New Cleft-Containing Heterosubstituted Cyclophosphazanes

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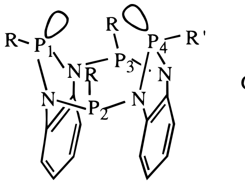
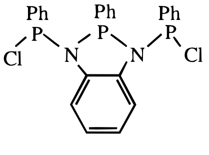
Molecules which contain donor atoms or reactive bonds within a molecular cavity or cleft are interesting because the chemistry within these regions can be unique.[1−4] Recently we reported such cyclotetraphosph(III)azanes, $[C_6H_4N_2(PR)_2]_2$ (**1**, **2**), molecules that are unusual because they incorporate an eight-membered P_4N_4 ring into a rigid orthocyclophane system.[5,6] The P(1,4) atoms possess lone-pair electrons which point into a molecular cleft formed between the upward pointing substituents on P(2,3). Preliminary studies showed that **1** displays highly selective and sometimes unusual coordination chemistry toward transition metals or metal moieties.[5b] Unfortunately, to date it has been possible to obtain **1** or **2** only from $RPCl_2$/1,2-$(NH_2)_2C_6H_4$ condensation reactions among mixtures of linear oligomers/polymers and phosphazane redox products.[6] We now report a synthetic route to these which not only is highly efficient but also allows synthesis of new classes of heteroatom-substituted derivatives.



1, R, R' = Ph; **2**, R, R' = Me
5, R = Ph, R' = Me



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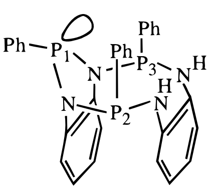
Triphosphazane **3**[6] reacts with 1,2-$(NH_2)C_6H_4$ and Et_3N in acetonitrile to precipitate $[Et_3NH]Cl$ and form cyclotriphosphazane **4**.[7] Compound **4** is the major product; only minor quantities of **1** and other unidentified phosphazanes are seen in the ^{31}P NMR spectrum of the reaction mixture. There is no evidence for other isomers of **4**. Cyclophosphazane **4** shows the expected spectral properties; the AX_2 ^{31}P NMR spectrum consists of coupled doublet (area 2) and triplet (area 1) resonances.



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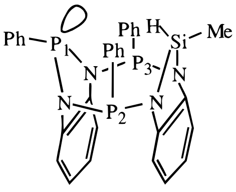

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Reactions of **4** with $RPCl_2$ (R = Me, Ph) or MeSi(H)Cl_2 and Et_3N in acetonitrile yield **1** and the heterosubstituted cyclophosphazanes **5** and **6**.[8,9] Whereas the $RPCl_2$ reactions proceed readily at 25 °C, the MeSi(H)Cl reaction requires a 2 h reflux. The ^{31}P NMR spectrum of **5** consists of two area 1 doublets ($J_{P1\cdots P4}$) of triplets ($^2J_{PNP}$) and an area 2 apparent triplet assigned to atoms P(1), P(4), and P(2,3), respectively. The spectrum of **6** is a coupled area 2 doublet [P(2,3)] and an area 1 triplet [P(1)]. The $^2J_{PNP}$ couplings in **5** and **6** are closely similar, ranging from 16.6 to 19.5 Hz; the similarity of these in **5** causes the P(2,3) resonance to appear as a triplet. The close transannular proximity of P(1) and P(4) in **5** and P(1) and the Si−H hydrogen in **6** produces strong through-space coupling. The $J_{P1\cdots P4}$ of 93.0 Hz in **5** is comparable to those reported earlier in molecules that contain phosphorus atoms separated by too many bonds to show normal through-bond coupling, but which exist in conformations that allow through-space coupling.[10] This coupling causes the P(1) and P(4) resonances, otherwise expected to be triplets, to appear as doublets of triplets. Similarly, the $J_{P1\cdots H1}$ coupling of 11.0 Hz in **6** is suprisingly large, causing a doublet of quartets for the Si−H proton ^1H NMR spectral resonance. Since these effects occur in rigid molecules, where the structure in solution is likely to be close to that in the solid, **5** and **6** offer fertile ground for further theoretical studies of through-space coupling effects.

The structures of **4** (Figure 1) and **6** (Figure 2) are verified by X-ray single-crystal analysis;[11] the structure of **5** is inferred from

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(1) (a) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713. (b) Gutsche, C. D. *Calixarenes*; The Royal Society of Chemistry: Cambridge, U.K., 1989.

(2) Cram, D. J.; Cram, J. M. *Container Molecules and their Guests*; Royal Society of Chemistry: Cambridge, 1994.

(3) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.

(4) (a) Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321. (b) Gerson, F.; Knobel, J.; Buser, U.; Vogel, E.; Zehnder, M. *J. Am. Chem. Soc.* **1986**, *108*, 3781.

(5) (a) Barendt, J. M.; Bent, E. G.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 6883. (b) Barendt, J. M.; Bent, E. G.; Young, S. M.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1991**, *30*, 325.

(6) Hands, R. M.; Katz, S. A.; Young, S. M.; Imiolczyk, T. W.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.*, submitted for publication.

(7) The 1, 2-$(NH_2)_2C_6H_4$ (3.24 g, 30 mmol) in acetonitrile was added to a mixture of **3** (14.9 g, 30 mmol) and Et_3N (17 mL, 120 mmol). Solid $[Et_3NH]Cl$ was filtered; upon reduction of filtrate volume, **4** crystallized (6.4 g, 40%). $^{31}P\{^1H\}$NMR (C_6D_6): δ 93.4 [d, 2P, $^2J_{PP} = 8.3$ Hz; P(2,3)], 73.2 [t, 1P; P(1)]. ^1H NMR (CD_2Cl_2): δ 7.78−7.81 (complex mult, 4H; C_6H_4), 7.17−7.42 (complex mult, 15H; C_6H_5), 6.85−6.93 (complex mult, 4H; C_6H_4), 5.88 (br d, 2H; NH). Anal. Calcd for $C_{30}H_{25}N_4P_3$: 534.1292 amu. Found (accurate mass MS): 534.1298 amu.

(8) To **4** (0.72 g, 1.3 mmol) in acetonitrile and Et_3N (21 mL, 6 mmol) was added $MePCl_2$ (0.11 mL, 1.2 mmol) dropwise. After 2 h solid $[Et_3NH]$Cl was filtered off; crystallization yielded **5** (1.4 g, 80%). $^{31}P\{^1H\}$ (C_6D_6): δ 88.2 [d of t, 1P, $J_{P1\cdots P4} = 93.0$ Hz, $^2J_{PNP} = 19.4$ Hz; P(4)], 98.5 [d of t, 1P, $J_{P1\cdots P4} = 93.0$ Hz, $^2J_{PNP} = 16.6$ Hz; P(2)], 112.2 [d of d (apparent triplet), 2P, $^2J_{PNP} = 18.0$ Hz (mean); P(1,3)]. ^1H NMR (C_6D_6): δ 7.87−6.98 (complex mult, 19H; C_6H_5's, C_6H_4), 6.75−6.63 (complex mult, 4H; C_6H_4), 1.04 (d, 3H, $^2J_{PH} = 9.7$ Hz; CH_3). MS (EI^+): *m/e* $[M^+]$ 578 $[C_{31}H_{26}N_4P_4{}^+]$. IR (KBr): 2254 (ν_{SiH}) cm^{-1}. Anal. Calcd for $C_{31}H_{26}N_4P_4$: 578.1108. Found (accurate mass MS) 578.1124.

(9) Compound **4** (1.6 g, 3.1 mmol), Et_3N (2.0 mL, 15 mmol), and MeSi(H)Cl_2 (0.36 mL, 3.4 mmol) in acetonitrile were refluxed for 2 h. After cooling and filtration to remove $[Et_3NH]Cl$, crystallization yielded **6** (1.3 g, 70%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 113.2 [d, 2P, $^2J_{PP} = 19.5$ Hz; P(2,3)], 88.4 [br t, 1P; P(1)]. ^1H NMR (C_6D_6): δ 7.90−7.87 complex mult, 4H; C_6H_4), 7.58−6.88 (complex mult, 15H; C_6H_5), 6.77−6.67 (complex mult, 4H; C_6H_4), 6.30 (d of q, 1H, $J_{PH} = 11.0$ Hz, $J_{HH} = 1.87$ Hz; Si*H*), 0.16 (d, 3H, $J_{HH} = 1.97$ Hz; CH_3). Anal. Calcd for $C_{31}H_{27}N_4P_3Si$: 576.128 amu. Found (accurate mass MS): 576.1199 amu.

(10) Keat, R.; Murray, L.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1982**, 1503.

(11) (a) Crystals of **4**, from toluene. Crystal data (151 K): space group $P\bar{1}$; $a = 8.6689(8)$ Å, $b = 12.7115(2)$ Å, $c = 14.882(2)$ Å, $\alpha = 110.033(6)°$, $\beta = 101.039(9)°$, $\gamma = 96.837(5)°$, $V = 1481.6(2)$ Å^3, $Z = 2$, $d_{calcd} = 1.300$ Mg/m^3; Siemens SMART diffractometer, sealed tube radiation

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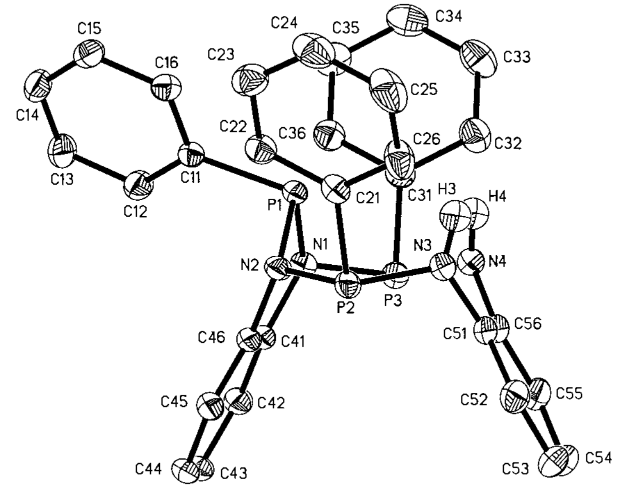

Figure 1. Structure and numbering scheme of **4**. Atoms are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P(1)−N(1), 1.7420(12); P(1)−N(2), 1.7507(12); P(2)−N(3), 1.7030(13); P(2)−N(2), 1.7423(12); P(3)−N(4), 1.7051(13); P(3)−N(1), 1.7395(12); N(3)−H(3), 0.890(8); N(4)−H(4), 0.893(8); N(1)−P(1)−N(2), 92.49(6); N(3)−P(2)−N(2), 108.10(6); N(4)−P(3)−N(1), 106.80(6); P(3)−N(1)−P(1), 120.16(7); P(2)−N(2)−P(1), 121.02(7); H(3)−N(3)−P(2), 118.5(12); H(4)−N(4)−P(3), 116.8(12).

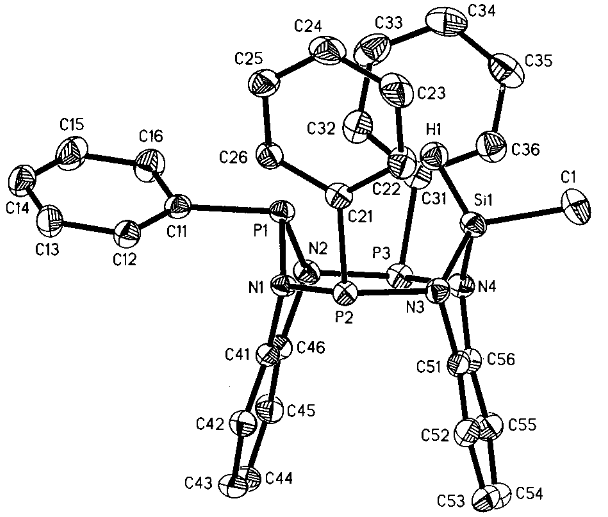

Figure 2. Structure and numbering scheme of **6**. Atoms are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si(1)−H(1), 1.38(2); Si(1)−N(4), 1.719(15); Si(1)−N(3), 1.7661(16); Si(1)−C(1), 1.848(2); P(1)−N(1), 1.7416(16); P(1)−N(2), 1.7506(15); P(2)−N(3), 1.7313(15); P(2)−N(1), 1.7354(15); P(3)−N(4), 1.7197(16); P(3)−N(2), 1.7564(16); H(1)−Si(1)−C(11), 110.2(9); H(1)−Si(1)−N(3), 114.7(9); H(1)−Si(1)−N(4), 115.7(9); N(4)−Si(1)−N(3), 94.94(7); N(4)−Si(1)−C(1), 109.95(9); N(3)−Si(1)−C(1), 110.56(9); N(1)−P(1)−N(2), 93.28(7); P(2)−N(3)−Si(1), 125.36(9); P(3)−N(4)−Si(1), 129.24(9).

spectral data. All contain 1,2-C_6H_4 groups bonded to adjacent nitrogen atoms in a cis orientation, thus providing the skeletal stabilization characteristic of molecules in this family.[5] Compound **6** is an analogue of **1** and **2**, in which a MeSi(H) moiety occupies one bowsprit position of the cyclophosphazane ring such that the Si−H bond points into the molecular cleft between the phenyl rings on phosphorus atoms P(2,3). In both **4** and **6**, the P(1) atoms are bonded to outward-pointing phenyl (exo) groups and contain inward pointing (*endo*) lone pairs, analogous to what is seen in **1**.[5] By analogy to that seen in **4** and **6**, it is assumed that in **5** the Ph and Me groups are also in exo positions. The absence of a bridging group in the bowsprit position of **4** leads to greater flexibility than is present in **1** and **6**. Distances between midpoints of both the 1,2-C_6H_4 groups (5.14 Å) and upward-pointing phenyl rings of **4** (7.85 Å), are appreciably greater than the corresponding distances (3.71 and 7.05 Å) and (4.01 and 6.72 Å) shown in **1** or **6**, respectively.[6] Bond distances in both **4** and **6** are as expected;[5,12,13] the mean P−N distances correspond closely to those observed earlier in **1** and its sulfide derivatives.[5]

Besides being a useful synthon for new heterosubstituted cyclophosphazanes, **4** might also be a novel PN_2-type tripodal ligand, capable of unique reactivity and coordination. Studies of **4**−**6** coordination chemistry and the use of **4** in the synthesis of other new skeletally stabilized cyclophosphazanes continue in our laboratories.

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Supporting Information Available: Crystallographic details and tables listing atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and nonbonded contacts (27 pages). Ordering information is given on any current masthead page.

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source; 6362 unique reflections of sphere 1.50° < θ < 28.27° collected and used in refinement. All non-hydrogen atoms refined anisotropically; hydrogen atoms rode on parent atoms; H(3) and H(4) were refined. No absorption correction applied; R1 [$I > 2\sigma(I)$] = 0.0358, wR2 (all data) = 0.0906, GOF = 1.031. (b) Crystals of **6**, from toluene. Crystal data (171 K): space group $P\bar{1}$; $a = 10.291(3)$ Å, $b = 17.108(8)$ Å, $c = 17.824(5)$ Å, $\alpha = 106.029(10)°$, $\beta = 106.254(6)°$, $\gamma = 96.298(8)°$, $V = 2835.4(18)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.351$ Mg/m^3; Siemens SMART diffractometer, MoKα sealed tube radiation source; 7480 unique reflections of sphere 1.47° < θ < 31.28° collected and used in the refinement. All non-hydrogen atoms refined anisotropically; hydrogen atoms rode on parent atom position; H(1) was refined. No absorption correction applied; R1 [$I > 2\sigma(I)$] = 0.0447, wR2 (all data) = 0.0980, GOF = 1.106.

(12) (a) Keat, R. *Top. Curr. Chem.* **1983**, *102*, 89. (b) Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101. (c) Zeiss, W.; Klehr, H. *Z. Naturforsch.* **1980**, *B35*, 1179.

(13) Corbridge, D. E. C. *The Structural Chemistry of Phosphorus*; Elsevier: Amsterdam, 1974.