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Cleft Reactivity in Skeletally-Stabilized Cyclotetraphosphazanes

Susan M. Young, Joseph M. Barendt, Vasili Carperos, R. Curtis Haltiwanger,
Robert M. Hands, and Arlan D. Norman*

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

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Molecular cleft selectivity and *exo*- vs *endo*-phosphorus site regioselectivity of cyclotetraphosphazanes $[C_6H_4N_2(PhP)_2]_2$ (**1**) and $[C_6H_4N_2(PhP)(PhPS)]_2$ (**2**) have been examined. Oxidation of **1** with O_3 or S_8 occurs regioselectively to form *exo*-phosphorus substituted $[C_6H_4N_2(PhP)(PhPO)]_2$ (**4**) and **2**, respectively; Ag^+ ion coordination and CH_3I quaternization occurs at *exo* sites with no apparent involvement of the cleft (*endo*-) phosphorus atoms. Insertion of O atoms into the cleft of **4** yields *endo*-substituted $(C_6H_4N_2)_2(PhP)(PhPO)_3$ (**5**) and $[C_6H_4N_2(PhPO)_2]_2$ (**6**); insertion of S, $AgNO_3$, or $Ni(CO)_2$ into the cleft of **2** yields $(C_6H_4N_2)_2(PhP)(PhPS)_3$ (**10**), $[C_6H_4N_2(PhPS)_2]_2$ (**11**), $\{[C_6H_4N_2(PhP)(PhPS)]_2{\cdot}Ag\}NO_3$ (**12**), and $[C_6H_4N_2(PhP)(PhPS)]_2Ni(CO)_2$ (**15**). Selenium oxidizing reagents (elemental Se and KCNSe), elemental Te, the larger metal moieties $Mo(CO)_3$ and $Mo(CO)_4$, and BH_3 and CH_3I are excluded from reactivity in the cleft of **2**. Complex **12** undergoes further reaction to form the mono- and dioxides $(C_6H_4N_2)_2(PhP)(PhPO)(PhPS)_2$ (**13**) and $[C_6H_4N_2(PhPO)(PhPS)]_2$ (**14**), via a process whereby oxidation by novel Ag^+ activation occurs. New compounds are characterized by spectral data; structures of **4**, **10**, **11**, and **15** were established by single crystal X-ray analysis: **4**, monoclinic, $C2/c$, a = 19.154(8) Å, b = 9.081(4) Å, c = 18.832(9) Å, β = 103.09(4)°, Z = 4, V = 3190(2) Å^3, d_{obs} = 1.400 g/cm^3, R = 0.041, R_w = 0.050; **10**, triclinic, $P\bar{1}$, a = 11.209(2) Å, b = 13.449(2) Å, c = 13.872(3) Å, α = 92.373(14)°, β = 96.703(14)°, γ = 105.718(14)°, Z = 2, V = 1993.4(6) Å^3, d_{obs} = 1.357 g/cm^3, R = 0.047, R_w = 0.060; **11**, monoclinic, $C2/c$, a = 26.674(5) Å, b = 9.976(2) Å, c = 19.732(5) Å, β = 120.47(1)°, Z = 4, V = 4525.5(17), d_{obs} = 1.358 g/cm^3, R = 0.045, R_w = 0.053; **15**, monoclinic, $C2/c$, a = 28.583(13) Å, b = 15.524(9) Å, c = 18.409(8) Å, β = 114.75(5)°, Z = 8, V = 7418(6) Å^3, d_{obs} = 1.467 g/cm^3, R = 0.075, R_w = 0.073. The basic cyclotetraphosphazane structure characterized by **1** and **2** is maintained upon insertion into the molecular cleft of one S atom (**10**) or a $Ni(CO)_2$ moiety (**15**); however, two S atoms in the cleft (**11**) causes severe distortion of the ring system.

Introduction

Molecules which contain cavities or clefts are currently of great interest,[2−4] in part because they offer opportunities for highly selective coordination of guest atoms or molecules. Although there are many examples of host molecules containing oxygen,[5−7] nitrogen,[8−10] or sulfur[11,12] donor atoms, ones containing phosphorus(III) donors[13−16] are less well studied. Recently, we reported members of a new phosphazane class, cyclotetraphosphazanes $[C_6H_4N_2(Ph)_2]_2$ (**1**) and $[C_6H_4N_2(PhP)(PhPS)]_2$ (**2**),[17−19] which, because of their structural rigidity and unique positioning of phosphorus donor sites relative to the molecular cavity, offer new host−molecule coordination potential.

Compounds **1** and **2** contain a molecular "cleft" defined by *endo*-phosphorus atoms [P(1,3)] and the pair of closely-spaced (ca. 6.5 Å at mid-points) nearly parallel phenyl rings attached

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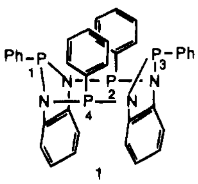

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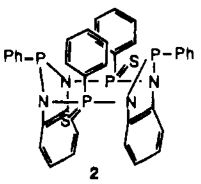

2

to *exo* phosphorus atoms P(2,4).[17] Lone-pair electrons on P(2,4) of **1** point outward from the ring and can be easily removed from coordination involvement by their sulfur oxidation, e.g., as in **2**. In contrast, atoms P(1,3) point into the region over the P_4N_4 ring and have significantly restricted accessibility. These phosphorus atoms, positioned 3.2 Å apart, offer opportunities for "cooperative coordination" to guest species in the region between the phenyl ring walls.

Earlier we reported that **1** reacts highly regioselectively with elemental sulfur (S_8) to form **2** and showed preliminarily that coordination of additional sulfur in the cavity of **2** occurs only under relatively forcing conditions.[17] We now report the continuation of our cavity reaction and regioselectivity studies, through examination of reactions between **1** and **2** with selected oxidizing agents (S_8, Se, O_3), Lewis acids (BH_3, CH_3^+), and metal moieties [Ag^+, $Ni(CO)_2$, $Mo(CO)_4$, and $Mo(CO)_3$]. The results of these studies are described below.

Experimental Section

Apparatus and Materials. ^{31}P, ^{11}B, and ^{19}F NMR spectra were obtained on Varian Gemini or VXR300S spectrometers at 121.4, 96.2, and 292.2 Hz, respectively. ^{31}P NMR spectra were also obtained with JEOL FX-90Q and Bruker WM-250 spectrometers at 36.5 and 101.2 MHz. ^1H NMR spectra were obtained on JEOL FX-90Q (90-MHz) and Varian Gemini-300 or VXR300S (300-MHz) NMR spectrometers. ^{31}P, ^1H, ^{11}B, and ^{19}F chemical shifts downfield from 85% H_3PO_4 (external), Me_4Si (internal), BF_3OEt_2 (external), and CF_3CO_2H (external), respectively, are reported as positive ($+\delta$). IR spectra (400–4000 cm^{-1}) were obtained using Beckman 4250 or IBM IR/32 Type 9132 spectrometers. Mass spectra were obtained at 70 eV with Varian MAT-CH5 or VG Analytical 7070 EQ-HF spectrometers. Mass spectral data refer to the major peak of the respective envelope. Chemical ionization (CI^+ and CI^-) was achieved using isobutane as the ionizing gas. Exact mass analyses were referenced to perfluorokerosene. Ozonolyses were carried out in a Welsbach Ozonator Model T-408 operating at 90 V. X-ray diffraction data were collected on a Nicolet P3/F automated diffractometer equipped with a graphite monochrometer and low temperature attachment. All manipulations were carried out using a standard vacuum line, a glovebag, or Schlenk techniques under dry N_2.[20] Flash chromatography was done as described by Still et al.[21] A 650- or 450-mL column was packed (15 cm) with silica gel 60 (230–400 mesh). Compounds were eluted with the necessary solvent mixture under N_2 pressure at 5 cm/min. Elemental analyses were performed by Huffman Laboratories Inc., Golden, CO, and Desert Analytics, Tucson, AZ.

$[C_6H_4N_2(PhP)_2]_2$ (**1**) and $[C_6H_4N_2(PhP)(PhPS)]_2$ (**2**) were prepared as described below, by a modification of the published procedure.[17] B_2H_6,[22] norMo(CO)$_4$ (nor = norbornadiene)[23] and CHT·Mo(CO)$_3$ (CHT = cycloheptatriene)[24] were prepared as described previously. 2,2′-Azobis(isobutyronitrile) (AIBN; Eastman Kodak), MeI (Aldrich), S_8 (EM Scientific), Se (Aldrich), Te (EM Scientific), BH_3THF (Aldrich), KNO_3 (Fisher Scientific), $AgNO_3$ (Aldrich), $(Ph_3P)_2Ni(CO)_2$ (Strem), silica gel (EM Science), and KBr (Baker, oven dried) were used as obtained. Toluene, tetrahydrofuran, and benzene (over sodium–benzophenone or CaH_2) and CH_2Cl_2 (CaH_2) were distilled before use. Acetonitrile (Fisher Scientific) was used as received.

$[C_6H_4N_2(PhP)_2]_2$ (1) and $[C_6H_4N_2(PhP)(PhPS)]_2$ (2). $PhPCl_2$ (10.1 mL, 0.074 mol) and Et_3N (25.0 mL, 0.18 mol) in toluene (400 mL) were heated under N_2. 1,2-Diaminobenzene (4.0 g, 0.037 mol) in toluene (350 mL) was added dropwise over 1 h to the mixture at 70 °C. After 18 h, the mixture was cooled, amine hydrochloride was filtered and washed with 100 mL of toluene, and the resulting filtrate was concentrated in vacuo to 100 mL. Cooling to 0 °C yielded a precipitate of **1** and Et_3NHCl. Extraction twice with hot toluene (80–90 °C) followed by removal of toluene in vacuo yielded pure **1** [$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 111.2 (t, 2 P, $^2J_{PP}$ = 18.3 Hz), 85.3 (t, 2 P)].[17]

Compound **1** was combined with a slight excess (10%) of S_8 in toluene and heated at 90 °C; **2** formed during 2 h and was purified by flash chromatography (toluene eluent).[17] When the **1**/S_8 reaction progress was monitored by ^{31}P NMR, resonances tentatively assigned to a monosulfide $C_6H_4N_2(PhP)_3(PhPS)$ (**3**) were seen initially: $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 99.3 (d of t, 1 P, $^2J_{PP}$ = 22.1 Hz, $^4J_{PP}$ = 22.9 Hz; PhP), 96.6 (d of d, 2 P, $^2J_{PP}$ = 44.6 Hz; $C_6H_4N_2PPh$), 63.5 (t of d, 1 P; PhPS). Attempts to isolate **3** failed.

Reactions of $[C_6H_4N_2(PhP)_2]_2$ (1). (A) With O_3. $[C_6H_4N_2(PhP)(PhPO)]_2$ (4), $(C_6H_4N_2)_2(PhP)(PhPO)_3$ (5), and $[C_6H_4N_2(PhPO)_2]_2$ (6). Ozone gas (O_3) was added to **1** (0.045 g, 0.70 mmol) in toluene (25 mL) for approximately 90 s. The first-formed precipitate was filtered and discarded. The remaining solution showed ^{31}P NMR spectral resonances due to **4**–**6** (mole ratio, 1.0:1.6:1.7) as well as other uncharacterized oxidation products (>50% of spectral area). Higher yields of **4** could be obtained by decreasing the time of O_3 addition to <60 s. Flash chromatography (ethyl acetate eluent) separated the mixture; first fractions contained **4**, followed by **5** and **6**. Repeated chromatography of **4**–**6** mixtures failed to completely separate the compounds; only **4** was characterizable by X-ray crystallography. $^{31}P\{^1H\}$ NMR: **4** (CD_2Cl_2), δ 91.4 (t, 2 P, $^2J_{PP}$ = 59.1 Hz; PhP=O), 15.9 (t, 2 P; $C_6H_4N_2PhP$); **5** (CD_2Cl_2), δ 101.6 (t, 1 P, $^2J_{PP}$ = 63.3 Hz; $C_6H_4N_2PPh$), 27.9 [s, 1 P; $C_6H_4N_2P(O)Ph$], 13.3 (d, 2 P; PhP=O); **6** (CD_2Cl_2), δ 22.8 [t, 2 P, $^2J_{PP}$ = 2.6 Hz; $C_6H_4N_2P(O)Ph$], 9.7 (t, 2 P; PhP=O). Anal. Calcd for $C_{36}H_{28}N_4P_4O_2$: C, 63.81; H, 4.25; N, 8.44. Found: C, 63.66; H, 4.14; N, 8.39.

(B) With Other Oxygen Oxidizing Compounds. Compound **1** (0.16 g, 0.25 mmol) was combined with AIBN (0.009 g) in toluene. Oxygen (O_2) was slowly added over the reaction solution at reflux. Small ^{31}P NMR resonances were initially seen that could be tentatively assigned to the monooxide, $C_6H_4N_2(PhP)_3(PhPO)$ (**7**). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 98.6 (d of t, 1 P, $^2J_{PP}$ = 20.5 Hz, $^4J_{PP}$ = 23.3 Hz; PhP), 91.8 (d of d, 2 P, $^2J_{PP}$ = 53.8 Hz; $C_6H_4N_2PPh$), 16.0 (t of d, 1 P; PhPO). As the reaction progressed **4** formed but in lower yield [by $^{31}P\{^1H\}$ NMR spectral integration] than in the ozonolysis reaction.

Me_3NO and PhIO were also allowed to react with **1**; however, it was not possible to dry either oxidizing agent thoroughly enough to see distinct formation of oxidation products. In both cases, ^{31}P NMR spectra showed only uncharacterized decomposition products.

(C) With CH_3I. $[(C_6H_4N_2)_2(PhP)_3(PhPMe)]I$ (8). A solution of **1** (0.006 g, 0.01 mmol) in CH_2Cl_2 was combined with CH_3I (0.03 mmol) in a sealed NMR tube. After 6 h at room temperature, the ^{31}P NMR spectrum showed resonances at δ 105.7 (complex multiplet) and 52.8 (t of d) tentatively assigned to a monoquaternized product (**8**, 36% spectral area); two equal-area triplets at δ 112 and 86 (**1**, 53% spectral area); and two singlets at δ 69.5 and 27.0 (11% spectral area). After 24 h, the spectrum showed resonances from **1** (3%), **8** (40%), and decomposition products [broad resonances (δ 96–120 and δ 26–54) and singlets (δ 70, 50, 42, 31, 30, 26, and 23); total area 57%]. Because decomposition products formed along with **8**, the latter could not be isolated from the reaction mixture. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): **8**, δ 105.7

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Table 1. Crystal Data and Details of Structure Determination of **4**, **10**, **11**, and **15**

	4	**10**	**11**	**15**
formula	$C_{36}H_{28}N_4P_4O_2$	$C_{36}H_{28}N_4P_4S_3{\cdot}C_6H_6$	$C_{36}H_{28}N_4P_4S_4{\cdot}2C_6H_6$	$C_{38}H_{28}N_4O_2P_4S_2Ni$
fw, amu	672.5	814.8	925.0	819.4
space group	$C2/c$	$P\bar{1}$	$C2/c$	$C2/c$
crystal system	monoclinic	triclinic	monoclinic	monoclinic
a, Å	19.154(8)	11.209(2)	26.674(5)	28.583(13)
b, Å	9.081(4)	13.449(2)	9.976(2)	15.524(9)
c, Å	18.832(9)	13.872(3)	19.732(5)	18.409(8)
α, deg	90	92.373(14)	90	90
β, deg	103.09(4)	96.703(14)	120.470(10)	114.75(5)
γ, deg	90	105.718(13)	90	90
V, Å^3	3190(2)	1993.4(6)	4525.5(17)	7418(6)
Z	4	2	4	8
d_{obs}, g/cm^3	1.400	1.357	1.358	1.467
μ, mm^{-1}	0.270	0.371	0.378	0.842
λ, Å (Mo Kα)	0.71073	0.71073	0.71069	0.71073
T, K	295−297	295−297	295−297	295−297
R, R_w	0.041, 0.050	0.047, 0.060	0.045, 0.053	0.075, 0.073

(complex multiplet, 3 P; $C_6H_4N_2PPh$, PhP), 52.8 (t of d, 1 P, $^2J_{PP}$ = 46.0 Hz, $^4J_{PP}$ = 21.4 Hz; PhPMe).

(D) With $AgNO_3$. Formation of Complex 9. Compound **1** (0.013 g, 0.02 mmol), when combined with a 10-fold excess of $AgNO_3$ in CH_2Cl_2, formed complex **9** quantitatively. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): at 25 °C, δ 113.8 (broad t, 2 P) and 80.7 (two, broad d of t); at −80 °C, δ 108.4 (t, 2 P, $^2J_{PP}$ = 26.9 Hz; $C_6H_4N_2PPh$), 78.4 [pair of d of t, 2 P, $^1J(^{109}Ag^{31}P)$ = 366 Hz, $^1J(^{107}Ag^{31}P)$ = 316 Hz; PhPAg]. The solution showed no changes during 3 days at room temperature.

Evaporation of solvent yielded **9** as an oil. Attempts at crystallization failed. MS (FAB$^+$), parent and six major peaks at *m*/*e* (% rel intens): 781 (5), 765 (28), 763 (23), 749 (98), 747 (100), 613 (10), 563 (15).

Reactions of 2. (A) With S_8. $(C_6H_4N_2)_2(PhP)(PhPS)_3$ (10) and $[C_6H_4N_2(PhPS)_2]_2$ (11). S_8 (ca. 5% excess) and **2** in toluene were allowed to react at 110 °C. After 10 days, the reaction solution showed ^{31}P NMR spectral resonances mainly from **10**. Removal of solvent in vacuo and recrystallization from CH_2Cl_2 yielded pure **10** (mp = 248−250 °C). Continued heating of a **10**/toluene solution with excess S_8 for an additional 10 days yielded **11**. Crystallization from CH_2Cl_2 yielded **11** (mp = 228−230 °C).

Compound 10. ^1H NMR (CS_2/CD_2Cl_2): δ 6.6−7.9 (complex mult, 28 H; *o*-C_6H_4 and C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 107.7 (t of d, 1 P, $^2J_{PP}$ = 47.4 Hz, $^4J_{PP}$ = 13.4 Hz; $C_6H_4N_2PPh$), 68.3 [d of t, 1 P, $^2J_{PP}$ = 15.6 Hz; $C_6H_4N_2P(S)Ph$], 58.5 (d of d, 2 P; PhPS). MS (EI$^+$), M$^+$, *m*/*e* (% rel intens): 736 (40).

Compound 11. ^1H NMR (CS_2/CD_2Cl_2): δ 6.4−7.8 (complex mult, 28 H; *o*-C_6H_4 and C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 65.2 [t, 2 P, $^2J_{PP}$ = 18.9 Hz; $C_6H_4N_2P(S)Ph$], 56.8 (t, 2 P; PhPS). MS (EI$^+$), M$^+$, *m*/*e* (% rel intens): 768 (15). Anal. Calcd for $C_{36}H_{28}N_4P_4S_4$: C, 55.73; H, 3.71; N, 7.37. Found: C, 55.68; H, 3.64; N, 7.30.

(B) With Se and Te. Compound **2** underwent no reaction with Se (in toluene solution), KSeCN (in CH_3CN) or Te (in toluene) in various ratios (1:1−100, m/m) at temperatures from 25 to 110 °C.

(C) With BH_3, BH_3THF, or CH_3I. Compound **2** (0.02 g, 0.03 mmol) with B_2H_6 (0.12 mmol) in toluene-d_8 or $BH_3{\cdot}THF$ (0.30 mL, 0.30 mmol) at 25 °C g, 0.028 mmol) in NMR tubes showed no reaction. Compound **2** and CH_3I were combined in various ratios (1:1−100, m/m) in CH_2Cl_2 and heated to 40 °C for up to 7 days without reaction. The ^{31}P NMR spectrum at −80 °C was unchanged from that at +25 °C.

(D) With $AgNO_3$. $\{[C_6H_4N_2(PhP)(PhPS)]_2{\cdot}Ag\}NO_3$ (12), $(C_6H_4N_2)_2(PhP)(PhPO)(PhPS)_2$ (13), and $[C_6H_4N_2(PhPO)(PhPS)]_2$ (14). Compound **2** (0.008 g, 0.012 mmol) in CH_2Cl_2 was combined with a 10-fold excess of $AgNO_3$. The ^{31}P NMR spectrum initially showed broad doublet resonances at δ 94.7 (d) and 58.7 (t) due to **12**. Removal of solvent in vacuo yielded an oil which did not crystallize and which could not be chromatographed.

Compound 12. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 94.7 (two d of t, 2 P, $^2J_{PP}$ = 24.8 Hz, $^1J(^{109}Ag^{31}P)$ = 392 Hz, $^1J(^{107}Ag^{31}P)$ = 341 Hz; $C_6H_4N_2P(Ag)Ph$), 58.7 (t, 2 P; PhPS). MS (FAB$^+$), (M − NO_3)$^+$ with correct isotope pattern and three major peaks at *m*/*e* (% rel intens): 811 (50), 737 (65), 705 (60), 673 (20).

During 3 h at room temperature, solutions of **12** underwent reaction; resonances from **12** disappeared and **13** and **14** appeared (**13**:**14** = 5.5:1), along with singlets at δ 15.8, 11.0, 10.5, 8.9, and 5.5. Using near equimolar reagent quantities (**2**:$AgNO_3$ = 1:1.2), after 18 h at room temperature the ^{31}P NMR spectrum showed resonances due mainly to **13** (**2**:**13**:**14**; mole ratio, 1.4:6.5:1). Solvent evaporation yielded **13**/**14** mixtures which were not separated by fractional crystallization or chromatography.

Compound 13. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 111.2 (t, 1 P, $^2J_{PP}$ = 52.7 Hz; $C_6H_4N_2PPh$), 56.5 (d of d, 2 P, $^2J_{PP}$ = 13.3 Hz; PhPS), 25.6 [t, 1 P; $C_6H_4N_2P(O)Ph$]. MS (FAB$^+$), M$^+$ and two main peaks at *m*/*e* (% rel intens): 721 (100), 705 (50), 597 (85).

Compound 14. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 52.8 (t, 2 P, $^2J_{PP}$ = 16.5 Hz; PhPS), 20.8 [t, 2 P; $C_6H_4N_2P(O)Ph$]. MS (FAB$^+$), M$^+$ and three main peaks at *m*/*e* (% rel intens): 737 (90), 705 (100), 597 (50), 457 (60). **13** and **14** showed no EI$^+$ mass spectral parent ions; hence, exact mass analyses were not performed.

Compound **2** (0.011 g, 0.015 mmol) with excess KNO_3 and CH_2Cl_2 (1.0 mL) in a capped NMR tube was allowed to sit at room temperature for 14 days; ^{31}P NMR showed only minor (<10% of spectral area) oxidation peaks. No **13** or **14** formed.

(E) With norMo(CO)$_4$ or CHTMo(CO)$_3$. Compound **2** with excess (>50%) norMo(CO)$_4$ or CHTMo(CO)$_3$ in toluene, when heated to 90 °C for 7 days in toluene, underwent no reaction.

(F) With $(Ph_3P)_2Ni(CO)_2$. $[C_6H_4N_2(PhP)(PhPS)]_2Ni(CO)_2$ (15). Compound **2** (0.010 g, 0.014 mmol) and $(Ph_3P)_2Ni(CO)_2$ (0.010 g, 0.035 mmol) were combined in CH_2Cl_2 (1.0 mL) in an NMR tube, and the solution was heated to reflux. After 4 days, the ^{31}P NMR spectrum showed resonances only due to **15**, unreacted $(Ph_3P)_2Ni(CO)_2$, $(Ph_3P)Ni(CO)_3$ (δ 42.4),[25] and Ph_3P (δ −10.0).[25] Recrystallization from CH_3CN yielded **15**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 131.2 (t, 2 P, $^2J_{PP}$ = 20.6 Hz; $C_6H_4N_2PhPNi$), 62.0 (t, 2 P; PhPS). MS, M$^+$, *m*/*e* (% rel intens): 817. IR (KBr pellet): ν_{CO}, 2960(w), 2038(m) cm^{-1}.

X-Ray Analysis of Various Compounds. (A) Compound 4. Slow evaporation of a CH_2Cl_2/toluene solution (~50:50) enriched in **4** yielded clear, colorless, hexagonal, cylinder (0.25 × 0.30 × 0.35 mm) crystals. Data collection details and values for cell parameters are listed in Table 1. Cell dimensions were determined by least-squares fit of the setting angles for 25 reflections, 2θ = 41.4−49.5°. Crystal integrity was monitored by measuring four check reflections after every 96 reflections. Only random variations were observed over the course of the data collection. The structure was solved by direct methods.[26] The molecule was refined anisotropically, except for the hydrogen atoms which were included in idealized positions. Final positional parameters are given in Table 2.

(B) Compound 10. Slow evaporation of a **10**/**11** benzene-d_6 solution yielded crystals of both **10** and **11**. By careful examination, we were able to separate the crystals and characterize each by X-ray crystal-

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[25] Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Topics in Phosphorus Chemistry*; Interscience: New York, 1963, Vol. 5.

[26] Sheldrick, G. M. *SHELXTL PLUS*: *A Program for Crystal Structure Determination*, Version 4.1; Siemens Analytical Instruments: Madison, WI, 1990; performed on a Micro VAX II.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [$(C_6H_4N_2)_2(PhP)_2(PhPO)_2$] (**4**)

atom[a]	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[b]
P(1)	−779(1)	14(1)	6912(1)	35(1)*
P(2)	584(1)	1205(1)	6597(1)	35(1)*
O(2)	831(1)	2376(2)	6179(1)	48(1)*
N(1)	−1043(1)	1236(2)	7516(1)	38(1)*
N(2)	−300(1)	1372(2)	6570(1)	34(1)*
C(11)	−1593(1)	−54(2)	6188(1)	37(1)*
C(12)	−1693(1)	666(3)	5528(1)	55(1)*
C(13)	−2311(1)	416(4)	4992(1)	66(1)*
C(14)	−2817(1)	−544(3)	5112(1)	62(1)*
C(15)	−2730(1)	−1277(3)	5766(2)	57(1)*
C(16)	−2114(1)	−1031(3)	6301(1)	47(1)*
C(21)	686(1)	−631(2)	6297(1)	39(1)*
C(22)	1338(1)	−1360(3)	6530(1)	51(1)*
C(23)	1436(2)	−2734(3)	6261(2)	64(1)*
C(24)	888(2)	−3394(3)	5750(2)	66(1)*
C(25)	259(1)	−2658(3)	5499(1)	58(1)*
C(26)	155(1)	−1282(3)	5764(1)	46(1)*
C(31)	−1035(1)	2688(2)	7197(1)	40(1)*
C(32)	−598(1)	2780(2)	6701(1)	38(1)*
C(33)	−477(1)	4123(2)	6405(1)	48(1)*
C(34)	−810(2)	5353(3)	6603(1)	63(1)*
C(35)	−1263(2)	5251(3)	7080(2)	70(1)*
C(36)	−1387(1)	3911(3)	7379(1)	56(1)*

[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 trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for [$(C_6H_4N_2)_2(PhP)(PhPS)_3$]·$C_6H_6$ (**10**)

atom[a]	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[b]
P(1)	6958(1)	8218(1)	3230(1)	31(1)*
P(2)	4403(1)	8006(1)	3937(1)	32(1)*
P(3)	4183(1)	6067(1)	2671(1)	33(1)*
P(4)	5809(1)	7108(1)	1208(1)	32(1)*
S(1)	7237(1)	7020(1)	3800(1)	42(1)*
S(2)	3426(1)	8899(1)	4319(1)	44(1)*
S(4)	5747(1)	7430(1)	−134(1)	44(1)*
N(1)	6575(3)	8183(2)	1976(2)	31(1)*
N(2)	5731(3)	8674(2)	3494(2)	31(1)*
N(3)	3573(3)	7046(2)	3100(2)	33(1)*
N(4)	4386(3)	6595(2)	1553(2)	32(1)*
C(11)	8295(4)	9336(3)	3481(3)	37(2)*
C(12)	9452(4)	9218(4)	3310(3)	52(2)*
C(13)	10507(5)	10032(4)	3530(4)	65(2)*
C(14)	10455(5)	10959(4)	3946(4)	64(2)*
C(15)	9330(5)	11074(4)	4123(4)	66(2)*
C(16)	8250(5)	10272(4)	3901(3)	53(2)*
C(21)	4970(4)	7414(3)	4958(3)	35(2)*
C(22)	4424(5)	6418(4)	5182(3)	49(2)*
C(23)	4802(6)	6065(4)	6047(4)	63(2)*
C(24)	5708(5)	6711(4)	6717(3)	57(2)*
C(25)	6276(5)	7708(4)	6510(3)	52(2)*
C(26)	5905(4)	8056(3)	5634(3)	42(2)*
C(31)	2711(4)	5070(3)	2289(3)	37(2)*
C(32)	2398(5)	4560(4)	1373(3)	53(2)*
C(33)	1397(5)	3699(4)	1175(4)	70(2)*
C(34)	677(5)	3325(4)	1879(4)	64(2)*
C(35)	969(5)	3817(4)	2798(4)	62(2)*
C(36)	1979(5)	4682(4)	2996(4)	55(2)*
C(41)	6681(4)	6192(3)	1462(3)	36(2)*
C(42)	7979(4)	6534(4)	1499(3)	47(2)*
C(43)	8676(5)	5847(4)	1626(4)	58(2)*
C(44)	8109(5)	4820(4)	1701(4)	62(2)*
C(45)	6824(5)	4468(4)	1633(4)	56(2)*
C(46)	6123(4)	5146(3)	1506(3)	42(2)*
C(51)	6096(4)	9079(3)	1882(3)	31(1)*
C(52)	5624(4)	9348(3)	2716(3)	33(1)*
C(53)	5238(5)	10233(3)	2791(3)	45(2)*
C(54)	5288(5)	10838(4)	2003(3)	52(2)*
C(55)	5745(5)	10570(3)	1170(3)	48(2)*
C(56)	6182(4)	9711(3)	1116(3)	40(2)*
C(61)	2948(4)	7361(3)	2220(3)	35(1)*
C(62)	3411(4)	7123(3)	1378(3)	34(1)*
C(63)	2898(4)	7344(4)	481(3)	46(2)*
C(64)	1956(5)	7827(4)	455(4)	56(2)*
C(65)	1498(5)	8053(4)	1280(4)	56(2)*
C(66)	1973(4)	7806(3)	2180(3)	47(2)*
C(71)	10214(11)	10490(7)	916(5)	105(4)*
C(72)	9192(8)	9643(8)	634(8)	111(5)*
C(73)	9003(8)	9160(5)	−293(9)	115(4)*
C(81)	8930(7)	4876(9)	4371(6)	117(5)*
C(82)	9865(10)	5805(7)	4478(6)	114(5)*
C(83)	10962(8)	5921(7)	5106(7)	113(5)*

[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 trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

lography. Clear, colorless parallelepiped (0.08 × 0.20 × 0.50 mm) crystals of **10** were mounted on a glass fiber. Data collection details and values for cell parameters are listed in Table 1. Cell dimensions were determined by least-squares fit of the setting angles for 25 reflections, 2θ = 22.0−33.2°. Crystal integrity was monitored by measuring four check reflections after every 96 reflections. Only random variations were observed over the course of the data collection. The structure was solved by direct methods.[26] The molecule was refined anisotropically, except for the hydrogen atoms which were included in idealized positions. Compound **10** cocrystallized with one molecule of benzene. Final positional parameters are given in Table 3.

(C) **Compound 11.** Clear, colorless parallelepiped (0.20 × 0.20 × 0.22 mm) crystals of **11** were mounted on a glass fiber. Data collection details and values for cell parameters are listed in Table 1. Cell dimensions were determined by least-squares fit of the setting angles for 25 reflections; 2θ = 30.9−34.8°. Crystal integrity was monitored by measuring three check reflections after every 97 reflections. Only random variations were observed over the course of the data collection. The structure was solved by direct methods.[26] The molecule was refined anisotropically, except for the hydrogen atoms which were included in idealized positions. Compound **11** cocrystallized with two molecules of benzene. Final positional parameters are given in Table 4.

(D) **Compound 15.** Slow cooling of a CH_3CN solution of **15** yielded clear, oblong, irregular (0.4 × 0.2 × 0.1 mm) crystals. Data collection details and values for cell parameters are listed in Table 1. Cell dimensions were determined by least-squares fit of the setting angles for 25 reflections, 2θ = 10.7−18.5°. Crystal integrity was monitored by measuring three check reflections after every 97 reflections. Only random variations were observed over the course of the data collection. The structure was solved by direct methods.[26] The molecule was refined anisotropically, except for the hydrogen atoms which were included in idealized positions. Final positional parameters are given in Table 5.

Results and Discussion

Cyclotetraphosphazane Regioselectivty. Reaction of **1** with O_3 occurs rapidly and, in comparison to reactions with S_8 or Se,[17] with much lower *endo*- vs *exo*-phosphorus site selectivity. Compound **1** and O_3 in CH_2Cl_2 react in 90 s to form an approximately equimolar mixture of [$C_6H_4N_2(PhPO)(PhP)$]$_2$ (**4**), ($C_6H_4N_2)_2(PhP)(PhPO)_3$ (**5**), and [($C_6H_4N_2)(PhPO)_2$]$_2$ (**6**) (Scheme 1). The mixture's ^{31}P NMR spectrum shows an A_2X_2[27] equal-area pair of triplets, a three-resonance triplet/singlet/doublet AM_2X pattern and a pair of equal-area A_2X_2 triplets assignable to **4**−**6**, respectively. The resonances occur in the regions expected for phosphadiazole and bridging ($PhPN_2$) phosphorus atoms, and their oxidized counterparts, based on comparison with the previously studied **1**, **2**,[17] $C_6H_4(NH)_2PPh$,[19,28] and C_6H_4-

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(28) Katz, S. A.; Allured, V. S.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1762.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[C_6H_4N_2(PhPS)_2]_2 \cdot 2C_6H_6$ (**11**)

atom[a]	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[b]
P(1)	737(1)	−603(1)	3524(1)	36(1)*
P(2)	523(1)	203(1)	1887(1)	35(1)*
S(1)	626(1)	−2464(1)	3363(1)	59(1)*
S(2)	838(1)	1445(1)	1449(1)	51(1)*
N(1)	201(1)	444(3)	3467(2)	33(2)*
N(2)	869(1)	354(3)	2899(2)	33(2)*
C(11)	1346(2)	−175(4)	4478(2)	41(2)*
C(12)	1277(2)	394(5)	5062(3)	50(2)*
C(13)	1748(2)	622(5)	5803(3)	61(3)*
C(14)	2290(3)	279(6)	5962(3)	74(3)*
C(15)	2369(2)	−306(7)	5396(3)	84(3)*
C(16)	1898(2)	−538(6)	4648(3)	67(3)*
C(21)	606(2)	−1486(5)	1647(3)	43(2)*
C(22)	220(2)	−1961(5)	899(3)	60(3)*
C(23)	306(3)	−3203(6)	672(4)	78(4)*
C(24)	783(3)	−3952(6)	1179(5)	88(5)*
C(25)	1178(3)	−3461(6)	1912(4)	75(4)*
C(26)	1092(2)	−2225(5)	2146(3)	56(3)*
C(31)	422(2)	1760(4)	3424(2)	35(2)*
C(32)	805(2)	1701(4)	3138(2)	35(2)*
C(33)	1100(2)	2819(5)	3123(3)	46(2)*
C(34)	984(2)	4028(5)	3350(3)	54(3)*
C(35)	592(2)	4100(5)	3618(3)	56(3)*
C(36)	324(2)	2969(4)	3675(3)	46(2)*
C(41)	2348(3)	4178(7)	6377(4)	82(4)*
C(42)	1904(3)	4507(7)	5663(4)	85(4)*
C(43)	1671(3)	5737(9)	5511(4)	87(4)*
C(44)	1879(3)	6679(7)	6103(5)	91(5)*
C(45)	2333(4)	6325(8)	6834(5)	97(5)*
C(46)	2564(3)	5068(8)	6960(4)	86(4)*

[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 trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$(NH)_2P(O)Ph$.[29] Typically, formation of **4**−**6** is accompanied by large quantitites (ca. 50%) of ill-defined uncharacterized materials, a situation which frustrated efforts to separate the mixtures. Flash chromatography of the reaction mixture yielded **4**; however, it was not possible to isolate **5** and **6**. In shorter reaction times, formation of **6** can be avoided, but it was never possible to obtain only dioxide **4**. Compound **4** was isolated and characterized by spectral and X-ray crystallographic analyses (see below).

Oxidation of **1** by other oxygen oxidizing agents was less successful. The reagents Me_3NO and PhIO could not be dried sufficiently to prevent unacceptable levels of competing hydrolysis. Reaction of **1** with O_2 in benzene in the presence of the radical initiator azobis(isobutyronitrile) (AIBN), a reaction known to be highly effective for trialkyl phosphite oxidation,[30] after 3 h showed resonances due to unreacted **1** and uncharacterized oxidation/cleavage products in the δ 0 to 30 region, in addition to the AM_2X resonances tentatively assigned to the monooxide $(C_6H_4N_2)_2(PhP)_3(PhPO)$ (**7**). Upon further reaction of **7** with O_2/AIBN, unidentifable products between δ 0 and 30 grew in faster than **4**, making this an impractical synthetic route.

Regioselectivity of *exo*- vs *endo*-phosphorus sites in **1** was further probed in reactions with CH_3I and Ag^+ ion, species known to react readily with tervalent phosphines.[31,32] Compound **1** reacted with excess CH_3I within 6 h, giving a ^{31}P NMR spectrum consisting of a complex multiplet at δ 105.7 and a triplet of doublets at δ 52.8 tentatively assigned to an *exo*-phosphorus monoquaternized product **8** (36% spectral area), along with resonances due to unreacted **1** and unassigned products. The relative yield of **8** did not improve with time. After 24 h, decomposition products predominated. Although ^{31}P NMR spectral data do not show conclusively which phosphorus site in **1** was quaternized, since we know that O_3 and S_8 react first at the *exo* phosphorus atoms, we assume that **8** involves similar regioselective bonding to an *exo*, noncavity, phosphorus atom [P(1,3)].

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $[C_6H_4N_2(PhP)(PhPS)]_2Ni(CO)_2$ (**15**)

atom[a]	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[b]
Ni(1)	4047(1)	1413(1)	4630(1)	37(1)*
P(1)	3888(1)	2733(2)	4781(2)	32(2)*
P(2)	2920(1)	2535(2)	3252(2)	34(2)*
P(3)	3908(1)	1672(2)	3421(2)	34(2)*
P(4)	4564(2)	3267(2)	3966(2)	35(2)*
S(2)	2360(2)	3210(3)	2487(2)	49(2)*
S(4)	4777(2)	4261(3)	3556(2)	48(2)*
N(1)	3287(4)	3116(6)	4100(6)	29(5)*
N(2)	4216(4)	3526(6)	4487(6)	34(5)*
N(3)	4225(4)	2545(7)	3220(5)	27(5)*
N(4)	3299(4)	2116(6)	2826(6)	32(5)*
C(11)	3946(5)	3173(9)	5721(7)	32(6)*
C(12)	4216(6)	3921(9)	6077(8)	46(7)*
C(13)	4236(6)	4197(11)	6813(9)	61(9)*
C(14)	3993(6)	3791(11)	7190(8)	54(8)*
C(15)	3727(6)	3047(11)	6857(9)	61(9)*
C(16)	3692(5)	2742(9)	6127(8)	43(7)*
C(21)	2691(5)	1634(9)	3618(8)	37(7)*
C(22)	2618(5)	1726(9)	4316(9)	47(7)*
C(23)	2378(6)	1082(10)	4542(10)	54(9)*
C(24)	2216(7)	344(11)	4122(12)	69(10)*
C(25)	2284(6)	265(9)	3419(11)	56(9)*
C(26)	2521(5)	906(10)	3170(9)	46(8)*
C(31)	3961(5)	846(8)	2762(7)	33(7)*
C(32)	3681(6)	109(9)	2655(9)	60(9)*
C(33)	3724(6)	−560(10)	2200(10)	64(9)*
C(34)	4074(6)	−501(10)	1854(9)	58(9)*
C(35)	4352(7)	227(11)	1955(10)	66(10)*
C(36)	4293(6)	910(10)	2390(9)	54(8)*
C(41)	5094(5)	2643(8)	4646(8)	32(6)*
C(42)	5284(6)	2770(10)	5476(9)	53(8)*
C(43)	5721(7)	2329(11)	5984(10)	71(9)*
C(44)	5984(7)	1825(11)	5667(11)	76(10)*
C(45)	5814(6)	1700(10)	4856(10)	60(8)*
C(46)	5368(5)	2129(10)	4367(9)	49(8)*
C(51)	3355(5)	4039(9)	4037(7)	26(6)*
C(52)	3860(6)	4252(9)	4248(8)	35(7)*
C(53)	4001(7)	5113(9)	4307(9)	49(8)*
C(54)	3631(7)	5744(10)	4139(8)	45(8)*
C(55)	3127(7)	5513(9)	3940(8)	48(8)*
C(56)	2985(6)	4659(9)	3887(7)	38(7)*
C(61)	3887(6)	2838(9)	2424(8)	37(7)*
C(62)	3379(6)	2585(9)	2191(8)	40(7)*
C(63)	3003(6)	2698(9)	1420(9)	46(8)*
C(64)	3157(6)	3087(9)	893(8)	44(7)*
C(65)	3661(7)	3342(10)	1106(8)	55(9)*
C(66)	4031(6)	3218(9)	1881(9)	43(8)*
C(91)	3636(6)	591(10)	4715(9)	44(7)*
O(91)	3425(5)	7(7)	4814(8)	84(7)*
C(92)	4659(7)	978(10)	5281(11)	64(10)*
O(92)	5030(5)	645(8)	5722(8)	87(7)*

[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 trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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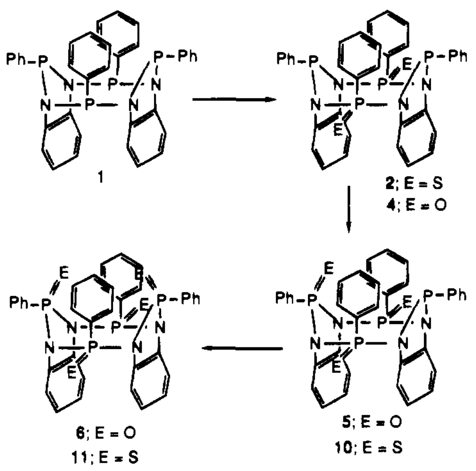
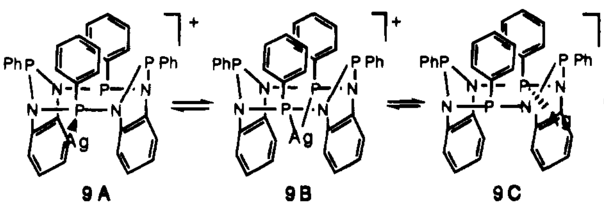
Scheme 1



Similarly, **1** coordinates the Ag^+ ion; excess $AgNO_3$ in CH_2Cl_2 reacts readily to form complex **9** whose ^{31}P NMR spectrum consists of an area 2 broad pair of doublets of triplets (δ 80.7) and an area 2 triplet (δ 113.8) assignable to the *exo* [P(2,4)] and uncoordinated *endo* [P(1,3)] phosphorus atoms, respectively. At −40 °C, the δ 80.7 resonance sharpens to two triplets due to $^1J(^{109}AgP)$ and $^1J(^{107}AgP)$ coupling. It has been shown previously that J_{AgP} values correlate with the number of coordinated phosphines; the J_{AgP} values for **9** are in the range expected for bis(phosphine)−Ag(I) complexes.[31,32,34] Continued cooling to −80 °C only sharpened these resonances. No further coordination of Ag^+ or association with the *endo*-phosphorus atoms of the molecular cavity was apparent. Since it was not possible to crystallize **9** and isolate it free of other minor reaction materials, its characterization depends on spectral data. Mass spectral (FAB$^+$) analysis showed the presence of a mono(silver) $\{[C_6H_4N_2(PhP)_2]_2Ag\}^+$ complex ion, no peaks due to doubly-charged disilver species were seen.

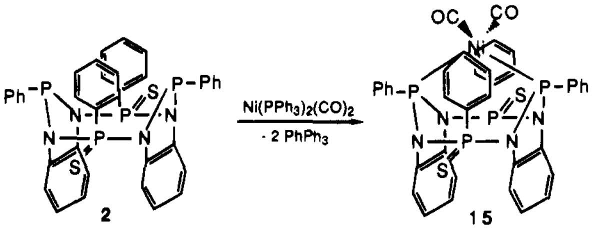
With the assumption that **9** is a mono(silver) complex, the symmetrical appearance of the ^{31}P NMR spectrum and the fact that the Ag^+ ion shows equivalent coupling to two phosphorus atoms must be explained. Possibly, at 25 °C the Ag^+ ion undergoes intramolecular exchange between *exo* phosphorus atoms of **9A** and **9C**, in a rapid argentotropic process,[35] such as that shown in eq 1. Such a process would require distortion outward of the orthophenylene rings in order to accommodate the Ag^+; spectral sharpening at −40 °C could result from slowed exchange of this process to an essentially frozen structure, in which Ag^+ is coordinated to both P(1) and P(3), between the orthophenylene rings. Other examples of such processes have been reported recently.[35]



(1)

Molecular cleft reactivity of the cyclotetraphosphazane system toward oxidizing agents was probed further in reactions of **2** with sulfur, selenium, and tellurium oxidizing agents. As described above, O_3 reacted easily with the *endo* atoms P(1,3) atoms of **4** to form tri- and tetraoxide products, **5** and **6**. However, much slower oxidation of these sites in **2** to the tri- and tetrasulfides, **10** and **11** is observed. Compound **10** forms in 30 min at 80 °C (Scheme 1); **11** forms in low yield only after refluxing in toluene at 95 °C for 10 days. Both **10** and **11** were isolated and characterized by spectral data and X-ray crystallography. Even though the cavity of **2** is large enough to allow reaction with elemental S_8 and ultimately to accommodate two sulfur atoms, insertion of selenium or tellurium atoms could not be effected. After heating **2** in refluxing toluene or CH_3CN for up to 7 days with elemental Se, KSeCN, or Te, the ^{31}P NMR spectrum of the mixture showed only unreacted **2**.

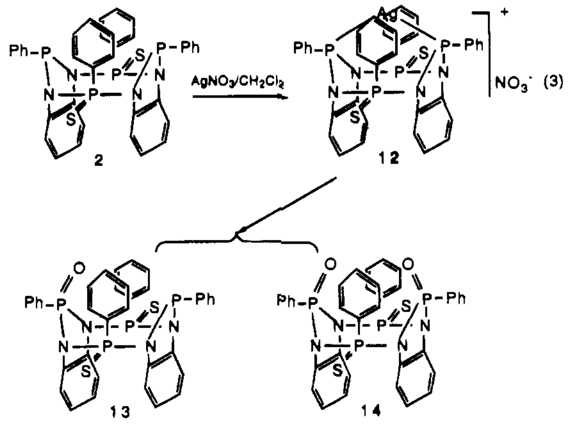
The coordination of metal moieties in the molecular cavity of **2** or **4** is potentially interesting because besides coordination to the two *endo*-phosphorus sites, secondary coordination to the cavity-wall phenyl groups might occur, leading to stabilization of metals in novel, low coordination states. Compounds **2** and **4** are structurally very similar (see below) and therefore are assumed to have similar reactivity and cavity characteristics. However, since **4** is much harder to obtain than **2**, only the latter was examined in subsequent coordination studies. Compound **2** did not react at 90 °C during 7 days with either nor·Mo(CO)$_4$ or CHT·Mo(CO)$_3$. In contrast, **2** reacted with excess $(Ph_3P)_2Ni(CO)_2$ in CH_2Cl_2 to yield the Ni(0) complex **15** (eq 2). The ^{31}P NMR spectrum of the reaction mixture showed mainly resonances from **15**, unreacted $(Ph_3P)_2Ni(CO)_2$, $(Ph_3P)Ni(CO)_3$, and Ph_3P. There was no evidence for other Ni-coordinated complexes of **2**. Complex **15** was stable in solution for periods of hours; it readily crystallized and was characterized by spectral and X-ray data.



(2)

Reaction of Ag^+ with **2** was more complex, showing not only metal ion coordination but also subsequent unexpected cyclotetraphosphazane oxidation. Reaction of $AgNO_3$ with **2** in CH_2Cl_2 immediately yields **12** (Scheme 2) whose ^{31}P NMR spectrum exhibits two broad doublets of triplets (δ 96.5) and a sharp triplet (δ 57.9). Cooling the solution to −60 °C sharpens the broad signals, and $^{31}P-^{107,109}Ag$ coupling becomes clear.

Scheme 2



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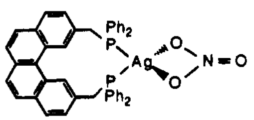
The spectral data show that there is either (i) one Ag^+ bridging the two *endo* cavity phosphorus atoms or (ii) two coordinated Ag^+, one attached to each *endo* phosphorus site (Scheme 2). Since **12** like **9** shows J_{AgP} values consistent with bis(phosphine) coordination,[31,32,34] two Ag^+, one coordinated to each *endo* phosphorus atom, seems unlikely. Also, experiments using equimolar quantities of reactants **2** and $AgNO_3$ resulted in complete formation of **12**, consistent with there being only one bridging Ag^+ in the cavity of **2**. Attempts to isolate **12** by rapid solvent evaporation failed. However, samples containing mostly **12** (70 mol %) gave FAB^+ mass spectral peaks at *m/e* 811 and 813 (**12** − NO_3^-) attributable to $\mathbf{2}\cdot{}^{107/109}Ag^+$, confirming the molecular formulation.

Over time, solutions containing **12** reacted further. Within 3 h, resonances from **12** disappeared and had been replaced by an AM_2X[27] pattern (triplet, δ 111.2; doublet of doublets, δ 56.5; triplet, δ 25.6), a pair of A_2X_2 triplets (δ 52.8 and 20.8), and numerous singlets between δ 15.8 and 5.5. The AM_2X pattern was assigned to the mixed oxidation product **13** containing two *exo*-located sulfur and one cavity (*endo*) oxygen atom, and the symmetrical A_2X_2 triplet pattern is attributed to the mixed disulfide−dioxide product **14**. If excess $AgNO_3$ remained in contact with the reaction solution, nearly complete conversion of **12** to **14** occurred.

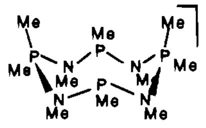
The ^{31}P NMR spectra of **13**/**14** mixtures typically showed substantial amounts of decomposition products (singlets and broad poorly defined resonances between δ 20.0 and 0.0) from which they could not be separated by crystallization or chromatography. However, by using either a deficiency or an excess of $AgNO_3$, it was possible to obtain samples enriched in **13** or **14**, respectively. The cavity phosphine oxide ^{31}P NMR chemical shifts in **13** (δ 25.6) and **14** (δ 20.8) are similar to the corresponding resonances in **5** (δ 27.9) and **6** (δ 22.8), while the phosphine sulfide resonances (**13**, δ 56.5; **14**, δ 52.8) are similar to those observed in **10** (δ 58.5) and **11** (δ 56.8). Both **13** and **14** exhibited the expected mass spectral data.

Oxidation of phosphines to phosphine oxides by $AgNO_3$ appears to be unusual. In order to determine if NO_3^- or extraneous H_2O or O_2 were responsible for the oxidation, **2** dissolved in CH_2Cl_2 was left in contact with KNO_3 or KNO_3 and added traces of H_2O and O_2 at room temperature for 14 days. The ^{31}P NMR of the solution showed only minor (<10%) resonances due to decomposition; however, no oxidation to **13** or **14** occurred. These results suggest that coordination of Ag^+ and NO_3^- in the molecular cavity of **2** is necessary and that Ag^+ coordination activates oxygen transfer from NO_3^- to the cavity phosphorus atoms. Equimolar reactions between **2** and $AgNO_3$ (**2**:$AgNO_3$ = 1:1.2) yielded mainly **13** (**2**:**13**:**14** = 1.4:6.5:1), suggesting that each NO_3^- in **12** transfers only one oxygen atom to **2**. Attempts to isolate a $[\mathbf{2}\cdot Ag]^+$ complex failed; the nitrate complex was too reactive, and the acetate complex failed to crystallize. Compound **2** was allowed to react with AgI in attempts to isolate a silver complex, however, the limited solubility of AgI in CH_2Cl_2 apparently prevented complex formation.

Mono(silver) complex **12** could not be unambiguously characterized because of its instability toward formation of **13**/**14**. However, other bis(phosphine)silver(I) nitrate complexes have been prepared,[36,37] and from what is known it is possible to suggest some aspects of a mechanism for formation of **13** and/or **14** from **12**. In bis(phosphino)silver(I) nitrate complexes such as **16**,[37] silver is typically four-coordinate, coordinating both phosphorus atoms of the bis(phosphine) ligand and two oxygen atoms of NO_3^-. Similar $AgNO_3$ coordination in the highly restricted cavity of **2** would locate NO_3^- proximate to a cavity phosphorus atom, possibly facilitating transfer of an oxygen from NO_3^- to an *endo*-phosphorus. Nitrite ion or other reduced nitrogen species might be formed during production of **13** and **14**, but such species have not yet been identified.



16



17

Small-molecule coordination, e.g., BH_3 or CH_3^+, in the cavity of **2** suprisingly did not occur. Borane (from $BH_3{\cdot}THF$ or B_2H_6), CH_3I, and Me_3OBF_4 were allowed to react with **2** under a variety of conditions. In each case the ^{31}P NMR spectra of the reaction mixtures showed only resonances from **2**. The ^{31}P and ^{11}B NMR spectra of **2** and B_2H_6 in toluene-d_8 was studied from +25 to −80 °C; however, even at −80 °C association was not evident. The absence of reactivity is suprising since other phenyl(bisaminophosphines) react readily with both BH_3 and CH_3I; e.g., both the phosphadiazole $C_6H_4(NH)_2PPh$ and Me_2NPPh_2 react quickly with $BH_3{\cdot}THF$ to form the borane complexes $C_6H_4(NH)_2PPh(BH_3)$[38] and $Me_2NPPh_2(BH_3)$.[39] It is possible that the two electron-withdrawing [PhPS] groups adjacent to the P(1,3) phosphorus atoms greatly lower the latter's basicity; however, the effect seems extreme. More likely, the lowered reactivity is a molecular cavity steric effect. If CH_3I is to react with the nucleophilic phosphine center in typical S_N2 fashion[40] to form a five-coordinate planar CH_3 unit, the transition state with its expected approximate van der Waals diameter of 4.0 Å[41] might be too large for the cavity. From models and molecular modeling analyses, we estimate that the cavity of **2** has only 3.0−3.5 Å of free space between the P(2,4) bonded phenyl rings. Interestingly, the nonrigid and sterically less incumbered cyclotetraphosphazane $(CH_3PNCH_3)_4$ reacts easily with CH_3I to form a stable diquaternized product **17**.[42,43]

Cyclotetraphosphazane Structural Studies. The cyclotetraphosphazane dioxide **4**, trisulfide **10**, tetrasulfide **11**, and $Ni(CO)_2$ complex **15** were structurally analyzed by X-ray crystallography. Compounds **4**, **10**, and **11** are members of a series which include the previously reported **1** and **2**.[17] Structures of **4**, **10**, and **11** are shown in Figures 1−3; selected bond lengths and angles are shown in Tables 6−8. The structural parameters of **4**, **10**, and **11**, where comparable, closely parallel those of **1** and **2**. The P−N distances between nitrogen and P(III) phosphorus atoms differ from those between nitrogen and oxidized phosphorus centers; e.g., the mean N−P(III) distances of 1.745 and 1.750 Å in **4** and **10** are significantly longer than the N−P(V) distances of 1.696, 1.717 (mean) and 1.724 Å in **4**, **10**, and **11**. Furthermore, P−N distances to

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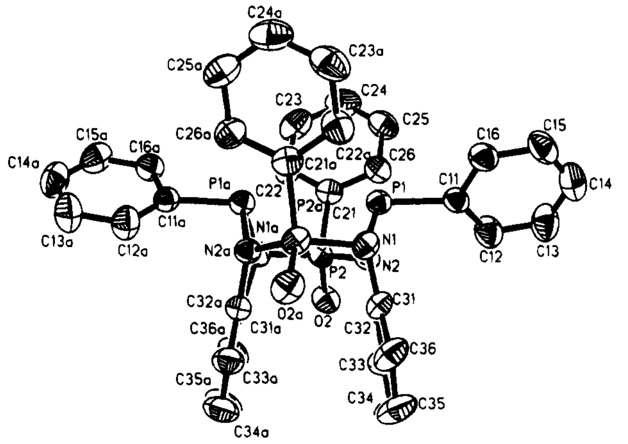

Figure 1. Structure and numbering scheme for $[C_6H_4N_2(PhP)(PhPO)]_2$ (**4**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

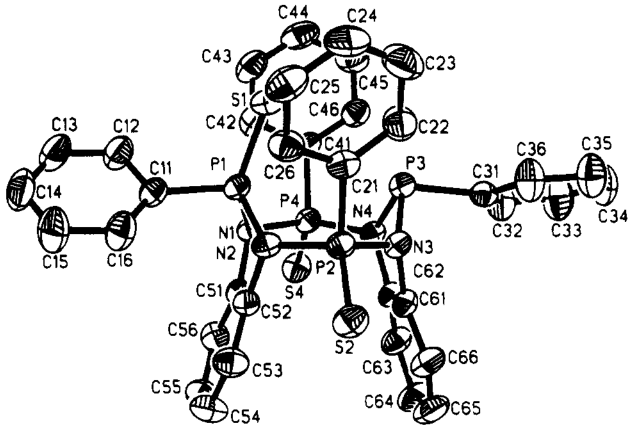

Figure 2. Structure and numbering scheme for $(C_6H_4N_2)_2(PhP)(PhPS)_3{\cdot}C_6H_6$ (**10**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

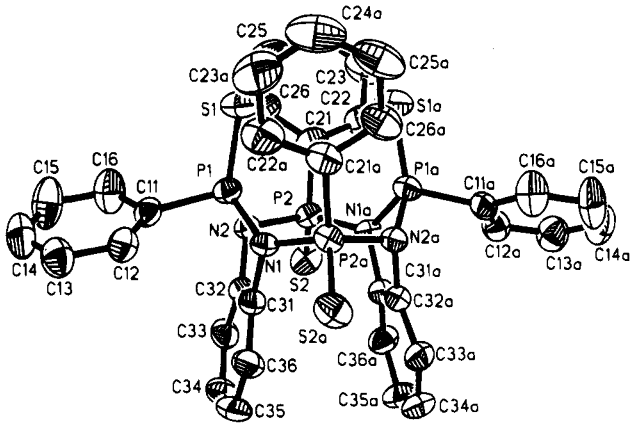

Figure 3. Structure and numbering scheme for $[C_6H_4N_2(PhPS)_2]_2{\cdot}2C_6H_6$ (**11**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 6. Selected Structural Parameters for $[C_6H_4N_2(PhP)(PhPO)]_2$ (**4**)

(a) Bond Distances, Å

P(1)–N(1)	1.743(2)	P(1)–N(2)	1.746(2)
P(1)–C(11)	1.825(2)	P(2)–O(2)	1.464(2)
P(2)–N(2)	1.690(2)	P(2)–C(21)	1.785(2)
P(2)–N(1A)	1.702(2)	N(1)–C(31)	1.451(3)
N(1)–P(2A)	1.702(2)	N(2)–C(32)	1.444(3)

(b) Bond Angles, deg

N(1)–P(1)–N(2)	92.6(1)	N(1)–P(1)–C(11)	100.6(1)
N(2)–P(1)–C(11)	100.3(1)	O(2)–P(2)–N(2)	111.2(1)
O(2)–P(2)–C(21)	115.9(1)	N(2)–P(2)–C(21)	104.8(1)
O(2)–P(2)–N(1A)	110.9(1)	N(2)–P(2)–N(1A)	108.6(1)
C(21)–P(2)–N(1A)	104.9(1)	P(1)–N(1)–C(31)	106.1(1)
P(1)–N(1)–P(2A)	117.9(1)	C(31)–N(1)–P(2A)	111.7(1)
P(1)–N(2)–P(2)	122.1(1)	P(1)–N(2)–C(32)	107.5(1)
P(2)–N(2)–C(32)	120.4(1)		

Table 7. Selected Structural Parameters for $(C_6H_4N_2)_2(PhP)(PhPS)_3{\cdot}C_6H_6$ (**10**)

(a) Bond Distances, Å

P(1)–S(1)	1.907(2)	P(1)–N(1)	1.739(3)
P(1)–N(2)	1.720(4)	P(1)–C(11)	1.800(4)
P(2)–S(2)	1.927(2)	P(2)–N(2)	1.713(3)
P(2)–N(3)	1.689(3)	P(2)–C(21)	1.789(4)
P(3)–N(3)	1.754(4)	P(3)–N(4)	1.745(3)
P(3)–C(31)	1.827(4)	P(4)–S(4)	1.927(2)
P(4)–N(1)	1.717(3)	P(4)–N(4)	1.691(3)
P(4)–C(41)	1.790(5)	N(1)–C(51)	1.451(6)
N(2)–C(52)	1.452(5)	N(3)–C(61)	1.471(5)
N(4)–C(62)	1.460(6)		

(b) Bond Angles, deg

S(1)–P(1)–N(1)	119.4(1)	S(1)–P(1)–N(2)	120.5(1)
N(1)–P(1)–N(2)	94.5(2)	S(1)–P(1)–C(11)	112.8(2)
N(1)–P(1)–C(11)	102.8(2)	N(2)–P(1)–C(11)	103.8(2)
S(2)–P(2)–N(2)	112.3(1)	S(2)–P(2)–N(3)	112.2(1)
N(2)–P(2)–N(3)	108.9(2)	S(2)–P(2)–C(21)	111.3(2)
N(2)–P(2)–C(21)	104.1(2)	N(3)–P(2)–C(21)	107.5(2)
N(3)–P(3)–N(4)	93.1(2)	N(3)–P(3)–C(31)	98.6(2)
N(4)–P(3)–C(31)	98.3(2)	S(4)–P(4)–N(1)	111.3(1)
S(4)–P(4)–N(4)	113.7(1)	N(1)–P(4)–N(4)	108.5(2)
S(4)–P(4)–C(41)	111.8(2)	N(1)–P(4)–C(41)	104.8(2)
N(4)–P(4)–C(41)	106.2(2)	P(1)–N(1)–P(4)	126.5(2)
P(1)–N(1)–C(51)	101.5(2)	P(4)–N(1)–C(51)	116.4(2)
P(1)–N(2)–P(2)	127.5(2)	P(1)–N(2)–C(52)	102.2(3)
P(2)–N(2)–C(52)	118.9(3)	P(2)–N(3)–P(3)	122.6(2)
P(2)–N(3)–C(61)	116.6(3)	P(3)–N(3)–C(61)	104.5(3)
P(3)–N(4)–P(4)	123.0(2)	P(3)–N(4)–C(62)	105.0(3)
P(4)–N(4)–C(62)	120.0(3)		

Table 8. Selected Structural Parameters for $[C_6H_4N_2(PhPS)_2]_2{\cdot}2C_6H_6$ (**11**)

(a) Bond Distances, Å

P(1)–S(1)	1.882(2)	P(1)–N(1)	1.727(4)
P(1)–N(2)	1.731(4)	P(1)–C(11)	1.807(4)
P(2)–S(2)	1.930(2)	P(2)–N(2)	1.731(3)
P(2)–C(21)	1.794(5)	P(2)–N(1A)	1.705(4)
N(1)–C(31)	1.458(5)	N(2)–C(32)	1.462(5)

(b) Bond Angles, deg

S(1)–P(1)–N(1)	122.0(1)	S(1)–P(1)–N(2)	119.8(1)
N(1)–P(1)–N(2)	94.7(2)	S(1)–P(1)–C(11)	113.0(1)
N(1)–P(1)–C(11)	101.6(2)	N(2)–P(1)–C(11)	102.3(2)
S(2)–P(2)–N(2)	111.2(1)	S(2)–P(2)–C(21)	110.2(2)
N(2)–P(2)–C(21)	108.7(2)	S(2)–P(2)–(N(1A))	112.7(1)
N(2)–P(2)–N(1A)	106.9(2)	C(21)–P(2)–N(1A)	106.9(2)
P(1)–N(1)–C(31)	101.7(3)	P(1)–N(1)–P(2A)	132.1(2)
C(31)–N(1)–P(2A)	120.6(2)	P(1)–N(2)–P(2)	126.3(2)
P(1)–N(2)–C(32)	100.2(3)	P(2)–N(2)–C(32)	111.8(2)

phosphadiazole P(V) centers are longer than those involving bridging $PhP(E)N_2$ (E = O, S) P(V) atoms; observed mean distances are 1.730 and 1.729 Å versus 1.703 and 1.718 Å in **10** and **11**, respectively. This shortening of bonds associated with the more highly oxidized phosphorus center is apparently typical for P(V) vs P(III) phosphazanes as it was also observed in the structure of **2**.[17] Similarly, the cyclotetraphosphazane internal ring angles are not much affected by oxidation. The N–P–N angles at phosphadiazole phosphorus atoms are 92.6°, 93.9° (mean), and 94.7° and the angles around bridging phosphorus atoms are 108.9°, 108.7° (mean), and 106.9° in **4**, **10**, and **1**, respectively. Small variations in the P–N–P ring angles occur; the observed mean angles are 120.0°, 124.4°, and 129.2°. Interestingly, oxidation of the *exo* P(2,4) phosphorus atoms does not have a large effect on the molecular cavity size. The nonbonded distances (P···P) between *endo*-phosphorus

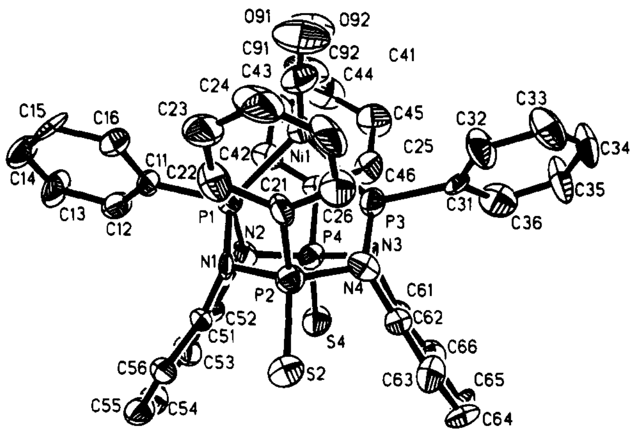

Figure 4. Structure and numbering scheme for $[C_6H_4N_2(PhP)(PhPS)]_2$-$Ni(CO)_2$ (**15**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

atoms increases only slightly, from 3.2 Å in **1**[17] to 3.3 Å in **4** and **2**.[17] The distance between the cavity walls, the upward oriented C_6H_5 groups, also remains relatively constant, 7.1 Å in **1** versus 6.9 Å in **4** and 6.5 Å in **2**.[17]

Conformational properties of the cyclotetraphosphazane system are not affected significantly by P(2,4) oxidation. However, further oxidation at P(1,3) sites causes significant conformational changes. The P_4N_4 skeleton in **10** distorts slightly with addition of a third sulfur atom whereas accommodation of the second S atom in the cage in **11** causes severe distortions. In **10**, the cavity-wall phenyl rings are twisted such that the ring carbons adjacent to S(1) [C(26) and C(42)] are farther apart than those adjacent to the unoxidized phosphorus atom P(3) [C(22) and C(46)], 7.5 Å vs 6.6 Å. The cavity sulfur S(1) is 3.47 Å from the unoxidized cavity phosphorus, P(3), slightly less than the calculated van der Waals distance (3.65 Å)[41] but significantly greater than a typical P−S bonding distance (1.85−2.0 Å).[16a,44] In **11** the mean distance between the cavity phenyl rings, [C(21)−C(26)] and [C(21A)−C(26A)], has increased substantially, from 6.5 Å in **2**[17] to 6.9 Å in **11**. The cavity sulfur atoms, S(1) and S(1A), are separated by 3.35 Å, slightly less than the calculated van der Waals distance (3.6 Å)[41] but again greater than a typical S−S bonding distance (2.0−2.1 Å).[41,44] Most importantly, the cavity P···P distance has increased from 3.3 Å in **2**[17] to 4.0 Å in **11**, and the P_2N_4 ring unit that is nearly planar in **2** [P(2,2a)/N(1,1a,2,2a)] is less planar in **11**. The dihedral angles betwen planes P(2)−P(2a)−N(1)−N(2) and P(2)−P(2a)−N(1a)−N(2a) in **2** and **11** are 10.2° and 15.8°, respectively. This close proximity of sulfur atoms forces the *endo* P atoms apart and forces closer approach between the two nearly parallel orthophenylene C_6H_4 rings. The distance between ring midpoints has decreased from 4.3 Å in **2**[17] to 3.7 Å in **11**, approaching the interplane separation of 3.35 Å seen in graphite.[45]

Table 9. Selected Structural Parameters for $[C_6H_4N_2(PhP)(PhPS)]_2Ni(CO)_2$ (**15**)

(a) Bond Lengths, Å			
Ni(1)−P(1)	2.142(4)	Ni(1)−P(3)	2.130(5)
Ni(1)−C(91)	1.786(17)	Ni(1)−C(92)	1.787(16)
P(1)−N(1)	1.753(10)	P(1)−N(2)	1.764(13)
P(1)−C(11)	1.801(14)	P(2)−S(2)	1.938(5)
P(2)−N(1)	1.727(10)	P(2)−N(4)	1.710(13)
P(2)−C(21)	1.791(16)	P(3)−N(3)	1.754(12)
P(3)−N(4)	1.762(9)	P(3)−C(31)	1.815(15)
P(4)−S(4)	1.926(6)	P(4)−N(2)	1.695(14)
P(4)−N(3)	1.721(10)	P(4)−C(41)	1.793(12)
N(1)−C(51)	1.457(17)	N(2)−C(52)	1.458(18)
N(3)−C(61)	1.449(15)	N(4)−C(62)	1.474(21)
C(91)−O(91)	1.145(21)	C(92)−O(92)	1.154(19)
(b) Bond Angles, deg			
P(1)−Ni(1)−P(3)	89.9(2)	P(1)−Ni(1)−C(91)	119.3(6)
P(3)−Ni(1)−C(91)	112.6(5)	P(1)−Ni(1)−C(92)	118.4(5)
P(3)−Ni(1)−C(92)	118.3(8)	C(91)−Ni(1)−C(92)	99.6(7)
Ni(1)−P(1)−N(1)	115.5(4)	Ni(1)−P(1)−N(2)	117.3(5)
N(1)−P(1)−N(2)	91.8(5)	Ni(1)−P(1)−C(11)	123.2(5)
N(1)−P(1)−C(11)	103.1(6)	N(2)−P(1)−C(11)	100.5(6)
S(2)−P(2)−N(1)	112.2(4)	S(2)−P(2)−N(4)	111.2(4)
N(1)−P(2)−N(4)	110.7(5)	S(2)−P(2)−C(21)	112.0(5)
N(1)−P(2)−C(21)	104.3(6)	N(4)−P(2)−C(21)	106.1(7)
Ni(1)−P(3)−N(3)	118.6(3)	Ni(1)−P(3)−N(4)	115.3(5)
N(3)−P(3)−N(4)	91.7(5)	Ni(1)−P(3)−C(31)	122.3(4)
N(3)−P(3)−C(31)	102.2(7)	N(4)−P(3)−C(31)	101.4(5)
S(4)−P(4)−N(2)	112.9(4)	S(4)−P(4)−N(3)	112.0(4)
N(2)−P(4)−N(3)	109.7(6)	S(4)−P(4)−C(41)	113.1(5)
N(2)−P(4)−C(41)	104.9(7)	N(3)−P(4)−C(41)	103.6(5)
P(1)−N(1)−P(2)	120.7(6)	P(1)−N(1)−C(51)	105.6(7)
P(2)−N(1)−C(51)	119.5(7)	P(1)−N(2)−P(4)	121.5(6)
P(1)−N(2)−C(52)	103.9(10)	P(4)−N(2)−C(52)	120.8(10)
P(3)−N(3)−P(4)	120.2(6)	P(3)−N(3)−C(61)	105.7(8)
P(4)−N(3)−C(61)	121.1(8)	P(2)−N(4)−P(3)	120.9(6)
P(2)−N(4)−C(62)	120.9(9)	P(3)−N(4)−C(62)	104.2(9)
P(1)−C(11)−C(12)	125.3(12)	P(1)−C(11)−C(16)	117.8(10)
P(2)−C(21)−C(22)	119.1(10)	P(2)−C(21)−C(26)	121.0(13)
P(3)−C(31)−C(32)	118.9(14)	P(3)−C(31)−C(36)	123.0(11)
P(4)−C(41)−C(42)	120.8(12)	P(4)−C(41)−C(46)	120.3(11)
N(1)−C(51)−C(52)	112.0(12)	N(1)−C(51)−C(56)	126.2(13)
C(52)−C(51)−C(56)	121.4(13)	N(2)−C(52)−C(51)	114.7(12)
N(2)−C(52)−C(53)	125.4(14)	C(51)−C(52)−C(53)	119.5(14)
N(3)−C(61)−C(62)	113.1(14)	N(3)−C(61)−C(66)	126.8(14)
C(62)−C(61)−C(66)	119.5(12)	N(4)−C(62)−C(61)	112.6(11)
N(4)−C(62)−C(63)	124.2(14)	C(61)−C(62)−C(63)	122.9(16)
Ni(1)−C(91)−O(91)	171.8(13)	Ni(1)−C(92)−O(92)	173.8(18)

Compound **15** is a metal complex of the cyclotetraphosphazane **2** (Figure 4), and, perhaps suprisingly, this coordination causes relatively small distortion of the cyclotetraphosphazane structure. Selected bonds and angles for **15** are shown in Table 9; these parameters are generally consistent with those of the other cyclotetraphosphazanes (**1**, **2**, **4**, and **10**) examined. The complex contains a $Ni(CO)_2$ moiety in the molecular cavity with the Ni in approximately tetrahedral coordination. The interplane angle between the P(1)−Ni(1)−P(3) and C(91)−Ni(1)−C(92) planes is 92.8°. The cavity-wall phenyl rings have bent apart to accommodate the $Ni(CO)_2$ group, rather than the coordination around Ni being distorted toward square planar geometry. In **2**, the cavity rings are 6.5 Å apart at their midpoints with an interplane dihedral angle of 40.8°. In **15**, the phenyl rings are forced to 8.3 Å apart at their midpoints and to a dihedral angle of 84.2°. The cavity P···P distance has decreased to 3.0 Å, most likely due to the small P−Ni−P angle (89.9°). Because of the decreased P···P distance, the orthophenylene (C_6H_4) ring midpoint interplane distance has increased from 4.3 Å in **2** to 5.4 Å in **15**.

Conclusions

Cyclotetraphosphazane **1** is readily oxidized regioselectively at the *exo*-phosphorus atoms [P(2,4)] to form the disulfide and dioxide derivatives **2** and **4** which are nearly structurally identical. Silver ion (Ag^+) also likely preferentially coordinates **1** at the *exo*-phosphorus position(s). In contrast, substitution at the cyclotetraphosphazane *endo*-phosphorus [P(1,3)] sites occurs with a high degree of selectivity. Thus, two oxygen atoms can be accommodated in the molecular cavity; however, with the larger sulfur atoms, it is only under highly forcing conditions that the additional two S atoms to form tetrasulfide **11** can be inserted. Addition of the second S atom into the

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[44] Shaw, R. A. *Phosphorus Sulfur Relat. Elem.* **1978**, *4*, 101.

[45] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, Pergamon Press: Oxford, U.K., 1984.

cavity occurs with considerable structural distortion of the basic eight-membered P_4N_4 ring system. It was not possible to insert Se or Te atoms or BH_3 or CH_3^+ moieties into the cavity.

With respect to metals, the relatively small Ag^+ ion and tetrahedrally-coordinating $Ni(CO)_2$ unit insert into the cavity of **2**, to form **12** and **15**, respectively; however, the more sterically demanding $Mo(CO)_3$ or $Mo(CO)_4$ fragments do not. In the case of Ag^+ coordination, when the Ag^+ source is $AgNO_3$, a suprising subsequent oxidation of the P(1,3) phosphorus atoms of **2** occurs in a process where activation towards oxidation is attributed to the proximate coordination of $AgNO_3$ in the molecular cavity. It appears that the cavity selectvity toward guest atoms and/or molecules is largely a function of kinetic steric inhibition; groups which exceed approximately 3.5 Å appear too large to coordinate within the cavity and form products. Further studies to determine more closely the size limits on stereoselectivity, and under what conditions unique reactivity resulting from the unusual coordination properties of the cavity might be seen, are in progress.

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Supporting Information Available: Tables of crystal data and refinement details, anisotropic thermal parameters, hydrogen atom positions, complete bond distances and angles, and least-squares planes (36 pages). Ordering information is given on any current masthead page.

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