

the formation of not inclusive complexes. The only important difference with respect to erbium complexes in the IR spectra is that all the nitrate groups in the Nd complexes are coordinated and those in the erbium complexes are ionic and coordinated, as is shown in Table II.

If inclusive complexes had been formed, larger shifts of $\nu_{\text{O-C}}$, $\nu_{\text{C-N-C}}$, $\nu_{\text{H-C-H}}$, and $\nu_{\text{C=C}}$ vibrations would be expected; important paramagnetic shifts in the NMR spectra that are characteristic of inclusive complexes were not observed for the neodymium cryptates, but neodymium does not give rise to important paramagnetic shifts of protons, as has been reported by Gansow²⁸ and Horrocks.²⁹

Concerning our 222BB complexes, it is important to state that the molar extinction coefficient of the free ligand 222BB is somewhat modified upon complexation and the new peak at 283 nm shows that the metal ion perturbs slightly the degenerate $\pi-\pi^*$

transition of the benzene rings in the metal complexes, resulting in a slight change in the degeneracy of the transition.

Conclusions

The experimental conditions are very important for the M:L ratio. According to our results, the 1:2 ratio is also possible for the lanthanide cryptates.

The M:L = 1:1 ratio in the Nd complexes is supported by the larger size of Nd^{3+} and therefore the probable major coordination number or its better arrangements to coordinate than Er^{3+} ; however it is still not clear if they are inclusive cryptates or not. The metal-ligand interaction suggests a not complete encryption of the metal ions by the ligands. The IR, UV, and NMR spectra afford evidence of complexation of the neodymium and erbium nitrates with the cryptands 222BB and 211. The IR spectra are too complex to allow a distinction between monodentate and bidentate nitrate groups.

IR and NMR spectra of the erbium complexes show a medium-strength metal-ligand interaction, enough to keep the metal between the two ligands with a sandwich configuration.

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New Orthocyclophane Cyclotetraphosphazanes: $[\text{C}_6\text{H}_4\text{N}_2(\text{PR})_2]_2$ (R = Ph, Me) and $[\text{C}_6\text{H}_4\text{N}_2(\text{PPh})(\text{PhPS})]_2$

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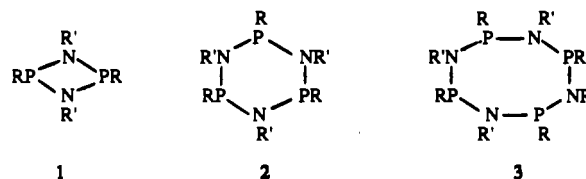
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The orthocyclophane cyclotetraphosphazanes $[\text{C}_6\text{H}_4\text{N}_2(\text{PR})_2]_2$ (R = Ph (4), Me (5)) have been obtained from $\text{RPCl}_2/1,2\text{-}(\text{NH}_2)_2\text{C}_6\text{H}_4/\text{Et}_3\text{N}$ reactions. S_8 oxidation of 4 yields $[\text{C}_6\text{H}_4\text{N}_2(\text{PhP})(\text{PhPS})]_2$ (6) and $[\text{C}_6\text{H}_4\text{N}_2]_2(\text{PhPS})_3(\text{PhP})$ (7). 4-7 are characterized by spectral (MS, IR, ^1H and ^{31}P NMR) data. 4 and 6 are further characterized by X-ray single-crystal analyses. 4: monoclinic, $C2/c$, $a = 18.629$ (4) Å, $b = 9.108$ (3) Å, $c = 18.874$ (3) Å, $\beta = 104.17$ (2)°, $V = 3105$ Å³, $Z = 4$, $d_{\text{calc}} = 1.37$ g cm⁻³. 6: triclinic, $P1$, $a = 10.8724$ (12) Å, $b = 11.1319$ (16) Å, $c = 14.219$ (2) Å, $\alpha = 99.812$ (11)°, $\beta = 93.707$ (10)°, $\gamma = 91.460$ (10)°, $V = 1691$ Å³, $Z = 2$, $d_{\text{calc}} = 1.384$ g cm⁻³. 4-7 contain eight-membered P_4N_4 rings, of alternating phosphorus and nitrogen atoms, made up of two diazaphosphole ring units bonded by bridging PhP groups. The two bridging PhP phosphorus atoms and four nitrogen atoms of 4 and 6 are coplanar. The P_4N_4 ring is in a boat conformation. The *o*-phenylene (C_6H_4) and bridging PhP phenyl rings are mutually cis oriented above and below the P_4N_4 ring. The bridging PhP phenyl rings create a molecular cleft into which the diazaphosphole phosphorus(III) atom electron pairs are directed. Formation of 4 and 5, regioselectivity in reactions of 4 with sulfur, and the potential of 4-6 for novel donor coordination are discussed.

Introduction

Cyclophosphazanes consisting of four- (1),²⁻⁵ six- (2),^{4,5,6-8} and eight-membered (3)^{4,5,9-14} rings of alternating phosphorus and

nitrogen atoms are known and, in several cases, have been the



object of detailed structural, reactivity, and mechanistic studies. Cyclodiphosphazanes (diazadiphosphetidines; 1) have been examined in considerable detail with respect to their structural,²⁻⁵

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isomeric and conformational,^{2,3,15} and reactivity^{2-4,16} properties. In contrast, much less is known about the larger ring cyclo-tetraphosphazanes (3). Stable cyclo-tetraphosphazanes (RPNMe)₄,^{9,10} [C₆H₄N(RN)P]₄,^{11,12} and (mesPNR)₄,¹³ have been obtained from RPCl₂/(Me₃Si)₂NMe (R = Me, Et, Ph), 1,2-(RNH)(NH₂)C₆H₄/(Me₂N)₃P (R = alkyl), and mesPCl₂/RNH₂ reactions, respectively; in addition the oxidation,¹⁷ quaternization,¹⁸ and metal moiety^{19,20} coordination of (RPNMe)₄ (R = Me, Ph) have been examined. In all cases, the uncoordinated cyclo-tetraphosphazanes appear to be conformationally nonrigid and to have equivalent phosphorus atoms in solution. Even in the solid, (MePNMe)₄ and [C₆H₄N(PrN)P]₄ assume 4-fold symmetric structures. Rings with other than crown-ring conformations and with phosphorus sites of different reactivities have not been available.

Recently, during studies of alkyl- and aryldichlorophosphine reactions with 1,2-(NH₂)₂C₆H₄, which were designed to produce high molecular weight skeletally stabilized phosphazane oligomers/polymers, we discovered and reported in preliminary form the moderate-yield formation of new cyclo-tetraphosphazanes²¹ that are novel orthocyclophane²² type ring molecules. These are unique because of the boat conformation assumed by the P₄N₄ ring and because they contain a molecular cleft (cavity) into which selective coordination might occur. The complete description of the synthesis and structural properties of these is reported below.

Experimental Section

Apparatus and Materials. Phosphorus-31 NMR spectra were obtained with JEOL FX-90Q, Bruker WM-250, and Varian VXR-500 spectrometers at 36.5, 101.2, and 202.3 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. ³¹P and ¹H chemical shifts downfield from 85% H₃PO₄ (external) and Me₄Si (internal) are reported as positive (+δ). IR spectra (4000–400 cm⁻¹) were obtained by using Beckman 4250 or IBM IR/32 Type 9132 spectrometers. Mass spectra were obtained at 70 eV with a Varian MAT-CH5 or VG Analytical 7070 EQ-HF spectrometer. Chemical ionization (CI⁺ and CI⁻) MS data were obtained by using 2-methylpropane or ammonia as the ionizing gas. Expected isotope patterns for parent ion envelopes are calculated with the program ISO supplied by V. G. Analytical. X-ray diffraction data were collected on a Nicolet P3/F automated diffractometer equipped with a graphite monochromator. All manipulations were carried out by using standard vacuum line, glovebag, or Schlenk techniques under dry N₂.²³

Flash chromatography was carried out as described by Still et al.²⁴ 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 N₂ pressure.

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

1,2-(NH₂)₂C₆H₄ (Aldrich) was recrystallized from toluene. Toluene (over Na/Pb or CaH₂) and CH₂Cl₂ (P₄O₁₀) were distilled before use. Et₃N (Baker), PhPCl₂, and MePCl₂ (Strem) were distilled from CaH₂. Butyllithium (Aldrich, 1.6 M in hexanes), *t*-BuPCl₂ (Strem), elemental sulfur (EM Scientific), petroleum ether, and silica gel (EM Science) were

used as received. C₆H₄(NH)₂PMe^es and CHT-Mo(CO)₃²⁶ (CHT = cycloheptatriene) were prepared as described previously.

Reaction of 1,2-(NH₂)₂C₆H₄ with Dichlorophosphines. In general, 1,2-diaminobenzene (0.037 mol) in toluene (400 mL) was added dropwise to a refluxed solution of RPCl₂ (0.074 mol) (R = Ph, Me) and Et₃N (0.17 mol) in toluene (350 mL). After 18–24 h, Et₃NHCl was filtered out and washed with 100 mL of toluene.

(A) With PhPCl₂. [C₆H₄N₂(PhP)]₂ (4). The filtrate, which showed ³¹P{¹H} NMR spectral triplets at δ 111.2 and 85.3 (4) and broad undefined resonances between δ 70 and 100 (uncharacterized; area 70% total), was concentrated to 100 mL. Upon cooling of the solution to 0 °C, crystallization occurred. Extraction with hot toluene, followed by recrystallization from toluene, yielded pure 4 (mp 290 °C dec; yield 15%). ³¹P{¹H} NMR (C₆D₆): δ 111.3 [t, area 2, ²J_{PP} = 18.0 Hz; P(1), P(1')], 85.4 [t, area 2; P(2), P(2')]. ¹H NMR (CS₂): δ 6.60 and 7.01 (A₂B₂ pattern, area 8; C₆H₄), 7.15, 7.28, and 7.65 complex multiplets, area 20; C₆H₅). MS: M⁺ (¹²C₃₆H₂₈N₄P₄⁺), *m/e* 640. IR (major absorptions, KBr, cm⁻¹): 1467 (vs), 1435 (s), 1226 (vs), 1100 (s), 926 (s), 918 (s), 875 (vs), 855 (vs), 830 (s), 749 (vs), 704 (vs), 689 (s), 530 (s), 438 (s). Anal. Calcd for C₃₆H₂₈N₄P₄: C, 67.50; H, 4.40; N, 8.75; P, 19.34. Found: C, 67.67; H, 4.60; N, 8.52; P, 19.20.

(B) With MePCl₂. [C₆H₄N₂(MeP)]₂ (5). The reaction filtrate, which showed ³¹P{¹H} NMR spectral equal-area triplets at δ 101.3 and 77.0 (5) (15% spectral area), equal-area quartets at δ 88.5 and 50.8 (*J* = 16.3 Hz) (<5% spectral area), and broad undefined resonances at δ 85–98 and 60–72 (uncharacterized; 80% of spectral area), was concentrated to 100 mL. Repeated attempts to crystallize 5 failed. Flash chromatography on a silica column (petroleum ether/ethyl ether eluent, 4:1) followed by solvent removal yielded solid 5; however, crystals adequate for X-ray analysis were not obtained.

Alternatively, prior to chromatography the MePCl₂/1,2-(NH₂)₂C₆H₄ reaction filtrate solution was pretreated by the addition of a toluene solution of CHT-Mo(CO)₃. The mixture initially turned orange, and then muddy yellow, along with concurrent formation of a precipitate. After 1.5 h at 25 °C, a precipitate formed and the broad unresolved ³¹P NMR resonances had decreased in the solution leaving the resonances from 5. The solid, which was insoluble in acetone and only slightly soluble in hot CH₃CN, exhibited ³¹P NMR resonances at δ 33.6 and 27. Addition of a second aliquot of CHT-Mo(CO)₃ produced small quantities of precipitate; after 3.5 h only the ³¹P NMR resonances from 5 along with the two trace quartets at δ 88.5 and 50.8 were seen. Flash chromatography on silica (petroleum ether/ethyl acetate eluent), followed by solvent removal, in vacuo, yielded white solid 5. ³¹P{¹H} NMR (CD₂Cl₂): δ 78.4 [t, area 2, ²J_{PP} = 18.3 Hz; P(2), P(4)], 101.3 [t, area 2; P(1), P(3)]. MS: M⁺ (¹²C₁₆H₂₀N₄P₄⁺), *m/e* 392. MS (exact mass, EI⁺): calcd for C₁₆H₂₀N₄P₄, 392.0638; found, 392.0645. Because samples contained traces of hydrocarbon impurities, ¹H NMR and IR spectral and chemical analytical data were inadequate.

The MePCl₂/1,2-(NH₂)₂C₆H₄/Et₃N reaction procedure described above was repeated with 0.043 mol of MePCl₂/100 mL of toluene (×4 as concentrated) and 0.017 mol of MePCl₂/800 mL of toluene (one-fifth as concentrated). Both reactions produced ca. 20% of 5. However, in the high-concentration reaction, most of the remaining area fell in the broad areas of resonance between δ 85 and 98 and 60 and 72. In the dilute reaction, there was less spectral area in these regions; most remaining spectral area fell in the δ 15–40 region.

(C) With *t*-BuPCl₂. Reactions of *t*-BuPCl₂ with 1,2-(NH₂)₂C₆H₄, carried out as above, yielded only unassignable complex ³¹P NMR resonance patterns between δ 0 and 170 ppm. No tractable products could be isolated.

[C₆H₄N₂(PhP)(PhPS)]₂ (6) and [C₆H₄N₂](PhPS)₃(PPh) (7). 4 (0.78 mmol) and S₈ (0.2 mmol) were refluxed in toluene (50 mL) for 2 h. Removal of solvent in vacuo and recrystallization from CH₂Cl₂ gave pure 6 (mp 341–345 °C; 60% yield). ³¹P{¹H} NMR (C₆D₆): δ 103.2 [t, area 2, ²J_{PP} = 46.4 Hz; P(1), P(3)], 61.0 [t, area 2; P(2), P(4)]. ¹H NMR (CS₂): δ 6.74 (1/2 A₂B₂ pattern, area 4; C₆H₄), 7.20–7.40, 7.50, 7.78 (complex multiplets, area 24; C₆H₅ and 1/2 C₆H₄). MS: M⁺, *m/e* 704. IR (major absorptions, KBr, cm⁻¹): 3062 (s), 3012 (s), 2974 (s), 1460 (vs), 1435 (s), 1216 (s), 1203 (s), 1100 (s), 1095 (vs), 949 (vs), 924 (vs), 869 (vs), 842 (vs), 748 (vs), 735 (vs), 725 (vs), 692 (vs), 640 (m, P=S), 455 (vs). Anal. Calcd for C₃₆H₂₈N₄P₄S₂: C, 61.36; H, 4.00; N, 7.95; P, 17.58. Found: C, 58.06; H, 4.09; N, 7.65; P, 16.27.

The electrochemistry of 6 in CH₂Cl₂ was studied: solution composition, 50 mL of CH₂Cl₂; 0.1 M electrolyte (Bu₄NBF₄); 10 mL of 10⁻³ M

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Table I. Crystallographic Data for $[C_6H_4N_2(PPh)_2]_2$ (**4**) and $[C_6H_4N_2(PhP)(PhPS)]_2$ (**6**)

formula	$C_{36}H_{28}N_4P_4$	$C_{36}H_{28}N_4P_4S_2$
fw	640.55	704.6
space group	$C2/c$	$P\bar{1}$
cryst system	monoclinic	triclinic
<i>a</i> , Å	18.629 (4)	10.8724 (12)
<i>b</i> , Å	9.108 (2)	11.1319 (16)
<i>c</i> , Å	18.874 (3)	14.2192 (18)
α , deg	90.00	99.812 (11)
β , deg	104.17 (2)	93.707 (10)
γ , deg	90.00	91.460 (10)
<i>V</i> , Å ³	3105 (1)	1691 (4)
<i>Z</i>	4	2
<i>d</i> _{calc} , g cm ⁻³	1.37	1.384
<i>F</i> (000), e	1330	728
μ , cm ⁻¹	2.7	3.485
radiation (λ , Å)	Mo K α (0.71069)	Cu K α (1.54184)
temp, K	294–296	295–297
transm coeff	0.922–0.960	0.577–0.867
<i>R</i> , <i>R</i> _w	0.045, 0.057	0.028, 0.039

Ph₃P; 10 mL of 10⁻³ M ferrocene internal standard; 10 mL of 10⁻³ M **3**. **6** displayed an irreversible oxidation at 1160 mV relative to Fe/Fe²⁺. No reversible redox behavior was evident.

6 (0.85 mmol) and **S**₈ (1.25 mmol) in toluene (60 mL) were refluxed for 7 days. At the end of this time the solution was cooled to 25 °C and then concentrated in vacuo. White solid mixed with amorphous intractable brown solid precipitated. Recrystallization of the white solid from CH₂Cl₂ yielded pure **7** (mp 363 °C dec; 80% yield). ³¹P{¹H} NMR (C₆D₆), AMX₂:²⁷ δ 107.6 [t of d, area 1, ²*J*_{PP} = 47.3 Hz, ⁴*J*_{PP} = 13.4 Hz; P(1)], 68.2 [t of d, area 1, ²*J*_{PP} = 15.6 Hz; P(3)], 58.8 [d of d, area 2; P(2), P(4)]. ¹H NMR (CS₂): δ 7.10–7.70 (broad, complex multiplet, area 20; C₆H₅), 6.80 and 7.00 (A₂B₂, area 8; C₆H₄). IR (KBr, cm⁻¹): 2978 (s), 2650 (m, br), 2505 (m), 1460 (m), 1443 (m), 1402 (w, sh), 1254 (s), 1198 (s), 1162 (m), 1080 (s, br), 948 (m, sh), 922 (m), 863 (s), 842 (m), 797 (s), 725 (m), 676 (m), 658 (m), 434 (m). Anal. Calcd for C₃₆H₂₈N₄P₄S₂: C, 58.69; H, 3.83; N, 7.61. Found: C, 58.55; H, 3.77; N, 7.66.

Reaction of 5 with S₈. Mixtures of **5** were allowed to react with excess **S**₈ while being monitored by ³¹P NMR spectral analysis. After 20 min at 25 °C, spectra showed evidence for a mixture of the mono- and disulfides of **5**. After 2 h at 84 °C, major resonances due to the disulfide, at δ 113.2 (t, ²*J*_{PP} = 29.9 Hz) and 72.9 (t), along with minor resonances due to presumed tri- and tetrasulfides were present. After an additional 12 h at 98 °C, resonances at δ 76.1 (t, area 2, *J* = 22.0 Hz) and 64.2 (t, area 2) attributed to tetrasulfide [C₆H₄N₂(MePS)₂]₂ were dominant. No reaction conditions were found that gave predominantly mono-, di-, or trisulfides as products. Separation of reaction mixtures by fractional crystallization or column flash chromatography was unsuccessful.

Reaction of C₆H₄(NH)₂PMe. (A) With MePCl₂. MePCl₂ (0.015 mol) and Et₃N (0.036 mol) in toluene (180 mL) were heated to reflux. C₆H₄(NH)₂PMe (0.015 mol in 20 mL of toluene) was added dropwise. After 4.5 h, Et₃NHCl was filtered from the solution and the resulting filtrate was concentrated in vacuo. The ³¹P{¹H} NMR spectrum of the mixture was essentially identical with the mixture formed by the reaction of MePCl₂ with 1,2-diaminobenzene described above; the area ratio of **5**:broad resonances at δ 85–98 and δ 60–73 was ca. 1:2. Similar results were obtained in reactions carried out at room temperature. As with the above reactions, **5** could not be separated fully from other reaction components.

(B) With PhPCl₂. PhPCl₂ (7.4 mmol) and Et₃N (16.5 mmol) in toluene (80 mL) were heated to reflux. C₆H₄(NH)₂PMe (7.4 mmol) in toluene was added dropwise. After 7 h, Et₃NHCl was filtered out and the solution concentrated in vacuo. ³¹P NMR: δ 87 and 96 (triplets, \approx 5% of reaction mixture).

X-ray Analysis of 4 and 6. Crystals of **4** from toluene and **6** from CH₂Cl₂ were coated with epoxy and mounted on glass fibers. Crystal data for **4** and **6** are given in Table I. Complete details of the experimental conditions for data collection and structural refinement are included in the supplementary material. Crystals of **4** were twinned. Details of the treatment of the twinning are given in the supplementary material. With data deconvoluted from that collected on the twinned crystal, the structure of **4** was solved. Structures for both **4** and **6** were solved by direct methods. Both compounds were refined by using full-matrix least-squares techniques with hydrogen atoms included in fixed

Table II. Positional ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[C_6H_4N_2(PPh)_2]_2$ (**4**)

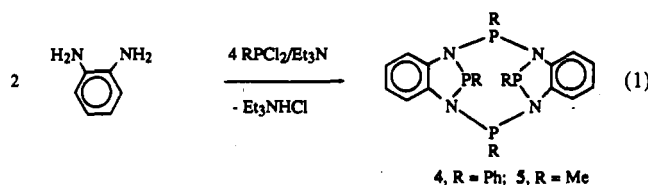
atom ^a	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b
P(1)	800 (1)	4985 (3)	-1929 (1)	37.0 (7)
P(2)	588 (1)	3656 (3)	-3437 (1)	39.8 (8)
N(1)	1080 (3)	3747 (8)	-2520 (3)	42 (2)
N(2)	339 (3)	3636 (7)	-1558 (3)	35 (2)
C(1)	1078 (5)	231 (1)	-2200 (4)	44 (3)
C(2)	636 (5)	225 (1)	-1693 (4)	39 (3)
C(3)	504 (5)	88 (1)	-1422 (4)	50 (4)
C(4)	824 (6)	-38 (1)	-1643 (5)	66 (4)
C(5)	1286 (6)	-25 (1)	-2122 (5)	73 (5)
C(6)	1410 (5)	110 (1)	-2401 (5)	56 (4)
C(11)	1658 (2)	5116 (6)	-1209 (2)	37 (3)
C(12)	2163 (2)	6147 (6)	-1343 (2)	43 (3)
C(13)	2799 (2)	6472 (6)	-801 (2)	56 (4)
C(14)	2931 (2)	5768 (6)	-125 (2)	57 (4)
C(15)	2426 (2)	4737 (6)	8 (2)	62 (4)
C(16)	1789 (2)	4411 (6)	-534 (2)	51 (4)
C(21)	-678 (4)	5524 (5)	-1259 (3)	36 (3)
C(22)	-94 (4)	6171 (5)	-749 (3)	47 (3)
C(23)	-185 (4)	7750 (5)	-461 (3)	63 (4)
C(24)	-861 (4)	8281 (5)	-683 (3)	71 (5)
C(25)	-1445 (4)	7634 (5)	-1193 (3)	65 (4)
C(26)	-1354 (4)	6256 (5)	-1481 (3)	56 (4)

^a Atoms have occupancies of 1.0. ^b Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

idealized positions. For **4**, phenyl rings were treated as rigid groups. Full tables of the derived results are included in the supplementary material. Positional parameters are given in Tables II and III. Selected bond distance and angle data are given in Tables IV and V.

Results and Discussion

Reactions of 1,2-(NH₂)₂C₆H₄ with RPCl₂ (R = Ph, Me) and Et₃N in refluxing toluene produce complex mixtures that apparently are of general composition [C₆H₄N₂(PR)₂]_n^{21b} and that include the new cyclotetraphosphazanes **4** and **5**.²⁸ Reactions occur as in eq 1. The presence of **4** and **5** was clearly evident



by the appearance of characteristic²⁷ sharp A₂X₂ ³¹P NMR triplet resonances. Reactions are affected by concentration; at higher dilution somewhat increased yields of **4** and **5** relative to higher oligomers/polymers are obtained. However, in these reactions larger quantities of hydrolysis products were observed, presumably resulting from traces of water in the 1,2-(NH₂)₂C₆H₄. Under all conditions the reaction mixtures are complex and product separation was generally difficult. **4** crystallizes from its reaction mixture and, after repeated crystallization, can be separated from traces of Et₃NHCl with which it seems to cocrystallize. Separation of **5** was more tedious, and even after chromatography, it retained traces (<5%) of hydrocarbon impurities. In the MePCl₂/1,2-(NH₂)₂C₆H₄ reactions, in addition to **5** and higher oligomers/polymers, very low yields of a product are seen that exhibits distinct quartet resonances at δ 88.5 and 50.8. This could be the next higher cyclooligomer in the [C₆H₄N₂(MeP)₂]_n series, the cyclohexaphosphazane [C₆H₄N₂(MeP)₂]₃; however, it has yet to be isolated and characterized.

Separation of reaction mixtures that contained **5** was achieved by column flash chromatography or, alternatively better, in a two-step process involving pretreatment of the reaction mixture with CHT·Mo(CO)₃. This process removes high molecular weight

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(28) Systematic nomenclature for **4**: 1,3,6,8-tetraaza-2,7-diphospha-2,7-diphenyl-3,6-(phenylphosphido)-1,8-(phenylphosphido)-syn-[3.3]orthocyclophane; see ref 22.

Table III. Positional ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_6\text{H}_4\text{N}_2(\text{PhP})(\text{PhPS})]_2$ (6)

atom ^a	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b
P(1)	4075 (1)	7862 (1)	6981 (1)	33 (1)
P(2)	1538 (1)	7567 (1)	6019 (1)	34 (1)
P(3)	1951 (1)	5919 (1)	7452 (1)	31 (1)
P(4)	3441 (1)	7709 (1)	8943 (1)	32 (1)
S(2)	284 (1)	8386 (1)	5375 (1)	51 (1)
S(4)	3406 (1)	8600 (1)	10230 (1)	48 (1)
N(1)	3855 (2)	8595 (2)	8142 (1)	33 (1)
N(2)	2758 (2)	8498 (2)	6506 (1)	33 (1)
N(3)	982 (2)	6845 (2)	6878 (1)	32 (1)
N(4)	2080 (2)	6964 (2)	8524 (1)	30 (1)
C(11)	5278 (3)	8867 (3)	6667 (2)	39 (1)
C(12)	5744 (3)	9938 (3)	7217 (2)	60 (1)
C(13)	6693 (3)	10604 (3)	6915 (3)	78 (2)
C(14)	7191 (3)	10187 (4)	6069 (3)	76 (2)
C(15)	6765 (4)	9120 (4)	5522 (3)	85 (2)
C(16)	5818 (3)	8457 (3)	5825 (2)	68 (1)
C(21)	2254 (3)	6388 (3)	5235 (2)	41 (1)
C(22)	1856 (3)	5173 (3)	5104 (2)	56 (1)
C(23)	2385 (4)	4310 (3)	4453 (3)	78 (2)
C(24)	3291 (4)	4647 (4)	3922 (3)	87 (2)
C(25)	3684 (4)	5849 (4)	4024 (2)	78 (2)
C(26)	3158 (3)	6724 (3)	4677 (2)	57 (1)
C(31)	774 (2)	4899 (2)	7799 (2)	33 (1)
C(32)	-67 (3)	4235 (3)	7127 (2)	50 (1)
C(33)	-842 (3)	3352 (3)	7362 (2)	60 (1)
C(34)	-796 (3)	3114 (3)	8276 (2)	51 (1)
C(35)	21 (3)	3771 (3)	8960 (2)	48 (1)
C(36)	803 (3)	4659 (2)	8727 (2)	41 (1)
C(41)	4572 (3)	6550 (3)	8810 (2)	38 (1)
C(42)	5799 (3)	6920 (3)	8800 (2)	52 (1)
C(43)	6714 (3)	6066 (4)	8765 (2)	67 (2)
C(44)	6406 (4)	4868 (4)	8758 (2)	70 (2)
C(45)	5202 (3)	4489 (3)	8776 (2)	62 (1)
C(46)	4283 (3)	5323 (3)	8808 (2)	49 (1)
C(51)	3176 (2)	9680 (2)	8052 (2)	35 (1)
C(52)	2579 (2)	9630 (2)	7150 (2)	35 (1)
C(53)	1967 (3)	10631 (3)	6919 (2)	48 (1)
C(54)	1973 (3)	11670 (3)	7612 (3)	60 (1)
C(55)	2568 (3)	11716 (3)	8506 (3)	59 (1)
C(56)	3185 (3)	10720 (3)	8735 (2)	47 (1)
C(61)	342 (2)	7561 (2)	7633 (2)	31 (1)
C(62)	947 (2)	7629 (2)	8542 (2)	30 (1)
C(63)	421 (3)	8228 (2)	9342 (2)	37 (1)
C(64)	-697 (3)	8774 (3)	9225 (2)	45 (1)
C(65)	-1278 (3)	8723 (3)	8331 (2)	47 (1)
C(66)	-773 (3)	8106 (2)	7526 (2)	40 (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.

Table IV. Selected Bond Lengths and Angles for $[\text{C}_6\text{H}_4\text{N}_2(\text{PPh})_2]_2$ (4)

(A) Bond Lengths (\AA)			
P(1)-N(1)	1.754 (7)	P(2)-N(1)	1.749 (7)
P(1)-N(2)	1.741 (7)	P(2)-N(2')	1.726 (6)
P(1)-C(11)	1.831 (5)	P(2)-C(21)	1.817 (5)
N(1)-C(1)	1.44 (1)	N(2)-C(2)	1.43 (1)
C(1)-C(2)	1.41 (1)		
(B) Bond Angles (deg)			
N(1)-P(2)-N(2')	106.7 (3)	N(1)-P(2)-C(21)	101.6 (3)
N(2)-P(2)-C(21)	100.2 (3)	N(2)-P(1)-C(11)	100.0 (3)
N(1)-P(1)-C(11)	99.9 (3)	N(1)-P(1)-N(2)	93.2 (3)
P(1)-N(1)-P(2)	119.6 (4)	P(2)-N(1)-C(1)	108.5 (5)
P(1)-N(1)-C(1)	106.5 (5)	P(1)-N(2)-C(2)	107.7 (5)
P(2)-N(2)-C(2)	116.0 (5)	P(1)-N(2)-P(2')	125.6 (4)
N(1)-C(1)-C(2)	112.7 (8)	N(1)-C(1)-C(6)	124.6 (8)
N(2)-C(2)-C(3)	128.1 (8)	N(2)-C(2)-C(1)	113.6 (8)

products, which tend to foul the chromatography column. Thus, $\text{CHT}\cdot\text{Mo}(\text{CO})_3$ was added in increments to the reaction mixture until the broad ill-defined resonances due to $[\text{C}_6\text{H}_4\text{N}_2(\text{PMe})_2]_n$ disappeared. The solution initially turned the orange color of the metal complex but, on sitting, turned yellow and a precipitate formed. The precipitate was not characterized. The ³¹P NMR

Table V. Selected Bond Lengths and Bond Angles for $[\text{C}_6\text{H}_4\text{N}_2(\text{PhP})(\text{PhPS})]_2$ (6)

(A) Bond Lengths (\AA)			
P(1)-N(1)	1.747 (2)	P(1)-N(2)	1.759 (2)
P(1)-C(11)	1.825 (3)	P(2)-S(2)	1.927 (1)
P(2)-N(2)	1.697 (2)	P(2)-N(3)	1.706 (2)
P(2)-C(21)	1.799 (3)	P(3)-N(3)	1.752 (2)
P(3)-N(4)	1.749 (2)	P(3)-C(31)	1.835 (3)
P(4)-S(4)	1.930 (1)	P(4)-N(1)	1.701 (2)
P(4)-N(4)	1.700 (2)	P(4)-C(41)	1.800 (3)
N(1)-C(51)	1.452 (3)	N(2)-C(52)	1.451 (3)
N(3)-C(61)	1.451 (3)	N(4)-C(62)	1.452 (3)
C(51)-C(52)	1.391 (4)	C(61)-C(62)	1.400 (4)
(B) Bond Angles (deg)			
N(1)-P(1)-N(2)	92.3 (1)	N(1)-P(1)-C(11)	100.1 (1)
N(2)-P(1)-C(11)	100.2 (1)	S(2)-P(2)-N(2)	113.4 (1)
S(2)-P(2)-N(3)	112.9 (1)	N(2)-P(2)-N(3)	109.0 (1)
S(2)-P(2)-C(21)	113.6 (1)	N(2)-P(2)-C(21)	102.6 (1)
N(3)-P(2)-C(21)	104.5 (1)	N(3)-P(3)-N(4)	93.0 (1)
N(3)-P(3)-C(31)	99.0 (1)	N(4)-P(3)-C(31)	96.9 (1)
S(4)-P(4)-N(1)	113.4 (1)	S(4)-P(4)-N(4)	113.0 (1)
N(1)-P(4)-N(4)	108.4 (1)	S(4)-P(4)-C(41)	114.0 (1)
N(1)-P(4)-C(41)	102.1 (1)	N(4)-P(4)-C(41)	105.0 (1)
P(1)-N(1)-P(4)	117.5 (1)	P(1)-N(1)-C(51)	106.6 (2)
P(4)-N(1)-C(51)	119.5 (2)	P(1)-N(2)-P(2)	119.3 (1)
P(1)-N(2)-C(52)	106.2 (2)	P(2)-N(2)-C(52)	120.9 (2)
P(2)-N(3)-P(3)	119.4 (1)	P(2)-N(3)-C(61)	118.2 (2)
P(3)-N(3)-C(61)	105.4 (2)	P(3)-N(4)-P(4)	121.4 (1)
P(3)-N(4)-C(62)	105.6 (1)	P(4)-N(4)-C(62)	119.9 (1)
P(1)-C(11)-C(12)	126.3 (2)	P(1)-C(11)-C(16)	115.9 (2)
P(2)-C(21)-C(22)	122.4 (2)	P(2)-C(21)-C(26)	118.5 (2)
C(22)-C(21)-C(26)	118.9 (3)	C(12)-C(11)-C(16)	117.7 (3)
P(3)-C(31)-C(32)	121.2 (2)	P(3)-C(31)-C(36)	120.5 (2)
P(4)-C(41)-C(42)	118.0 (2)	P(4)-C(41)-C(46)	122.9 (2)
C(32)-C(31)-C(36)	117.8 (3)	C(42)-C(41)-C(46)	118.9 (3)
N(1)-C(51)-C(52)	113.1 (2)	N(1)-C(51)-C(56)	125.4 (2)
N(2)-C(52)-C(51)	113.1 (2)	N(2)-C(52)-C(53)	126.3 (2)
N(3)-C(61)-C(62)	113.3 (2)	N(3)-C(61)-C(66)	126.2 (2)
N(4)-C(62)-C(61)	112.9 (2)	N(4)-C(62)-C(63)	126.8 (2)

spectrum of the remaining solution showed only the triplets due to **5** and the trace pair of quartet resonances (δ 88.5 and 50.8). The $\text{CHT}\cdot\text{Mo}(\text{CO})_3$ /phosphazane filtrate solution was separated by flash chromatography with a solvent mixture of petroleum ether and ethyl acetate (4:1). Surprisingly, **5** was stable to silica gel and could be separated on a silica gel column.

It appears that, in a mixture containing members of the oligomer series $[\text{C}_6\text{H}_4\text{N}_2(\text{PMe})_2]_n$, $\text{CHT}\cdot\text{Mo}(\text{CO})_3$ coordinates more readily to the higher oligomer members than it does to the $n = 2$ product, **5**. The higher members are precipitated from solution as $\text{Mo}(\text{CO})_3$ complexes. Phosphazane-molybdenum(0) coordination is not surprising, since it is well-known that aminophosphines readily coordinate $\text{Mo}(\text{CO})_3$ and $\text{Mo}(\text{CO})_4$ units.^{29,30} Although, it has been shown by Paddock et al.¹⁹ that the cyclotetraphosphazane $(\text{PMeNMe})_4$ tricoordinates $\text{Mo}(\text{CO})_3$ to form $(\text{PMeNMe})_4\cdot\text{Mo}(\text{CO})_3$, $(\text{PMeNMe})_4$ is not conformationally rigid and therefore perhaps is more able than the rigid **5** (see below) to adopt a conformation that allows it to coordinate to a $\text{Mo}(\text{CO})_3$ unit.

t-BuPCl₂ also reacts with 1,2-(NH₂)₂C₆H₄; however, it was not apparent that products analogous to **5** and **6** formed. Typically, ³¹P NMR spectra of reaction mixtures were complex with only low-intensity, well-defined small doublet patterns apparent. These could be due to two-phosphorus intermediates,^{25b} although none were isolated. Perhaps the steric bulk of the *t*-Bu groups prevents formation of the eight-membered-ring product, at least under the reaction conditions used.

Compound **4** has been unambiguously characterized by single-crystal X-ray analysis as a cyclotetraphosphazane. The structure is shown in Figure 1. **4** crystallizes with four molecules

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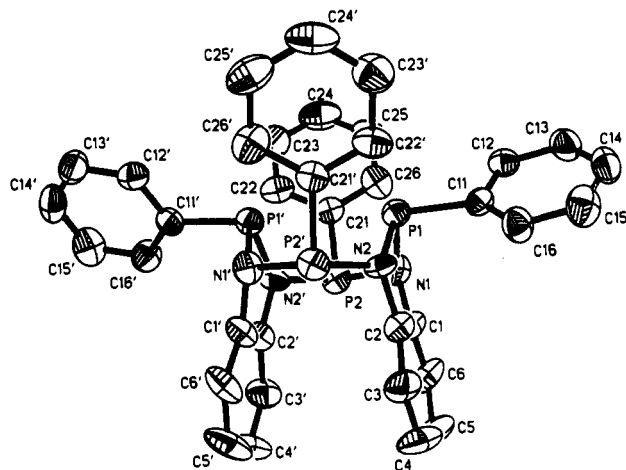
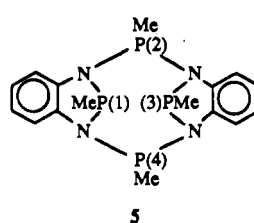


Figure 1. Structure and numbering system for $[\text{C}_6\text{H}_4\text{N}_2(\text{PPh})_2]_2$ (**4**). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

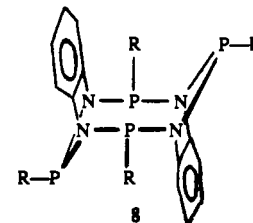
in the unit cell. The molecule is an orthocyclophane²² which contains two phosphadiazole units connected by bridging PhP groups to form an eight-membered ring of alternating phosphorus and nitrogen atoms. The P_4N_4 ring assumes a boat type conformation. The bridging PhP phosphorus atoms [P(2), P(2')] and four nitrogen atoms [N(1), N(1'), N(2), N(2')] are within experimental error coplanar. The *o*-phenylene (C_6H_4) rings and bridging PhP phenyl groups [Ph(2) and Ph(2'), C(21)–C(26) and C(21')–C(26')] are mutually cis-oriented. The *o*-phenylene C_6H_4 ring interplane dihedral angles are 14.8° . The rings are 3.71 Å apart at their midpoints. This separation is essentially equal to the van der Waals distance of 3.7 Å³¹ and is typical for the ring separation in orthocyclophanes.²² Phenyl groups Ph(2) and Ph(2') point upward; the interplane angle between the C(21)–C(24) and C(21')–C(24') vectors is 51.7° , and the rings are 7.05 Å apart at their midpoints. Phosphorus atoms P(1) and P(1') are 3.30 Å apart, above the P_2N_4 plane by 1.19 Å, and oriented with their electron pairs pointing between phenyl rings Ph(2) and Ph(2'). Bond distances (Table IV) are not surprising; all P–N distances are within the range expected for P(III)–N compounds^{2,4,5,9,32} and phosphadiazoles.^{9,25,33} Mean P–N phosphadiazole distances [1.747 (7) Å] are, within experimental error, equal to the bridging [1.733 (7) Å] distances. Bond angles are generally as expected except for the somewhat small angles around N(1) and N(2) and the large N(1)–P(2)–N(2) angle (106.7°), which arise because the atoms are constrained in the eight-membered ring.

The structure of **4** is novel among cyclophosphazanes, because the ring is in a unique conformation and because the ring contains phosphorus atoms of two different types. The electron pairs of the phosphadiazole phosphorus atoms [P(1), P(1')] point into and between the Ph(2)/Ph(2') rings; those of the bridging P atoms [P(2), P(2')] point out from the P_4N_4 ring. This is different from previously reported phosph(III)azane rings in $(\text{MePNMe})_4$ ⁹ and $[\text{C}_6\text{H}_4\text{N}(\text{PrN})\text{P}]_4$ ¹² which are in crown conformations and which contain equivalent phosphorus atoms both in solution and in the solid state. The molecular dimensions and conformation adopted by **4** make it a unique new cleft-containing molecule. Phenyl rings Ph(2) and Ph(2') are separated enough to allow entrance by small molecules or atoms but not enough to allow entrance of larger ones. Further, the lone pairs on P(1) and P(1'), which point into this cleft, offer the additional advantages of selective dicoordination in this highly protected environment.

On the basis of the close similarity of spectral data (³¹P and ¹H NMR, MS) between **4** and **5**, we conclude that **5** is also a



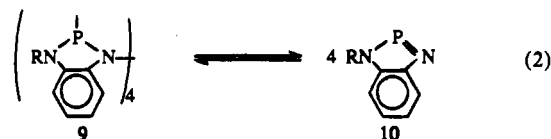
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cyclophosphazane structurally analogous to **4**. **4** and **5** exhibit mass spectral parent ions³⁴ at m/e 640 and 392, respectively. Both show A_2X_2 ³¹P NMR spectra²⁷ consistent with a ring containing two pairs of chemically different phosphorus atoms. **4** exhibits two coupled equal-area triplets at δ 111.2 and 85.3; these resonances occur at δ 101.3 and 77.0 for **5**. Further, the $^2J_{\text{PP}}$ coupling constants of 18.3 and 19.5 Hz for **4** and **5**, respectively, indicate closely similar trans conformations with respect to rotation of the P(1) and P(2) atoms' lone-pair electrons around the P(1)–N(1)–P(2) bond unit.^{35,36} The angle of 165° in **4** and the associated coupling constant correlate well with data for P(III)–N bis-(phosphino)amines reported previously by Keat.³⁶

It is of interest to compare the properties of **4** to those of the cyclophosphazanes **9** prepared earlier by Malavaud and co-workers.¹² Compounds **9** (where R = Pr, *i*-Pr, *s*-Bu, PhCH_2) are completely associated tetramers at ambient temperatures; however, above 100 °C dissociation to the monomer phosphinimines **10**



occurs. Monomers **10** show characteristic dicoordinate-phosphorus ³¹P NMR spectral resonances at δ 226–236; at 120 °C in xylene the *s*-Bu derivative (**9**) is 15% dissociated to **10**. Similar behavior is not observed for **4**. At 110 °C in toluene, only resonances due to **4** are seen in the ³¹P NMR spectrum.

It is interesting that in the $\text{PhPCl}_2/1,2\text{-(NH}_2)_2\text{C}_6\text{H}_4$ or $\text{MePCl}_2/1,2\text{-(NH}_2)_2\text{C}_6\text{H}_4$ systems no clear evidence for other than the *syn*-cyclophosphazane isomers is seen. Although broad ³¹P NMR peaks in the reaction mixtures due to higher molecular weight $[\text{C}_6\text{H}_4\text{N}_2(\text{PR})_2]_n$ materials are evident, it is expected that if significant quantities of other $[\text{C}_6\text{H}_4\text{N}_2(\text{RP})_2]_2$ isomers were present, e.g. **8**, clearly distinctive A_2X_2 patterns²⁷ would be apparent. Also, there is no evidence that thermal isomerization of the *syn* isomers occurs; heating **4** or **5** to 110 °C for 36 h produces no ³¹P NMR spectral change. Either **4** or **5** are too rigid to isomerize or they are formed in their thermodynamically most stable form.

The effects on product distribution of varying reaction conditions in the $1,2\text{-(NH}_2)_2\text{C}_6\text{H}_4/\text{R}_2\text{PCl}_2$ reactions were noticeable but smaller than expected. The reactions were initially carried out by adding $1,2\text{-(NH}_2)_2\text{C}_6\text{H}_4$ in toluene dropwise to a solution of R_2PCl_2 and Et_3N in toluene. Under these conditions, the R_2PCl_2 reagent is always in excess. Product yields of 15–20% attain. It seemed likely that polymer formation might be favored if the $1,2\text{-(NH}_2)_2\text{C}_6\text{H}_4:\text{R}_2\text{PCl}_2$ reactant ratios were maintained rigorously at 2:1 but that at other ratios **4** (or **5**) might be favored. However, in reactions in which both reagents were combined dropwise at the same rate to maintain the 2:1 ratio, the product distribution was not greatly different than observed at 2.0–1.5:1.0 reactant ratios. Similarly, dilution of reaction mixtures was expected to favor small (eight-membered) ring products over high oligomer/polymers. At high dilution higher yields of **4** or **5** were ob-

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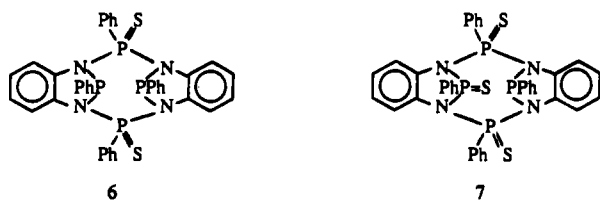
served, e.g. 20% **5**; however, in these, more unwanted amino-phosphine oxide hydrolysis material was formed. This is expected if traces of water in the diamine reactant, which are extremely difficult to remove, were present.

The mechanism by which **4** and **5** form in the 1,2-(NH₂)₂C₆H₄/R₂PCl₂ reactions is of interest. A possible reaction pathway is depicted in Scheme I, in which the phosphadiazole **11** forms early and subsequently reacts to form the chloroaminodiphosphazane **12**. Phosphadiazoles **11** have been synthesized recently by transamination reactions of RP(NEt₂)₂ (R = Me, Et, Ph, *t*-Bu) with 1,2-(NH₂)₂C₆H₄.²⁵ When C₆H₄-(NH)₂PMe and MePCl₂ were allowed to react in a 1:1 ratio in the presence of excess Et₃N under reaction conditions similar to those used in the MePCl₂/1,2-(NH₂)₂C₆H₄ reactions described above, the resulting reaction mixtures exhibited ³¹P NMR spectra that were essentially identical with those from the MePCl₂/1,2-(NH₂)₂C₆H₄ reactions. This suggests that **11** and **12**, or the analogous Ph-substituted species, might indeed be intermediates in the formation of the cyclotetraphosphazanes **4** and **5**. Coupling of the chlorodiphosphazane **12**, or the stepwise addition of additional **11** and MePCl₂ to **12**, could then lead to the final products.

Efforts to isolate the chlorodiphosphazane intermediate **12** have so far been unsuccessful. This intermediate is of particular interest because it is an AB monomer,³⁷ which contains both sites of condensation reactivity (the P-Cl bond and the N-H bond) in the same molecule. Reactions of MePCl₂ with **11** and 1 equiv of Et₃N produced a product that showed two doublets with a small coupling constant; however, the product was not isolated. Alternatively, synthesis of **12** was attempted by reaction of **11** with 1 equiv of BuLi followed by 1 equiv of MePCl₂. However, again a mixture of products was obtained with some doublet patterns evident, but no products were isolated.

We attempted to synthesize a cyclotetraphosphazane containing mixed R groups, e.g. [C₆H₄N₂(PR)(PMe)]₂. When **11** was allowed to react with PhPCl₂ and Et₃N, a complex ³¹P NMR spectrum developed that indicated that PhP and MeP group exchange had taken place at the elevated temperatures needed for reaction. Precedence for such exchange with phosphadiazoles was reported by Zuckerman et al.,³⁸ who observed exchange of RAs and RB groups with the RP moieties of (CH₂)₃(NMe)₂PR.

Reactions of **4** and **5** with S₈ occur regioselectively and thus show clearly the difference in reactivity between the two types of phosphorus atoms in the structure. These reactions support the idea that the molecular cleft, especially in **4**, shows regioselective reactivity. Reaction of **4** with S₈ in 2 h in toluene forms cleanly the disulfide [C₆H₄N₂(PhPS)(PhP)]₂ (**6**). Only under



forcing conditions, 7 days at 110 °C, is the trisulfide (C₆H₄N₂)₂(PhPS)₂(PhP) (**7**) obtained. In contrast, **5** shows evidence in the ³¹P{¹H} NMR spectrum for formation of its disulfide and some tri- and tetrasulfide after only 2 h at 84 °C. The two equal-area triplet resonances at δ 113.5 and 62.7 (²J_{PP} = 39.1 Hz) are closely similar to the spectral pattern observed for **6**. Further reaction with S₈ (12 h at 98 °C) causes formation of mainly the tetrasulfide as shown by the two new triplet pairs at δ 76.1 and 64.2 (²J_{PP} = 22.0 Hz). Although the sulfides of **5** could not be separated, the reaction pattern indicates strongly that the cavity size of **5** is larger than that of **4** and unrestricted enough to easily accommodate two sulfur atoms. In contrast, the cavity of **4**, formed by the two phenyl groups, is much smaller and only with

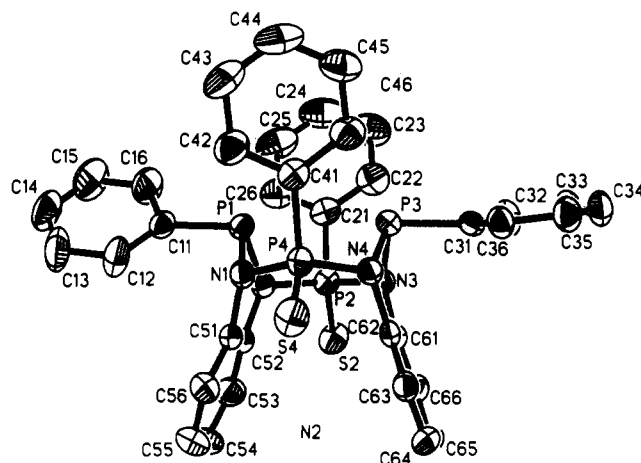
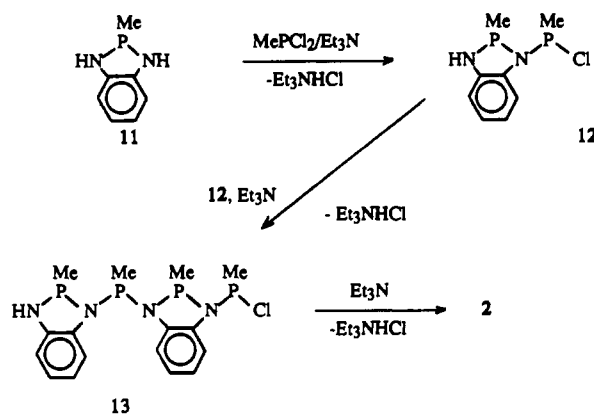


Figure 2. Structure and numbering system for [C₆H₄N₂(PhP)(PhPS)]₂ (**6**). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

Scheme I



difficulty reacts with further sulfur. Similar selectivity was reported in the stabilized triphosphazane disulfide C₆H₄[NP(S)-Et₂]₂PNEt₂,³⁹ where the highly sterically restricted center phosphorus was relatively unreactive toward sulfur. Whether the high selectivity of **5** toward sulfur will be general in all coordination reactions of **5** remains to be studied.

X-ray analysis of **6** confirms its structure and that preferential oxidation of the phosphorus atoms P(2) and P(2') of **4** occurred. The structure of **6** is shown in Figure 2; the structure is surprisingly close to that of **4**. Oxidation has occurred at the PhP units that are in the coplanar P₂N₄ ring. The unoxidized phosphorus atoms P(1) and P(3) are 3.30 Å apart. The P-N bond distances in **6** are typical for phosphazanes; however, the mean P-N distances involving the oxidized phosphorus atoms P(2) and P(4) are significantly shorter (1.702 Å) than the corresponding ring distances in **4** (1.733 Å). This foreshortening of P-N bonds associated with the P(V) center is typical for P(V) vs P(III) phosphazanes^{5,39,40} and λ³-λ⁵ systems.⁴¹ Bond angles in **4** and **6** are also closely similar. The internal P-N-P distances in **6** are somewhat smaller (119.4°) than in **4** (122.6°), and the internal N-P-N angles involving the oxidized phosphorus atoms P(2) and P(4) are slightly larger (108.7°) than the angles in the unoxidized **4** (106.7°). The N-P-N phosphadiazole angles are closely similar, 92.6° in **6** and 93.2° in **4**. Even the molecular cleft in **6** is very close dimensionally to that of **4**; the Ph(2) and Ph(4) [C(21)-C(26) and C(41)-C(46)] separation in **6** is 6.48 Å (at ring midpoints), and the rings are tilted apart by a dihedral angle of 40.8°.

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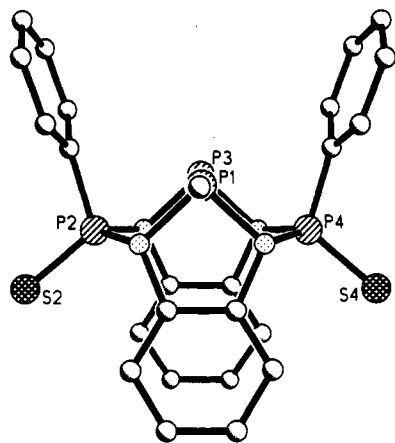


Figure 3. View of **6** down the P(1)–P(3) vector, showing the cavity between phenyl groups Ph(2) and Ph(4). Hydrogen atoms and phenyl groups Ph(1) and Ph(3) are omitted for clarity.

The cavity contained in molecules **4** and **6** (Figure 3), and that can be expected in other $[C_6H_4N_2(PhPX)(PhP)]_2$ compounds where X = O, Se, NPh, etc., could show novel coordination to both metal and non-metal atom species. Given that the van der Waals thickness of the cavity phenyl rings is about 3.7 Å,³¹ there should be, without molecular distortion, around 3.0–3.5 Å of free

space to allow coordination. With small but reasonable distortions of the P_4N_4 ring systems, cleft widths of at least 4.5 Å seem possible. This should make the cavity highly selective, allowing coordination/reactivity with only relatively small guest species. Cavity coordination in a myriad of other guest–host and cleft-containing systems is under investigation;⁴² however, such behavior in diphosphorus systems would be new. This coordination, and the effect such coordination has on the coordinated species, is currently being studied in our laboratories.

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Supplementary Material Available: Listings of all crystal collection and refinement data, hydrogen atom coordinates, anisotropic thermal displacement parameters, bond lengths and angles, least-squares planes, and interplane dihedral angles (22 pages); listings of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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Notes

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Five-Coordinate Nickel(III) Phosphines: Spectroscopic and EXAFS Studies

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Although once regarded as very rare, nickel(III) complexes have been shown by recent research to be obtainable with F, O, and particularly N donor ligands, the last including bi- and multi-dentate amines, peptides, oximes, and aza macrocycles.¹ A much smaller number of examples with second- and third-row p-block donors are known, including *trans*-[Ni(L-L)₂X₂]⁺ (L-L = diphosphine or diarsine, X = Cl or Br).² All these complexes contain Ni(III) in a tetragonal-octahedral geometry, consistent with the Jahn–Teller distortion expected for a low-spin d⁷ ion. In marked contrast to the isoelectronic Co(II), for which many five-coordinate complexes are known,³ Ni(III) rarely exhibits five-coordination. Distorted square-pyramidal structures are established for two series of complexes, [Ni(diphosphine)X₃] (diphosphine = *o*-C₆H₄(PPh₂)₂, Ph₂P(CH₂)_nPPh₂ (n = 2, 3), and *cis*-Ph₂PCHCHPPh₂),⁴ and [Ni{C₆H₃(CH₂NMe₂)₂o,o'}X₂] (X = Cl, Br, I, NO₂, NO₃).⁵ The sole examples of trigonal-bipyramidal

geometry are the very unstable [Ni(PR₃)₂X₃], first reported in 1936⁶ but relatively little studied since.^{7–9} We recently reported a combined spectroscopic and EXAFS (extended X-ray absorption fine structure) study of the more stable Co(III) analogues [Co(PR₃)₂X₃]¹⁰ and report here similar data for the Ni(III) complexes.

Experimental Section

The complexes [Ni(PR₃)₂X₃] were made as described previously.⁹ All measurements were made on samples that were <48 h old and that had been stored at –20 °C in the dark. UV–visible spectra were recorded from freshly prepared dichloromethane solutions, on Perkin-Elmer PE554 and Varian Cary 2300 spectrometers, and diffuse-reflectance spectra were recorded on a Beckman Acta M IV instrument using BaSO₄ as diluent and reference.

Nickel and bromine K-edge EXAFS measurements were made in transmission mode on Station 7.1 at the Daresbury Synchrotron Radiation Source (operating at 2 GeV with an average current of 150 mA), using a silicon (111) order-sorting monochromator. Data were collected from room-temperature samples diluted with boron nitride (ca. 10% Ni by weight) and held between Sellotape strips in 1 mm thick aluminum holders.

Background-subtracted spectra were obtained by using the program PAXAS.¹¹ Removal of the pre-edge background was achieved by using a polynomial of order 2. For the nickel K-edge data the post-edge background was subtracted by fitting the post-edge region with a polynomial of order 6; however, a similar treatment of the bromine K-edge data failed to remove low-frequency contributions in the spectra. A more satisfactory background was achieved by fitting coupled polynomials of order 7 to the post-edge region. Curve-fitting analysis, by least-squares

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