Acknowledgment. J.V.Z.K. gratefully acknowledges the financial support of this project received from the Research Corp., the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation, Grant No. CHE-8416730. The department of Chemistry and Biochemistry at San Francisco State University acknowledges support received from the National Institutes of Health, Grant No. RR02684, and the National Science Foundation, Grant No. DMB-8516065, for purchase of the General Electric QE-300 and GN-300 NMR spectrometers.

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Intermediates in the 1,2-$(NH_2)_2C_6H_4$/$P(NEt_2)_3$ Transamination Reaction

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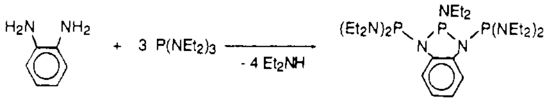
Received May 14, 1990

The diazaphosphole intermediates $C_6H_4(NH)_2PNEt_2$ (**2**), $C_6H_4(NH)P(NEt_2)NP(NEt_2)_2$ (**3**), and $[C_6H_4(NH)P(NEt_2)N][P(NH)_2C_6H_4]$ (**6**), the addition-coupled product of **2**, formed in the 1,2-$(NH_2)_2C_6H_4/P(NEt_2)_3$ transaminative formation of $C_6H_4[NP(NEt_2)_2]_2PNEt_2$ (**1**), have been characterized. Sulfur oxidation of P(III) product mixtures yields isolatable sulfides $C_6H_4(NH)_2P(S)NEt_2$ (**7**), $[C_6H_4(NH)_2P(S)][C_6H_4(NH)(N)P(S)NEt_2]$ (**8**), $C_6H_4(NH)PS(NEt_2)NPS(NEt_2)_2$ (**9**), and $(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2$ (**10**). **2**, **3**, and **6–10** are characterized by spectral data (MS, IR, and ^{31}P and ^1H NMR). **7**, **8**, and **10** are characterized by X-ray single-crystal analysis. **7**: monoclinic, $P2_1/c$, $a = 14.736$ (6) Å, $b = 8.872$ (5) Å, $c = 21.581$ (8) Å, $\beta = 104.38$ (3)°, $V = 2606$ (2) Å^3, $Z = 8$, $d_{calc} = 1.19$ g cm^{-3}. **8**: monoclinic, $P2_1/c$, $a = 21.384$ (9) Å, $b = 9.341$ (4) Å, $c = 22.293$ (8) Å, $\beta = 118.06$ (3)°, $V = 3930$ (3) Å^3, $Z = 8$, $d_{calc} = 1.38$ g cm^{-3}. **10**: triclinic, $P\bar{1}$, $a = 9.741$ (7) Å, $b = 11.655$ (5) Å, $c = 20.240$ (10) Å, $\alpha = 73.41$ (4)°, $\beta = 76.23$ (5)°, $\gamma = 79.17$ (5)°, $V = 2121$ (2) Å^3, $Z = 2$, $d_{calc} = 1.20$ g cm^{-3}. The $\mathbf{2} \rightleftharpoons \mathbf{6}$ equilibrium process and the oligomerization of **2** and **3** that occurs upon Et_2NH elimination have been examined. The role of 1,2- versus 1,4-transaminative addition in the coupling of **2** and **3** is discussed. Results are compared and contrasted with those of the $(Me_2N)_3P/1,2\text{-}(RNH)(NH_2)C_6H_4$ transamination reported recently. The reactions of **2** with Ph_2PCl and Et_3N yields tentatively characterized $C_6H_4(NPPh_2)_2PNEt_2$ (**11**); the reaction of **7** with Ph_2PCl and Et_3N forms the λ^3–λ^5–λ^3 mixed-valence triphosphazane $C_6H_4(NPPh_2)_2PSNEt_2$ (**13**).

Introduction

Synthesis of the skeletally stabilized triphosphazane **1** was reported recently from the transamination of 1,2-$(NH_2)_2C_6H_4$ with $P(NEt_2)_3$[2,3]. Formation of **1** is quantitative when excess $P(NEt_2)_3$ (>3:1) is used; however, at lower $P(NEt_2)_3$:1,2-$(NH_2)_2C_6H_4$ reactant ratios, tentative ^{31}P NMR spectral evidence for mono- (**2**) and diphosphazane (**3**) intermediates was obtained.[2b] This observation is of particular interest, since it contrasts earlier studies of $P(NMe_2)_3$/1,2-$(NH_2)(NHR)C_6H_4$ (R = H, Me, *i*-Pr) reactions by Malavaud and co-workers[4,5] in which only the cyclotetramers (**4**) and, at high temperatures, the phosphinimines (**5**) were observed. No evidence was reported for the presence of the monophosphorus analogue of **2**, which might precede **4**, or for two- or three-phosphorus intermediates between **4** and **5**. Thus, in order to better understand the $P(NR_2)_3$/1,2-$(NH_2)_2C_6H_4$ transamination reactions, we have studied the $P(NEt_2)_3$/1,2-$(NH_2)_2C_6H_4$ system in greater detail. We have isolated and characterized reaction intermediates and studied their elimination and subsequent condensation chemistry. The results of our work are reported below.



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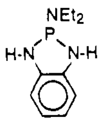

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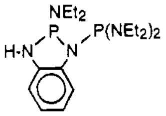

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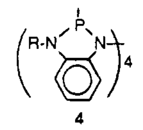

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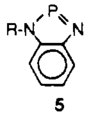

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Table I. Reactions of 1,2-$(NH_2)_2C_6H_4$ with $(Et_2N)_3P$

$(Et_2N)_3P$: 1,2-$(NH_2)_2C_6H_4$^{b}	time, h^a	amt of product, mol %^{c}			
		$(Et_2N)_3P$	**2**	**3**	**1**
0.5:1	140 (45 °C)	37	16	3	
0.8:1	24 (60 °C)	0	80^d	0	0
2:1	1.5	33	15	47	5
4:1	1.5	79	0	16	5
2:1	2.5	25	15	54	7
3:1	2.5	68	2	22	7
4:1	2.5	77	0	15	8
2:1	4	19	21	52	8
4:1	4	73	0	14	13
2:1	9	7	23	54	16

^{a}All reactions at 85 °C except as noted. ^{b}Mole ratios. ^{c}Determined from ^{31}P NMR spectral areas. ^{d}20% of the reaction mixture was due to compound **6**.

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 or a Varian Gemini-300 NMR spectrometer at 300 MHz. ^{31}P and ^1H chemical shifts downfield from 85% H_3PO_4 (external) and Me_4Si (internal) are reported as positive (+δ). IR spectra (4000–400 cm^{-1}) were obtained on a Beckman 4250 or IBM IR/32 Type 9132 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 respective envelope. Chemical ionization (CI$^+$ and CI$^-$) was achieved with isobutane as the ionizing gas. Exact mass analyses were referenced to perfluorokerosene. X-ray diffraction data were collected on a Nicolet P3/F automated diffractometer equipped with a graphite monochromator and low-tem-

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perature attachment. All manipulations were carried out by using standard vacuum-line, glovebag, or Schlenk techniques under dry N_2.[6]

Flash chromatography was carried out according to the method of Still et al.[7] A 650- or 450-mL column was packed with 15 cm of silica gel 60 (230–400 mesh). Compounds were eluted with the necessary solvent mixture under N_2 pressure at 0.8 cm/min. Fractions of 25 mL were collected, analyzed by TLC, and combined according to their R_f values.

Elemental analyses were performed by Huffman Laboratories Inc., Golden, CO.

1,2-$(NH_2)_2C_6H_4$ (Aldrich) was recrystallized from toluene. Toluene (over Na/Pb or CaH_2) and CH_2Cl_2 (P_4O_{10}) were distilled before use. Et_2NH (Aldrich), Et_3N (Baker), $PhPCl_2$ (Strem), Ph_2PCl (Strem), and Me_3SiCl (Petrarch) were distilled from CaH_2. Butyllithium (Aldrich; 1.6 M in hexanes), elemental sulfur (EM Scientific), silica gel (EM Science), KBr (Baker; oven dried), petroleum ether, ethyl acetate, and deuterated solvents were used as received. $P(NEt_2)_3$[8] and (nor)Mo$(CO)_4$[9] (nor = norbornadiene) were prepared as described previously.

$(Et_2N)_3P$/1,2-$(NH_2)_2C_6H_4$ Reactions. (A) General Considerations. Reactions of $P(NEt_2)_3$ with 1,2-$(NH_2)_2C_6H_4$ were carried out at a variety of reactant ratios as shown in Table I. Reaction mixtures typically showed major $^{31}P\{^1H\}$ NMR spectral resonances at δ 117.4 [s, $(Et_2N)_3P$)], δ 89.0 [s, $C_6H_4(NH)_2PNEt_2$ (**2**)], δ 107.2 (d, a 1) and 94.8 (d, a 1, $^2J_{PP}$ = 42.7 Hz) [$C_6H_4(NH)P(NEt_2)NP(NEt_2)_2$ (**3**)], and δ 100.5 (t, a 1, $^2J_{PP}$ = 43.5 Hz) and 106.5 (d, a 2) [$C_6H_4[NP(NEt_2)_2]_2PNEt_2$, (**1**)] in the relative quantities shown in the table.

(B) $C_6H_4(NH)_2PNEt_2$ (2) and $[C_6H_4(NH)P(NEt_2)N][P(NH)_2C_6H_4]$ (6). $P(NEt_2)_3$ (11.7 mmol) and 1,2-$(NH_2)_2C_6H_4$ (13.6 mmol, 0.8:1.0 mole ratio) were heated at 60 °C under N_2. After 24 h, the mixture was dissolved in toluene, and the resultant mixture was filtered through 3 mm of silica gel. The filtrate was treated with activated charcoal and refiltered through Filter-Cel. The resulting solution showed a major $^{31}P\{^1H\}$ NMR resonance at δ 88.9 (s) and a minor doublet pair at δ 78.2 (d) and 90.6 (d, $^2J_{PP}$ = 122.1 Hz) attributable to **2** and **6**, respectively (Figure 1A). The ^1H NMR spectrum (toluene-d_8) showed resonances at δ 1.0 (t, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3) and 2.5 (q, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), [free Et_2NH] and δ 0.9 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), 2.8 (pent, $^3J_{HH} \cong$ 7.0, CH_2CH_3, $^3J_{PH}$ = 14.0 Hz), 5.3 (broad s, NH), 5.7 (broad s, NH), and 6.3–6.8 (m, C_6H_4) (**2**) [**2**:Et_2NH ratio = 1:3.5]. Attempts to isolate and/or separate **2** and **6** were unsuccessful due to their high reactivity toward H_2O and their tendency to decompose in the absence of Et_2NH.

A toluene solution of **2**/**6** (mainly **2**) with $(Et_2N)_3P$ (1:1 ratio) was heated at 50–65 °C. After 37 h, the $^{31}P\{^1H\}$ NMR spectrum showed $(Et_2N)_3P$, **3**, and **2** (ratio 1:6:4). Further heating did not increase the yield of **3**.

(C) $C_6H_4(NH)P(NEt_2)NP(NEt_2)_2$ (3). $P(NEt_2)_3$ (0.014 mol) and 1,2-$(NH_2)_2C_6H_4$ (0.007 mol) were heated at 85 °C under N_2. After 2.5 h, the mixture was dissolved in toluene. The $^{31}P\{^1H\}$ NMR spectrum showed two doublets at δ 107.2 and 94.8 ($^2J_{PP}$ = 43.5 Hz, 54%) attributable to **3** and singlets at δ 117.4 (25%) and 89.0 (15%) attributable to $P(NEt_2)_3$ and **2**, respectively. Small quantities of **1** (ca. 7%) were also present [mol % **3**, $P(Et_2N)_3$, **2**, and **1** = 54, 25, 15, and 7]. Attempts to isolate **3** were unsuccessful due to its high reactivity toward H_2O and instability in the absence of Et_2NH.

Excess (nor)Mo$(CO)_4$ in toluene was added to a solution containing mainly **3** (85%) in toluene. After 17 h at 25 °C and 4.5 h at 60 °C, ^{31}P NMR spectral analysis indicated no reaction.

$C_6H_4(NH)_2P(S)NEt_2$ (7) and $[C_6H_4(NH)_2P(S)][C_6H_4(NH)(N)P(S)NEt_2]$ (8). S_8 ($\cong$10% excess) was added to a **2**/**6** mixture in toluene (prepared as described above). Immediate reaction occurred at room temperature. After 40 min at 25 °C, the $^{31}P\{^1H\}$ NMR spectrum showed only phosphorus sulfide resonances at δ 67.6 (s) and a doublet pair at δ 71.0 (d, $^2J_{PP}$ = 33.0 Hz) and 52.8 (d), attributable to **7** and **8**, respectively [**7**:**8** $\cong$ 92:8; mol %].

Flash chromatography using a petroleum ether/ethyl acetate eluent (4.5:1 v/v) separated the **7**/**8** mixture (elution order S_8, **7**, and **8**). Pure crystalline **7** (mp = 142.5–144.5 °C) and **8** (mp = 245–248 °C) were obtained from petroleum ether/ethyl acetate and MeCN solutions, respectively. **7**: soluble in toluene and CH_2Cl_2; $^{31}P\{^1H\}$ NMR (toluene) δ 67.2 (s); ^{31}P NMR (^1H coupled, toluene) δ 67.1 (pent, $^3J_{PH}$ = 14.4 Hz); ^1H NMR (C_6D_6) δ 0.9 (t, a 6, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), 3.0 (d of q, a 4, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.5 Hz, CH_2CH_3), 4.8 (broad s, a 2, NH), 6.3–6.9 (complex m, a 4, C_6H_4); MS (EI) m/e 241 (M^+) [$C_6H_4(NH)_2PSNEt_2^+$]; IR (KBr, cm^{-1}) 3384 (s), 3264 (s, NH), 1494 (vs), 1395 (s), 1283 (s), 1204 (m), 1173 (w), 1066 (w), 1026 (s), 958 (m), 949 (m), 924 (w), 882 (s), 787 (m), 745 (s), 737 (s), 713 (vs, P=S), 686 (m), 593 (m), 547 (m). Anal. Calcd for $C_{10}H_{16}N_3PS$ (mol wt 241.0802): C, 49.78; H, 6.68; N, 17.41. Found (mol wt (exact mass MS) 241.0802): C, 50.03; H, 6.79; N, 17.32. **8**: soluble in ethyl acetate and hot MeCN; $^{31}P\{^1H\}$ NMR (CD_3CN) δ 68.2 (d, $^2J_{PP}$ = 27.5 Hz), 52.2 (d); ^1H NMR (CD_3CN) δ 1.0 (t, a 6, $^3J_{HH}$ = 7.01 Hz; CH_2CH_3), 2.6–3.6 (m, a 4, coupling to CH_3 and P, CH_2CH_3 (diasteriotopic protons)), 6.4–7.0 (m, C_6H_4), NH protons not observed; IR (KBr, cm^{-1}) 3270 (s, broad, NH), 2971 (m), 2932 (w), 1491 (vs), 1470 (m), 1382 (vs), 1271 (vs), 1205 (s), 1169 (m), 1115 (m), 1030 (s), 971 (vs), 910 (vs), 882 (m), 786 (w), 735 (vs, P=S), 710 (m), 504 (m), 429 (w), 419 (w); MS (EI) m/e 409 (M^+), [$(C_6H_4)_2(NH)_3NP_2S_2NEt_2^+$], ($CI^+$) 410 (M + 1), ($CI^-$) 408 (M − 1). Anal. Calcd for $C_{16}H_{21}N_5P_2S_2$ (mol wt 409.0714): C, 46.93; H, 5.17; N, 17.10; P, 15.13; S, 15.66. Found (mol wt (exact mass MS) 409.0704): C, 47.24; H, 5.34; N, 16.84; P, 14.83; S, 15.97.

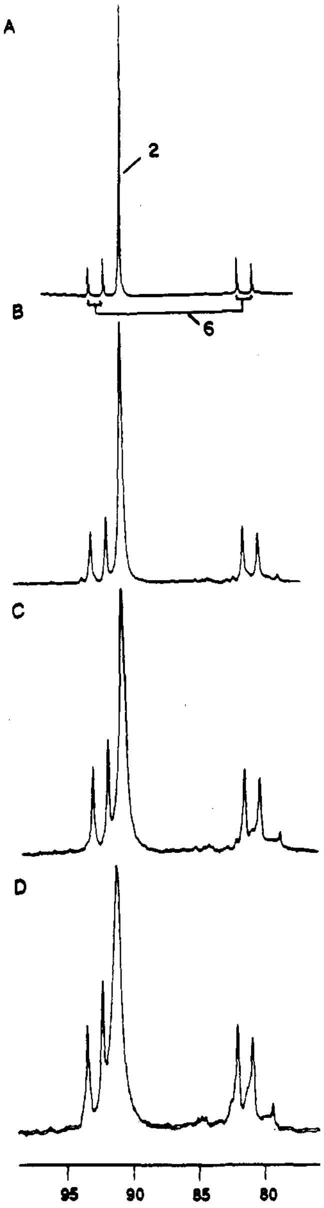

Figure 1. $^{31}P\{^1H\}$ NMR spectra of a **2**/**6** mixture (mainly **2**) at (A) 30, (B) 80, (C) 130, and (D) 150 °C.

Thermolysis of **7** at 100–105 °C for 75 min showed no ^{31}P NMR spectral change.

$C_6H_4(NH)PS(NEt_2)NPS(NEt_2)_2$ (9) and $(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2$ (10). A typical reaction mixture containing primarily **3** (described above) was allowed to react at room temperature with S_8 (ca. 10% excess). The product mixture was separated by flash chromatography using a petroleum ether/ethyl acetate (4.3:1 ratio) eluent solution. Fractions eluted in the order S_8, $(Et_2N)_3PS$, **9**, and **7** last. Upon crystallization of a fraction containing **9** and $(Et_2N)_3PS$, a trace of **10**, a compound not seen in the ^{31}P NMR spectrum, was obtained. **9**: soluble in benzene and toluene; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 69.0 (d, $^2J_{PP}$

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= 20.8 Hz, a 1), 64.3 (d, a 1); ^{1}H NMR (C_6D_6) δ 0.96 [t, $^3J_{HH}$ = 7.1 Hz, $(CH_2CH_3)_a$], 0.98 [t, $^3J_{HH}$ = 7.1 Hz $(CH_2CH_3)_b$], 1.2 [t, $^3J_{HH}$ = 7.0 Hz, $(CH_2CH_3)_c$], 2.5–3.9 (complex m, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), 4.3 (br d, NH), 6.7–6.9 (m, meta), 6.2–6.4 (m, ortho), 7.8–8.0 (m, ortho); MS (EI) *m/e* 447 (M^+) [$C_6H_4(NH)P(S)NEt_2NP(S)(NEt_2)_2{}^+$]. **10**: Since only trace quantities of **10** formed, only limited spectral characterization data were obtained; MS (EI) *m/e* 717 (M^+) [$(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2{}^+$].

Thermolysis of **9** for 99 h at 80–100 °C caused no decomposition.

Reaction of 2 with Ph_2PCl and S_8. $C_6H_4(NPPh_2)_2PNEt_2$ (11). **2** (ca. 0.5 mmol) in toluene was allowed to react with excess Ph_2PCl at room temperature. The $^{31}P\{^1H\}$ NMR spectrum showed evidence for a three-phosphorus product **11** at δ 36.7 (d, a 2, $^2J_{PP}$ = 110.1 Hz) and 106.5 (t, a 1, $^2J_{PP}$ = 110.4 Hz) along with resonances at δ 81.6 (s, Ph_2PCl) and 61.0 (s, Ph_2PNEt_2). Addition of Et_3N did not change the appearance of the NMR spectrum. Excess S_8 was added to the solution. After 12 h, the $^{31}P\{^1H\}$ NMR spectrum showed evidence for the disulfide of **11**, with the exo phosphorus atoms oxidized. $^{31}P\{^H\}$ NMR: δ 98.1 (t, $^2J_{PP}$ = 62.6 Hz, a 1) and 54.6 (d, a 2) [$C_6H_4[NP(S)Ph_2]_2PNEt_2$ (**12**)]. Attempts to isolate **11** or **12** failed.

$C_6H_4(NPPh_2)_2PSNEt_2$ (13). **7** and Ph_2PCl (1:4 mole ratio) in toluene with excess Et_3N were allowed to react at 65 °C. After 3 h, the ^{31}P NMR spectrum showed only a three-phosphorus product at δ 87.9 (t, a 1, $^2J_{PP}$ = 102.5 Hz) and 27.0 (d, a 2) (**13**) along with unreacted Ph_2PCl. Flash chromatography of the mixture using a petroleum ether/ethyl acetate (7:1) eluent mixture resulted in isolation of pure **13** (mp = 176 °C dec). **13**: soluble in CH_2Cl_2 and hot toluene; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 87.8 (t, a 1, $^2J_{PP}$ = 102.5 Hz), 27.7 (d, a 2); ^{1}H NMR (CD_2Cl_2) δ 0.87 (t, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), 3.2 (d of q, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 14.0 Hz, CH_2CH_3), 6.3 (br s, a 20, C_6H_5), 7.1–7.8 (m, C_6H_4); MS (EI) *m/e* 609 (M^+) [$C_6H_4(NPPh_2)_2P(S)NEt_2{}^+$]; IR (KBr, cm^{-1}) 3432 (m, br), 2967 (s), 2924 (s), 2854 (w), 1476 (vs), 1435 (m), 1242 (vs), 1207 (s), 1171 (w), 1116 (s), 1098 (m), 1037 (s), 1026 (s), 944 (vs), 929 (s), 921 (m), 746 (m), 729 (s), 721 (w), 697 (m); mol wt calcd for $C_{34}H_{34}P_3N_3S$ 609.1686, found (exact mass MS) 609.1686.

$C_6H_4[NP(NEt_2)_2]_2P(S)NEt_2$ (14). **7** (1.1 mmol) in 10 mL of toluene was allowed to react with $(Et_2N)_3P$ (3.8 mmol). The mixture was heated at 88 °C and monitored by $^{31}P\{^1H\}$ NMR spectral analysis. After 1 h, only the two singlets of the starting materials at δ 117.4 [$P(NEt_2)_3$] and 66.6 (**7**) were observed. After 24 h, two doublets at δ 115.5 and 72.7 ($^2J_{PP}$ = 74.5 Hz) appeared, which were slowly replaced by the AX_2 pattern of compound **14**: δ 117.9 (d, $^2J_{PP}$ = 62.3 Hz), 77.3 (t). After 120 h at 88–94 °C, the majority (≅75%) of the spectral area were attributed to compound **14**; however, attempts to isolate it for complete characterization failed.

Equilibrium Studies. (A) 2/6. Removal of Et_2NH. A **2/6** mixture (**2**:**6** = 6:1 by ^{31}P NMR spectroscopy) was maintained under vacuum for 20 h. As Et_2NH was removed, the sample became extremely viscous and was only slightly soluble in toluene. The toluene-soluble portion exhibited a sharp $^{31}P\{^1H\}$ NMR spectral resonance at δ 88.0 and broad ill-defined resonances between δ 75 and 85. When Et_2NH was readded to the mixture, the material dissolved and the solution yielded $^{31}P\{^1H\}$ NMR spectral resonances at δ 89.6 (s, 64%) (**2**) and 77.1 (s, 21%). The remaining spectral area appeared in the P(V) phosphorus[10] region. The singlet at δ 77.1 disappeared after 36 h; attempts to isolate this compound were unsuccessful. Reaction of S_8 with this mixture yielded mainly **7**.

Excess Et_2NH was added to a **2/6** mixture (**2**:**6** = 6:1) at room temperature, while the reaction was monitored by ^{31}P NMR spectroscopy. After 10 min at 25 °C, the **2**:**6** ratio increased to 10:1. The **2**:**6** ratio remained unchanged upon further standing at 25 °C.

(B) 3. Removal of Et_2NH. A mixture containing **3** [**3**:**2**:$P(NEt_2)_3$ ≅ 66:16:18] was placed under vacuum for 6.5 days at 25 °C. Et_2NH and $P(NEt_2)_3$ were removed slowly. The resulting viscous gold-colored solution was soluble in toluene. It exhibited ^{31}P NMR spectral resonances at δ 118 [$P(NEt_2)_3$, 16%], 92–115 (complex mixture of sharp peaks with traces of **3**; 53%), and 72–88 (broader, ill-defined resonances; 28%).

Excess Et_2NH was readded to the above mixture in toluene. Reaction occurred slowly. After 7.5 h the solution contained the following (area %): $P(NEt_2)_3$ (19), **3** (16), and **2** (4) along with material that gave broad, equal-area resonances between δ 72 and 88 (20). The remaining ^{31}P NMR spectral area (40%) occurred between δ 92 and 115. After 32 h, the relative area percentages of $(Et_2N)_3P$, **3**, **2**, broad resonances at δ 72–88, and the complex resonances at δ 92–115 were 17, 27, 8, 13, and 36. These remained essentially unchanged thereafter.

The above **3**/Et_2NH mixture was dissolved in toluene, and the resulting mixture was allowed to react with excess S_8. After 45 min at 25 °C, ^{31}P NMR spectral resonances attributable to $PS(NEt_2)_3$ [δ 78.0 (s)] and $C_6H_4[NP(S)NEt_2)_2]_2PNEt_2$ [δ 64.9 (d) 98.1 (t)] (area % 18 and 23) appeared. The remaining phosphorus products exhibited broad resonances at δ 80–103 and 55–75. No spectral change occurred after 3 days at room temperature. Sulfur addition to a **3**/**2**/$(NEt_2)_3P$ mixture in toluene that had been placed under vacuum on a Schlenk line for 23 h was also carried out. The ^{31}P NMR spectrum from this reaction showed $(Et_2N)_3PS$, **9**, and **7**, and two broad resonances at δ 80–93 and 45–58. There was also extra area under the resonances for **9** and **7** between δ 58 and 75 ppm.

Table II. Crystal Data for $C_6H_4(NH)_2P(S)NEt_2$ (**7**), $[C_6H_4(NH)_2P(S)]C_6H_4(NH)NP(S)NEt_2$ (**8**), and $(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2$ (**10**)

	7	**8**	**10**
formula	$C_{10}H_{16}PN_3S$	$C_{16}H_{21}P_2N_5S_2$	$C_{32}H_{59}P_4N_9S_3$
fw	241.3	409.5	789.9
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	14.736 (6)	21.384 (9)	9.741 (7)
b, Å	8.872 (5)	9.341 (4)	11.655 (5)
c, Å	20.581 (8)	22.293 (8)	20.240 (10)
α, deg	90.0	90.0	73.41 (4)
β, deg	104.38 (3)	118.06 (3)	76.23 (5)
γ, deg	90.0	90.0	79.17 (5)
V, Å^3	2606 (2)	3930 (3)	2121 (2)
Z	8	8	2
d_{calc}, g cm^{-3}	1.23	1.38	1.20
abs coeff, mm^{-1}	0.334	0.430	0.348
$F(000)$, e$^-$	1024	1712	844
λ(Mo Kα), Å	0.71073	0.71073	0.71073
temp, °C	25	23	25
R, R_w	0.069, 0.094	0.036, 0.038	0.057, 0.078

(C) 1 or 3. Addition of Et_2NH. A mixture of mainly **3** [**3**:**2**:$P(NEt_2)_3$ = 2.5:1:2] was heated at 55 °C with excess Et_2NH for 38 h. No reaction occurred. **1**, when heated at 80 °C with a 20-fold molar excess of Et_2NH for 2 days, yielded ca. 4% **3** along with unreacted **1**.

(D) Variable-Temperature NMR Studies of 2/6. A **2/6** mixture (**2**:**6** = 5:1) in an NMR tube at 28 °C initially showed ^{31}P NMR spectral resonances from **2** [δ 89.8 (s)] and **6** [δ 91.7 and 79.7 (d, $^2J_{PP}$ = 121.8 Hz)]. Upon heating, the **2**:**6** ratio decreased as follows (**2**:**6** ratio, temperature): 5:1, 30 °C; 4.5:1, 50 °C; 3:1, 130 °C; 2.5:1, 150 °C. When the mixture was cooled to 30 °C, the **2**:**6** ratio returned to 5:1. In a separate experiment, a 5:1 **2**:**6** mixture was dissolved in mesitylene and the ^{31}P NMR spectrum examined as a function of temperature. Between 30 and 150 °C no significant change in the **2**:**6** ratio was observed.

Excess S_8 was added to a **2/6** mixture at 110 °C. The product mixture showed a $^{31}P\{^1H\}$ NMR singlet resonance at δ 66.6 (**7**) and a minor doublet resonance at δ 68.2 and 52.2 (**8**). No other resonances appeared.

X-ray Analyses of 7, 8, and 10. Crystals of **7** (from toluene), **8** (from MeCN), and **10** (from petroleum ether/ethyl acetate) were obtained suitable for X-ray analyses. Crystals of **8** and **10** tended to be twinned. **8** was solved by using Wykoff data, but the crystals were not of adequate quality to merit collection of 2θ data. A mixture containing mainly **9**, $P(S)(NEt_2)_3$, and traces of **10** yielded crystals of **10** as the solvent evaporated. All crystals were coated with epoxy. All structures were solved by direct method and refined by full-matrix least-squares calculations treating non-hydrogen atoms anisotropically. Atom scattering factors were those used for neutral atoms. Hydrogen atoms were refined as fixed groups. Calculations were carried out with programs in the SHELXTL package.

Results and Discussion

Reactions of $P(NEt_2)_3$ and 1,2-diaminobenzene were carried out under a range of conditions [$P(NEt_2)_3$:1,2-$(NH_2)_2C_6H_4$ ratios of 0.5:1.0 to 4:1.0, temperatures of 45–85 °C, and reaction times of 1.5–140 h] in order to determine the order of intermediate formation, the range of intermediates that can be seen, and the conditions under which major intermediate formation can be optimized. Example reaction conditions are listed in Table I. Typically, the ^{31}P NMR spectra of these mixtures show the presence of three intermediate species (**2**, **3**, and **6**), two of which (**2** and **3**) precede formation of the final triphosphazane **1** (Scheme I).

The first intermediate observed in the 1,2-$(NH_2)_2C_6H_4$/$P(NEt_2)_3$ transamination (eq 2a) is the diazaphosphole **2**. Reaction

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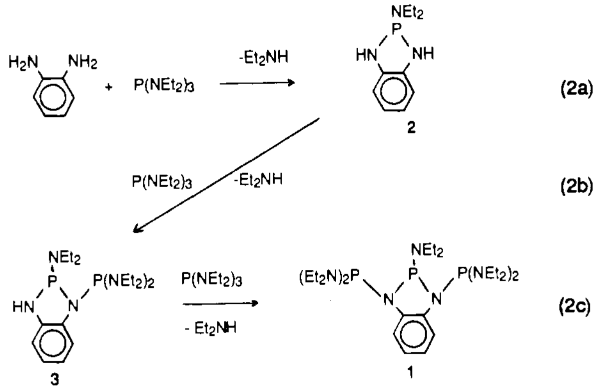
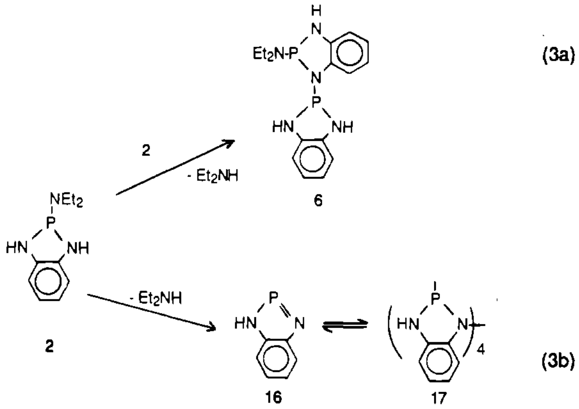
[10] Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van-Wazer, J. R. *Topics in Phosphorus Chemistry*; Interscience: New York, 1967; Vol. 5.

Scheme I



of $P(NEt_2)_3$ with 1,2-$(NH_2)_2C_6H_4$ in a 0.8:1.0 ratio at 60 °C during 24 h results in Et_2NH elimination and formation of a reaction mixture that shows (Figure 1A) a major singlet (δ 88.9) and minor doublet resonances [δ 78.2, 90.6 ($^2J_{PP}$ = 122.1 Hz)] due to **2** and a coupled secondary reaction species **6**, respectively (Scheme II). Typically, **2** and **6** are formed in a (4–6):1 mole ratio. The ^{31}P NMR spectral resonances for both are in the region for P(III) diazaphospholes reported previously.[2,4,5,11,12] The ^1H NMR spectra of the mixtures show the presence of free Et_2NH as well as the Et_2N, NH, and phenylene (C_6H_4) resonances attributable to the two products.[13]

Scheme II



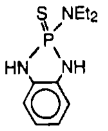
At intermediate reaction times and $P(NEt_2)_3$:1,2-$(NH_2)_2C_6H_4$ reactant ratios (2 h, 2.0:1.0) at 85 °C, doublet resonances [δ 107.2, 94.6 (^2J = 42.7 Hz)] due to the second intermediate in the transamination series, **3** (Scheme I, eq 2b), are optimized (Figure 2A). The higher field ^{31}P NMR resonance occurs in the diazaphosphazole region,[2,4,5] and the lower field resonance is in the region characteristic of acyclic tris(amino)phosphines.[2,4,10,14] Typically, **3** constitutes about 50% of the products formed. Singlets at δ 89.0 and 117.4 due to **2** and unreacted $P(NEt_2)_3$ along with the minor doublet–triplet resonances at δ 100.5 and 106.5 characteristic of the final product **1** are seen. Alternatively, a product mixture containing mainly **3** forms from a 1:1 $P(NEt_2)_3$:**2** (**2** from a **2**/**6** mixture, above) reaction during 35 h at 60 °C. Intermediates **2**, **3**, and **6** could not be isolated from their reaction mixtures either by crystallization or by column chromatography, because they are unstable in the absence of Et_2NH and upon exposure to traces of ambient moisture. Placing the mixtures under vacuum appears to cause higher condensation products to form (see below), as evidenced by the formation of additional broad peaks in the ^{31}P NMR spectra. Compounds **2**, **3**, and **6** could be isolated and unambiguously structurally characterized only as their sulfide oxidation products.

Table III. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $C_6H_4(NH)_2P(S)NEt_2$ (**7**)

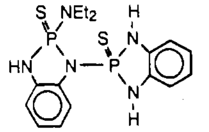
	x/a	*y/b*	*z/c*	U_{eq}[b]
P(1)	4669 (1)	7242 (2)	1847 (1)	76 (1)
S(1)	4140 (1)	7186 (2)	2621 (1)	92 (1)
N(1)	5509 (4)	8497 (6)	1862 (3)	86 (3)
N(2)	5396 (3)	5834 (6)	1778 (3)	82 (2)
N(3)	3863 (3)	7386 (7)	1158 (3)	101 (3)
C(1)	6382 (4)	7852 (7)	1862 (3)	70 (2)
C(2)	6317 (4)	6310 (6)	1808 (3)	66 (2)
C(3)	7092 (4)	5449 (7)	1790 (3)	76 (3)
C(4)	7933 (4)	6203 (9)	1829 (3)	81 (3)
C(5)	8002 (4)	7703 (9)	1881 (3)	84 (3)
C(6)	7223 (4)	8591 (7)	1898 (3)	75 (2)
C(7)	2847 (5)	7583 (9)	1122 (5)	114 (4)
C(8)	2348 (6)	6154 (11)	1009 (6)	177 (6)
C(9)	4153 (7)	7416 (23)	488 (6)	178 (7)
C(10)	3845 (25)	6461 (40)	20 (15)	228 (20)
C(10′)*	4028 (15)	8633 (27)	92 (13)	164 (12)
P(2)	724 (1)	1004 (2)	1119 (1)	71 (1)
S(2)	308 (1)	−1030 (2)	1246 (1)	88 (1)
N(4)	1822 (3)	1426 (6)	1513 (3)	81 (2)
N(5)	950 (5)	1431 (7)	398 (3)	82 (3)
N(6)	10 (4)	2252 (6)	1287 (3)	85 (2)
C(11)	2385 (4)	1797 (6)	1083 (3)	71 (2)
C(12)	1871 (4)	1798 (7)	423 (3)	71 (2)
C(13)	2277 (5)	2139 (7)	−87 (3)	88 (3)
C(14)	3224 (6)	2479 (9)	74 (4)	108 (4)
C(15)	3747 (5)	2477 (9)	724 (5)	112 (4)
C(16)	3339 (5)	2127 (8)	1248 (3)	95 (3)
C(17)	220 (7)	3865 (9)	1203 (5)	113 (4)
C(18)*	−382 (10)	4678 (14)	718 (7)	118 (6)
C(18′)*	418 (15)	4606 (32)	1701 (14)	137 (13)
C(19)	−873 (7)	1877 (10)	1495 (5)	119 (4)
C(20)*	−841 (14)	1929 (22)	1045 (14)	165 (12)
C(20′)*	−1666 (13)	1865 (24)	2144 (9)	144 (10)

[a] Atoms have occupancies of 1.0 except those marked with * above: C(10), 0.5; C(10′), 0.5; C(18), 0.6; C(18′), 0.4; C(20), 0.5; C(20′), 0.5. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Oxidation of mixtures containing mainly **2** (with minor **6**) and **3** by their reaction with sulfur results in formation of stable derivatives that can be separated by crystallization and column chromatography. The $^{31}P\{^1H\}$ NMR spectrum of the **2**/**6**/S_8 reaction mixture shows a singlet resonance at δ 67.6 and two doublets at δ 71.0 and 52.8 ($^2J_{PP}$ = 33.0 Hz) due to **2** and to **7** and **8**, the sulfides of **2** and **6**, respectively, in the chemical shift region characteristic of P(V) phosphazanes.[10,15,16] No significant amounts of other phosphorus sulfides are evident.



7



8

7 and **8** both can be separated by crystallization and column chromatography. **7** was reported previously from reaction of the chlorodiazaphosphole $C_6H_4(NH)_2PCl$ with Et_2NH; however, it was not characterized.[17] Both are stable indefinitely in air. **8** is more soluble in polar solvents than **7** and therefore is the second fraction eluted from the flash column. The ^{31}P NMR spectra of **7** and **8** are entirely consistent with those of other diazaphosphole sulfides.[2b] The ^1H NMR spectrum of **7** displays the expected CH_3 [δ 0.9 (t, $^3J_{HH}$ = 7.1 Hz)], aryl [δ 6.3–6.9 (m)], and NH [δ 4.8 (br s)] resonances; the CH_2 resonance is a doublet of quartets due to coupling to the phosphorus atom ($^3J_{PNCH}$ = 14.5 Hz) and the CH_3 protons ($^3J_{HCCH}$ = 7.2 Hz). The mass spectral (EI$^+$) parent

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(17) Croce, P. D.; Maiorana, S. *Synthesis* **1984**, *11*, 980.

Table IV. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[C_6H_4(NH)_2P(S)]C_6H_4(NH)NP(S)NEt_2$ (**8**)

	x/a	*y/b*	*z/c*	U_{eq}[b]
P(1)	-541 (1)	-807 (1)	12350 (1)	49 (1)
P(2)	-13 (1)	2748 (1)	11451 (1)	52 (1)
S(1)	890 (1)	-858 (1)	13155 (1)	67 (1)
S(2)	1036 (1)	1569 (1)	11226 (1)	69 (1)
N(1)	-1117 (2)	-2834 (3)	11723 (2)	64 (2)
N(2)	-1258 (2)	-751 (3)	12882 (2)	58 (1)
N(3)	-852 (1)	1139 (3)	11570 (1)	49 (1)
N(4)	-928 (2)	3794 (4)	10487 (2)	74 (2)
N(5)	424 (2)	4339 (3)	12333 (1)	61 (1)
C(1)	-1842 (2)	-3609 (4)	11947 (2)	57 (2)
C(2)	-1918 (2)	-2407 (4)	12631 (2)	57 (2)
C(3)	-2598 (2)	-2839 (4)	12959 (2)	70 (2)
C(4)	-3185 (2)	-4557 (5)	12598 (2)	92 (2)
C(5)	-3109 (2)	-5761 (5)	11922 (2)	92 (2)
C(6)	-2435 (2)	-5306 (4)	11577 (2)	75 (2)
C(7)	-1871 (2)	1625 (4)	10874 (2)	56 (2)
C(8)	-1882 (2)	3156 (4)	10268 (2)	65 (2)
C(9)	-2779 (2)	3891 (5)	9538 (2)	92 (2)
C(10)	-3659 (2)	3041 (6)	9435 (2)	106 (2)
C(11)	-3648 (2)	1542 (5)	10036 (2)	96 (2)
C(12)	-2757 (2)	806 (4)	10760 (2)	72 (2)
C(13)	-266 (2)	5516 (4)	12551 (2)	84 (2)
C(14)	1495 (2)	4845 (4)	12903 (2)	76 (2)
C(15)	-358 (3)	4772 (5)	13409 (3)	124 (3)
C(16)	1810 (2)	6568 (5)	12470 (2)	116 (3)
P(1′)	7768 (1)	-415 (1)	5825 (1)	47 (1)
P(2′)	7148 (1)	3260 (1)	4508 (1)	52 (1)
S(1′)	6346 (1)	-622 (1)	5355 (1)	71 (1)
S(2′)	6049 (1)	2159 (1)	3353 (1)	75 (1)
N(1′)	8389 (2)	-2300 (3)	5661 (2)	58 (1)
N(2′)	8486 (2)	-500 (3)	7010 (2)	55 (1)
N(3′)	8029 (1)	1659 (3)	5362 (1)	48 (1)
N(4′)	8027 (2)	4323 (4)	4312 (2)	68 (2)
N(5′)	6767 (1)	4797 (3)	5070 (1)	60 (1)
C(1′)	9058 (2)	-3258 (4)	6518 (2)	53 (2)
C(2′)	9110 (2)	-2219 (4)	7301 (2)	52 (2)
C(3′)	9728 (2)	-2888 (4)	8222 (2)	73 (2)
C(4′)	10281 (2)	-4628 (5)	8334 (2)	97 (2)
C(5′)	10229 (2)	-5662 (5)	7555 (2)	92 (2)
C(6′)	9612 (2)	-4990 (4)	6626 (2)	69 (2)
C(7′)	9035 (2)	2295 (4)	5596 (2)	54 (2)
C(8′)	9003 (2)	3833 (4)	4975 (2)	60 (2)
C(9′)	9873 (2)	4710 (4)	5067 (2)	79 (2)
C(10′)	10778 (2)	4048 (5)	5794 (2)	92 (2)
C(11′)	10812 (2)	2562 (5)	6422 (2)	92 (2)
C(12′)	9939 (2)	1668 (4)	6333 (2)	72 (2)
C(13′)	5736 (2)	5467 (5)	4732 (2)	86 (2)
C(14′)	7515 (2)	5815 (5)	5949 (2)	91 (2)
C(15′)	5516 (3)	7484 (5)	4232 (3)	158 (3)
C(16′)	7610 (3)	4891 (5)	6864 (2)	152 (3)

[a] Atoms have occupancies of 1.0. Atoms in molecule B are primed. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

ion (M^+) *m/e* 241 and infrared N—H and P═S stretching absorptions at 3384 and 713 cm^{-1} are observed. The ^{1}H NMR spectrum of **8** exhibits a triplet at δ 1.0 from the Et$_2$N group CH$_3$ protons and a multiplet at δ 2.6–3.6 from the CH$_2$ diastereotopic protons coupled to the CH$_3$ protons and to the phosphorus atoms. Complex resonances due to the aryl protons are seen at δ 6.1–7.1. The NH protons were not observed, perhaps because of exchange with trace water in the CD$_3$CN solvent. **8** shows the expected $^2J_{PNP}$ coupling constants[15] and mass spectral parent (EI$^+$), M + 1 (CI$^+$), and M − 1 (CI$^-$) ions at *m/e* 409, 410, and 408, respectively.[18] Distinct N—H and P═S stretches at 3270 and 735 cm^{-1}, respectively, are present.

Structural confirmation for **7** and **8** was obtained by X-ray single-crystal analyses. Their structures are shown in Figures 3 and 4. Both **7** and **8** crystallize in the space group $P2_1/c$ with

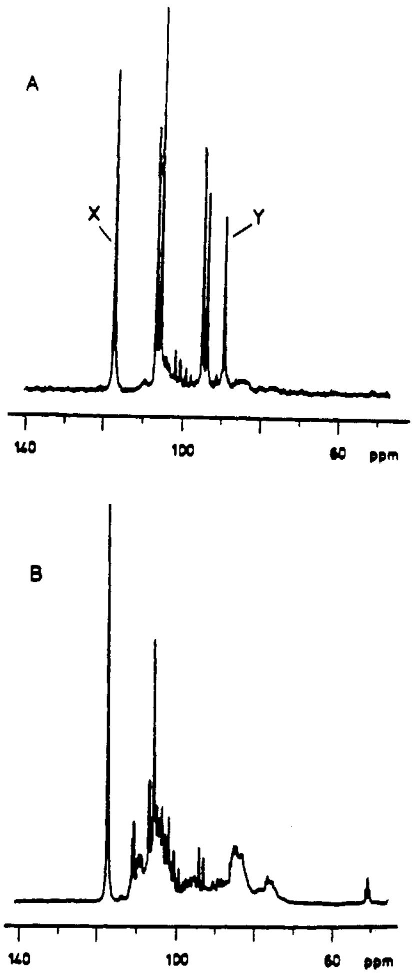

Figure 2. $^{31}P\{^1H\}$ NMR spectra of (A) a reaction solution enriched in **3** at 25 °C and (B) the solution after removal of Et$_2$NH for 6.5 h in vacuo. Resonances x and y are from (Et$_2$N)$_3$P and **2**, respectively.

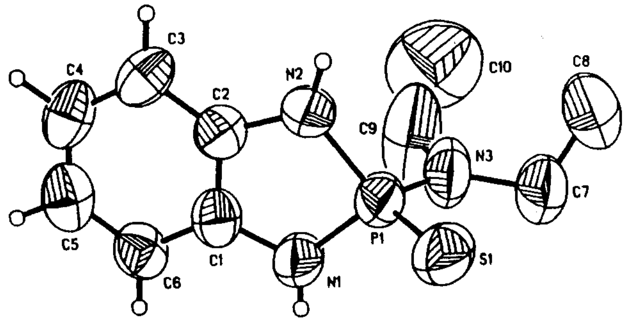

Figure 3. Structure and numbering system for **7**. Thermal ellipsoids are shown at the 50% level, and hydrogen atoms are omitted for clarity.

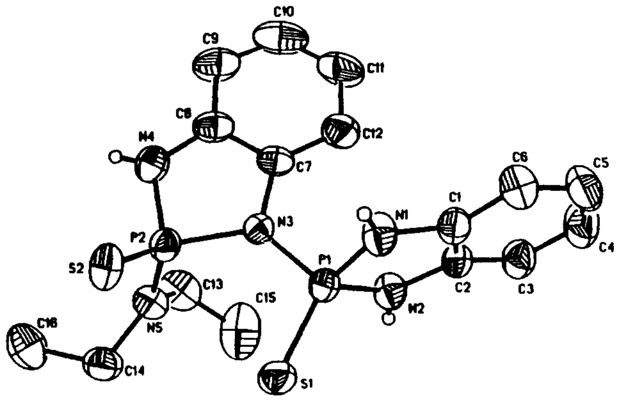

Figure 4. Structure and numbering system for **8**. Thermal ellipsoids are shown at the 50% level, and hydrogen atoms are omitted for clarity.

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Table V. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2$ (**10**)

	x/a	*y/b*	*z/c*	U_{eq}[b]
P(1)	−39 (2)	3380 (1)	7807 (1)	56 (1)
P(2)	267 (2)	4806 (1)	8750 (1)	51 (1)
P(3)	2543 (2)	6133 (1)	7825 (1)	54 (1)
P(4)	3225 (2)	7778 (2)	6391 (1)	64 (1)
S(1)	−792 (2)	4941 (2)	7287 (1)	69 (1)
S(2)	−1678 (2)	4857 (2)	9251 (1)	68 (1)
S(4)	3587 (2)	9391 (2)	6310 (1)	92 (1)
N(1)	868 (5)	3605 (4)	8381 (2)	49 (2)
N(2)	1505 (6)	4384 (5)	9236 (3)	61 (3)
N(3)	719 (5)	6094 (4)	8212 (3)	50 (2)
N(4)	2032 (6)	7230 (4)	7112 (2)	53 (2)
N(5)	−1261 (6)	2519 (5)	8237 (3)	70 (3)
N(6)	1191 (6)	2541 (4)	7372 (3)	61 (2)
N(7)	3130 (6)	6893 (5)	8250 (3)	80 (2)
N(8)	4680 (6)	6783 (5)	6462 (3)	73 (2)
N(9)	2548 (7)	7641 (5)	5752 (3)	79 (3)
C(1)	1921 (6)	2783 (5)	8740 (4)	56 (2)
C(2)	2240 (7)	3240 (6)	9243 (3)	58 (2)
C(3)	3218 (8)	2629 (6)	9652 (4)	81 (2)
C(4)	3878 (9)	1516 (7)	9562 (5)	103 (2)
C(5)	3576 (8)	1043 (7)	9078 (5)	94 (2)
C(6)	2583 (7)	1661 (6)	8657 (4)	76 (2)
C(7)	−165 (6)	7149 (5)	7886 (3)	51 (2)
C(8)	599 (7)	7777 (5)	7269 (3)	53 (2)
C(9)	−37 (7)	8847 (5)	6886 (4)	66 (2)
C(10)	−1444 (8)	9267 (6)	7133 (4)	77 (2)
C(11)	−2181 (8)	8647 (6)	7748 (4)	84 (2)
C(12)	−1531 (7)	7577 (6)	8136 (4)	73 (2)
C(13)	−931 (9)	1304 (7)	8665 (5)	112 (2)
C(14)*	−1263 (13)	1212 (11)	9395 (6)	119 (2)
C(14′)*	−1729 (27)	511 (22)	8900 (22)	131 (2)
C(15)	−2773 (8)	2968 (7)	8267 (5)	99 (2)
C(16)	−3428 (10)	2583 (10)	7784 (6)	147 (2)
C(17)	2479 (8)	3076 (6)	6993 (4)	80 (2)
C(18)	3732 (8)	2192 (8)	6796 (5)	114 (2)
C(19)	738 (8)	1811 (6)	6993 (4)	86 (2)
C(20)	423 (11)	2474 (9)	6279 (5)	130 (2)
C(21)	2482 (12)	8108 (8)	8363 (6)	123 (2)
C(22)*	1407 (16)	8087 (11)	9016 (7)	142 (2)
C(22′)*	3438 (31)	8631 (24)	8380 (22)	156 (2)
C(23)	4525 (12)	6271 (10)	8493 (7)	152 (2)
C(24)*	4480 (16)	5900 (17)	9241 (7)	149 (2)
C(24′)*	4937 (23)	6871 (25)	8897 (17)	161 (2)
C(25)	5933 (8)	7040 (8)	6654 (5)	107 (2)
C(26)	7066 (11)	7473 (10)	6057 (7)	168 (2)
C(27)	4667 (10)	5546 (7)	6378 (5)	108 (2)
C(28)*	5627 (18)	5294 (17)	5660 (9)	116 (2)
C(28′)*	5948 (24)	5284 (18)	5966 (14)	170 (2)
C(29)	3163 (13)	8305 (5)	5044 (5)	165 (2)
C(30)	2274 (17)	9289 (12)	4739 (7)	242 (2)
C(31)	1331 (10)	6993 (8)	5821 (4)	103 (2)
C(32)	1432 (12)	6261 (10)	5353 (5)	155 (2)

[a] Atoms have occupancies of 1.0 except as marked with * above: C(14), 0.77; C(14′), 0.23; C(22), 0.77; C(22′), 0.23; C(24), 0.66; C(24′), 0.34; C(28), 0.51; C(28′), 0.49. [b] The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Selected Bond Lengths and Angles for $C_6H_4(NH)_2P(S)NEt_2$ (7)

(a) Bond Lengths (Å)

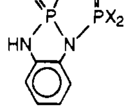
molecule A		molecule B	
P(1)–S(1)	1.941 (3)	P(2)–S(2)	1.944 (3)
P(1)–N(1)	1.659 (6)	P(2)–N(4)	1.663 (5)
P(1)–N(2)	1.675 (6)	P(2)–N(5)	1.643 (7)
P(1)–N(3)	1.613 (6)	P(2)–N(6)	1.623 (6)
N(1)–C(1)	1.409 (8)	N(4)–C(11)	1.395 (9)
N(2)–C(2)	1.407 (8)	N(5)–C(12)	1.384 (9)
N(3)–C(7)	1.491 (9)	N(6)–C(17)	1.483 (10)
N(3)–C(9)	1.541 (14)	N(6)–C(19)	1.505 (12)
C(1)–C(2)	1.373 (8)	C(11)–C(12)	1.381 (7)

(b) Bond Angles (deg)

molecule A		molecule B	
S(1)–P(1)–N(1)	116.9 (2)	S(2)–P(2)–N(4)	116.4 (2)
S(1)–P(1)–N(2)	116.5 (2)	S(2)–P(2)–N(5)	118.5 (2)
N(1)–P(1)–N(2)	90.7 (3)	N(4)–P(2)–N(5)	89.8 (3)
S(1)–P(1)–N(3)	111.5 (2)	S(2)–P(2)–N(6)	111.2 (2)
N(1)–P(1)–N(3)	110.2 (3)	N(4)–P(2)–N(6)	110.3 (3)
N(2)–P(1)–N(3)	109.3 (3)	N(5)–P(2)–N(6)	108.8 (3)
P(1)–N(1)–C(1)	113.9 (4)	P(2)–N(4)–C(11)	113.8 (4)
P(1)–N(2)–C(2)	113.7 (4)	P(2)–N(5)–C(12)	116.0 (4)
P(1)–N(3)–C(7)	124.3 (6)	P(2)–N(6)–C(17)	117.9 (6)
P(1)–N(3)–C(9)	118.8 (5)	P(2)–N(6)–C(19)	124.2 (5)
C(7)–N(3)–C(9)	116.8 (6)	C(17)–N(6)–C(19)	117.9 (6)
N(1)–C(1)–C(2)	111.0 (5)	N(4)–C(11)–C(12)	110.9 (5)
N(1)–C(1)–C(6)	127.7 (6)	N(4)–C(11)–C(16)	128.2 (5)
N(2)–C(2)–C(1)	110.5 (5)	N(5)–C(12)–C(11)	109.2 (6)
N(2)–C(2)–C(3)	128.8 (5)	N(5)–C(12)–C(13)	129.5 (5)

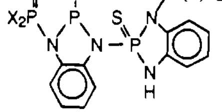
eight molecules per unit cell. In both, the six phenyl ring carbon atoms and the two diazadiphosphole ring nitrogen atoms are in the same plane; however, the phosphorus atoms are bent out of this plane by 3.6° in **7** and **4** and 5.6° in **8**. Selected bond distances and angles are given in Tables VI and VII. The internal N–P–N angles of the diazaphosphole rings are 90.3° for compound **7** and 91.9° [N(1)–P(1)–N(2)] and 90.9° [N(3)–P(2)–N(4)] for **8**. These small angles are consistent with those seen for compound **1** and in Malavaud's diazaphosphole, **5** (R = *n*-Pr).[1,5] The P–N bond lengths generally are in the 1.62–1.65 Å range observed for other P(V) diazaphospholes,[19] except for the long P(1)–N(3) distance of 1.69 Å and the P(2)–N(3) distance of 1.732 (5) Å in **8**. The latter makes the substituted diazaphosphole ring of **8** somewhat unsymmetrical. The dihedral angle between the two diazaphosphole ring planes in **8** [C(1)–C(6),N(1),N(2) and C(7)–C(12),N(3),N(4)] is 86.2°, making them surprisingly close to perpendicular.

Just as the **2**/**6** mixture was oxidized and separated, so was **3** sulfur oxidized and isolated by flash chromatography. Typically, mixtures containing mainly **3**, along with $P(NEt_2)_3$ and **2**, were oxidized at room temperature with excess S_8. The $^{31}P\{^1H\}$ NMR spectrum of a reaction mixture showed that all compounds in the system were oxidized to their sulfides by the upfield shifts of all resonances relative to those of the P(III) compounds. These sulfide mixtures were eluted from flash columns with solvent mixtures of petroleum ether and ethyl acetate (4.3:1 ratio by volume). The fractions eluted in the following order: excess S_8, $PS(NEt_2)_3$, **9**, and **7**. In addition, trace quantities of a crystalline product **10** were obtained from flash chromatography of fractions that contained mainly **9**.



9

(X = NEt2)



10

Characterization of **9** as the disulfide of the two-phosphorus intermediate **3** was readily accomplished by spectral data. A mass spectral parent ion at *m*/*e* 447 and the expected fragments due to loss of Et_2N (*m*/*e* 376) and Et_2N and S (*m*/*e* 343) groups are seen. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet resonance pair at δ 69.0 and 64.3 ($^2J_{PP}$ = 20.8 Hz); the high-field resonance is tentatively assigned to the diazaphosphole ring phosphorus.[2b] The ^1H NMR spectrum exhibits triplet resonances at δ 0.96 and 0.98 ($^3J_{HH}$ = 7.1 Hz) attributable to the two types of CH_3 groups on the Et_2N groups of the ring and exocyclic phosphorus atoms.[15] The CH_2 resonances are complex because they are split by the adjacent CH_3 groups and the phosphorus atom. A broad singlet at δ 4.4 corresponds to the NH proton, and multiplets at δ 6.8 and 7.9 correspond to aryl ring meta and ortho protons, respectively.

10 was present only in trace amounts in chromatographic fractions of **9**. No ^{31}P NMR spectral evidence for it or for its

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(19) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101.

Table VII. Selected Bond Lengths and Angles for $[C_6H_4(NH)_2P(S)]C_6H_4(NH)NP(S)NEt_2$ (**8**)

(a) Bond Lengths (Å)

molecule A		molecule B	
P(1)–S(1)	1.927 (1)	P(1′)–S(1′)	1.922 (2)
P(1)–N(1)	1.650 (3)	P(1′)–N(1′)	1.653 (4)
P(1)–N(2)	1.655 (5)	P(1′)–N(2′)	1.663 (3)
P(1)–N(3)	1.687 (3)	P(1′)–N(3′)	1.686 (3)
P(2)–S(2)	1.944 (2)	P(2′)–S(2′)	1.941 (1)
P(2)–N(3)	1.732 (3)	P(2′)–N(3′)	1.738 (3)
P(2)–N(4)	1.651 (3)	P(2′)–N(4′)	1.656 (5)
P(2)–N(5)	1.616 (3)	P(2′)–N(5′)	1.622 (4)
N(1)–C(1)	1.399 (6)	N(1′)–C(1′)	1.401 (4)
N(2)–C(2)	1.408 (5)	N(2′)–C(2′)	1.409 (5)
N(3)–C(7)	1.447 (4)	N(3′)–C(7′)	1.448 (5)
N(4)–C(8)	1.383 (6)	N(4′)–C(8′)	1.388 (4)
N(5)–C(13)	1.466 (6)	N(5′)–C(13′)	1.460 (5)
N(5)–C(14)	1.475 (4)	N(5′)–C(14′)	1.476 (4)
C(1)–C(2)	1.388 (6)	C(1′)–C(2′)	1.383 (6)
C(7)–C(8)	1.385 (6)	C(7′)–C(8′)	1.397 (6)

(b) Bond Angles (deg)

molecule A		molecule B	
S(1)–P(1)–N(1)	119.6 (1)	S(1′)–P(1′)–N(1′)	120.1 (1)
S(1)–P(1)–N(2)	117.9 (1)	S(1′)–P(1′)–N(2′)	116.9 (2)
N(1)–P(1)–N(2)	92.0 (2)	N(1′)–P(1′)–N(2′)	91.8 (2)
S(1)–P(1)–N(3)	109.6 (1)	S(1′)–P(1′)–N(3′)	109.8 (1)
N(1)–P(1)–N(3)	107.1 (1)	N(1′)–P(1′)–N(3′)	106.2 (2)
N(2)–P(1)–N(3)	109.2 (2)	N(2′)–P(1′)–N(3′)	110.6 (1)
S(2)–P(2)–N(3)	118.4 (1)	S(2′)–P(2′)–N(3′)	120.3 (1)
S(2)–P(2)–N(4)	113.7 (2)	S(2′)–P(2′)–N(4′)	113.1 (1)
N(3)–P(2)–N(4)	91.0 (2)	N(3′)–P(2′)–N(4′)	90.7 (2)
S(2)–P(2)–N(5)	112.3 (1)	S(2′)–P(2′)–N(5′)	112.3 (1)
N(3)–P(2)–N(5)	109.3 (2)	N(3′)–P(2′)–N(5′)	107.4 (1)
N(4)–P(2)–N(5)	110.3 (2)	N(4′)–P(2′)–N(5′)	111.1 (2)
P(1)–N(1)–C(1)	113.7 (3)	P(1′)–N(1′)–C(1′)	113.3 (3)
P(1)–N(2)–C(2)	112.8 (3)	P(1′)–N(2′)–C(2′)	112.2 (3)
P(1)–N(3)–P(2)	125.5 (1)	P(1′)–N(3′)–P(2′)	125.4 (2)
P(1)–N(3)–C(7)	123.7 (3)	P(1′)–N(3′)–C(7′)	123.9 (2)
P(2)–N(3)–C(7)	110.8 (2)	P(2′)–N(3′)–C(7′)	110.6 (2)
P(2)–N(4)–C(8)	115.3 (3)	P(2′)–N(4′)–C(8′)	115.0 (3)
P(2)–N(5)–C(13)	119.9 (2)	P(2′)–N(5′)–C(13′)	125.7 (2)
P(2)–N(5)–C(14)	124.0 (3)	P(2′)–N(5′)–C(14′)	119.0 (3)
N(1)–C(1)–C(2)	110.4 (3)	N(1′)–C(1′)–C(2′)	110.4 (3)
N(1)–C(1)–C(6)	128.4 (4)	N(1′)–C(1′)–C(6′)	127.9 (4)
N(2)–C(2)–C(1)	110.9 (4)	N(2′)–C(2′)–C(1′)	111.2 (3)
N(2)–C(2)–C(3)	127.6 (4)	N(2′)–C(2′)–C(3′)	128.4 (4)
N(3)–C(7)–C(8)	110.4 (3)	N(3′)–C(7′)–C(8′)	110.2 (3)
N(3)–C(7)–C(12)	129.5 (3)	N(3′)–C(7′)–C(12′)	129.5 (4)
N(4)–C(8)–C(7)	112.2 (3)	N(4′)–C(8′)–C(7′)	111.9 (4)
N(4)–C(8)–C(9)	126.7 (4)	N(4′)–C(8′)–C(9′)	127.2 (4)

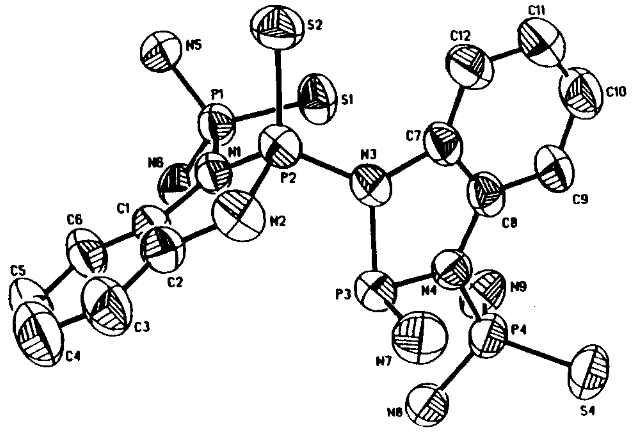


Figure 5. Structure and numbering system for **10**. Thermal ellipsoids are shown at the 50% level, and hydrogen atoms are omitted for clarity.

Table VIII. Selected Bond Lengths and Angles for $(C_6H_4)_2N_3(NH)(PS)(PNEt_2)[P(S)(NEt_2)_2]_2$ (**10**)

(a) Bond Lengths (Å)

P(1)–S(1)	1.931 (3)	P(1)–N(1)	1.718 (6)
P(1)–N(5)	1.624 (6)	P(1)–N(6)	1.647 (5)
P(2)–S(2)	1.923 (3)	P(2)–N(1)	1.715 (5)
P(2)–N(2)	1.651 (6)	P(2)–N(3)	1.649 (5)
P(3)–N(3)	1.767 (5)	P(3)–N(4)	1.736 (5)
P(3)–N(7)	1.647 (8)	P(4)–S(4)	1.932 (3)
P(4)–N(4)	1.680 (5)	P(4)–N(8)	1.661 (6)
P(4)–N(9)	1.642 (7)	N(1)–C(1)	1.444 (7)
N(2)–C(2)	1.388 (8)	N(3)–C(7)	1.449 (7)
N(4)–C(8)	1.424 (8)	C(1)–C(2)	1.393 (11)
C(7)–C(8)	1.375 (7)		

(b) Bond Angles (deg)

S(1)–P(1)–N(1)	108.0 (2)	S(1)–P(1)–N(5)	113.2 (2)
N(1)–P(1)–N(5)	109.7 (3)	S(1)–P(1)–N(6)	118.1 (2)
N(1)–P(1)–N(6)	101.6 (3)	N(5)–P(1)–N(6)	105.5 (3)
S(2)–P(2)–N(1)	114.8 (2)	S(2)–P(2)–N(2)	116.3 (2)
N(1)–P(2)–N(2)	91.6 (3)	S(2)–P(2)–N(3)	115.5 (2)
N(1)–P(2)–N(3)	112.8 (3)	N(2)–P(2)–N(3)	103.0 (3)
N(3)–P(3)–N(4)	88.2 (2)	N(2)–P(3)–N(7)	105.0 (3)
N(4)–P(3)–N(7)	104.0 (3)	S(4)–P(4)–N(4)	114.0 (2)
S(4)–P(4)–N(8)	111.8 (3)	N(4)–P(4)–N(8)	103.9 (3)
S(4)–P(4)–N(9)	114.9 (3)	N(4)–P(4)–N(9)	102.7 (3)
N(8)–P(4)–N(9)	108.6 (3)	P(1)–N(1)–P(2)	119.2 (3)
P(1)–N(1)–C(1)	129.1 (4)	P(2)–N(1)–C(1)	110.2 (4)
P(2)–N(2)–C(2)	114.8 (5)	P(2)–N(3)–P(3)	116.9 (3)
P(2)–N(3)–C(7)	129.9 (4)	P(3)–N(3)–C(7)	111.9 (3)
P(3)–N(4)–P(4)	121.9 (3)	P(3)–N(4)–C(8)	112.6 (4)
P(4)–N(4)–C(8)	124.1 (3)	N(1)–C(1)–C(2)	111.3 (5)
N(4)–C(8)–C(7)	112.9 (5)		

presumed P(III) precursor was seen in the reaction solutions. Since **10**, or its P(III) precursor, contains four chemically inequivalent phosphorus atoms, their phosphorus NMR spectra are expected to be complex and the resonances apparently are lost in the baseline noise. Pure samples of **10** large enough for ^{31}P NMR spectral analysis were not obtained. However, **10** does display a mass spectral parent ion at *m*/*e* 789 (M^+).

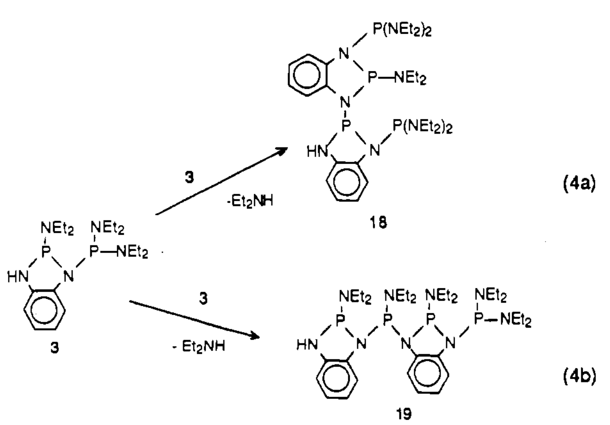
X-ray single-crystal analysis of **10** shows it to be a coupled, two-diazaphosphole ring derivative of **3**, oxidized as a trisulfide in which the ring phosphorus atom [P(3)], which contains the Et_2N substituent, remains unoxidized (Figure 5). This phosphorus atom is in a highly sterically protected environment analogous to that of the central phosphorus atom of **1**, which is known to remain unoxidized during reaction with S_8 at room temperature.[2b] Selected bond lengths and angles in **10** are given in Table VIII. The unoxidized phosphorus, P(3), is bent further out of its diazaphosphole C_6N_2 ring plane, 17.1°, than is the P(V) atom [P(2)], 9.5°, from its ring. This geometry is consistent with the slightly longer bond lengths of the P(III)–N bonds than of the P(V)–N bond in the two rings. The ring mean P–N bond lengths of the P(3) diazaphosphole ring are 1.76 Å, whereas the analogous P–N distance for the P(2) diazaphosphole ring is 1.69 Å. The internal N(4)–P(3)–N(3) and N(2)–P(2)–N(1) angles are 88.2 and 91.6° for the two rings. Both coupled condensation compounds, **6** and **10**, contain one phosphorus atom of a diazaphosphole ring connected to one of the ring nitrogen atoms of the other diazaphosphole ring. In **10**, this P(3)–N(3)–P(2) angle is 117.0°, while the P(1)–N(3)–P(2) angle in **6** is wider at 125.5°. It is worth noting that both P(1) and P(2) in **6** are P(V) atoms whereas one of the phosphorus atoms in **10**, P(3), is a P(III) atom.

In general, we have been successful using flash chromatography to separate new P(V) phosphazanes. Once separated, the compounds can usually be recrystallized for X-ray crystallographic analysis. However, other attempts to derivatize and/or separate **2**, **3**, or **6** failed. A major difficulty with these separations results from the reactive N–H bonds, which can react, with amine elimination, under vacuum to form condensation products. We attempted to replace the N–H functionality of **2** by BuLi deprotonation of the N–H groups followed by silylation with Me_3SiCl. Although silylation might have occurred, the reactions were not clean. Reaction of mixtures containing **3** with (nor)Mo(CO)$_4$ were attempted to determine if a two-phosphorus coordination complex **3**·Mo(CO)$_4$ could form analogous to other reported (bis(phosphino)amido)Mo(CO)$_4$ complexes reported recently.[20] After 4.5 h at 60 °C, **3** and (nor)Mo(CO)$_4$ showed no reaction perhaps because the bulky Et_2N groups make the P(III) donor sites relatively inaccessible.

The formation of primarily **2** and **3** from 1,2-$(NH_2)_2C_6H_4/(Et_2N)_3P$ reactions suggests behavior that is different from Malavaud's previously studied $(RNH)(NH_2)C_6H_4/(Me_2N)_3P$ systems. The data indicate that the reactions are significantly influenced by the R_2N substituents; the more bulky Et_2N groups behave differently from the smaller Me_2N units. In Malavaud's system, the cyclotetraphosphazanes[4,5] (**5**) are formed predominantly. At high temperatures these dissociate to the monomer phosphinimines (**4**). No spectral evidence for the Me_2N-substituted analogues of **2** and **3** was reported. In contrast, in our 1,2-$(NH_2)_2C_6H_4/(Et_2N)_3P$ reactions no phosphinimine, e.g. **16** (eq 3b), was apparent. No characteristic ^{31}P NMR resonances in the low-field region (δ 400–450) were seen[21] either in 1,2-$(NH_2)_2C_6H_4/(Et_2N)_3P$ reaction mixtures or in solutions of **2** at elevated temperatures. Instead, as Figure 2 shows, only the yield of the coupled product **6** increased with an increase in temperature. At room temperature, the **2**:**6** ratio is about 5:1; at 150°, this ratio decreases to approximately 2.5:1. The spectrum returns to its original appearance after the sample is returned to room temperature. Also, even when Et_2NH was removed in vacuo from **2**/**6** mixtures, no ^{31}P NMR resonance clearly attributable to a cyclotetraphosphazane (**17**, eq 3b) was seen. A small singlet appeared at δ 88.0 in the range observed earlier for cyclotetraphosphazanes; however, this singlet never became a major spectral feature.

The formation of **6** along with **2** and presumably **18**, the P(III) precursor to **10**, and **3** in the $(Et_2N)_3P$/1,2-$(NH_2)_2C_6H_4$ reactions (Scheme III) seems to be the result of coupling two molecules of **2** or **3** upon Et_2NH elimination. Coupling of **2** yields **6** (eq 3a), and coupling of **3** would yield **18** (eq 4a). **18** could form during the oxidation of the mixture containing **9**, or it could be present in minor amounts before the oxidation. Although oxidation is carried out at room temperature, some heat is generated in the exothermic process. The coupling reactions are consistent with the 1,2-addition of the N–H bond of a **2** (or **3**) to a phosphinimine intermediate; however, they might more likely be the result of transaminative exchange of the N–H of one diazaphosphole for the Et_2N group of another. Removal of Et_2NH from **2** or **3** results in the formation of higher molecular weight condensation products. **2** produces a viscous oil that consists of **6** and other materials that give broad ill-defined ^{31}P NMR resonances typical of higher oligomer/polymer products. Readdition of Et_2NH to this reaction mixture re-forms **2**, providing evidence for slow reversibility of the oligomer/polymer condensation processes. Addition of Et_2NH to a **2**/**6** reaction mixture causes the **2**:**6** ratio to increase. However, other resonances appear in the ^{31}P NMR spectrum suggesting the formation of other condensation products.

Scheme III

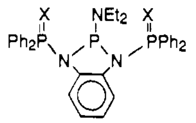


Similarly, mixtures containing **3**, when placed under vacuum to remove Et_2NH, form a viscous gold-colored oil. In contrast to the oil obtained from **2**, this oil is soluble in toluene. The ^{31}P NMR spectrum of the mixture is shown in Figure 2B. Broad unresolved resonances occur between δ 72 and 88. Readdition of Et_2NH slowly converts the mixture back to starting material. The sharper resonances, which appeared on removal of Et_2NH, are the first to disappear; the broader area resonances disappear more slowly over a few days. It is expected that relatively low molecular weight materials yield sharp NMR spectral resonances whereas higher molecular weight products yield the broader area resonances.

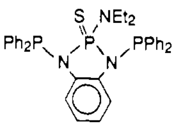
The behavior of **3** upon removal of Et_2NH is only tentatively understood. It seems likely that coupling of **3** could occur by both 1,2- and 1,4-addition processes. Transaminative coupling of the 1,2-type would yield **18** (eq 4a). Coupling through formal 1,4-addition could yield **19**, a more clearly linear oligomer/polymer product (eq 4b). This difference could explain why products from the oligomerization of **3** are more soluble than those from **2**. Since no additional **18** (or **10**, after S_8 oxidation) is formed upon Et_2NH removal from **3**, it is possible that the 1,4-process is dominant and occurs to the near exclusion of the 1,2-process. This might be because access to the diazaphosphole NEt_2 group is sterically more difficult than access to the Et_2N unit of the appended $-P(NEt_2)_2$ group.

Sulfur oxidation of the higher condensation product mixtures obtained from **2**/**6** or **3** did not result in readily separable products. Broad, ill-defined area resonances appear except for the sharp resonances due to **7**–**9**. In fact, oxidation of **2**/**6** condensation mixtures with sulfur seems to form more **7** than would be expected on the basis of spectral areas seen in the unoxidized spectra. An example of this was seen when we attempted to achieve high yields of **6** by oxidizing high-temperature **2**/**6** equilibrium mixtures. Sulfur reaction produced high yields of **7** and almost no **8**. At room temperature, the percentage of the coupled product **8** also decreased when the mixture was oxidized with sulfur. This suggests the **7** $\rightleftharpoons$ **8** equilibrium is facile and that **7** oxidizes faster than **8**, shifting the equilibrium to **7** during the reaction.

The reactivity of the N–H groups of **2** and those of its sulfide derivative, **7**, was explored preliminarily to determine if use of this functionality in synthesis of longer chain phosphazanes[22] is possible. Generally, reactivity of a phosphorus center decreases upon oxidation.[18,23] Consistent with this, we found that reactions with **7** were typically cleaner and easier to characterize than analogous reactions with unoxidized **2**. Reactions of Ph_2PCl with the **2**/**6** reaction mixture showed formation of a three-phosphorus product $C_6H_4(NPPh_2)_2PNEt_2$ (**11**), that would be expected if two Ph_2PCl molecules reacted at the N–H bonds of **2**. Unfortunately, **11** and the disulfide obtained upon S_8 oxidation (**12**) were difficult to isolate and only tentatively characterized. The $^{31}P\{^1H\}$ NMR spectra of **11** and **12** showed the triplet and doublet patterns characteristic of λ^3 P(III) and λ^5-λ^3-λ15 triphosphazanes, respectively. In contrast, **7** reacts cleanly with Ph_2PCl in the presence of Et_3N at 70 °C to form **13** quantitatively. This λ^3-λ^5-λ^3 mixed valence compound[24] is a rare example of a triphosphazane oxidized only at the endo, middle phosphorus, position.[25] **13** was stable enough to purify by silica column flash



11 (X = lone pair)
12 (X = S)



13

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chromatography. The $^{31}P\{^1H\}$ NMR spectrum exhibits characteristic triplet and doublet resonances at δ 87.8 and 27.7 ($^2J_{PP}$ = 102.5 Hz), and the ^1H NMR spectrum shows the expected triplet and doublet of quartets seen previously for ethyl resonances of NEt_2 groups attached to phosphorus. Mass spectra show the M^+ peak at *m/e* 609 and fragments at *m/e* 537 due to loss of NEt_2 and at *m/e* 217 due to the $P(S)Ph_2NEt_2^+$ ion.

Similarly, **2** and **7** are reactive toward transamination. Reaction of **2** with $P(NEt_2)_3$ in a 1:1 ratio produces **3** in a mixture with $P(NEt_2)_3$ and **1** ($P(NEt_2)_3$:**3**:**1** = 1:6:4). **7** is less reactive but also reacts with $P(NEt_2)_3$ to produce the mixed-valence compound **14**. Our results indicate that the intermediates which form in the reaction of $P(NEt_2)_3$ with 1,2-diaminobenzene are reactive enough that they may useful in the building of longer chain P–N phosphazane molecules. Further work must be done on the condensation mixtures that are formed upon Et_2NH elimination to determine what types of products form.

Acknowledgment. Support for this work by National Science Foundation (Grant CHE 8714951) and the Colorado Advanced Materials Institute Polymer Center is gratefully acknowledged.

Supplementary Material Available: Tables giving the details of the crystal structure determination, hydrogen atom coordinates, anisotropic thermal displacement parameters, complete bond angles and distances, and least-squares planes and dihedral angles (29 pages); listings of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Organochromium(III) Macrocyclic Complexes. Factors Controlling Homolytic vs Heterolytic Cleavage of the Chromium–Carbon Bond

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Received February 12, 1990

Kinetics studies were done of the homolytic and heterolytic cleavage reactions of the chromium–carbon bonds in the complexes $RCr(L)A^{n+}$ (where L = [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane; A = H_2O, OH^-). Activation parameters (ΔH^*/kJ mol^{-1}, ΔS^*/J mol^{-1} K^{-1}) for homolysis of $RCrL(H_2O)^{2+}$ are as follows: 111 ± 2, 54 ± 6 (R = $p\text{-}CH_3C_6H_4CH_2$); 103 ± 2, 28 ± 5 ($C_6H_5CH_2$); 101 ± 3, 22 ± 9 ($p\text{-}BrC_6H_4CH_2$); 110 ± 3, 62 ± 6 ($i\text{-}C_3H_7$). The ΔH^* and ΔS^* parameters are considerably smaller than those for homolysis of $(H_2O)_5CrR^{2+}$ analogues. Primary alkyl macrocyclic complexes do not undergo homolysis. The complexes $RCrL(OH)^+$ slowly hydrolyze for R = $n\text{-}C_3H_7$ and $i\text{-}C_3H_7$ whereas those for which R = $ArCH_2$ do not. The activation parameters for hydrolysis are 78 ± 1, −53 ± 2 (R = $i\text{-}C_3H_7$) and 83 ± 3, −46 ± 9 ($n\text{-}C_3H_7$). This pathway shows no solvent deuterium isotope effect. The complexes $RCrL(H_2O)^{2+}$ are not subject to acidolysis by H_3O^+ or H_2O, unlike their $(H_2O)_5CrR^{2+}$ analogues.

Introduction

Conventional ligand substitution reactions of inorganic and organometallic complexes are two-electron processes. They are relatively well understood in terms of the electronic and structural factors that control the rate.[1-3] In contrast, much less is known about the factors controlling the rates of unimolecular bond homolysis reactions, $L_5M^n\text{–}R \rightarrow L_5M^{n-1} + R^\bullet$ (R = alkyl, aralkyl). The data available for complexes such as $(H_2O)_5CrR^{2+}$[4,5] and macrocyclic organocobalt complexes[6] suggest that both steric and electronic factors must be considered.

We consider here a family of organochromium(III) macrocycles, $RCrL(H_2O)^{2+}$ (L = [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane) in aqueous solution. With a trans ligand A (A = H_2O, OH^-), we consider the possibilities of homolysis (eq 1) and heterolysis (eq 2). Neither reaction type has been examined previously for these complexes.

$$RCr^{III}L(A)^{n+} \rightarrow Cr^{II}L(A)^{n+} + R^\bullet \qquad (1)$$

$$RCr^{III}L(A)^{n+} + H_2O \rightarrow HOCr^{III}L(A)^{n+} + RH \qquad (2)$$

The presence of the macrocyclic ligand offers certain advantages in studying the reactivity of the metal–carbon bond. Most significantly, the macrocycle permits variation of the pH over a wide range, in contrast to the complexes $(H_2O)_5CrR^{2+}$ that rapidly decompose above pH ~ 4. This allows examination of the species with A = OH^-. In this article we present data showing that variation of A changes the mechanism of the Cr–C bond cleavage from homolytic to heterolytic. We explain this finding by the stabilizing effect of the strongly electron-donating OH^- group on the 3+ oxidation state of chromium. The same phenomenon helps in the understanding of the reactivity order when the R group is changed.

Experimental Section

Materials. The complexes $RCrL(H_2O)^{2+}$ were prepared by the known reaction of RBr or RI with $(H_2O)_2CrL^{2+}$ and separated by ion-exchange chromatography on Sephadex C25 columns.[7] The electronic spectra matched the reported values.[7] Radical scavengers were $[Co(NH_3)_5Br](ClO_4)_2$[8] and HTMPO[9] (Aldrich). The ESR and UV-visible spectra of HTMPO matched the literature values.[10]

Techniques. ESR spectra were recorded on aqueous solutions with an IBM-Bruker ER-200 spectrometer. Since the activation energies of metal–alkyl homolysis are in general rather large,[4-6] homolysis can be promoted at elevated temperature. This approach was used to conduct the ESR study. Samples of the complex $RCrL(A)^{n+}$ in the presence of a 3-fold excess of HTMPO were immersed in a water bath at 40 °C to initiate decomposition. At a fixed time, decomposition was quenched by immersing the sample in an ice–water bath. The sample was then warmed back to 15 °C and the ESR spectrum recorded. With bath temperature and timing controlled, the method was reproducible.

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