 (11) | 91.7 (2) | P(4)–N(3)–C(3) | 121.9 (18) | 121.0 (4) |
| N(1)–P(2)–N(6) | 106.0 (12) | 106.6 (3) | N(1)–C(1)–C(2) | 109.0 (24) | 109.2 (5) |
| N(2)–P(2)–N(6) | 108.6 (12) | 109.0 (3) | N(1)–C(1)–C(6) | 134.0 (26) | 133.8 (5) |
| E(3)–P(3)–N(2) | 114.2 (8) | 114.4 (2) | C(2)–C(1)–C(6) | 117.0 (26) | 116.9 (5) |
| E(3)–P(3)–N(3) | 119.4 (8) | 118.5 (2) | N(2)–C(2)–C(1) | 115.8 (25) | 116.8 (5) |
| E(3)–P(3)–N(7) | 114.5 (10) | 114.3 (2) | N(2)–C(2)–C(3) | 120.2 (25) | 116.5 (5) |
| N(2)–P(3)–N(3) | 91.2 (10) | 91.2 (2) | C(1)–C(2)–C(3) | 123.8 (27) | 126.7 (6) |
| N(2)–P(3)–N(7) | 108.6 (12) | 109.1 (3) | N(3)–C(3)–C(2) | 107.2 (25) | 109.2 (5) |
| N(3)–P(3)–N(7) | 106.2 (12) | 107.0 (3) | N(3)–C(3)–C(4) | 130.3 (26) | 133.2 (6) |
| E(4)–P(4)–N(3) | 110.0 (8) | 111.5 (2) | C(2)–C(3)–C(4) | 122.5 (26) | 117.6 (6) |
| E(4)–P(4)–N(8) | 113.5 (11) | 115.5 (2) | C(3)–C(4)–C(5) | 113.9 (26) | 117.9 (6) |
| E(4)–P(4)–N(9) | 114.0 (10) | 113.1 (2) | C(4)–C(5)–C(6) | 123.8 (30) | 122.7 (6) |
| N(3)–P(4)–N(8) | 102.7 (12) | 100.9 (3) | C(1)–C(6)–C(5) | 118.9 (27) | 118.2 (6) |
| N(3)–P(4)–N(9) | 107.2 (12) | 106.0 (3) | | | |

atoms. That only one $AX_2$ pattern is seen indicates that the $P_3N_2$ units of the molecule are equivalent, perhaps because the exo $P(NEt_2)_2$ groups are on average equivalent in solution. The $^{31}P$ NMR spectrum (Figure 1A) of **6** consists of two resonances (δ 110.6 and 109.2) in an AA′BB′ pattern. From spectral simulation, it was possible to ascertain the pertinent coupling constants (Figure 1B). Since only one set of resonances is seen, we conclude that **6** also is present in solution in only one isomeric form.

Complete structural characterization of **4** has been achieved by single-crystal X-ray analysis at −100 °C. The structure of **4** is shown in Figure 2. The molecule consists of an arene ring with two phosphadiazole rings fused at the arene 1,2- and 4,5-positions to create a tricyclic ring system. There are two molecules of **4** per unit cell; a crystallographic inversion center at the center of the $C_6$ ring relates the two $P_3N_2$ moieties of the molecule to each other. Each phosphadiazole unit has a $(Et_2N)_2P$ group bonded at each nitrogen atom. The $C_6$ ring and four bonded nitrogen atoms are coplanar; the phosphorus atoms of the phosphadiazole rings [P(2) and P(2′)] are displaced out of this plane by 0.009 Å, and the exo phosphorus atoms [P(1) and P(3) or P(1′) and P(3′)] are displaced by 0.228 Å in the opposite directions. The dihedral angle between the $C_6N_4$ plane and the N(1)/P(2)/N(2) plane is 17.0°, similar to that seen (21.4°) for the analogous angle in **2**.[2] The exo $(Et_2N)_2P$ units of **4** are rotated in the solid such that the lone-pair of electrons on each phosphorus atom is approximately trans oriented relative to the lone pair of the central P(2) atom. An analogous confirmation was reported for **2**. A similar conformational situation may predominate in solution where a$^2J_{PP}$ coupling constant between the exo and central [P(2)] phosphorus atoms of 54.7 Hz occurs, a situation consistent with that expected for phosphorus(III) diphosphazanes, which prefer a mostly trans conformation.[25] Because the $(Et_2N)_2P$ units are

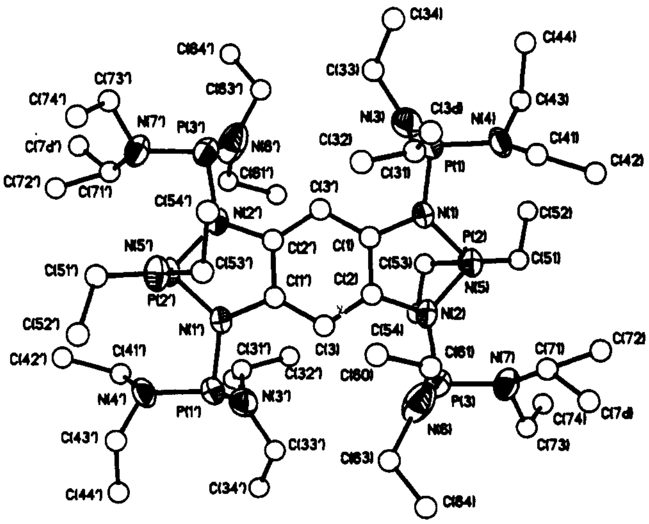

**Figure 2.** Structure and numbering scheme for $C_6H_2\{N_2[P(NEt_2)_2]_2PNEt_2\}_2$ (**4**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

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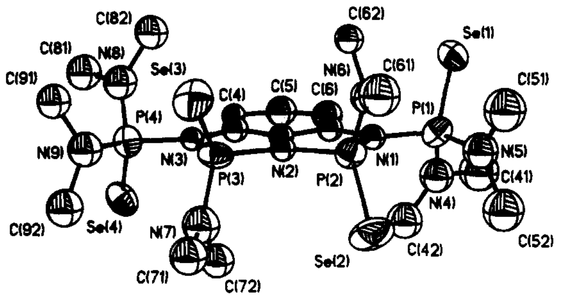


**Figure 3.** Structure and numbering scheme for $C_6H_3N_3[PSe(NMe_2)_2]_2[P(Se)NMe_2]_2$ (**8**). Thermal ellipsoids are shown at the 50% probability level.

very bulky, a protected cleft is created around the central phosphorus, P(2).

Bond lengths and angles in **4** (Table VI and VII) are generally as expected for aminophosphines[8,9,26] and phosphadiazoles;[2,4,6,27] the P–N$_{aryl}$ distances (mean 1.726 Å) are slightly longer than the P–N$_{alkyl}$ distances (mean 1.676 Å), but both are with the range of values seen in other P(III) phosphazanes. The P–N distances in the phosphazadiazole $C_2N_2P$ ring (mean 1.706 Å) are significantly longer than the exo ring bonds (mean 1.679 Å), although both are within the range of previously observed P–N bond distances. The phosphadiazole N(1)–P(2)–N(2) angle is small at 88.1°, but close to that of the analogous angle in **2** (87.5°) and in diazadiphosphetidines.[23a,28]

Reaction of **4** with sulfur provides initial insight into reactivity of the bis(triphosphazane) system and allows the reactivity of **4** to be compared with that of **2**. Compound **4**, like **2**, reacts readily in toluene with sulfur at the exo $(Et_2N)_2P$ phosphorus atoms (Scheme I). Reaction is regioselective to the complete exclusion of the central [P(2) and P(2′)] sites, to form the tetrasulfide $C_6H_2\{N_2[P(S)(NEt_2)_2]_2PNEt_2\}_2$ (**5**) quantitatively. Reaction occurs in 4–6 h at room temperature; under these conditions there is no evidence for formation of more completely oxidized penta- or hexasulfide products. Mass spectra show only the characteristic parent ion for **5** at *m/e* 621. **5** exhibits a characteristic symmetrical two-resonance triplet and doublet $AX_2$ $^{31}P$ NMR spectral pattern at δ 100.9 and 63.1, indicating that the $(Et_2N)_2P(S)$ groups are, on average, equivalent in solution.

Oxidation of **6** with sulfur and selenium (Scheme II) leads to new diselenide, tetrasulfide, and tetraselenide products. With sulfur, reaction occurs rapidly at 25 °C to form the completely oxidized tetraphosphazane **10**. There is little tendency toward regioselective reaction at either the exo or the endo phosphorus atom positions. The tetrasulfide is the dominant product, even from reactions deficient in $S_8$ or carried out at temperatures as low as −78 °C. In contrast, reactions of **6** with elemental selenium are regioselective. After 6 h at 25 °C, mainly the diselenide **7** is present. Only under much more vigorous conditions, 40 °C for 3 days, does the tetraselenide **8** form. This higher degree of regioselectivity in reactions of **6** with selenium compared to sulfur is consistent with the generally lower reactivity of selenium towards aminophosphines.[29] In addition, there might be a steric factor involved; the central phosphorus atoms P(2) and P(2′) are in a region more difficult to attack by the larger selenium reagent.[29]

The structures of **8** and **10**, and indirectly those of **6** and **7**, were established through single-crystal X-ray analyses. Both **8** and **10** were examined in order to determine if there is any structural dependence of the systems on sulfur versus selenium substitution. **8** and **10** crystallize from $CH_2Cl_2$ in space group *Pbca*. They are isomorphous with cell constants that differ by less than 2%. The structures of the molecules are shown in Figures 3–5. **8** and **10** are tricyclic molecules that contain a pair of fused phosphadiazole rings at the 1,2- and 2,3-positions of a benzene ring. The phosphazane $P_4N_3$ chain, which contains nitrogen atoms N(1), N(2), and N(3), is close to coplanar with the $C_6$ ring. The average out-of-plane distance for the phosphorus atoms is 0.056 Å. **8** and **10** possess approximate $C_2$ molecular symmetry, with the $C_2$ axis bisecting N(2), C(2), and C(5). The endo P═E (E = S, Se) bonds are oriented approximately trans relative to the exo P═E bonds; e.g. in **10** the torsional angles between P(1)-S(1) and P(2)-S(2) and between P(3)-S(3) and P(4)-S(4) are 156.5° and 159.3°, respectively. The endo P═E bonds are oriented more closely orthogonal; the P(2)–S(2) to P(3)–S(3) angle in **10** is 102.8°. Therefore **8** and **10** are the trans-*d,l* diastereomers of the possible two diastereomer systems, trans-*d,l* and cis-*meso*, that could occur.

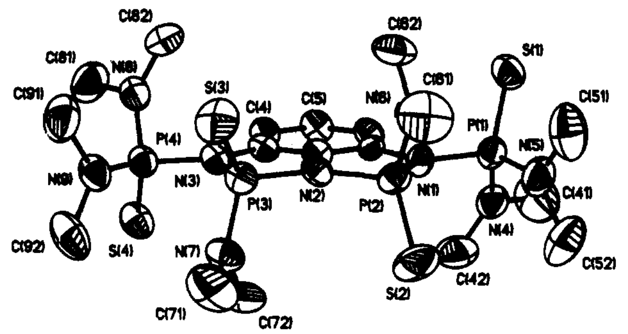


**Figure 4.** Structure and numbering scheme for $C_6H_3N_3[PS(NMe_2)_2]_2[P(S)NMe_2]_2$ (**10**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

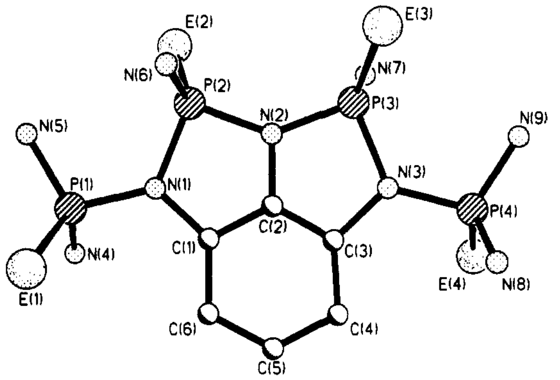
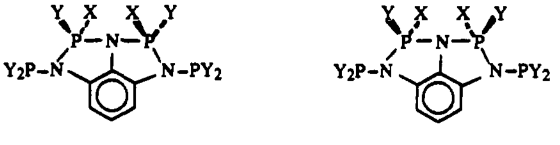


**Figure 5.** View of **8** (**10**) perpendicular to the $C_6N_3P_4$ molecular plane. $Me_2N$ carbon atoms are omitted for clarity.



trans - d,l (Y = NMe2, X = S, Se) cis - meso

Bond lengths in both **8** and **10** are close to those seen in **4** and the previously reported **2**; only the C(2)–N(2) bond at 1.390 Å is exceptionally short (see discussion below). The N–C distances and angles around the nitrogen atoms in the bridging $Me_2N$–P and exo peripheral $(Me_2N)_2P$ groups are not unusual; mean N–C distances are 1.49 Å (**8**) and 1.46 Å (**10**) and the P–N–C and C–N–C angles are 121 (3) and 116 (3)° (**8**) and 122 (3) and 114 (1)° (**10**).

Spectral data confirm that the structures of **8** and **10** in solution are closely similar to those seen in the solid and that **6**–**8** and **10** are present in only one diastereomeric form. **8** and **10** show only two P═E (E = S, Se) infrared stretching absorptions, attributable

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to the endo and exo P═E bond units of a single diastereomer. **6**–**8** and **10** each exhibit a single AA′BB′ (or AA′XX′) $^{31}$P NMR spectral pattern. All were simulated, for example Figure 1B for **6**, in order to obtain accurate coupling constant and chemical shift data. The P(2)-P(3) $^2J_{PP}$ coupling constants of 70.4 Hz in **6** and 82.0 Hz in **8** are as expected for approximately trans-oriented P lone pair electrons in a $\lambda^3$–$\lambda^3$ phosphazane. Likewise, the P(2)–P(3) coupling constants of 11.0 Hz in both **8** and **10** are consistent with that expected for trans oriented P═S bond units in a $\lambda^5$–$\lambda^5$ diphosphazane.[25,30] In fact, **6**–**8** and **10**, are rare examples of systems that, because their conformations in solution and in the solid must be essentially identical, allow confirmation of the correlations between $^2J_{PP}$ values and conformational angles. The $^2J_{PP}$ coupling between the endo and exo phosphorus atoms, P(1)–P(2), of 66.4 and 70.7 Hz in **6** and **7**, respectively, and 15.5 and 18.2 Hz in **8** and **10**, respectively, indicate that in these the lone pair electrons or P═S bonds, as in **3**, are on average in trans conformations in solution.[25,29–32]

Reactions of **4**–**8** and **10** with HCl are of interest to compare with those of the previously studied **2**.[2,3] As with **2**, anhydrous HCl reacts with **4**–**6** nonselectively to give a variety of uncharacterized products.[2] In contrast, neither **8** nor **10** react with HCl in toluene during extended periods at 25 °C. Addition of gaseous HCl to the diselenide **7** yields the dichloride **9** nearly quantitatively. Although **9** could not be crystallized, spectral data confirm clearly that it is the dichloride derivative and that it is monodiastereomerically formed. The $^{31}$P NMR spectrum appears as two coupled ($^2J_{PP}$ = 71.2 Hz) equal-area doublets at $\delta$ 147.8 and 66.1, in a $(AX)_2$ pattern. The relatively simple spectrum is unexpected in light of spectra of **6**–**8** and **10** being more complex AA′BB′ or AA′XX′ patterns. This suggests that coupling between the endo and exo phosphorus atoms is small or zero, eliminating the magnetic inequivalence of A and B (or X) type atoms.[17] This could be a substituent effect, i.e. the result of replacing $NMe_2$ groups by Cl atoms; however, it could also indicate that **9** is a different diastereomer than compounds in the **6**, **7**, **9**, and **10** series.

Tetraphosphazane **6** is first examples of a linear P(III) phosphazane that contains an extended phosphorus–nitrogen atom skeleton of more than three phosphorus atoms. Because the substituent geometry at phosphorus atoms P(2) and P(3) is fixed by their being in phosphadiazole rings, two diastereomers, cis-*meso* and trans-*d*,*l*, are possible. However, even in the 1,2,3-$(NH_2)_3C_6H_3/P(NMe_2)_3$ reaction mixture only the trans-*d*,*l* isomer is seen. This diasteromerically selective formation of **6** is relatively rare in phosphazane formation reaction chemistry. Only in the synthesis of *meso*-*i*-PrN[PhP(*i*-RNH)]$_2$ (R = Me, Et, *i*-Pr) from $PhPCl_2$/*i*-$PrNH_2$/$Et_3N$ has diasteromer selection been unambigously established previously.[33] The diastereoselective formation of **6** and the implications this process has for formation of higher order skeletally stabilized phosphazanes will be studied further.

As indicated in the Introduction, it is of interest to determine to what extent phosphazane formation around the periphery of a benzene ring can be developed, ultimately to form cyclohexaphosphazanes of type **3**. Some indication of this feasibility can be obtained by comparing the "fit" between the phosphazane unit and the arene ring in **4** versus that which occurs in **10** (or **8**). Although the fit of the phosphadiazole rings in **4** is quite good, they are not perfect since the internal angles around C(1) and C(2) [C(1)–C(2)–N(2) and C(2)–C(1)–N(1)] of the phosphadiazole ring are 111.0° (mean), somewhat less that the ideal angles of 120°. The analogous internal angles in **10** (**8**) around C(1) and C(3) [N(3)–C(3)–C(2) and C(2)–C(1)–N(1)] are 109.2°, only slightly smaller than those in **4**. Having the two fused phosphadiazole rings in **10** (**8**) causes extra strain on the system, which might in part be relieved by (i) foreshortening the phosphadiazole center C–N bond distance [C(2)–N(2)] to 1.39 Å relative to that of the outer C–N distances [C(3)–N(3) and C(1)–N(1)] of 1.44 Å (mean), and (ii) more significantly, distorting the hexagonal $C_6$ ring in **10** (**8**) relative to that in **4**. In **10** the C(1)–C(2)–C(3) and transannular C(4)–C(5)–C(6) angles are 126.7 and 122.7°, respectively, whereas the other angles are uniformly around 118°. This distortion decreases the C(2)⋯C(5) distance relative to that of the other C⋯C transannular vectors and in effect compresses the $C_6$ hexagon along the C(2)⋯C(5) axis (Figure 5). However, in spite of the observed distortions in bond angles and distances, these are not enough to distort the $C_6$ ring carbon atoms and the attached three [in **10** (**8**)] or four (in **4**) nitrogen atoms from coplanarity. Thus, it appears possible to fit a tetra- or pentaphosphazane, or even a cyclohexaphosphazane, around a $C_6$ arene ring. However, it seems likely that the cumulative effect of attaching three or more fused phosphadiazole rings might lead to enough distortion that a "dishing" of the system will be required in order to accommodate the fit. Further studies of the synthesis and structural properties of higher order phosphazanes appear warranted.

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**Supplementary Material Available:** Listings of complete crystallographic data, hydrogen atom coordinates, anisotropic thermal parameters, least-squares planes and equations, and complete bond distance and bond angle parameters (25 pages); listings of observed and calculated structure factors (75 pages). Ordering information is given on any current masthead page.

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