

handedness of the structure was determined by a SHELXTL routine in which a variable of either 1 or -1 refines all  $\Delta f''$  values. Disorder in the two dichloromethane molecules was modeled by assigning 70, 70, and 60% weights to three chlorines of one molecule and 100, 60, and 40% weights to the three chlorines of the other. The carbons of these two molecules were not included in the structure factor calculation, although they did appear as small peaks in the final difference map. The carbon of the carbonyl group was reset during refinement to a distance of 1.85 (2) Å from the iridium. Phenyl rings were refined as rigid hexagons with C-C distances of 1.395 Å. Hydrogen atoms were included at calculated positions by using a riding model and C-H distances of 0.96 Å. The thermal parameters for the hydrogen atoms were fixed at 1.2 times the thermal parameter of the bonded carbon. Two low angle reflections, 020 and 002, were omitted from the data set, since they appeared to suffer from extinction. An absorption correction was applied.<sup>23</sup> Final refinement was carried out with anisotropic thermal parameters for the Ir, Pb, Cl, P, N, and O atoms. The largest peak in a final difference map had a value of 1.7 e Å<sup>-3</sup>, located 0.93 Å from Pb.

[ClSn(crown-P<sub>2</sub>)Ir(CO)Cl]I·3CH<sub>2</sub>Cl<sub>2</sub>. The structure was refined by direct methods with the Siemens SHELXTL PLUS (VMS) programs. No constraints were applied to the phenyl carbons; however, the Ir-C distance was reset to 1.85 (2) Å with each cycle of refinement. Neutral-atom scattering factors and corrections for anomalous dispersion were taken from a standard source. Hydrogen atoms were included at calculated positions by using a riding model and C-H distances of 0.96 Å. The thermal parameters for the hydrogen atoms were fixed at a *U* of 0.04 Å<sup>2</sup>. The handedness was determined as above. An absorption correction was applied. Final refinement was carried out with anisotropic thermal pa-

rameters for the Ir, Sn, Cl, and P atoms. The largest peak in a final difference map had a value of 3.0 e Å<sup>-3</sup>, 1.2 Å from Sn(2).

[K(crown-P<sub>2</sub>)Ir(CO)I]I·3CH<sub>2</sub>Cl<sub>2</sub>. Determination of the space group followed from the observed conditions  $0kl$ ,  $k = 2n$ ,  $h0l$ ,  $l = 2n$ , and  $hko$ ,  $h = 2n$ . The structure was solved by direct methods with the Siemens SHELXTL PLUS (VMS) programs. Hydrogen atoms were included at calculated positions by using a riding model and C-H distances of 0.96 Å. The thermal parameters for the hydrogen atoms were fixed at a *U* = 0.03 Å<sup>2</sup> except for those of the dichloromethanes, which were fixed at 0.06 Å<sup>2</sup>. An absorption correction was applied. Final refinement was carried out with anisotropic thermal parameters for the Ir, K, Cl, P, and I atoms. The largest peak in a final difference map had a value of 1.2 e Å<sup>-3</sup>, 1.3 Å from I(2).

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**Registry No.** 9-CHCl<sub>3</sub>, 135107-48-1; 10, 135107-50-5; 11, 135107-52-7; 12-Cl, 135107-47-0; 12-Cl·2CH<sub>2</sub>Cl<sub>2</sub>, 135107-63-0; 12-BPh<sub>4</sub>, 135107-54-9; 13 (X = Br), 135107-57-2; 13 (X = I), 135107-58-3; 14, 135107-60-7; (crown-P<sub>2</sub>)Ir(CO)Cl, 132673-23-5; [Na(crown-P<sub>2</sub>)Ir(CO)Cl][BPh<sub>4</sub>], 135107-56-1; [K(crown-P<sub>2</sub>)Ir(CO)I]I, 135107-61-8; [K(crown-P<sub>2</sub>)Ir(CO)I]I·3CH<sub>2</sub>Cl<sub>2</sub>, 135107-64-1.

**Supplementary Material Available:** Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal refinement data for [ClPb(crown-P<sub>2</sub>)Ir(CO)Cl]·Cl·2CH<sub>2</sub>Cl<sub>2</sub>, [ClSn(crown-P<sub>2</sub>)Ir(CO)Cl](SnCl<sub>3</sub>)·CHCl<sub>3</sub>, and [K(crown-P<sub>2</sub>)Ir(CO)I]I·3CH<sub>2</sub>Cl<sub>2</sub> (21 pages); listings of observed and calculated structure factors (63 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, The University of Calgary, Calgary, Alberta, T2N 1N4, Canada, and Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

## Preparation of 1,1,5,5-Tetraphenyl-3,7-diaryl-1,5-diphosphatetrazocines and 1,1,3,3,5-Pentaphenyldiphosphatriazine and the X-ray Structure of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>

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The reactions of Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] or ArCN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> (Ar = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4, C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-4) with Ph<sub>2</sub>PCl<sub>3</sub> produce 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>Ar<sub>2</sub> (Ar = C<sub>6</sub>H<sub>5</sub> (4a), 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (4c)) and, as a minor product, the six-membered ring Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>CPh (1b). Compound 1b is also obtained from the reaction of PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPPh<sub>2</sub>) with 2 molar equiv of benzeneselenenyl chloride in CH<sub>2</sub>Cl<sub>2</sub>. Compounds 1b and 4a-c exhibit high thermal stability with no indication of polymer formation below 250 °C. An X-ray structural determination of 4b showed that it consists of an eight-membered ring in a distorted boat-boat conformation with the phosphorus atoms out of and on the same side of the plane and the carbon atoms on the other side of the plane. One of the nitrogen atoms also deviates significantly from the best plane. The crystals of 4b are monoclinic, space group *P*2<sub>1</sub>/*c*, with *a* = 17.236 (3) Å, *b* = 19.558 (1) Å, *c* = 20.694 (3) Å, β = 107.66 (1)°, *V* = 6647 (2) Å<sup>3</sup>, and *Z* = 8. Two crystallographically independent molecules of 4b are present in the asymmetric unit. The final *R* and *R<sub>w</sub>* values were 0.059 and 0.039, respectively. The average P-N and C-N bond lengths are ca. 1.60 and 1.31 Å, respectively, and the endocyclic bond angles at phosphorus are ca. 126°. There are two distinct bond angles at nitrogen for both molecules with values of ca. 127 and 139°.

### Introduction

Phosphorus-nitrogen heterocycles that contain a third heteroatom (heterocyclophosphazenes) are of interest from the viewpoint of structure and bonding<sup>1</sup> and as precursors for inorganic polymers with unusual properties.<sup>2</sup> Several examples of the hybrid inorganic ring systems P<sub>2</sub>N<sub>3</sub>C (diphosphatriazines) (1)<sup>3</sup> and PN<sub>3</sub>C<sub>2</sub> (phosphatriazines) (2)<sup>4</sup> are known, and very recently the first examples of poly(carbophosphazenes) have been obtained via

thermolysis of 1a.<sup>2c</sup> Two derivatives of the eight-membered 1,3- and 1,5-P<sub>2</sub>N<sub>4</sub>C<sub>2</sub> rings (diphosphatetrazocines), 3 and 4 (R = Ph,

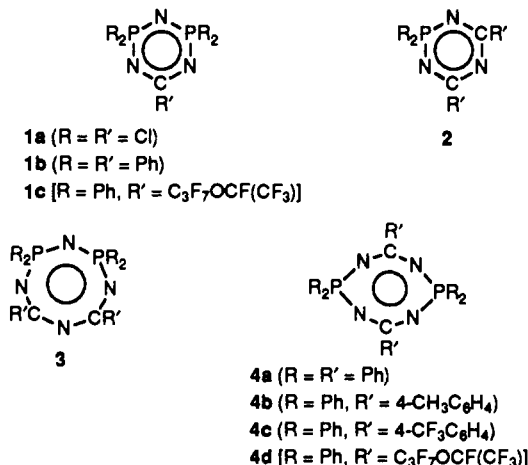
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R' = perfluoroalkyl ether), have also been prepared.<sup>5</sup> To date, however, there have been no structural studies of these PNC heterocycles, with the exception of the 12-membered ring (Cl<sub>2</sub>PN<sub>2</sub>CCl)<sub>3</sub>.<sup>6</sup>

The trifunctional reagents ArCN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub><sup>7</sup> are potential sources of ring systems of type 4 via cyclocondensation reactions with phosphorus(V) halides. In this investigation, we have examined the reactions of trisilylated amidines with Ph<sub>2</sub>PCl<sub>3</sub>, PhPCl<sub>4</sub>, and PCl<sub>5</sub>. In the case of Ph<sub>2</sub>PCl<sub>3</sub>, this reaction produced the heterocycles 4a–c and, as a minor product, 1b. The first X-ray structural characterization of a P<sub>2</sub>N<sub>4</sub>C<sub>2</sub> ring, 4b, is also reported. In contrast, the reaction of PhCN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> with phosphorus(III) halides R<sub>2</sub>PCl<sub>2</sub> (R = Ph,<sup>8a</sup> (Me<sub>3</sub>Si)<sub>2</sub>CH<sup>8b</sup>) yields either a bicyclic system (R = Ph) or a five-membered ring [R = (Me<sub>3</sub>Si)<sub>2</sub>CH], both of which contain phosphorus(III)–phosphorus(V) linkages.



## Experimental Section

**Reagents and General Procedures.** All experiments were performed under an atmosphere of dry nitrogen (99.99% purity). Solvents were dried by heating under reflux with the appropriate drying agents: methylene dichloride and carbon tetrachloride (P<sub>4</sub>O<sub>10</sub>), tetrahydrofuran (CaH<sub>2</sub>), pentane and hexane (CaH<sub>2</sub>), and acetonitrile (P<sub>4</sub>O<sub>10</sub>, CaH<sub>2</sub>). They were then distilled and stored in bottles fitted with a Teflon stopcock and a septum-sealed T-joint.

The following commercially available reagents were used as received: PCl<sub>3</sub>, PhPCl<sub>2</sub>, and Ph<sub>2</sub>PCl (all from Alfa), PhSeCl, PhCN, and (Me<sub>3</sub>Si)<sub>2</sub>NH (all from Aldrich), and *n*-BuLi in hexane (Alfa). Ph<sub>2</sub>PCl<sub>3</sub> (δ<sup>31</sup>P) +42.6 ppm) and PhPCl<sub>4</sub> (δ<sup>31</sup>P) +34.1 ppm) were obtained by treatment of Ph<sub>2</sub>PCl and PhPCl<sub>2</sub>, respectively, with an equimolar amount of SO<sub>2</sub>Cl<sub>2</sub> in carbon tetrachloride at -15 °C. This procedure was found to be preferable to the literature method, which uses gaseous Cl<sub>2</sub>,<sup>9</sup> because the amount of chlorinating agent is more easily controlled and complications due to the use of an excess of Cl<sub>2</sub> are thus avoided. The reagents Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] and ArCN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> (Ar = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4, C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-4) were prepared by the literature methods.<sup>7</sup>

**Instrumentation.** Infrared spectra were recorded as Nujol mulls on KBr windows by using a Nicolet DX-5 FTIR spectrometer. <sup>1</sup>H NMR spectra were obtained on a Bruker ACE 200 spectrometer, and chemical shifts are reported relative to Me<sub>4</sub>Si. <sup>31</sup>P NMR spectra were recorded on a Varian XL-200 instrument, and <sup>31</sup>P chemical shifts are referenced to external 85% H<sub>3</sub>PO<sub>4</sub>. Mass spectra were obtained by using a Kratos

Table I. Crystallographic Data for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>

chem formula: C <sub>40</sub> H <sub>34</sub> N <sub>4</sub> P <sub>2</sub>	fw: 632.68
a = 17.236 (3) Å	space group: P <sub>2</sub> /c, No. 14
b = 19.558 (1) Å	T = 23 (2) °C
c = 20.694 (3) Å	λ = 0.71073 Å
β = 107.66 (1)°	ρ <sub>calcd</sub> = 1.264 g cm <sup>-3</sup>
V = 6647 (2) Å <sup>3</sup>	μ = 1.6 cm <sup>-1</sup>
Z = 8	R = 0.059
	R <sub>w</sub> = 0.039

MS80 RFA instrument operating at 70 eV. Chemical analyses were performed by the Analytical Services Division of the Department of Chemistry, The University of Calgary. Melting points were obtained in sealed glass capillaries and are uncorrected.

**Reaction of Ph<sub>2</sub>PCl<sub>3</sub> with Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>].** A solution of Ph<sub>2</sub>PCl<sub>3</sub> (1.58 g, 5.4 mmol) in THF (30 mL) was added dropwise to Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] (5.4 mmol) in THF (20 mL) at -78 °C. The reaction mixture was stirred at 23 °C for 16 h, and then solvent was removed under vacuum to give a yellow solid, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-pentane to give white crystals of Ph<sub>4</sub>P<sub>2</sub>N<sub>3</sub>CPh (100 mg, 0.20 mmol), mp 225 °C. Anal. Calcd for C<sub>31</sub>H<sub>25</sub>N<sub>3</sub>P<sub>2</sub>: C, 74.25; H, 5.02; N, 8.38. Found: C, 74.36; H, 5.18; N, 8.24. NMR (δ, ppm): <sup>31</sup>P in CH<sub>2</sub>Cl<sub>2</sub>, +18.4. MS (EI, 70 eV) [m/e (%): 501 (100), M<sup>+</sup>. IR (Nujol, cm<sup>-1</sup>): 1439 vs, 1422 s, 1360 vs, 1183 m, 1130 vs, 1121 vs, 1097 m, 1025 m, 931 m, 888 m, 863 m, 751 m, 747 sh, 725 vs, 696 s, 692 s, 545 vs, 522 s, 450 m. Solvent was evaporated from the mother liquor to give white crystals of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>Ph<sub>2</sub> (500 mg, 0.83 mmol, 31%), mp 115 °C. Anal. Calcd for C<sub>38</sub>H<sub>30</sub>N<sub>4</sub>P<sub>2</sub>: C, 75.49; H, 5.00; N, 9.27. Found: C, 75.05; H, 4.94; N, 9.11. NMR (δ, ppm): <sup>31</sup>P in CH<sub>2</sub>Cl<sub>2</sub>, +0.3. IR (Nujol, cm<sup>-1</sup>): 1596 s, 1547 s, 1522 s, 1517 s, 1510 s, 1496 s, 1419 vs, 1395 vs, 1301 m, 1113 s, 1027 m, 961 m, 927 m, 902 m, 872 s, 748 s, 725 vs, 691 vs, 647 m, 537 s, 525 s.

**Reaction of Ph<sub>2</sub>PCl<sub>3</sub> with 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub>.** A solution of 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> (0.84 g, 2.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dropwise to a solution of Ph<sub>2</sub>PCl<sub>3</sub> (0.70 g, 2.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at -78 °C. The mixture was stirred for 16 h at 23 °C and then solvent was removed under vacuum to give a viscous solid. This residue was washed with acetonitrile (20 mL) and dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The removal of solvent under vacuum gave 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub> as a white solid (80 mg, 0.13 mmol, 11%), which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:1) to give an analytically pure sample, mp 239–240 °C. Anal. Calcd for C<sub>40</sub>H<sub>34</sub>N<sub>4</sub>P<sub>2</sub>: C, 75.94; H, 5.42; N, 8.86. Found: C, 75.85; H, 5.32; N, 8.93. NMR (δ, ppm): <sup>1</sup>H in CDCl<sub>3</sub>, 8.53–7.19 (m, 28 H, C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>4</sub>), 2.49 (s, 6 H, CH<sub>3</sub>); <sup>31</sup>P in CH<sub>2</sub>Cl<sub>2</sub>, -0.6. IR (Nujol, cm<sup>-1</sup>): 1594 vs, 1584 vs, 1553 vs, 1479 s, 1438 s, 1432 s, 1401 s, 1386 vs, 1372 vs, 1303 m, 1290 m, 1178 m, 1158 m, 1115 s, 1109 s, 1027 m, 1021 m, 872 s, 835 m, 828 m, 796 m, 750 s, 741 s, 724 vs, 692 s, 593 m, 534 vs, 508 m, 481 m, 455 m, 435 m, 427 m.

**Reaction of Ph<sub>2</sub>PCl<sub>3</sub> with 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub>.** A solution of 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> (1.0 g, 2.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise to a solution of Ph<sub>2</sub>PCl<sub>3</sub> (0.73 g, 2.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at -78 °C. The reaction mixture was stirred at 23 °C for 16 h, and then solvent was removed under vacuum. The solid residue was washed with acetonitrile to give a white solid (150 mg, 0.20 mmol, 16%), which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to give white crystals of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>-4)<sub>2</sub>, mp 230–232 °C. Anal. Calcd for C<sub>40</sub>H<sub>28</sub>F<sub>6</sub>N<sub>4</sub>P<sub>2</sub>: C, 64.87; H, 3.81; N, 7.57. Found: C, 64.06; H, 3.86; N, 7.22. NMR (δ, ppm): <sup>31</sup>P in CH<sub>2</sub>Cl<sub>2</sub>, +1.8. IR (Nujol, cm<sup>-1</sup>): 1593 m, 1556 m, 1518 s, 1500 vs, 1446 s, 1428 m, 1411 m, 1400 vs, 1325 vs, 1156 m, 1119 vs, 1066 s, 1018 m, 967 m, 892 s, 852 m, 767 m, 726 vs, 694 s, 653 m, 624 m, 551 s, 522 s, 508 m, 466 m, 429 m.

**Preparation of PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPPh<sub>2</sub>).**<sup>10</sup> Benzonitrile (10.3 g, 0.1 mol) was added dropwise to a solution of (Me<sub>3</sub>Si)<sub>2</sub>NLi (0.1 mol) in THF (100 mL), which was prepared at 0 °C from (Me<sub>3</sub>Si)<sub>2</sub>NH (0.1 mol) and *n*-BuLi (0.1 mol, 2.5 M solution in hexane). The reaction mixture was stirred at 23 °C for 2 h and then cooled to -78 °C. Chlorodiphenylphosphine (22.1 g, 0.1 mol) in THF (50 mL) was added dropwise, and the reaction mixture was stirred and allowed to reach room temperature. The precipitate of LiCl was removed by filtration and solvent was evaporated under vacuum. The residue was treated with *n*-hexane (2 × 100 mL), and then hexane was removed under vacuum to give a red viscous oil (39.2 g, 0.088 mol). Yellow crystals of PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPPh<sub>2</sub>) were obtained by recrystallization from pentane, mp 71–72 °C.

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**Table II.** Atomic Coordinates and Isotropic Thermal Parameters for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>

	x	y	z	$U_{eq}^a \text{ \AA}^2$		x	y	z	$U_{eq}^a \text{ \AA}^2$
Molecule A									
P(1)	0.21308 (9)	0.46798 (8)	0.16774 (8)	0.0380 (6)	C(19)	0.1515 (5)	0.5395 (4)	-0.0245 (3)	0.069 (3)
P(2)	0.38956 (9)	0.44911 (9)	0.29936 (8)	0.0370 (6)	C(20)	0.0824 (5)	0.5750 (4)	-0.0297 (4)	0.069 (3)
N(1)	0.2303 (3)	0.5282 (2)	0.2224 (2)	0.043 (2)	C(21)	0.0526 (4)	0.5792 (4)	0.0233 (4)	0.070 (3)
N(2)	0.3640 (3)	0.5283 (2)	0.3008 (2)	0.036 (2)	C(22)	0.0920 (4)	0.5469 (3)	0.0840 (3)	0.053 (3)
N(3)	0.4054 (3)	0.4115 (2)	0.2359 (2)	0.040 (2)	C(23)	0.1382 (3)	0.4145 (3)	0.1869 (3)	0.039 (3)
N(4)	0.2783 (3)	0.4183 (2)	0.1498 (2)	0.041 (2)	C(24)	0.1171 (4)	0.3529 (4)	0.1545 (3)	0.056 (3)
C(1)	0.2896 (4)	0.5527 (3)	0.2721 (3)	0.037 (2)	C(25)	0.0600 (5)	0.3122 (4)	0.1686 (4)	0.077 (3)
C(2)	0.3525 (3)	0.3976 (3)	0.1760 (3)	0.033 (2)	C(26)	0.0231 (5)	0.3309 (5)	0.2152 (4)	0.085 (4)
C(3)	0.2699 (4)	0.6177 (3)	0.3017 (3)	0.038 (3)	C(27)	0.0420 (5)	0.3922 (5)	0.2463 (4)	0.087 (4)
C(4)	0.3191 (4)	0.6440 (3)	0.3618 (3)	0.051 (3)	C(28)	0.0995 (4)	0.4338 (4)	0.2328 (3)	0.059 (3)
C(5)	0.2963 (4)	0.7016 (4)	0.3890 (3)	0.054 (3)	C(29)	0.4870 (3)	0.4438 (3)	0.3621 (3)	0.041 (3)
C(6)	0.2254 (4)	0.7357 (3)	0.3594 (3)	0.052 (3)	C(30)	0.5121 (4)	0.4915 (4)	0.4121 (3)	0.061 (3)
C(7)	0.1766 (4)	0.7098 (4)	0.2987 (3)	0.061 (3)	C(31)	0.5844 (4)	0.4854 (4)	0.4625 (3)	0.072 (3)
C(8)	0.1972 (4)	0.6522 (3)	0.2706 (3)	0.053 (3)	C(32)	0.6330 (4)	0.4315 (5)	0.4626 (3)	0.070 (4)
C(9)	0.2003 (4)	0.7981 (3)	0.3910 (3)	0.082 (3)	C(33)	0.6107 (4)	0.3837 (4)	0.4141 (4)	0.081 (3)
C(10)	0.3828 (3)	0.3483 (3)	0.1332 (3)	0.028 (2)	C(34)	0.5373 (4)	0.3892 (4)	0.3635 (3)	0.073 (3)
C(11)	0.4577 (4)	0.3161 (3)	0.1578 (3)	0.048 (3)	C(35)	0.3204 (3)	0.3981 (3)	0.3299 (3)	0.038 (3)
C(12)	0.4823 (4)	0.2695 (3)	0.1178 (3)	0.056 (3)	C(36)	0.3016 (4)	0.3324 (4)	0.3075 (3)	0.051 (3)
C(13)	0.4360 (4)	0.2551 (3)	0.0538 (3)	0.040 (3)	C(37)	0.2481 (5)	0.2950 (4)	0.3318 (4)	0.071 (4)
C(14)	0.3633 (4)	0.2884 (3)	0.0297 (3)	0.041 (3)	C(38)	0.2146 (4)	0.3223 (5)	0.3775 (4)	0.075 (4)
C(15)	0.3373 (3)	0.3339 (3)	0.0687 (3)	0.037 (2)	C(39)	0.2338 (4)	0.3863 (5)	0.3989 (4)	0.073 (4)
C(16)	0.4632 (4)	0.2028 (3)	0.0108 (3)	0.070 (3)	C(40)	0.2859 (4)	0.4253 (3)	0.3757 (3)	0.053 (3)
C(17)	0.1620 (3)	0.5100 (3)	0.0900 (3)	0.035 (2)					
C(18)	0.1911 (3)	0.5068 (3)	0.0356 (3)	0.048 (3)					
Molecule B									
P(3)	0.11202 (9)	0.02829 (9)	0.20087 (8)	0.0395 (6)	C(59)	-0.0788 (4)	-0.0140 (4)	0.0369 (3)	0.067 (3)
P(4)	0.28861 (9)	0.01346 (9)	0.33335 (8)	0.0389 (6)	C(60)	-0.1295 (4)	0.0397 (5)	0.0349 (3)	0.086 (4)
N(5)	0.0947 (3)	0.0660 (2)	0.2638 (2)	0.044 (2)	C(61)	-0.1094 (5)	0.0871 (5)	0.0846 (4)	0.128 (5)
N(6)	0.2231 (3)	0.0631 (2)	0.3500 (2)	0.041 (2)	C(62)	-0.0391 (4)	0.0824 (4)	0.1360 (3)	0.090 (4)
N(7)	0.2719 (3)	-0.0511 (2)	0.2842 (2)	0.045 (2)	C(63)	0.1788 (3)	0.0809 (4)	0.1698 (3)	0.038 (3)
N(8)	0.1420 (3)	-0.0499 (2)	0.2005 (2)	0.047 (2)	C(64)	0.1836 (4)	0.1504 (4)	0.1818 (3)	0.062 (3)
C(41)	0.1471 (3)	0.0821 (3)	0.3217 (3)	0.036 (2)	C(65)	0.2346 (5)	0.1908 (4)	0.1581 (4)	0.082 (4)
C(42)	0.2148 (3)	-0.0751 (3)	0.2321 (3)	0.039 (3)	C(66)	0.2812 (5)	0.1639 (5)	0.1224 (4)	0.085 (4)
C(43)	0.1155 (3)	0.1317 (3)	0.3626 (3)	0.032 (2)	C(67)	0.2773 (5)	0.0944 (5)	0.1101 (4)	0.080 (4)
C(44)	0.1588 (3)	0.1481 (3)	0.4284 (3)	0.042 (3)	C(68)	0.2271 (4)	0.0539 (4)	0.1338 (3)	0.055 (3)
C(45)	0.1301 (4)	0.1950 (3)	0.4650 (3)	0.044 (3)	C(69)	0.3456 (3)	-0.0205 (3)	0.4149 (3)	0.037 (3)
C(46)	0.0579 (4)	0.2280 (3)	0.4383 (3)	0.043 (3)	C(70)	0.3637 (3)	0.0197 (3)	0.4714 (3)	0.057 (3)
C(47)	0.0139 (3)	0.2122 (3)	0.3733 (3)	0.055 (3)	C(71)	0.4094 (4)	-0.0042 (4)	0.5327 (3)	0.061 (3)
C(48)	0.0413 (3)	0.1649 (3)	0.3363 (3)	0.047 (3)	C(72)	0.4372 (4)	-0.0697 (4)	0.5389 (3)	0.060 (3)
C(49)	0.0292 (4)	0.2786 (3)	0.4805 (3)	0.074 (3)	C(73)	0.4201 (4)	-0.1113 (4)	0.4847 (4)	0.083 (3)
C(50)	0.2351 (4)	-0.1409 (3)	0.2045 (3)	0.039 (3)	C(74)	0.3748 (4)	-0.0861 (4)	0.4226 (3)	0.068 (3)
C(51)	0.3052 (4)	-0.1759 (3)	0.2334 (3)	0.055 (3)	C(75)	0.3602 (3)	0.0675 (4)	0.3093 (3)	0.040 (3)
C(52)	0.3240 (4)	-0.2357 (4)	0.2068 (3)	0.064 (3)	C(76)	0.3682 (4)	0.1342 (4)	0.3271 (4)	0.069 (3)
C(53)	0.2736 (4)	-0.2620 (3)	0.1476 (3)	0.048 (3)	C(77)	0.4252 (5)	0.1747 (4)	0.3117 (5)	0.091 (4)
C(54)	0.2034 (4)	-0.2264 (4)	0.1188 (3)	0.066 (3)	C(78)	0.4738 (5)	0.1487 (6)	0.2772 (5)	0.100 (5)
C(55)	0.1853 (4)	-0.1673 (3)	0.1457 (3)	0.056 (3)	C(79)	0.4669 (5)	0.0822 (6)	0.2594 (4)	0.098 (5)
C(56)	0.2941 (4)	-0.3275 (3)	0.1198 (3)	0.078 (3)	C(80)	0.4109 (4)	0.0420 (4)	0.2752 (3)	0.072 (3)
C(57)	0.0140 (3)	0.0302 (3)	0.1375 (3)	0.043 (3)					
C(58)	-0.0068 (3)	-0.0182 (4)	0.0879 (3)	0.057 (3)					

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j a_i a_j$$

Anal. Calcd for C<sub>25</sub>H<sub>33</sub>N<sub>2</sub>PSi<sub>2</sub>: C, 66.92; H, 7.41; N, 6.24. Found: C, 66.42; H, 7.38; N, 6.13. IR (cm<sup>-1</sup>): 1590 s, 1574 s, 1566 s, 1445 s, 1434 s, 1253 s, 1241 m, 1172 m, 1083 s, 1067 s, 1023 m, 938 s, 921 s, 909 m, 883 s, 838 s, 825 s, 788 s, 763 m, 750 m, 739 s, 694 s, 680 m, 511 s, 492 m, 415 m. NMR spectra ( $\delta$ , ppm): <sup>1</sup>H in CDCl<sub>3</sub>, 7.63–7.27 (m, 15 H, C<sub>6</sub>H<sub>5</sub>), 0.12 (s, 18 H, Me<sub>2</sub>Si); <sup>31</sup>P in CH<sub>2</sub>Cl<sub>2</sub>, +35.1.

#### Reaction of PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPH<sub>2</sub>) with Benzeneselenenyl Chloride.

A solution of benzeneselenenyl chloride (1.38 g, 7.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dropwise to a solution of PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPH<sub>2</sub>) (1.61 g, 3.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C. The reaction mixture was stirred at 23 °C for 16 h, and then solvent was removed under vacuum. The residue was washed with hexane (2 × 25 mL) and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to give white crystals of Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>CPh (150 mg, 0.30 mmol). Anal. Calcd for C<sub>31</sub>H<sub>25</sub>N<sub>3</sub>P<sub>2</sub>: C, 74.25; H, 5.02; N, 8.38. Found: C, 73.53; H, 4.99; N, 8.31. NMR ( $\delta$ , ppm): <sup>31</sup>P in CH<sub>2</sub>Cl<sub>2</sub>, +18.35. The IR spectrum was identical with that of an authentic sample of Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>CPh. No other pure product could be isolated from the mother liquor. Solvent was removed from the hexane extract to give Ph<sub>2</sub>Se<sub>2</sub> (0.81 g, 2.6 mmol).

**X-ray Analysis of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>.** A suitable colorless crystal with approximate dimensions of 0.18 × 0.25 × 0.20 mm, obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexane, was glued on the top of a glass fiber and mounted on an Enraf-Nonius CAD-4F diffractometer. Unit cell dimensions and their standard deviations were determined from the

setting angles of 15 reflections in the range 20.14° <  $\theta$  < 20.87° in four alternate settings.<sup>11</sup> The scattering power of the studied crystals was weak, and no observable intensities could be measured with  $\theta > 21^\circ$ . The space group was derived from the observed systematic absences and checked for the presence of higher metrical symmetry.<sup>12</sup> Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 2 h of X-ray exposure time; there was no indication of crystal decomposition. A 360°  $\psi$ -scan for a reflection close to axial (0,-8,0) showed a variation in intensity of less than 2% about the mean value. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects, but not for absorption. Standard deviations  $\sigma(I)$  in the intensities were increased according to an analysis of the excess variance of the reference reflection: Variance was calculated based on counting statistics and the term ( $P^2/I^2$ ) where  $P$  (=0.025) is the instability constant<sup>13</sup> as derived from the excess variance in the reference reflections. To provide an adequate ratio of observations to parameters, only reflections where  $I$  was less than 2.0 $\sigma(I)$  were considered unobserved and were not included

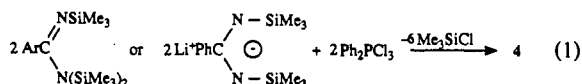
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in the refinement. The structure was solved by direct methods with SHELXS86,<sup>14</sup> and the positional and anisotropic thermal parameters for the nonhydrogen atoms were refined with block-diagonal least-squares procedures (XTAL), minimizing the function  $Q = \sum_i [w(|F_o| - |F_c|)^2]$ . Most of the hydrogen atom positions could be located on a difference Fourier map. The hydrogen atoms were ultimately included with their positions calculated by using sp<sup>2</sup> or sp<sup>3</sup> hybridization at the C atom as appropriate and a fixed C-H distance of 1.0 Å; thereby, the found H atoms served to determine the conformation of the methyl groups. Due to the low observation to parameter ratio in the final calculation, H atoms were refined in the riding mode with a fixed C-H bond length of 1.0 Å and one common temperature factor. Weights were introduced in the final refinement cycles. Refinement on *F* by blocked full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one common isotropic thermal parameter for the hydrogen atoms converged at  $R = 0.059$  ( $R_w = 0.039$ ). The asymmetric unit contains two independent molecules. In the refinement each block contains the parameters of one independent molecule. A final difference Fourier map did not show residual peaks outside the range  $\pm 0.32$  e/Å<sup>3</sup>. The details of the final refinements are included in Table I. The final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table II. Tables of hydrogen atom positions, thermal parameters, comprehensive lists of bond distances and tables of ( $F_o$ ), ( $F_c$ ), and  $\sigma(F)$  are given as supplementary material for this paper. Scattering factors were taken from Cromer and Mann.<sup>15</sup> Anomalous dispersion factors were taken from Cromer and Liberman<sup>16</sup> and were included in  $F_c$ . All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL,<sup>17</sup> EUCLID<sup>18</sup> (calculation of geometric data), and ORTEP.<sup>19</sup>

## Results and Discussion

### Synthesis of 1,5-Diphosphatetrazocines and Diphosphatriazines.

The reactions of the trisilylated amidines or Li[PhC(NSiMe<sub>3</sub>)<sub>2</sub>] with Ph<sub>2</sub>PCl<sub>3</sub> were shown by <sup>31</sup>P NMR spectroscopy to occur at room temperature in methylene dichloride to give a complex mixture of products. The cyclocondensation reaction (eq 1) was successful for the preparation of **4a-c** from Ph<sub>2</sub>PCl<sub>3</sub>,<sup>20</sup> but the yields were low ( $\leq 30\%$ ) and, in one case, **1b**, was also isolated as a minor product.<sup>21</sup> The formation of six-membered rings of types **1** and **2**, in addition to **4**, has been reported previously for the reaction of Ph<sub>2</sub>PCl<sub>3</sub> with the amidine, R<sub>F</sub>C(NH)(NH<sub>2</sub>) (R<sub>F</sub> = perfluoroalkyl ether).<sup>5</sup>



The <sup>31</sup>P NMR chemical shifts of **4a-c** are observed close to 0 ppm. In the case of **4a** the <sup>31</sup>P NMR resonance is ca. 20 ppm upfield of that of the related six-membered ring **1b**. A similar upfield shift is observed for eight-membered cyclophosphazenes compared to their six-membered homologues.<sup>22</sup>

1,5-Diphosphatetrazocines are potential precursors of polymers with alternating R<sub>2</sub>PN and RCN units in the backbone via ring opening thermolysis. The new heterocycles **4a-c** exist as air-stable, colorless crystals, which exhibit weak molecular ions in the

**Table III.** Selected Bond Lengths (Å) and Bond Angles (deg) for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>

molecule A		molecule B	
Distances			
P(1)-N(1)	1.597 (4)	P(3)-N(5)	1.602 (5)
P(1)-N(4)	1.612 (5)	P(3)-N(8)	1.615 (4)
P(1)-C(17)	1.783 (6)	P(3)-C(57)	1.798 (6)
P(1)-C(23)	1.797 (6)	P(3)-C(63)	1.802 (7)
P(2)-N(2)	1.613 (4)	P(4)-N(6)	1.604 (5)
P(2)-N(3)	1.599 (5)	P(4)-N(7)	1.592 (4)
P(2)-C(29)	1.787 (6)	P(4)-C(69)	1.802 (6)
P(2)-C(35)	1.809 (6)	P(4)-C(75)	1.806 (7)
N(1)-C(1)	1.302 (8)	N(5)-C(41)	1.302 (7)
N(2)-C(1)	1.328 (8)	N(6)-C(41)	1.316 (8)
N(3)-C(2)	1.325 (7)	N(7)-C(42)	1.307 (7)
N(4)-C(2)	1.293 (8)	N(8)-C(42)	1.322 (7)
Angles			
N(1)-P(1)-N(4)	127.9 (3)	N(5)-P(3)-N(8)	125.4 (2)
N(1)-P(1)-C(17)	103.5 (3)	N(5)-P(3)-C(57)	102.6 (3)
N(1)-P(1)-C(23)	105.3 (3)	N(5)-P(3)-C(63)	108.9 (3)
N(4)-P(1)-C(17)	104.9 (2)	N(8)-P(3)-C(57)	104.3 (3)
N(4)-P(1)-C(23)	107.3 (3)	N(8)-P(3)-C(63)	107.4 (3)
C(17)-P(1)-C(23)	106.0 (3)	C(57)-P(3)-C(63)	106.8 (3)
N(2)-P(2)-N(3)	124.9 (2)	N(6)-P(4)-N(7)	127.9 (3)
N(2)-P(2)-C(29)	104.1 (3)	N(6)-P(4)-C(69)	104.0 (2)
N(2)-P(2)-C(35)	108.1 (3)	N(6)-P(4)-C(75)	106.8 (3)
N(3)-P(2)-C(29)	102.3 (3)	N(7)-P(4)-C(69)	104.3 (3)
N(3)-P(2)-C(35)	109.1 (3)	N(7)-P(4)-C(75)	107.1 (3)
C(29)-P(2)-C(35)	106.7 (3)	C(69)-P(4)-C(75)	104.5 (3)
P(1)-N(1)-C(1)	139.8 (5)	P(3)-N(5)-C(41)	127.7 (5)
P(2)-N(2)-C(1)	124.7 (4)	P(4)-N(6)-C(41)	138.2 (4)
P(2)-N(3)-C(2)	128.5 (4)	P(4)-N(7)-C(42)	139.2 (4)
P(1)-N(4)-C(2)	139.6 (4)	P(3)-N(8)-C(42)	127.4 (4)
N(1)-C(1)-N(2)	129.9 (5)	N(5)-C(41)-N(6)	131.3 (5)
N(1)-C(1)-C(3)	114.5 (6)	N(5)-C(41)-C(43)	114.1 (5)
N(2)-C(1)-C(3)	115.5 (5)	N(6)-C(41)-C(43)	114.6 (5)
N(3)-C(2)-N(4)	129.8 (5)	N(7)-C(42)-N(8)	129.7 (5)
N(3)-C(2)-C(10)	114.7 (5)	N(7)-C(42)-C(50)	114.9 (5)
N(4)-C(2)-C(10)	115.4 (5)	N(8)-C(42)-C(50)	115.5 (5)

electron-impact (70 eV) mass spectra. They are thermally stable up to at least 250 °C. For comparison, we note that **4d** undergoes decomposition at 316 °C for 24 h to give **1c** (69%) with the elimination of C<sub>3</sub>F<sub>7</sub>OCF(CF<sub>3</sub>)CN.<sup>23</sup>

Allcock et al. have proposed that two pathways are available for the polymerization of cyclophosphazenes.<sup>24</sup> The initial step in the polymerization process involves heterolytic cleavage of either (a) an exocyclic P-X bond or (b) an endocyclic P-N bond. Pathway a is favored when X is a readily ionizable substituent, e.g. a halogen, and provides a more efficient route to high polymer formation. Consistent with this notion, the diphosphatriazine **1b** does not decompose below its melting point (225 °C) whereas **1a** produces the polymer [ClCN(NPCl<sub>2</sub>)<sub>2</sub>]<sub>n</sub> upon heating at 120 °C.<sup>2c</sup> Consequently, we also investigated the reactions of PhCN<sub>2</sub>(SiMe<sub>3</sub>)<sub>3</sub> with PhPCl<sub>4</sub> and with PCl<sub>5</sub> in order to prepare 1,5-diphosphatetrazocines with chlorine substituents attached to phosphorus. The <sup>31</sup>P NMR spectra of the reaction mixtures revealed a very complex assortment of products. In the case of PhPCl<sub>4</sub>, at least six major resonances were observed in the region +20 to 0 ppm. This complexity may arise in part from the formation of both cis and trans isomers for **4** (and **1**) with different exocyclic substituents (Ph and Cl) on phosphorus. In the reaction with PCl<sub>5</sub>, a very broad resonance centered at ca. -12.0, possibly due to polymer formation, and a sharp signal at +40.2 ppm were observed, in addition to weaker resonances at +12.0 and +6.0 ppm. Attempts to isolate pure crystalline materials from these reaction mixtures were unsuccessful.

**Reaction of PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPH<sub>2</sub>) with Benzeneselenenyl Chloride.** Recently we have found that the reaction of PhCN<sub>2</sub>-

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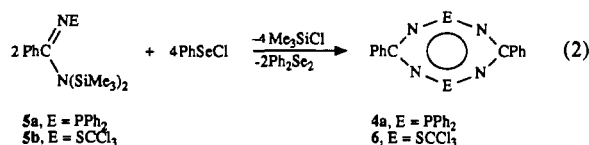
**Table IV.** Selected Dihedral Angles (deg) and Deviations (Å) from Least-Squares Plane for 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub>

Dihedral Angles					
molecule A			molecule B		
N(4)–P(1)–N(1)–C(1)	–10.3 (8)		N(8)–P(3)–N(5)–C(41)	66.8 (6)	
N(1)–P(1)–N(4)–C(2)	19.2 (7)		N(5)–P(3)–N(8)–C(42)	–72.1 (6)	
N(3)–P(2)–N(2)–C(1)	77.5 (6)		N(7)–P(4)–N(6)–C(41)	–23.5 (7)	
N(2)–P(2)–N(3)–C(2)	–66.5 (6)		N(6)–P(4)–N(7)–C(42)	23.2 (8)	
N(2)–C(1)–N(1)–P(1)	–7 (1)		N(6)–C(41)–N(5)–P(3)	–13.3 (9)	
N(1)–C(1)–N(2)–P(2)	–23.2 (9)		N(5)–C(41)–N(6)–P(4)	–2 (1)	
N(4)–C(2)–N(3)–P(2)	10.5 (9)		N(8)–C(42)–N(7)–P(4)	–2 (1)	
N(3)–C(2)–N(4)–P(1)	3 (1)		N(7)–C(42)–N(8)–P(3)	21.1 (9)	

Deviations from Least-Squares Plane					
molecule A			molecule B		
P(1)	–0.22 (2)	P(2)	–0.48 (2)	P(3)	0.466 (7)
N(1)	–0.05 (2)	N(3)	0.08 (2)	N(5)	–0.123 (9)
C(1)	0.18 (2)	C(2)	0.20 (2)	C(41)	–0.19 (1)
N(2)	0.23 (2)	N(4)	0.06 (2)	N(6)	–0.04 (1)
				P(4)	0.255 (9)
				N(7)	–0.02 (1)
				C(42)	–0.17 (1)
				N(8)	–0.173 (9)

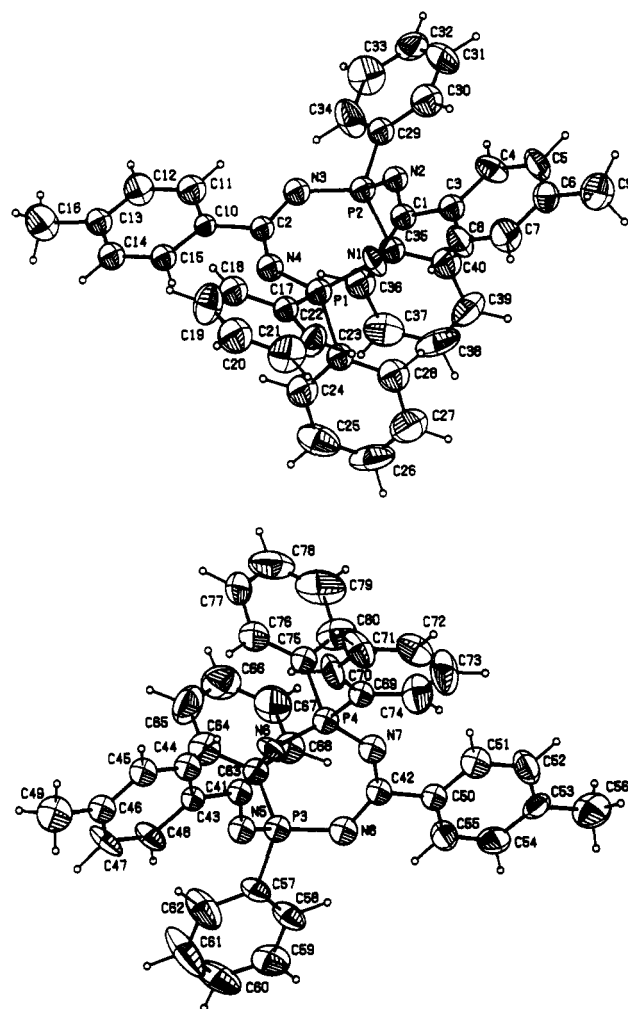
(SiMe<sub>3</sub>)<sub>2</sub>(SCCl<sub>3</sub>) (**5b**) with 2 molar equiv of PhSeCl produces the eight-membered rings Ph<sub>2</sub>C<sub>2</sub>N<sub>4</sub>S<sub>2</sub>(CCl<sub>3</sub>)<sub>2</sub> (**6**) in ca. 70% yield.<sup>25</sup>



By analogy, we envisaged that the reaction of the known reagent PhC[N(SiMe<sub>3</sub>)<sub>2</sub>](NPPh<sub>2</sub>)<sup>10</sup> with PhSeCl in a 1:2 molar ratio might provide a preferred alternative to reaction 1 for the synthesis of **4a**. Indeed this reaction proceeds rapidly at 0 °C in methylene dichloride with the spontaneous elimination of Ph<sub>2</sub>Se<sub>2</sub>, which was obtained in 72% yield, but the only heterocycle that could be isolated was the six-membered ring **1b**.

**Crystal and Molecular Structures of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>Ph<sub>2</sub> (**4b**).** An ORTEP plot of the two independent molecules of **4b** and the atomic numbering schemes are illustrated in Figure 1, and selected bond lengths and bond angles are given in Table III. Selected dihedral angles and deviations from the least-squares plane are given in Table IV. Each asymmetric unit contains two independent molecules with no atom setting at special positions. The monoclinic unit cell contains eight discrete molecules of **4b** separated by normal van der Waals distances. The P<sub>2</sub>N<sub>4</sub>C<sub>2</sub> rings of both molecules adopt a distorted boat–boat conformation<sup>26</sup> with the phosphorus atoms out of and on the same side of the plane by ca. 0.24 and 0.47 Å and the carbon atoms on the other side of the plane by ca. 0.17 and 0.20 Å. One of the nitrogen atoms in each of the P<sub>2</sub>N<sub>4</sub>C<sub>2</sub> rings also deviates significantly (by ca. 0.23 and 0.17 Å) from the best plane, but the other three N atoms lie within ca. 0.1 Å of the best plane. In contrast, the heterocyclic ring in Ph<sub>8</sub>P<sub>4</sub>N<sub>4</sub> adopts a conformation intermediate between the ideal boat and ideal saddle forms.<sup>27</sup>

The average P–N bond lengths are 1.605 (4) and 1.603 (5) Å for the two molecules in **4b** are comparable to the value of 1.590 (3) Å found for Ph<sub>8</sub>P<sub>4</sub>N<sub>4</sub>.<sup>27</sup> The average C–N bond lengths are 1.312 (9) (molecule A) and 1.311 (5) Å (molecule B). These values are similar to the C–N bond distance of 1.319 Å in *s*-triazine,<sup>28</sup> consistent with a C–N bond order of 1.5. The endocyclic bond angles at phosphorus of 127.9 (3) (molecule A) and 125.4 (2)° (molecule B) are significantly larger than those of Ph<sub>8</sub>P<sub>4</sub>N<sub>4</sub>, which are 119.9°.<sup>27</sup> An interesting feature of the structure of both molecules in **4b** is that there are two distinct pairs of endocyclic bond angles at N in **4b** with values of ca. 127 and 139°; cf. 127.9°



**Figure 1.** ORTEP plots (50% probability ellipsoids) of the two independent molecules (A, top; B, bottom) of 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>C<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-4)<sub>2</sub> (**4b**).

for Ph<sub>8</sub>P<sub>4</sub>N<sub>4</sub>.<sup>27</sup> The nitrogen atoms involved in the large bond angles are attached to the phosphorus atoms with the least deviation from the best plane. The endocyclic bond angles at carbon fall within the narrow range 129.7 (5)–131.1 (5)°.

### Conclusions

This investigation has provided the first structural characterization of a 1,5-diphosphatetrazocine. The eight-membered ring in **4a** adopts a distorted boat–boat conformation, and there are no indications of significant ring strain from the observed structural parameters. Consistently, these new heterocycles do not readily undergo thermal polymerization, and alternative approaches, e.g.

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acid catalysis, will be necessary in order to prepare poly(carbo-phosphazenes) with organic groups attached to phosphorus from the corresponding ring systems.

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**Supplementary Material Available:** Listings of hydrogen atom parameters, thermal parameters, bond distances, bond angles, torsion angles, and crystallographic parameters (14 pages); a table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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## Molecular Structure of a Cobalt(I) Complex Lacking a Carbonyl Ligand. A Unique Example of Co-N Bond Shortening

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The following compound,  $[(\text{CH}_3)_4\text{N}][\text{Co}(\text{dmgBF}_2)_2\text{py}]$ , where  $\text{py} = \text{C}_5\text{H}_5\text{N}$  and  $(\text{dmgBF}_2)_2^{2-} = \text{bis}[(\text{difluoroboryl})\text{dimethylglyoximate}]$ , was crystallized and its molecular structure determined by X-ray diffraction. The distances between Co(I) and the nitrogen of the macrocycle are unusually short (1.839 Å), even shorter than the corresponding bond (1.878 Å) in the cobalt(II) analogue. The cobalt atom is displaced 0.257 Å above the axial plane toward pyridine. Reasons for this unusual Co-N bond shortening are discussed along with the electronic structure of the  $d^8$  cobalt(I) anion.

### Introduction

It is well-known that vitamin  $\text{B}_{12}$  (=cyanocobalamin) and its derivative  $\text{B}_{12a}$  (aquocobalamin) can be reduced by one electron to  $\text{B}_{12r}$  (=cobalt(II) cobalamin) and by two electrons to  $\text{B}_{12s}$ .<sup>1</sup> The crystal structure of  $\text{B}_{12r}$  was also determined recently.<sup>2</sup> Vitamin  $\text{B}_{12a}$  exists in solution as the cobalt(I) complex, although at higher acidities it is in equilibrium with its conjugate acid,  $\text{HCo}(\text{corrin})$ , with  $\text{p}K_a = 1$ .<sup>3-5</sup> In a localized valence formalism, the latter is referred to as a hydridocobalt(III). The  $\text{B}_{12}$  model complexes  $\text{Co}(\text{dmgH})_2\text{py}^-$  and  $\text{HCo}(\text{dmgH})_2\text{py}$  are also known; here the acidity is lower ( $\text{p}K_a = 9$ ),<sup>6-9</sup> and the rate of acid-base interconversion, sufficiently low that the two forms undergo separate and not always identical chemical reactions.<sup>9-12</sup>

We have now succeeded in isolating single crystals of a closely related model complex that is an example of a nonporphyrin cobalt(I) macrocycle, and that lacks a carbonyl or phosphine ligand. The compound studied is  $[(\text{CH}_3)_4\text{N}][\text{Co}(\text{dmgBF}_2)_2\text{py}]\cdot\text{CH}_3\text{CN}$  crystallized from acetonitrile. It contains the anion  $\text{Co}(\text{dmgBF}_2)_2\text{py}^-$  ( $\text{py} = \text{C}_5\text{H}_5\text{N}$ ;  $(\text{dmgBF}_2)_2^{2-} = \text{bis}[(\text{difluoroboryl})\text{dimethylglyoximate}]$ ), which was first prepared by Schrauzer.<sup>13</sup> Not only is this of interest because of the biological role of  $\text{B}_{12}$  but also, aside from species containing carbonyl, phosphine, or porphyrin ligands,<sup>14-20</sup> it is the first co-

**Table I.** Crystallographic Data for  $[(\text{CH}_3)_4\text{N}][\text{Co}(\text{dmgBF}_2)_2\text{py}]\cdot\text{CH}_3\text{CN}$

chem formula	$\text{C}_{18}\text{H}_{29}\text{B}_2\text{NO}_4\text{F}_4\text{Co}\cdot\text{CH}_3\text{CN}$	$\gamma$ , deg	103.72 (2)
fw	579.02	$V$ , Å <sup>3</sup>	1280.9 (7)
space group	$P\bar{1}$	$Z$	2
$a$ , Å	12.492 (4)	$T$ , °C	-75 (1)
$b$ , Å	12.883 (3)	$\lambda$ , Å	0.710 73
$c$ , Å	8.996 (3)	$d_{\text{calc}}$ , g cm <sup>-3</sup>	1.501
$\alpha$ , deg	99.39 (2)	$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	7.338
$\beta$ , deg	109.25 (2)	$R(F_o)$	0.045
		$R_w(F_o^2)$	0.061

bal(I) macrocyclic complex to be so characterized. Moreover, the structure is of interest in its own right because of the considerable variations in distances, angles, and displacements that are found in it, compared to those in the cobalt(II) analogue. Cobalt(I) macrocycle complexes are often short-lived owing to high reactivity with protic solvents or to internal metal-ligand decompositions. The species examined here is moderately stable, even more so than the cobaloxime parent,  $\text{Co}(\text{dmgH})_2\text{py}^-$ . In general cobalt(I) complexes are strong nucleophiles<sup>2,12,13,21-24</sup> and Bronsted (as well as Lewis) bases.<sup>6-9,24</sup> As expected from inductive effects, the complex  $\text{Co}(\text{dmgBF}_2)_2\text{py}^-$  is much less nucleophilically reactive than the  $(\text{dmgH})_2$  and  $\text{B}_{12a}$  analogues.<sup>13</sup> Several catalytic reactions of cobalt(I) macrocycles are known.<sup>23-25</sup>

### Results and Discussion

The pentacoordinated structure of the cobalt(I) monoanion  $\text{Co}(\text{dmgBF}_2)_2\text{py}^-$  is depicted in the ORTEP diagram given in Figure 1. The structure is square-pyramidal. The closest analogues are cobalt(I) porphyrins.<sup>26,27</sup> Most often cobalt(I) needs to be stabilized by CO (or phosphine) coordination.<sup>25-30</sup>

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