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Synthesis of Mono- and Diphosphorus Phosphazane Oligomer/Polymer Precursors

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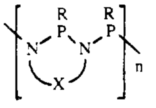
Reactions of $RP(NEt_2)_2$ (R = Me, Et, *t*-Bu, Ph) with $1,2\text{-}(NH_2)_2C_6H_4$ (0.8:1.0 ratio) yield the 1,3,2-diazaphospholes $C_6H_4(NH)_2PR$ [R = Me (**4**), Et (**5**), *t*-Bu (**6**), Ph (**7**)]. At higher ratios (2:1) the diphosphazanes $C_6H_4(NH)PRNP(NEt_2)R$ [R = Me (**9**), Et (**10**), *t*-Bu (**11**), Ph (**12**)] form. **4**–**7** and **9**–**12** were characterized in solution by spectral data; **9**–**12** form as mixtures of diastereomers. **4** and **10** upon reaction with S_8 are converted to $C_6H_4(NH)_2P(S)Me$ (**8**) and two diastereomers of $C_6H_4(NH)PEt(S)NP(NEt_2)(S)Et$ (**13a,b**). **4** with cycloheptatriene·$Mo(CO)_3$ forms the derivative complex *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ (**15**). **15** crystallizes from MeCN with Ph_3PO as the cocrystallate *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3\cdot 3Ph_3PO\cdot MeCN$ (**16**). X-ray analyses of **13a** and **16** were carried out. **13a**: monoclinic, *Pn*, $a = 8.561$ (3) Å, $b = 7.705$ (3) Å, $c = 14.036$ (4) Å, $\beta = 95.97$ (2)°, $V = 920.8$ (5) Å^3, $d_{calc} = 1.304$ g/cm^3, $Z = 2$. **16**: monoclinic, $P2_1$, $a = 12.869$ (5) Å, $b = 16.312$ (5) Å, $c = 18.853$ (7) Å, $\beta = 108.15$ (3)°, $V = 3761$ (2) Å^3, $d_{calc} = 1.322$ g/cm^3, $Z = 2$. **16** contains three Ph_3PO molecules H-bonded to the six N–H bonds of the diazaphosphole rings in an approximate 3-fold symmetry pattern.

Introduction

The synthesis of high molecular weight polymers often depends upon the availability of appropriate polymer precursors.[2-4] Designing systems with the necessary functionality and with the desired level of reactivity to be effective precursors can be critical. A particularly desirable condensation polymer precursor is an A–B[2-4] type monomer, one which contains both sites of reactivity necessary for polymer formation in the same molecule. Thus, in connection with our studies of linear phosphazanes that can be stabilized by the introduction of bridging groups between nitrogen atoms (**1**: X = *o*-phenylene),[5] we became interested in 1,3,2-diazaphosphole-based mono- and diphosphorus P(III) and P(V) phosphazanes (**2** and **3**: R = alkyl, aryl; X = O, S, lone pair; Y = halogen, NR_2), which might be used as polymer precursors. The diphosphazanes were also of interest structurally because this information could help predict and determine the stereochemistry of polymers of type **1**. We now report studies of the transamination of $RP(NEt_2)_2$ by $1,2\text{-}(NH_2)_2C_6H_4$ as a route to such compounds. Preliminary reports of parts of this work have been presented.[6]



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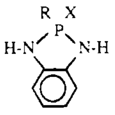

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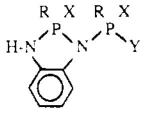

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Experimental Section

Apparatus and Materials. Phosphorus-31 NMR spectra were obtained 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 ($+\delta$). In cases where ^{31}P NMR relative spectral areas were critical (e.g. **10a**:**10b**, below), spectra were measured over a range of data collection conditions and the areas measured in decoupled ($^{31}P\{^1H\}$) spectra were compared with those measured in undecoupled (^{31}P) experiments. IR spectra (4000–400 cm^{-1}) were obtained by using a Beckman 4250 or an IBM IR/32 Type 9132 spectrometer. Mass spectra were obtained at 70 eV with a Varian MAT-CH5 or a VG Analytical 7070 EQ-HF spectrometer. Mass spectral data refer to the major peak of the respective envelope. Chemical ionization (CI$^+$ and CI$^-$) data were obtained by using 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-temperature attachment. All manipulations were carried out by using standard vacuum-line, glovebag, or Schlenk techniques under dry N_2.[7]

Flash chromatography was carried out according to the method of Still et al.[8] A 650- or 450-mL column was packed with 15 cm of silica gel 60 (230–400 mesh). Compounds were eluted at 5 cm/min with the necessary solvent mixture under N_2 pressure.

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

$1,2\text{-}(NH_2)_2C_6H_4$ (Aldrich) was recrystallized from toluene. Toluene (over Na/Pb or CaH_2), CH_2Cl_2 (P_4O_{10}), and CH_3CN (CaH_2) were distilled before use. Elemental sulfur (EM Scientific), silica gel (EM Scientific), KBr (Baker, oven dried), $Mo(CO)_6$ (Aldrich), triphenylphosphine oxide (Aldrich), petroleum ether, ethyl acetate, EtOH, and deuterated solvents were used as received. $MeP(NEt_2)_2$,[9] $EtP(NEt_2)_2$,[9] $PhP(NEt_2)_2$,[10] and CHT·$Mo(CO)_3$[11] (CHT = cycloheptatriene) were prepared as described previously. *t*-$BuP(NEt_2)_2$ (^{31}P NMR, δ 110.0) was prepared like the other $RP(NEt_2)_2$ compounds[9] except longer reaction times were required (reflux $\cong$ 60 h in toluene with periodic filtration from amine hydrochloride).

Reactions of $RP(NEt_2)_2$ with $1,2\text{-}(NH_2)_2C_6H_4$. (A) $C_6H_4(NH)_2PR$ [R = Me (4), Et (5), *t*-Bu (6), Ph (7)]. Reactions of $RP(NEt_2)_2$ with $1,2\text{-}(NH_2)_2C_6H_4$ were carried out under N_2 at the following $RP(NEt_2)_2$:$1,2\text{-}(NH_2)_2C_6H_4$ mole ratios, reaction times, and reaction temperatures: R = Me, 0.8–3:1, 3–15 h, 60–70 °C; R = Et, 1–6:1, 46 h, 45–85 °C; R = *t*-Bu, 0.8–2:1, 5 days 70–85 °C; R = Ph, 0.8–3:1, 2–38 h, 80 °C. Reaction progress as a function of time was monitored by ^{31}P NMR spectral analysis. Reaction mixtures that exhibited resonances attributable primarily to the monophosphines $C_6H_4(NH)_2PMe$ (**4**), $C_6H_4(NH)_2PEt$ (**5**), $C_6H_4(NH)_2P$-*t*-Bu (**6**), and $C_6H_4(NH)_2PPh$ (**7**) at δ 88.5, 92.7, 101.1, and 77.1, respectively, were obtained at the following $RP(NEt_2)_2$:$1,2\text{-}(NH_2)_2C_6H_4$ mole ratios, reaction times, and reaction temperatures: **4**, 0.9:1.0, 4 h, 60 °C; **5**, 0.8:1.0, 3 h, 70 °C; **6**, 0.8:1.0, 24 h, 80 °C; 7, 0.8:1.0, 50 h, 80 °C. In the $RP(NEt_2)_2/1,2\text{-}(NH_2)_2C_6H_4$ (R = Me, Et, *t*-Bu) reactions, **4**–**6** were major products (>90%). Only minor resonances due to uncharacterized products were seen. The $PhP(NEt_2)_2/1,2\text{-}(NH_2)_2C_6H_4$ reaction mixture was more complex, exhibiting ^{31}P NMR spectral resonances (45–50 area %) at δ 80–90 and 50–65. Attempts to isolate **4**–**7** from their reaction mixtures for further characterization by fractional crystallization or silica-gel flash chromatography were unsuccessful. ^1H NMR spectra of reaction mixtures could not be unambiguously assigned due to the presence of Et_2NH, unreacted

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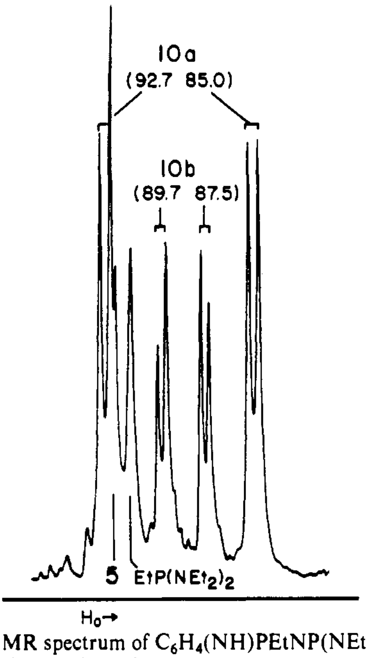


Figure 1. ^{31}P NMR spectrum of $C_6H_4(NH)PEtNP(NEt_2)Et$ diastereomers (**10a**/**10b**) in reaction mixture.

1,2-$(NH_2)_2C_6H_4$, and other minor impurities. Placing a mixture containing mainly **4** under vacuum seemed to increase the yield of other products, further complicating the ^{1}H NMR spectrum. Mass spectral data on samples completely free of other reaction materials and oxidation species could not be obtained; however, for **4** a distinct parent ion (M^+) at *m/e* 152 was observed.

(B) $C_6H_4(NH)_2P(S)Me$ (8). S_8 (ca. 10% excess) was allowed to react at room temperature with a toluene solution of **4** prepared as described above. Within 0.5 h, the product mixture showed mainly a singlet ^{31}P NMR spectral resonance attributable to **8**. Flash chromatography of the mixture using a petroleum ether/ethyl acetate eluent (4.5:2 v/v) separated the mixtures; first fractions contained unreacted S_8, and later fractions contained **8**. Evaporation of solvent in vacuo yielded pure **8** (mp = 159–162 °C). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 76.6 (s). ^{1}H NMR (C_6D_6): δ 1.6 (d, a 3, $^2J_{PH}$ = 14.5 Hz, CH_3), 4.1 (br d, a 2, NH), 6.2–6.3 (m, a 2, 4-line pattern, aryl), 6.5–6.7 (m, a 2, aryl). IR (KBr), cm^{-1}: 3253 (s, br, NH), 3059 (m), 2965 (w), 2905 (w), 1489 (vs), 1468 (m), 1390 (vs), 1281 (vs), 1294 (m), 1249 (s), 1103 (m), 1021 (m), 914 (s), 800 (m), 764 (s), 740 (s, P=S), 651 (s), 587 (m), 502 (m), 423 (m). MS (EI): *m/e* 184 (M^+ ($C_7H_9N_2PS^+$)). Anal. Calcd for $C_7H_9N_2PS$: mol wt 184.02240; C, 45.65; H, 4.92; N, 15.21; P, 16.82. Found: mol wt (exact mass MS) 184.0224; C, 45.73; H, 5.11; N, 15.06; P, 16.66.

(C) $C_6H_4(NH)PRNP(NEt_2)R$ [R = Me (9), Et (10), *t*-Bu (11), Ph (12)]. Maximum yields of diphosphino products $C_6H_4(NH)PRNP(NEt_2)R$, as determined by ^{31}P NMR spectral analysis on reactions in toluene solution, were obtained at the following $RP(NEt_2)_2$:1,2-$(NH_2)_2C_6H_4$ mole ratios, reaction times, and reaction temperatures: $C_6H_4(NH)PMeNP(NEt_2)Me$ (**9**), 2:1, 15 h, 70 °C; $C_6H_4(NH)PEtNP(NEt_2)Et$ (**10**), 2:1, 46 h, 70 °C; $C_6H_4(NH)P(t\text{-}Bu)NP(NEt_2)\text{-}t\text{-}Bu$ (**11**), 2:1, 5 days, 80 °C; $C_6H_4(NH)PPhNP(NEt_2)Ph$ (**12**), 2:1, 21 h, 70 °C in vacuo. Typically, reaction mixtures contained 80–85% **9**–**12** as mixtures of two diastereomers (**a** and **b**), 10–15% monophosphorus products **4**–**7**, and minor amounts of unreacted $RP(NEt_2)_2$ and/or other uncharacterized products (Figure 1). In the $EtP(NEt_2)_2$/1,2-$(NH_2)_2C_6H_4$ reaction, after 23 h, resonances clearly attributable to the three-phosphorus product $C_6H_4N_2[PEt(NEt_2)]_2PEt$ were seen. Attempts to separate **9**–**12** from their monophosphorus precursors **4**–**7** by fractional crystallization or column chromatography failed and resulted instead in decomposition and formation of condensation products of the reaction mixtures. Consequently, unambiguous ^{1}H NMR, IR, and mass spectral and elemental analytical data could not be obtained. ^{31}P NMR spectral data (obtained on species in the reaction mixtures): **9a** δ 82.5 (d, $^2J_{PP}$ = 22.0 Hz), 76.5 (d) and **9b** δ 87.2 (d, $^2J_{PP}$ = 18.3 Hz), 71.6 (d), **9a**:**9b** = 3:1; **10a** δ 92.7 (d, $^2J_{PP}$ = 18.3 Hz), 85.0 (d) and **10b** δ 89.7 (d, $^2J_{PP}$ = 14.6 Hz), 87.5 (d), **10a**:**10b** = 2.5:1; **11a** δ 100 (d, $^2J_{PP}$ = 1 Hz), 113 (d) and **11b** δ 117.3 (d, $^2J_{PP}$ = 32.3 Hz), 105.0 (d), **11a**:**11b** = 1:1; **12a** δ 85.0 (s), 86.4 (s) and **12b** δ 85.9 (d, $^2J_{PP}$ = 23.3 Hz), 91.9 (d), **12a**:**12b** = 1:1.

Table I. Crystal Data for $C_6H_4(NH)PEt(S)NP(NEt_2)(S)Et$ (**13a**) and $[C_6H_4(NH)_2PMe]_3Mo(CO)_3\cdot 3Ph_3PO\cdot MeCN$ (**16**)

	13a	16
formula	$C_{14}H_{25}P_2N_3S_2$	$C_{80}H_{75}N_7O_6P_6Mo$
fw	361.4	1512.2
space group	monoclinic, *Pn*	monoclinic, $P2_1$
a, Å	8.561 (3)	12.869 (5)
b, Å	7.705 (3)	16.312 (5)
c, Å	14.036 (4)	18.853 (7)
β, deg	95.97 (2)	108.15 (3)
V, Å^3	920.8 (5)	3761 (2)
Z	2	2
d_{calcd}, g cm^{-3}	1.304	1.322
abs coeff, mm^{-1}	0.446	0.350
F(000), e	384	1568
λ(Mo Kα), Å	0.71073	0.71073
T, °C	23	-80
μ, cm^{-1}	4.46	3.50
transm coeff	0.96, 0.89	0.948, 0.937
R and R_w (obs data)	0.038, 0.047	0.046, 0.053

(D) $C_6H_4(NH)P(S)EtNP(S)(NEt_2)Et$ (13a,b). A toluene solution of a **10a**/**10b** mixture, obtained as described above, was allowed to react with excess S_8 at 70 °C. After 4 h, $EtP(S)(NEt_2)_2$ [δ 86.4 (s)], $C_6H_4(NH)_2P(S)Et$ [δ 87.1 (s)], **13a** [δ 92.0 (d, ^2J = 4.9 Hz, a 1), 75.5 (d, a 1)], and **13b** [δ 95.8 (d, ^2J = 19.5 Hz, a 1), 73.3 (d, a 1)] formed (**13a**:**13b** area = 1.5:1). The solution was filtered from excess S_8, and toluene was removed in vacuo. Separation of the mixture was achieved partially by flash chromatography using a petroleum ether/ethyl acetate (45:25 v/v) eluent solvent. Elution order: S_8, $C_6H_4(NH)_2P(S)Et$, **13a**, **13b**, and $EtP(S)(NEt_2)_2$. Crystallization from a mainly **13a** fraction yielded large rectangular crystals of **13a**. **13b** was not obtained free of **13a**. Recrystallization of **13a** from ethanol/toluene ($\cong$1:1) produced an X-ray-quality crystalline product (mp = 163.5–164 °C). $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 93.7 (d, a 1, $^2J_{PP}$ = 7.3 Hz) and 76.4 (d). ^{1}H NMR (CD_2Cl_2): δ 1.0 (t, a 6, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3), 1.1 (t of d, a 3, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 3.9 Hz, CH_2CH_3), 1.4 (t of d, a 3, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 3.7 Hz, CH_2CH_3), 1.8–2.7, 2.9–3.8 (m, a 8, methylenes), 4.9 (br d, a 1, NH), 6.6–7.0, 7.2–7.4 (m, a 4, aryl). MS (EI): *m/e* 361 (M^+ ($C_{14}H_{25}N_3P_2S_2^+$)). MS (CI^+): *m/e* 362 (M^+ + 1). IR (KBr), cm^{-1}; 3252 (s, br), 2967 (w), 1488 (vs), 1370 (m), 1263 (s), 1190 (m), 1166 (m), 1113 (w), 1030 (m), 1002 (w), 949 (vs), 895 (vs), 875 (m), 771 (w), 745 (s), 723 (s), 716 (s), 680 (w), 628 (m), 578 (m). Anal. Calcd for $C_{14}H_{25}N_3P_2S_2$: mol wt 361.0965. Found: mol wt (exact mass MS) 361.0974.

Reaction of 6 with $MeP(NEt_2)_2$. **6** (0.66 mmol) and $MeP(NEt_2)_2$ (0.54 mmol) were heated at 70 °C. After 14 h, the ^{31}P NMR spectrum showed **6** (δ 101.9) and the two diastereomers of $C_6H_4(NH)P(t\text{-}Bu)NP(NEt_2)Me$ (**14a**:**14b**) in a 3:1 mole ratio: **14a** δ 96.7 (d, $^2J_{PP}$ = 15.9 Hz), 82.6 (d); **14b** δ 102.5 (d, $^2J_{PP}$ = 80.6 Hz), 90.0 (d) (mole ratio **14a**:**14b**= 3.2:1). The reaction was repeated at 45 °C; **14a** and **14b** formed in a 2.5:1 ratio. **14a** and/or **14b** could not be isolated.

***fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ (15).** **4** (8.0 mmol) and $CHT\cdot Mo(CO)_3$ (1.9 mmol) at 25 °C in toluene were allowed to react. After 1.5 h at 25 °C, toluene was removed in vacuo. The resulting brown solid was slurried in 50 mL of refluxing toluene. The slurry was filtered, leaving white solid **15** (mp = 210 °C dec). $^{31}P\{^1H\}$ NMR (CH_3CN): δ 132.6 (s). ^{1}H NMR (CD_3CN): δ 1.5 (s, a 9, CH_3), 5.3 (br s, a 6, N–H), 6.6 (s, a 12, aryl). MS (CI^-): *m/e* 638 (M^+) with correct isotope pattern, 486 (loss of one molecule of **4**). IR (KBr), cm^{-1}: 3411 (s), 3379 (s, NH), 3048 (w), 3019 (w), 1954 (vs, C=O), 1867 (vs, C=O), 1838 (m), 1486 (s), 1373 (s), 1278 (m), 1248 (vs), 888 (s), 874 (s), 830 (m), 746 (s), 707 (m), 601 (m), 574 (m), 488 (m), 447 (w).

***fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3\cdot 3Ph_3PO\cdot MeCN$ (16).** **15** (66 mmol) and Ph_3PO (204 mmol) in 20 mL of MeCN were heated to 70 °C until all solid dissolved. Upon cooling, after 4 h, large cubic white crystals of **16** (mp = 192–194 °C) crystallized. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 132.5 (s), 26.2 (s). ^{1}H NMR (CD_3CN): δ 1.5 (s, CH_3), 5.4 (br s, NH), 6.6 (m, phenylene), 7.5–7.7 (m, phenyl). MS (EI): *m/e* 638 (**12**$^+$), 277 (Ph_3PO; M^+ − 1). IR (KBr), cm^{-1}: 3256 (m, br), 3057 (m), 2965 (w), 1952 (vs, C=O), 1862 (vs, C=O), 1489 (s), 1439 (m), 1399 (m), 1270 (m), 1249 (s), 1169 (m), 1120 (m), 1090 (w), 887 (m), 873 (m), 849 (m), 722 (s), 694 (m), 541 (s), 480 (w).

X-ray Analysis. (A) $C_6H_4(NH)P(S)EtNP(S)(NEt_2)Et$ (13a). Clear colorless parallellepipeds were obtained from toluene/ethanol (50:50). Experimental conditions for data collection and structure solution are given in Table I. Positional parameters are given in Table II. Crystal integrity was monitored by measuring four check reflections every 96 reflections. Only random variations were observed over the course of the data collection. The amine hydrogen atoms were refined with no constraints. The thermal parameters of each hydrogen atom were refined independently.

Table II. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $C_6H_4(NH)PEt(S)NP(NEt_2)(S)Et$ (**13a**)

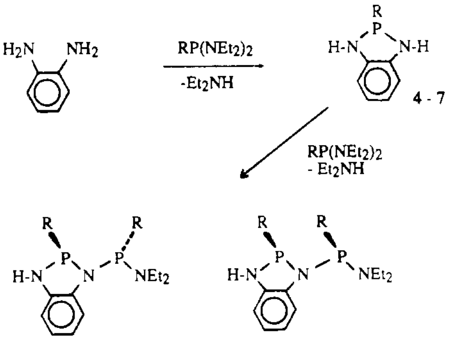
	x/a	y/b	z/c	U_{eq}[b]
P(1)	5800	2607 (1)	5600	31 (1)
P(2)	2236 (1)	2997 (1)	4990 (1)	28 (1)
S(1)	6484 (1)	4846 (1)	6095 (1)	44 (1)
S(2)	828 (1)	1054 (1)	4641 (1)	41 (1)
N(1)	4136 (3)	2524 (3)	4806 (2)	30 (1)
N(2)	6879 (3)	1646 (4)	4831 (2)	44 (1)
N(3)	1755 (3)	4780 (3)	4397 (2)	35 (1)
C(1)	4530 (3)	2048 (4)	3870 (2)	31 (1)
C(2)	6109 (3)	1557 (4)	3898 (2)	38 (1)
C(3)	6755 (4)	1076 (5)	3076 (3)	49 (1)
C(4)	5785 (5)	1067 (6)	2213 (3)	52 (1)
C(5)	4234 (4)	1555 (5)	2185 (2)	46 (1)
C(6)	3587 (4)	2057 (4)	3013 (2)	38 (1)
C(7)	2748 (4)	6327 (4)	4569 (3)	44 (1)
C(8)	3680 (7)	6777 (7)	3747 (4)	75 (2)
C(9)	371 (4)	4961 (5)	3692 (3)	45 (1)
C(10)	−861 (5)	6168 (8)	4016 (4)	73 (2)
C(11)	2373 (3)	3474 (5)	6257 (2)	40 (1)
C(12)	831 (5)	4124 (8)	6559 (3)	72 (2)
C(13)	5659 (4)	1044 (4)	6550 (2)	41 (1)
C(14)	4957 (5)	−685 (5)	6229 (3)	56 (1)

[a] 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.

(B) $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (16). Clear colorless parallelepipeds were obtained from MeCN. A summary of crystal data, details of the data collection, and structure refinement data are given in Table I. Only random variations were observed over the course of the data collection. Positional parameters are given in Table III. Crystal integrity was monitored by measuring three check reflections every 97 reflections. Anisotropic refinement was carried out on Mo, P, N, and O atoms as well as the C atoms of carbonyl groups and the MeCN molecule. Hydrogen atoms were included in fixed idealized positions.

Results and Discussion

Transamination of $RP(NEt_2)_2$ (R = Me, Et, *t*-Bu, Ph) with $1,2-(NH_2)_2C_6H_4$ under carefully controlled conditions yields primarily monophosphorus (**4–7**) and diphosphorus (**9–12**) diazaphospholes stepwise as



(1)

(2)

9 - 12 (a/b)

R = Me (**4, 9**), Et (**5, 10**), *t*-Bu (**6, 11**), Ph (**7,12**)

Reactions under a variety of conditions were monitored by ^{31}P NMR spectral analysis, and from these studies optimum conditions were determined for formation of the desired products. Although reaction rates depend on temperature, they are most dependent on the R group of the $RP(NEt_2)_2$ reactant. Reaction products are dependent on the reactant ratio. At lower ratios (<0.8:1.0) relatively large amounts of unreacted $1,2-(NH_2)_2C_6H_4$ remain in the reaction mixtures; at higher ratios (>2:1) significant quantities of products tentatively identified as triphosphazanes arise.

Reactions of $RP(NEt_2)_2$ with $1,2-(NH_2)_2C_6H_4$ (0.8:1 mole ratio) yield product mixtures with **4–7** as the primary phosphorus-containing products. After **3–4** h at 60–70 °C, $1,2-(NH_2)C_6H_4$ reactions with $MeP(NEt_2)_2$ and $EtP(NEt_2)_2$ show singlet $^{31}P\{^1H\}$ NMR spectral resonances at δ 88.5 and 92.7 attributable **4** and **5**, respectively. Typically, reaction mixtures show only minor resonances from uncharacterized products and traces of unreacted $RP(NEt_2)_2$. Reactions of $t\text{-}BuP(NEt_2)_2$ and $PhP(NEt_2)_2$ with $1,2-(NH_2)_2C_6H_4$ proceed more slowly; at 80 °C, **6** and **7** form in 24 and 50 h, respectively. **6** and **7** exhibit characteristic ^{31}P NMR spectral peaks at δ 101.0 and 77.1. **4–6** form quite cleanly (80–90 mol %); **7** typically shows ca. 50% of the spectral area due to uncharacterized high molecular weight material. The chemical shifts for **4–7** are in the region observed for N-substituted 1,3,2-diazaphospholes reported previously.[12–16]

Reactions of $RP(NEt_2)_2$ (R = Me, Et, *t*-Bu, Ph) with $1,2-(NH_2)_2C_6H_4$ in a 2:1 ratio produce mixtures containing primarily the diphosphazanes **9–12** (Figure 1), although the reaction mixtures also contain small quantities of reactant $RP(NEt_2)_2$, monophosphines **4–7**, and minor amounts of higher condensation products, e.g. triphosphazanes. Similar to the reactions that form **4–7**, reactions with $MeP(NEt_2)_2$ and $EtP(NEt_2)_2$ were faster than those of $t\text{-}BuP(NEt_2)_2$ and $PhP(NEt_2)_2$. The former required 15 and 46 h at 70 °C to maximize the yields of **9** and **10**, respectively, while it required 5 days at 80 °C to maximize the yield of **11** and 21 h at 70 °C in vacuo to optimize the yield of **12**.

Product mixtures containing **9–12** are complicated because the diphosphorus compounds occur as mixtures of two diasteromers. **9–12** contain chiral centers at both phosphorus atoms. A ^{31}P NMR spectrum of a reaction mixture containing mainly $C_6H_4(NH)PEtNP(NEt_2)Et$ (**10a/10b**) (Figure 1) exhibits two doublets, at δ 92.7 and 85.0 (J = 18.3 Hz) and δ 89.7 and 87.5 (J = 14.6 Hz), assigned to diastereomers **10a** and **10b**, respectively. Closely similar spectral properties are seen for **9a/9b**, **11a/11b**, and **12a/12b**. The $^2J_{PNP}$ coupling constants for **9a/9b–12a/12b** are close to those reported earlier for the diphosphazane disulfides $MeN[(Me_2N)PX][PX_2]$.[16] On the basis of comparison with other diazaphospholes[12–15] and **4–7**, the lower field resonances are assigned to the ring phosphorus atoms. The higher field resonances occur in the region expected for alkylaminophosphino [$-P(NEt_2)R$] moieties.[16–21]

The **9–12** diasteromer ratios (**a**:**b**) indicate that a modest degree of diastereomer selectivity occurs in some cases. Compounds **9** and **10** exhibit a diastereomeric formation selectivity under optimum ratios of 3:1 (**9a**:**9b**) and 2.5:1 (**10a**:**10b**). The harsher conditions required to form **11** and **12** presumably preclude selective diastereomer formation because at these temperatures inversion at phosphorus is faster.[22] Reaction of $EtP(NEt_2)_2$ with $1,2-(NH_2)_2C_6H_4$ at lower temperature (45 °C) does not improve diastereomer selectivity in the reaction to form **10a** and **10b**, perhaps because the transamination reactions at this temperature are very slow.

Attempts to separate **4–7** and **9–12** from other reaction materials by fractional crystallization or column chromatography were unsuccessful. **4–7** and **9–12** showed no tendency to crystallize from their respective reaction mixtures. Separation is complicated by the high sensitivity of the compounds to ambient moisture and

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Table III. Atomic Coordinates[a] ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (**16**)

	x/a	*y/b*	*z/c*	*U*[b]		*x/a*	*y/b*	*z/c*	*U*[b]
Mo(1)	-1 (1)	5000	-1479 (1)	27.2 (1)*	C(32)	6199 (9)	5825 (7)	969 (6)	55 (3)
P(1)	-1532 (2)	4724 (1)	-2621 (1)	31 (1)*	C(33)	6598 (9)	5214 (7)	1489 (6)	60 (3)
P(2)	3408 (2)	7576 (2)	-3617 (1)	36 (1)*	C(34)	6004 (10)	4512 (8)	1459 (7)	73 (3)
P(3)	386 (2)	6443 (2)	-1695 (1)	36 (1)*	C(35)	5005 (9)	4427 (8)	950 (6)	62 (3)
P(4)	4608 (2)	6520 (2)	-249 (1)	32 (1)*	C(36)	4596 (7)	5032 (8)	420 (5)	45 (2)
P(5)	-603 (2)	1606 (2)	-3124 (1)	33 (1)*	C(37)	5732 (7)	7142 (6)	-316 (5)	35 (2)
P(6)	-3408 (2)	7576 (2)	-3617 (1)	36 (1)*	C(38)	6290 (7)	7681 (6)	254 (5)	40 (2)
O(1)	-117 (6)	3134 (5)	-1080 (4)	53 (3)*	C(39)	7190 (8)	8100 (7)	196 (6)	50 (3)
O(2)	1759 (5)	5148 (5)	104 (3)	60 (3)*	C(40)	7530 (9)	8008 (7)	-417 (6)	57 (3)
O(3)	-1821 (6)	5458 (5)	-764 (4)	67 (3)*	C(41)	6996 (9)	7484 (7)	-971 (6)	58 (3)
O(4)	3961 (5)	6160 (3)	-976 (3)	36 (2)*	C(42)	6079 (8)	7041 (7)	-928 (6)	51 (3)
O(5)	-287 (5)	2468 (4)	-2879 (3)	41 (2)*	C(43)	-2059 (7)	1479 (6)	-3360 (5)	32 (2)
O(6)	-2371 (5)	7098 (4)	-3331 (3)	48 (3)*	C(44)	-2642 (8)	2055 (7)	3120 (5)	49 (3)
N(1)	-2063 (6)	5374 (4)	-3345 (4)	38 (3)*	C(45)	-3787 (9)	2002 (7)	-3296 (6)	57 (3)
N(2)	-1366 (6)	4013 (4)	-3232 (4)	35 (3)*	C(46)	-4315 (9)	1339 (7)	-3703 (6)	60 (3)
N(3)	1495 (6)	3621 (5)	-2286 (4)	40 (3)*	C(47)	-3740 (8)	746 (7)	-3936 (6)	54 (3)
N(4)	2710 (5)	4703 (4)	-1719 (4)	39 (3)*	C(48)	-2607 (8)	814 (6)	-3771 (5)	46 (3)
N(5)	1662 (6)	6669 (5)	-1725 (4)	43 (3)*	C(49)	-9 (8)	893 (6)	-2389 (5)	39 (2)
N(6)	-149 (6)	6936 (5)	-2525 (4)	48 (3)*	C(50)	98 (7)	50 (7)	-2509 (5)	43 (2)
C(1)	-2036 (7)	4162 (5)	-3963 (5)	31 (2)	C(51)	487 (9)	-455 (8)	-1904 (6)	65 (3)
C(2)	-2473 (6)	4952 (6)	-4026 (4)	33 (2)	C(52)	776 (9)	-155 (8)	-1193 (7)	75 (4)
C(3)	-3155 (7)	5237 (6)	-4690 (5)	43 (3)	C(53)	659 (11)	640 (9)	-1059 (8)	83 (4)
C(4)	-3405 (8)	4714 (6)	-5320 (5)	48 (3)	C(54)	315 (9)	1188 (8)	-1672 (6)	64 (3)
C(5)	-2954 (8)	3946 (6)	-5252 (5)	47 (3)	C(55)	-212 (7)	1331 (6)	-3932 (5)	41 (2)
C(6)	-2291 (7)	3656 (6)	-4576 (5)	42 (2)	C(56)	802 (10)	999 (7)	-3849 (7)	68 (3)
C(7)	2565 (7)	3400 (5)	-2210 (4)	31 (2)	C(57)	1141 (11)	871 (9)	-4491 (7)	83 (4)
C(8)	3286 (7)	4049 (5)	-1876 (5)	30 (2)	C(58)	461 (10)	1103 (8)	-5175 (7)	69 (3)
C(9)	4400 (8)	3971 (6)	-1732 (5)	42 (2)	C(59)	-535 (10)	1413 (8)	-5270 (7)	64 (3)
C(10)	4787 (8)	3227 (6)	-1899 (5)	47 (3)	C(60)	-877 (9)	1542 (7)	-4640 (6)	56 (3)
C(11)	4113 (8)	2565 (7)	-2197 (5)	46 (3)	C(61)	-3603 (7)	7944 (6)	-4552 (5)	33 (2)
C(12)	2959 (7)	2671 (6)	-2355 (5)	41 (2)	C(62)	-4335 (8)	8543 (6)	-4882 (5)	49 (3)
C(13)	1667 (7)	7249 (6)	-2276 (5)	36 (2)	C(63)	-4466 (9)	8799 (7)	-5615 (6)	55 (3)
C(14)	606 (7)	7406 (6)	-2735 (5)	37 (2)	C(64)	-3822 (10)	8464 (8)	-5984 (7)	70 (3)
C(15)	411 (8)	7952 (6)	-3319 (5)	43 (2)	C(65)	-3122 (10)	7833 (8)	-5691 (7)	78 (4)
C(16)	1308 (8)	8338 (7)	-3438 (6)	54 (3)	C(66)	-2994 (9)	7576 (7)	-4958 (6)	63 (3)
C(17)	2364 (8)	8155 (7)	-2985 (5)	54 (3)	C(67)	-4555 (8)	6976 (6)	-3621 (5)	41 (2)
C(18)	2552 (8)	7622 (6)	-2414 (5)	44 (2)	C(68)	-4544 (12)	6630 (9)	-2968 (8)	91 (4)
C(19)	-2754 (8)	4349 (7)	-2433 (5)	51 (3)	C(69)	-5405 (12)	6114 (10)	-2901 (9)	102 (5)
C(20)	1122 (7)	5074 (7)	-3054 (4)	47 (2)	C(70)	-6206 (10)	5903 (8)	-3508 (7)	72 (3)
C(21)	176 (9)	7150 (7)	-1014 (6)	55 (3)*	C(71)	-6184 (12)	6182 (9)	-4181 (8)	86 (4)
C(22)	1137 (7)	5109 (6)	-488 (5)	41 (4)*	C(72)	-5372 (9)	6740 (7)	-4235 (7)	66 (3)
C(23)	-103 (7)	3818 (6)	-1237 (5)	34 (4)*	C(73)	-3406 (7)	8446 (6)	-3039 (5)	40 (2)
C(24)	-1144 (8)	5298 (6)	-1019 (5)	39 (4)	C(74)	-4381 (8)	8822 (7)	-3029 (5)	51 (3)
C(25)	3788 (7)	7178 (5)	123 (5)	33 (2)	C(75)	-4347 (10)	9497 (8)	-2587 (6)	65 (3)
C(26)	3627 (8)	7989 (6)	-106 (5)	44 (2)	C(76)	-3365 (9)	9814 (8)	-2150 (6)	72 (3)
C(27)	2926 (8)	8501 (7)	101 (5)	54 (3)	C(77)	-2404 (9)	9462 (8)	-2131 (6)	64 (3)
C(28)	2375 (9)	8193 (7)	563 (6)	54 (3)	C(78)	-2410 (8)	8766 (6)	-2589 (5)	47 (3)
C(29)	2482 (9)	7402 (7)	788 (6)	51 (3)	N(7)	-1507 (45)	-505 (24)	-4705 (34)	514 (52)*
C(30)	3205 (8)	6877 (6)	581 (5)	45 (3)	C(79)	-1100 (17)	-864 (17)	-4986 (16)	206 (14)*
C(31)	5179 (7)	5736 (6)	441 (5)	35 (2)	C(80)	-533 (23)	-1525 (16	-5518 (15)	202 (19)*

[a] Atoms have occupancies of 1.0. [b] For atoms marked with an asterisk the equivalent isotropic *U* is defined as one-third of the orthogonalized tensor.

their marginal thermal stability. Similar low thermal stability was reported for the N-Me diazaphospholes $C_6H_4(NMe)_2PNR_2$ (R = Me, Et), which decomposed during attempted isolation.[23] Furthermore, additional peaks in the $^{31}P\{^1H\}$ NMR spectrum of **9**–**12**, likely due to higher molecular weight oligomer/polymer products, appear on Et_2NH removal. Thus it was expedient to derivatize representative members of each series in order to allow complete separation and unambiguous characterization.

Compound **4** from a typical reaction mixture was converted to $C_6H_4(NH)_2P(S)Me$ (**8**) by reaction with elemental sulfur. **8** is hydrolytically stable and can be purified by flash chromatography. It exhibits a mass spectral parent ion at *m/e* 184 and characteristic fragments[24] at *m/e* 169 and 151 due to loss of CH_3 and S + H units, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **8** shows the expected downfield shift of the singlet resonance on oxidation.[17,25] The ^1H NMR spectrum in CD_2Cl_2 exhibits a doublet at δ 1.6 due to the CH_3 protons coupled to phosphorus and a broad doublet at δ 4.1 and a singlet at δ 6.6 from the N-H and aryl protons, respectively.[26] In C_6D_6, the singlet aryl resonance splits into two four-line patterns at δ 6.2 and 6.6 from the ortho and meta hydrogens, respectively. Infrared N—H and P=S stretching absorptions are seen at 3253 and 740 cm^{-1}, respectively.[27] Compounds similar to **8** have been reported from RP(S)Cl_2 (R = Et, Ph)/1,2-$(NH_2)_2C_6H_4$ reactions;[28] however, characterization of the latter was limited to elemental analysis.

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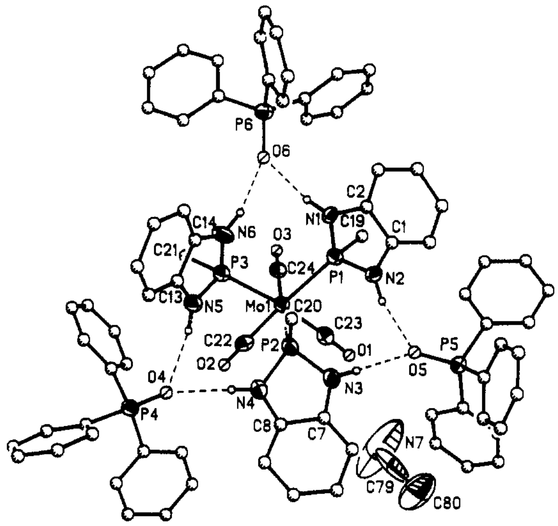


Figure 2. Structure and numbering scheme for $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (**16**). Thermal ellipsoids are at the 50% level. Phenyl carbons, which were refined isotropically, are included as simple spheres with a fixed radius for clarity.

Table IV. Selected Structural Parameters for $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (**16**)

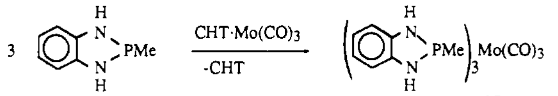
(a) Bond Lengths (Å)

Mo(1)–P(1)	2.464 (2)	Mo(1)–P(2)	2.479 (3)
Mo(1)–P(3)	2.466 (3)	Mo(1)–C(22)	1.991 (8)
Mo(1)–C(23)	1.995 (10)	Mo(1)–C(24)	1.986 (11)
P(1)–N(1)	1.696 (7)	P(1)–N(2)	1.695 (8)
P(1)–C(19)	1.823 (11)	P(2)–N(3)	1.683 (8)
P(2)–N(4)	1.711 (7)	P(2)–C(20)	1.827 (9)
P(3)–N(5)	1.701 (8)	P(3)–N(6)	1.701 (8)
P(3)–C(21)	1.807 (12)	P(4)–O(4)	1.486 (6)
P(5)–O(5)	1.497 (6)	P(6)–O(6)	1.494 (6)
O(1)–C(23)	1.156 (13)	O(2)–C(22)	1.156 (10)
O(3)–C(24)	1.150 (14)	N(1)–C(2)	1.407 (10)
N(2)–C(1)	1.399 (10)	N(3)–C(7)	1.386 (12)
N(4)–C(8)	1.382 (12)	N(5)–C(13)	1.407 (12)
N(6)–C(14)	1.389 (13)	C(1)–C(2)	1.397 (13)
C(7)–C(8)	1.420 (11)	C(13)–C(14)	1.394 (11)
N(7)–C(79)	1.035 (69)	C(79)–C(80)	1.776 (43)

(b) Bond Angles (deg)

P(1)–Mo(1)–P(2)	90.4 (1)	P(1)–Mo(1)–P(3)	100.2 (1)
P(2)–Mo(1)–P(3)	87.1 (1)	P(1)–Mo(1)–C(22)	172.0 (3)
P(2)–Mo(1)–C(22)	94.0 (3)	P(3)–Mo(1)–C(22)	86.7 (3)
P(1)–Mo(1)–C(23)	86.1 (2)	P(2)–Mo(1)–C(23)	88.7 (3)
P(3)–Mo(1)–C(23)	172.4 (2)	C(22)–Mo(1)–C(23)	87.3 (4)
P(1)–Mo(1)–C(24)	85.8 (2)	P(2)–Mo(1)–C(24)	176.2 (2)
P(3)–Mo(1)–C(24)	93.1 (3)	C(22)–Mo(1)–C(24)	89.8 (4)
C(23)–Mo(1)–C(24)	91.5 (4)	Mo(1)–P(1)–N(1)	127.0 (3)
Mo(1)–P(1)–N(2)	118.9 (2)	N(1)–P(1)–N(2)	89.1 (4)
Mo(1)–P(1)–C(19)	113.3 (3)	N(1)–P(1)–C(19)	102.1 (4)
N(2)–P(1)–C(19)	101.6 (4)	Mo(1)–P(2)–N(3)	118.1 (3)
Mo(1)–P(2)–N(4)	122.2 (3)	N(3)–P(2)–N(4)	89.0 (3)
Mo(1)–P(2)–C(20)	117.0 (3)	N(3)–P(2)–C(20)	102.7 (5)
N(4)–P(2)–C(20)	103.0 (4)	Mo(1)–P(3)–N(5)	117.3 (3)
Mo(1)–P(3)–N(6)	123.9 (3)	N(5)–P(3)–N(6)	89.2 (4)
Mo(1)–P(3)–C(21)	114.2 (4)	N(5)–P(3)–C(21)	104.2 (5)
N(6)–P(3)–C(21)	104.2 (5)	O(4)–P(4)–C(25)	111.6 (4)
O(4)–P(4)–C(31)	111.7 (4)	O(4)–P(4)–C(37)	112.9 (4)
O(5)–P(5)–C(43)	110.3 (4)	O(5)–P(5)–C(49)	111.3 (4)
O(5)–P(5)–C(55)	111.9 (4)	O(6)–P(6)–C(61)	111.3 (4)
O(6)–P(6)–C(67)	111.3 (4)	O(6)–P(6)–C(73)	111.3 (4)
P(1)–N(1)–C(2)	111.8 (6)	P(1)–N(2)–C(1)	112.4 (6)
P(2)–N(3)–C(7)	114.2 (6)	P(2)–N(4)–C(8)	113.2 (5)
P(3)–N(5)–C(13)	113.4 (6)	P(3)–N(6)–C(14)	113.8 (5)
N(2)–C(1)–C(2)	110.6 (7)	N(1)–C(2)–C(1)	110.3 (6)
N(3)–C(7)–C(8)	110.1 (8)	N(4)–C(8)–C(7)	110.5 (7)
N(5)–C(13)–C(14)	110.7 (8)	N(6)–C(14)–C(13)	111.0 (8)
Mo(1)–C(22)–O(2)	176.2 (9)	Mo(1)–C(23)–O(1)	177.2 (7)
Mo(1)–C(24)–O(3)	178.4 (7)	N(7)–C(79)–C(80)	174.2 (35)

Further characterization of **4** as a representative member of the **4**–**7** series, and some indication of its properties, is obtained from formation of a Mo(0) complex $[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ (**15**). A 3-equiv sample of **4** reacts with $CHT \cdot Mo(CO)_3$ to form



(3)

15

15 essentially quantitatively. After toluene and cycloheptatriene are removed in vacuo and the resulting brown solid is washed with hot toluene, pure **15** is obtained. **15** is soluble in acetone, ethyl acetate, and hot MeCN; from the last were obtained tiny needles inadequate for X-ray analysis. Spectral data show conclusively the structure and composition of **15**. A mass spectral parent ion occurs at *m/e* 638 ($C_{24}H_{27}P_3N_6O_3Mo^+$). The singlet ^{31}P NMR resonance at δ 132.6 is in the region expected for a Mo-coordinated aminophosphine.[29] The two carbonyl (CO) IR stretching absorptions at 1954 and 1867 cm^{-1} are consistent with those observed for other facial tris complexes, e.g. $(CO)_3Mo(PMe_3)_3$.[30]

Confirmation of the structure of **15**, and indirectly that of **4**, was achieved by single-crystal X-ray analysis of **15**. **15** was cocrystallized with 3 equiv of Ph_3PO[31] from MeCN to form $[C_6H_4(NH)_2PMe]_3Mo(CO)_3 \cdot 3Ph_3PO \cdot MeCN$ (**16**). Crystals of **16** varied in size, but when grown slowly, they could be obtained routinely as cubes in excess of 2 mm on edge. After 3 days at ambient temperature they darken but appear to be stable indefinitely under N_2. Compound **16** crystallizes with three molecules of Ph_3PO in the novel structure shown in Figure 2. Structural parameters are given in Table IV. Three Ph_3PO molecules are H-bonded in nearly symmetrical fashion to the *fac*-$[C_6H_4(NH)_2PMe]_3Mo(CO)_3$ molecule. Hydrogen bonding takes place between the phosphoryl P=O units and the N—H bonds of two diazaphospholes in an approximately equilateral triangular arrangement. **16** was approximate C_s symmetry in the solid; two of the diazaphosphole P–Me groups point upward and one points downward relative to the three-atom P(1),P(2),P(3) plane. The bonding within the metal complex, e.g. mean Mo–P [2.470 (2) Å], Mo–C [1.992 (10) Å], and C–O [1.151 (13) Å] distances, is consistent with previous observations in aminophosphine $Mo(CO)_3$ complexes.[29,32] Apparently, the diazaphosphole units exhibit only slightly greater steric repulsion than carbonyl ligands, since the cis carbonyl group bond angles are close to 90° [mean C–Mo–C angle = 89.5 (4)°]. Owing to the unsymmetrical orientation of the diazaphospholes on the $Mo(CO)_3$ moiety, the P–Mo–P angles differ somewhat. The angles P(1)–Mo–P(2), P(2)–Mo–P(3), and P(3)–Mo–P(1) are 90.4 (1), 87.1 (1), and 100.2 (1)°, respectively. Molecular parameters for the $C_6H_4(NH)_2PMe$ diazaphosphole units, i.e. the mean P–N distance of 1.701 (8) Å and the mean N–P–N internal ring angle of 89.3 (4)°, are closely similar to and within the range of those reported earlier for substituted systems.[5,13,14,15b]

Etter et al. have shown that cocrystallization of many organic compounds with Ph_3PO (TPPO) induces them to crystallize readily as large cubic crystals.[31] The factors contributing to the effect that TPPO has on crystal growth properties are thought to be a strong hydrogen bond, which imparts partial ionic character to the crystal, and the bulky shape of the TPPO molecule, which inhibits the formation of lamellar structures that cause crystals to fracture easily and to grow as thin plates. Compound **16** appears to be the first example of an organometallic molecule that cocrystallizes with Ph_3PO to improve its crystal form.

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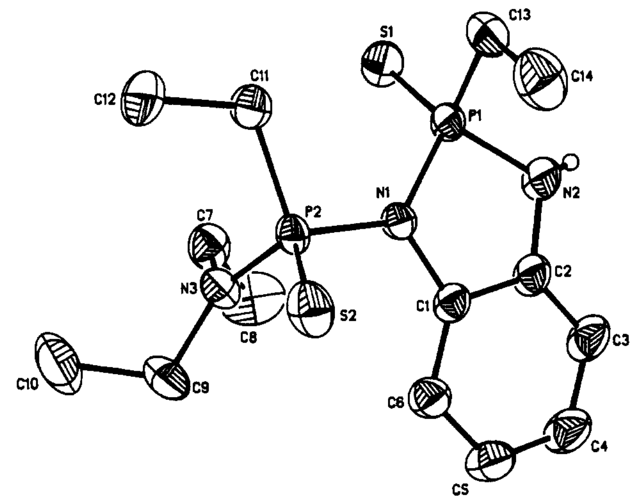

Figure 3. Structure and numbering scheme for $C_6H_4(NH)PEt(S)NP(NEt_2)(S)Et$ (**13a**). Thermal ellipsoids are at the 50% level.

Characterization of the diphosphazane **9–12** series is based on spectral data and, in addition, on analysis of **10a**/**10b** as representative of the series as the P(V) sulfide derivative. Sulfur oxidation of the P(III) diphosphazanes **9–12** yields the P(V) diphosphazane sulfides. Treatment of **10a**/**10b** reaction mixture with S_8 yields P(V) sulfides of all the P(III) species in solution, in approximately the same area ratios. The $^{31}P\{^1H\}$ spectrum after oxidation shows a downfield shift of all spectral resonances.[25] Two sets of doublets at δ 92.0 and 75.5 ($^2J_{PP}$ = 4.9 Hz) and δ 95.8 and 73.3 ($^2J_{PP}$ = 19.5 Hz) are assigned to the disulfides of **10a** and **10b** (**13a** and **13b**), along with resonances at δ 86.4 and 87.1 due to $EtP(S)(NEt_2)_2$ and $C_6H_4(NH)_2P(S)Et$. Separation of the mixture was achieved by flash chromatography followed by crystallization of **13a** from a **13a**/**13b** mixture. Diastereomer **13a** is the major diastereomer and the diastereomer having the smaller $^2J_{PNP}$ coupling constant.

Characterization of **13a** and **13b** as a mixture of diphosphazane disulfide diastereomers, and of **13a** separately, is based on spectral data. In addition, the structure of **13a** was determined by single-crystal X-ray analysis. The ^1H NMR spectrum shows a triplet (δ 1.0) for the diethylamino (Et_2N–) CH_3 groups and two triplets of doublets (δ 1.1 and 1.4) for the two CH_3 groups of the P–Et groups. The expected CH_2 resonances for these ethyl groups are complex multiplets in the regions between δ 1.8–2.7 and 2.9–3.8. A broad doublet due to the N–H protons (δ 4.9) and two aryl multiplets (δ 6.8 and 7.3) are seen. Mass spectral data support the proposed structure for **13a**; a parent ion occurs at *m/e* 361, and strong peaks at *m/e* 164 and 137 due to $C_6H_4N_2PEt^+$ and $C_6H_4(NH)_2P^+$ are seen.

Confirmation of the structure of **13a** is accomplished by a single-crystal X-ray analysis. **13a** crystallizes from an ethanol/toluene mixture ($\cong$1:1) in space group *Pn* with two molecules per unit cell. The molecule consists of a diazaphosphole unit to which a $-PEt(S)NEt_2$ unit is appended (Figure 3). The conformation around the P–N–P skeletal unit has the two P=S bonds on P(1) and P(2) oriented approximately trans to each other, similar to that reported earlier for $MeN[P(S)(NH_2)_2][P(S)(NH_2)(NHMe)]$.[33] Bond distances and angles, listed in Table V, are as expected for an aminophosphine.[13,18,33] The N(2)–P(1)–N(1) internal angle is 92.1°. The phenyl carbon atoms and two bonded nitrogen atoms [C(1)–C(6), N(1), N(2)] are coplanar within experimental error. Phosphorus atom P(1) is displaced out of this plane; the [C(1)–C(6),N(1),N(2)]/P(1),N(1),N(2) interplane dihedral angle is 11.8°. This value is intermediate between previously reported values for the analogous angle in similar diazaphospholes; the triphosphazane disulfide $C_6H_4[NP(S)(NEt_2)_2]_2PNEt_2$ exhibits a dihedral angle of 21.2°[15b] whereas the trisulfide of this same compound contains a dihedral angle of only 2.3°.[34]

Table V. Selected Structural Parameters for $C_6H_4(NH)PEt(S)NP(NEt_2)(S)Et$ (**13a**)

	(a) Bond Lengths (Å)		
P(1)-S(1)	1.928 (1)	P(1)-N(1)	1.716 (2)
P(1)-N(2)	1.665 (3)	P(1)-C(13)	1.810 (3)
P(2)-S(2)	1.952 (1)	P(2)-N(1)	1.713 (2)
P(2)-N(3)	1.637 (3)	P(2)-C(11)	1.808 (3)
N(1)-C(1)	1.438 (4)	N(2)-C(2)	1.405 (4)
N(3)-C(7)	1.469 (4)	N(3)-C(9)	1.470 (4)
C(1)-C(2)	1.400 (4)		
	(b) Bond Angles (deg)		
S(1)-P(1)-N(1)	117.9 (1)	S(1)-P(1)-N(2)	117.6 (1)
N(1)-P(1)-N(2)	92.4 (1)	S(1)-P(1)-C(13)	111.8 (1)
N(1)-P(1)-C(13)	109.8 (1)	N(2)-P(1)-C(13)	105.4 (2)
S(2)-P(2)-N(1)	111.7 (1)	S(2)-P(2)-N(3)	113.6 (1)
N(1)-P(2)-N(3)	107.1 (1)	S(2)-P(2)-C(11)	112.3 (1)
N(1)-P(2)-C(11)	103.1 (1)	N(3)-P(2)-C(11)	108.5 (2)
P(1)-N(1)-P(2)	129.2 (1)	P(1)-N(1)-C(1)	110.2 (2)
P(2)-N(1)-C(1)	120.6 (2)	P(1)-N(2)-C(2)	112.8 (2)
P(2)-N(3)-C(7)	119.1 (2)	P(2)-N(3)-C(9)	124.4 (2)
C(7)-N(3)-C(9)	116.5 (3)	N(1)-C(1)-C(2)	111.1 (2)
N(1)-C(1)-C(6)	128.7 (3)	N(2)-C(2)-C(1)	111.8 (3)
N(2)-C(2)-C(3)	127.0 (3)		

Diastereomerically selective P–N–P bond formation reactions are important because, if they can be used in polyphosphazane formation, they could produce new classes of stereoregular polymers. Unfortunately, the known diastereoselective phosphazane formation reactions are rare. Reports of diastereoselectivity in $MeN[P(Cl)NMe_2]_2$,[20] $MeN(ClPBr)_2$,[20] and $MeN[P(Cl)Me]_2$[20,35] formation, but based on only minimal structural characterization, have appeared. Only recently, we showed conclusively that reaction of $PhPCl_2$ with *i*-$PrNH_2$ in the presence of Et_3N produces *meso*-*i*-PrN[PhP(*i*-PrNH)]$_2$ diastereoselectively (*meso*:*d,l* > 15:1);[18] however, it is yet unclear how isomer selection occurs. In compounds **9–12**, the major diastereomer that forms, albeit the selection is small, appears to be the least sterically hindered. Thus, if P(2) is rotated so its sulfur atom, S(2), is trans to S(1), which is the conformation it adopts in the solid state, the bulky diethylamino group has more room in compound **13a** than it would if it were exchanged with the ethyl group on P(2) giving compound **13b**.

The new P(III) mono- (**4–7**) and diphosphorus phosphazanes (**9–12**) prepared in this study are reactive enough that they might have limited use in oligomeric/polymeric phosphazane synthesis. Both series, **4–7** and **9–12**, are sufficiently reactive to water and O_2 that their use will require inert-atmosphere handling. **9–12** are A–B type monomers that might be used directly in condensation polymer formation. Since they condense to oligomers/polymers of type **1** upon removal of Et_2NH, they will be difficult to isolate in pure form unless separations at low temperatures can be devised. However, the P(V) derivatives offer greater potential because they are much more stable. Studies of their use in polyphosphazane formation reactions are in progress currently.

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Supplementary Material Available: Tables giving details of the structure determination and crystal structure data, positional parameters, anisotropic thermal parameters, bond distances, bond angles, and least-squares equations and planes (18 pages); tables of structure factors (39 pages). Ordering information is given on any current masthead page.

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