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Structural Chemistry of

1-Oxo-2,8-dimethyl-4,6-bis[3-(trifluoromethyl)phenyl]-2,4,6,8-tetraaza-1 λ^3 ,5 λ^5 -diphosphabicyclo[3.3.0]octane-3,7-dione and the Synthesis, Structure, and Reactions of 2,4,6,8-Tetramethyl-2,4,6,8-tetraaza-1 λ^3 ,5 λ^3 -diphosphabicyclo[3.3.0]octane-3,7-dione. Bicyclic Compounds with Phosphorus-Phosphorus Bonds

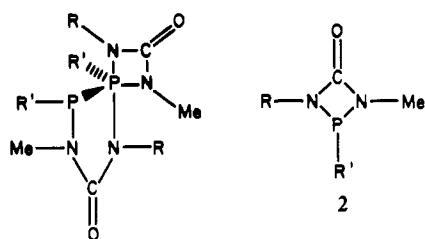
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Received December 12, 1980

The structure of 1-oxo-2,8-dimethyl-4,6-bis[3-(trifluoromethyl)phenyl]-2,4,6,8-tetraaza-1 λ^3 ,5 λ^5 -diphosphabicyclo[3.3.0]octane-3,7-dione (**3**) has been determined by single-crystal X-ray diffraction. **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell constants $a = 10.780$ (3) Å, $b = 15.448$ (6) Å, $c = 6.588$ (3) Å, $\alpha = 94.13$ (7)°, $\beta = 95.73$ (5)°, $\gamma = 98.01$ (5)°, and $Z = 2$. Full-matrix least-squares refinement of the structure converged with $R = 0.057$ and $R_w = 0.058$ for 2922 reflections with $I \geq 2.0\sigma(I)$. Individual molecules of **3** feature a P-P(O) moiety incorporated in a bicyclic structure, and centrosymmetric pairs of molecules of **3** exhibit rather short P...O nonbonded distances of 2.805 and 2.984 Å. 2,4,6,8-Tetramethyl-2,4,6,8-tetraaza-1 λ^3 ,5 λ^3 -diphosphabicyclo[3.3.0]octane-3,7-dione (**4**) has been synthesized by the action of PCl_3 on $[\text{Me}(\text{Me}_3\text{Si})\text{N}]_2\text{CO}$. The structure of **4** has been determined by single-crystal X-ray diffraction. **4** crystallizes in the monoclinic space group $P2_1/n$ with unit cell constants $a = 6.577$ (3) Å, $b = 19.276$ (6) Å, $c = 8.531$ (2) Å, $\beta = 92.64$ (3)°, and $Z = 4$. The structure was refined by full-matrix least-squares methods to the terminal values $R = 0.065$ and $R_w = 0.055$ for 982 reflections with $I \geq 2.0\sigma(I)$. A short nonbonded P(1)...P(1)' distance of 3.345 Å is observed with P(1)' taking up an axial position in an incipient (ψ)-trigonal-bipyramidal geometry at P(1). The $\lambda^3\text{P}-\lambda^3\text{P}$ bond in **4** is 0.05 Å longer than the $\lambda^3\text{P}-\lambda^5\text{P}$ bond in **3**. **4** forms a $\text{Cr}(\text{CO})_5$ complex, **9**, upon treatment with $\text{Cr}(\text{CO})_5\text{THF}$. 1,1,1-Trichloro-2,4-dimethyl-1,2,4-phosphadiazetin-3-one (**11**) and 4-chloro-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4-phosphaspiro[3.3]heptane-2,6-dione (**12**) resulted from the reaction of **4** with Cl_2 . **12** can also be formed by the reaction of equimolar quantities of **4** with SO_2Cl_2 .

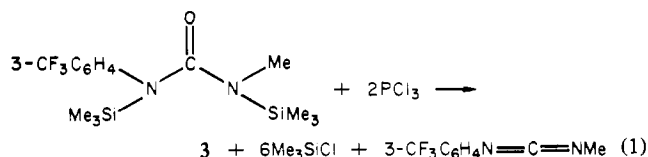
Introduction

Otherwise labile bonding situations can often be stabilized by incorporation of the bonded atoms into cyclic structures. For example, this strategy has been employed recently in the isolation of the first compounds with $\lambda^5\text{P}-\lambda^5\text{P}^2$ and $\lambda^3\text{P}-\lambda^5\text{P}^3$ bonds. Compounds such as **1** are formed by the action of

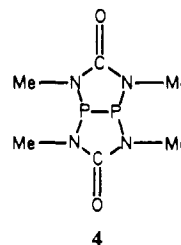


- 1A, R = 3-CF₃C₆H₄, R' = C₆F₅
 B, R = Me, R' = Ph
 C, R = R' = Ph

dichlorophosphines, $\text{R}'\text{PCl}_2$, on silyl-substituted ureas, $\text{Me}_3\text{SiN}(\text{Me})\text{C}(\text{O})\text{N}(\text{R})\text{SiMe}_3$, and presumably arise from initially formed **2**, one molecule of which undergoes P-N bond cleavage followed by oxidative addition to an intact ring. When PCl_3 was substituted for $\text{R}'\text{PCl}_2$ in one of these reactions, a phosphorus-oxygen bonded compound **3** was formed according to eq 1.^{3b} The main purpose of the present work



was to determine the solid-state structure of **3**. While the work was in progress we found that, interestingly, the reaction of $[(\text{Me}_3\text{Si})(\text{Me})\text{N}]_2\text{CO}$ with PCl_3 does not proceed as indicated in eq 1 but results in a $\lambda^3\text{P}-\lambda^3\text{P}$ compound, **4**, rather than a

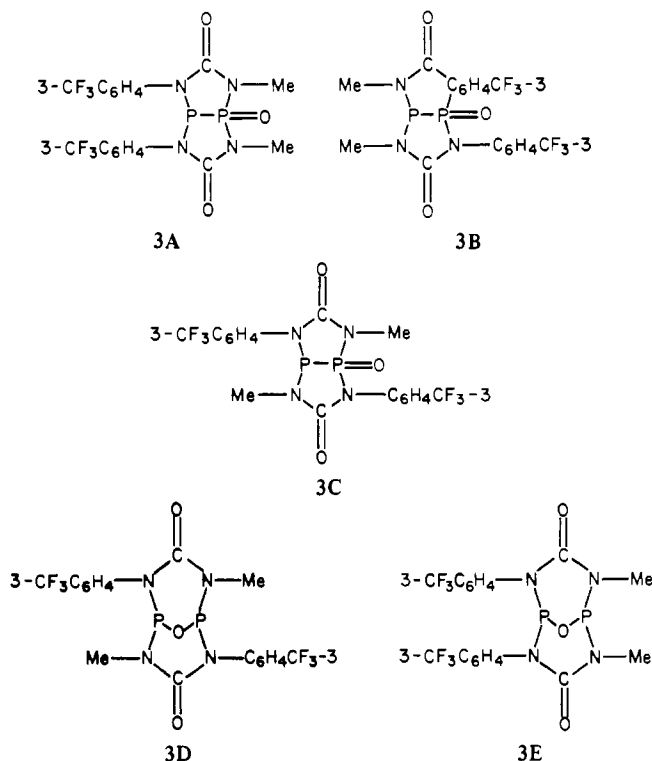


spirocyclic species. We have also determined the structure of **4** by single-crystal X-ray diffraction and report some of its reaction chemistry.

Results and Discussion

Crystal Structure and Dynamic Stereochemistry of $\text{OP}_2[3\text{-CF}_3\text{C}_6\text{H}_4\text{NC}(\text{O})\text{NMe}]_2$ (3**).** As noted in the Introduction, the reaction of PCl_3 with the silyl-substituted urea 3-CF₃C₆H₄-(Me₃Si)NC(O)N(SiMe₃)(Me) results in a phosphorus-oxygen bonded product, the plausible structures for which are **3A-3E**. Initially, structure **3D** was assigned to this product principally because the ambient-temperature ³¹P NMR spectrum appeared to comprise a singlet.^{3b} However, it has now been discovered that, on cooling, the ³¹P{¹H} spectrum changes to a typical AB pattern (Figure 1a and Table I). The uncoupled ³¹P spectrum is a somewhat distorted AB pattern (Figure 1b) due to the presence of unresolved ¹H coupling on the two lower frequency signals. The ¹⁹F NMR spectrum remains a singlet throughout this temperature range. The changes in the ³¹P spectra are conveniently explained by postulating a process in which there is a net transfer of the oxygen atom between phosphorus atoms. Deferring a discussion of possible mechanisms for the oxygen-exchange process, it is clear from the temperature sensitivity of the ³¹P spectra that the solution-state structure cannot be **3D** or **3E**. Unfortunately, however, it is not possible to choose between

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 (2) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955.
 (3) (a) Roesky, H. W.; Ambrosius, K.; Sheldrick, W. S. *Chem. Ber.* **1979**, *112*, 1365-1371. (b) Roesky, H. W.; Ambrosius, K.; Banek, M.; Sheldrick, W. S. *Ibid.* **1980**, *113*, 1847-1854.



structures **3A**, **3B**, and **3C** on the basis of NMR data. Even though the solution and solid-state structures of **3** could, in fact, differ, we considered that single-crystal X-ray diffraction data on this compound were highly desirable.

The crystal structure consists of discrete molecules of **3A**. The molecule is depicted in Figure 2, and a summary of bond lengths and angles appears in Table II. The molecular skeleton consists of an "open-book" arrangement of the two five-membered P_2N_2C rings. However, the five-membered rings are somewhat puckered, with the deviations from planarity being more marked for the P(1)-N(1)-C(2)-N(3)-P(2) ring than for the P(1)-N(4)-C(5)-N(6)-P(2) ring. The following distances (Å) are observed for the member atoms from least-squares planes: ring one P(1) -0.074, N(1) 0.078, C(2) -0.017, N(3) -0.057, P(2) 0.069; ring two, P(1) -0.034, N(4) 0.032, C(5) 0.001, N(6) -0.035, P(2) 0.036 Å. The average bond angles at P(1) and P(2) are 93.7 and 109.1°, respectively. These are typical of the values expected for tri- and tetracoordinate phosphorus atoms. The differing coordination numbers of the two phosphorus atoms influence, e.g., the P-N bond lengths. Thus, the average P-N bond length at P(2) is ~0.07 Å shorter than that at P(1). This shortening can be attributed to the fact that P(2), being tetrahedral, features approximately 25% P(3s) character in the bonding orbitals, while at the tricoordinate center, P(1), the percent of 3s character is ~3%.

P-P bond lengths have normally been observed in the range 2.16–2.24 Å, independent of oxidation state and the nature of the substituents.^{4,5} The P-P bond lengths in **3A** and **4** (vide infra) are 2.172 (1) and 2.222 (2) Å, respectively. There is thus a significant decrease in the P-P bond length as the coordination number of P(2) is changed from 3 to 4. An intermediate value of 2.195 (2) Å was found for the $\lambda^3P-\lambda^5P$ bond in **1A**.^{3a} However, bearing in mind that a distance of 2.264 (2) Å has been reported for a $\lambda^5P-\lambda^5P$ bond,² it is clear

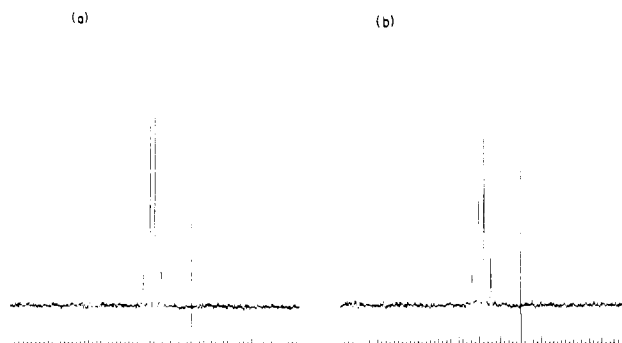


Figure 1. (a) 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of **3A** at $-75^\circ C$. (b) 36.43-MHz ^{31}P NMR spectrum of **3A** at $-75^\circ C$.

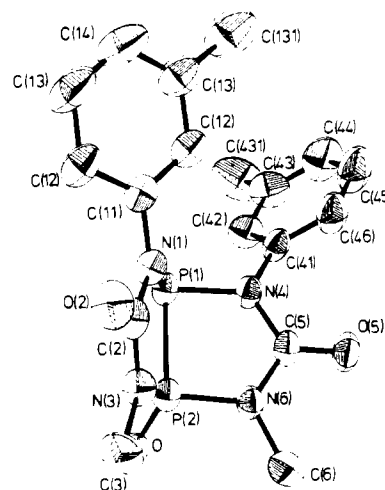
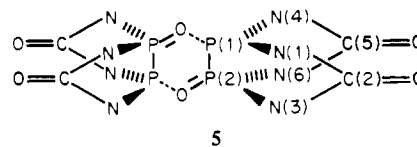


Figure 2. Perspective view of **3A**, illustrating the atom numbering scheme. The hydrogen atoms are omitted; all other atoms are shown as ellipsoids of 50% probability.

that there is no overall correlation between P-P bond length and coordination number.

The P-O bond length in **3A** is quite normal and typical of those found in amido-substituted phosphine oxides.⁶ The most interesting aspect of the crystal structure is the fact that remarkably short intermolecular P(1)···O' and P(2)···O' distances of 2.805 and 2.984 Å to the symmetry equivalent oxygen O' at $-x, -y, -z$ are observed. Since the sum of the van der Waals radii for P and O is 3.32 Å,⁷ this observation implies that **3A** crystallizes in pairs of molecules which are related by a center of symmetry. In the incipient dimer **5**, the incoming oxygen,

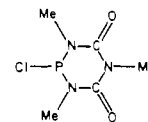


O', must take up an axial position in a distorted (ψ)-trigo-

(6) See, for example: Clardy, J. C.; Kolpa, R. C.; Verkade, J. G. *Phosphorus* **1974**, *4*, 133–141.

(7) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441–451.

(8) When this solid residue was heated to 110–120 °C in vacuo, a viscous liquid and a polymeric material were formed. The liquid (bp 95 °C (0.2 torr)) has been shown to be



(4) Cowley, A. H. *Chem. Rev.* **1965**, *65*, 617–634. Cowley, A. H. "Compounds Containing Phosphorus-Phosphorus Bonds"; Dowden, Hutchinson, and Ross: Stroudsburg, PA, 1973, and references therein.

(5) See also: Khaikin, L. S.; Vilkov, L. V. *Russ. Chem. Rev. (Engl. Transl.)* **1971**, *40*, 1014–1029. Baxter, S. G.; Cowley, A. H.; Davis, R. E.; Riley, P. E. *J. Am. Chem. Soc.* **1981**, *103*, 1699–1702.

Table I. Summary of NMR Data for 3A, 4, and 9

compd (temp, °C)	chem shifts, ppm ^a			coupling constants, Hz
	¹ H	¹⁹ F	³¹ P	
OP ₂ [3-CF ₃ C ₆ H ₄ NC(O)NMe] ₂ (3A) (-75)	3.15	63.1	AB pattern: δ _A 21.11; δ _B 16.09	J _{PP} = 118.37, J _{PNCH} = 6.4
P ₂ [MeNC(O)NMe] ₂ (4)	3.40		27.3	J _{PNCH} = 5.0
P ₂ [MeNC(O)NMe] ₂ Cr(CO) ₅ (9)	3.10, 3.13			J _{PNCH} = 9.0

^a See Experimental Section for statement of references used.

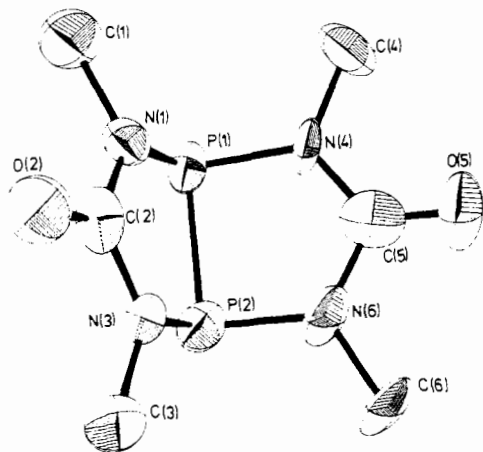
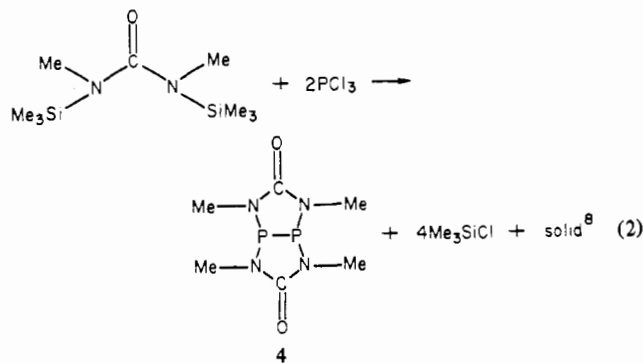


Figure 3. Perspective view of 4, illustrating the atom numbering scheme. The hydrogen atoms are omitted; all other atoms are shown as ellipsoids of 50% probability.

nal-bipyramidal geometry at P(1). The other axial position is occupied by N(1), and P(2), N(4), and a phosphorus lone pair occupy the equatorial positions. Some of the pertinent angles observed at P(1) in the dimer are O'...P(1)-N(1) 159.9°, O'...P(1)-P(2) 72.4°, and O'...P(1)-N(4) 77.3°.

Synthesis and Crystal Structure of P₂[MeNC(O)NMe]₂ (4). The reaction of PCl₃ with silyl-substituted ureas is evidently dependent on the nitrogen substituents because the reaction of [Me(Me₃Si)N]₂CO with PCl₃ does not proceed according to eq 1 (Introduction). In fact, as indicated in eq 2, no car-



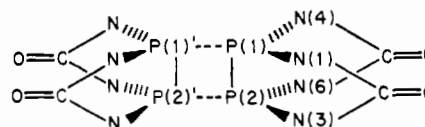
bodiimide is formed, and the sublimable product 4 does not contain a phosphorus-oxygen bond. Compound 4 has been characterized by elemental analysis, single-crystal X-ray diffraction, and NMR and mass spectroscopy. Like 3A, 4 exhibits an "open-book" arrangement of two five-membered P₂N₂C rings joined along a P-P bond (Figure 3). However, in 4, both phosphorus atoms are tricoordinate. The two five-membered rings show deviations from planarity, N(3) and N(6) being displaced by 0.069 and 0.082 Å, respectively from the least-squares planes passing through the four remaining atoms of the five-membered rings. Other distances (Å) from the least-squares planes are as follows: ring one, P(1) 0.000, N(1) -0.001, C(2) 0.000, P(2) 0.000; ring two, P(1) -0.005, N(4) 0.007, C(5) -0.005, and P(2) 0.003. As in the case of 3A, the most interesting aspect of the crystal structure of 4

Table II. Bond Lengths (Å) and Bond Angles (Deg) in OP₂[3-CF₃C₆H₄NC(O)NMe]₂ (3A)^{a,b}

P(1)-P(2)	2.172 (1)	C(131)-F(134)	1.308 (22)
P(1)-N(1)	1.740 (3)	C(131)-F(136)	1.306 (13)
P(1)-N(4)	1.715 (3)	C(41)-C(46)	1.370 (6)
P(2)-N(3)	1.658 (3)	C(43)-C(44)	1.375 (7)
P(2)-N(6)	1.648 (3)	C(45)-C(46)	1.391 (6)
P(2)-O	1.466 (3)	C(431)-F(431)	1.332 (9)
N(1)-C(2)	1.404 (4)	C(431)-F(433)	1.308 (12)
N(1)-C(11)	1.428 (5)	C(431)-F(435)	1.318 (12)
N(3)-C(2)	1.377 (5)	C(11)-C(16)	1.381 (5)
N(3)-C(3)	1.469 (4)	C(13)-C(14)	1.369 (7)
N(4)-C(5)	1.397 (4)	C(15)-C(16)	1.380 (7)
N(4)-C(41)	1.432 (4)	C(131)-F(131)	1.335 (7)
N(6)-C(5)	1.372 (4)	C(131)-F(133)	1.312 (12)
N(6)-C(6)	1.472 (5)	C(131)-F(135)	1.320 (21)
C(2)-O(2)	1.209 (4)	C(41)-C(42)	1.385 (5)
C(5)-O(5)	1.212 (4)	C(42)-C(43)	1.386 (5)
C(11)-C(12)	1.376 (5)	C(44)-C(45)	1.368 (8)
C(12)-C(13)	1.383 (6)	C(43)-C(431)	1.480 (8)
C(14)-C(15)	1.364 (7)	C(431)-F(432)	1.283 (11)
C(13)-C(131)	1.476 (7)	C(431)-F(434)	1.311 (17)
C(131)-F(132)	1.324 (9)	C(431)-F(436)	1.349 (18)
P(2)-P(1)-N(1)	87.5 (1)	N(3)-C(2)-O(2)	123.3 (3)
P(2)-P(1)-N(4)	89.0 (1)	N(4)-C(5)-O(5)	123.8 (3)
N(1)-P(1)-N(4)	104.7 (1)	N(6)-C(5)-O(5)	122.6 (3)
P(1)-P(2)-N(3)	96.6 (1)	N(1)-C(11)-C(12)	118.3 (3)
P(1)-P(2)-N(6)	96.0 (1)	C(12)-C(11)-C(16)	119.4 (4)
N(3)-P(2)-N(6)	108.5 (1)	C(12)-C(13)-C(14)	120.6 (4)
P(1)-P(2)-O	128.8 (1)	C(14)-C(15)-C(16)	121.4 (5)
N(3)-P(2)-O	111.2 (1)	C(12)-C(13)-C(131)	118.1 (4)
N(6)-P(2)-O	113.3 (1)	N(4)-C(41)-C(42)	119.3 (3)
P(1)-N(1)-C(2)	122.9 (2)	C(42)-C(41)-C(46)	119.7 (3)
P(1)-N(4)-C(5)	121.8 (2)	C(42)-C(43)-C(44)	120.7 (4)
P(2)-N(3)-C(2)	119.4 (2)	C(44)-C(45)-C(46)	121.0 (5)
P(2)-N(6)-C(5)	119.2 (2)	C(42)-C(43)-C(431)	119.2 (5)
P(1)-N(1)-C(11)	116.8 (2)	N(1)-C(11)-C(16)	122.3 (3)
P(1)-N(4)-C(41)	118.3 (2)	C(11)-C(12)-C(13)	120.2 (4)
P(2)-N(3)-C(3)	121.8 (2)	C(13)-C(14)-C(15)	119.0 (5)
P(2)-N(6)-C(6)	122.1 (2)	C(11)-C(16)-C(15)	119.4 (4)
C(11)-N(1)-C(2)	118.9 (3)	C(14)-C(13)-C(131)	121.4 (4)
C(41)-N(4)-C(5)	117.9 (3)	N(4)-C(41)-C(46)	120.9 (3)
C(3)-N(3)-C(2)	118.8 (3)	C(41)-C(42)-C(43)	119.8 (4)
C(6)-N(6)-C(5)	118.5 (3)	C(43)-C(44)-C(45)	119.1 (4)
N(1)-C(2)-N(3)	112.2 (3)	C(41)-C(46)-C(45)	119.8 (4)
N(4)-C(5)-C(6)	113.7 (3)	C(44)-C(43)-C(431)	120.1 (4)
N(1)-C(2)-O(2)	124.5 (3)		

^a Numbers in parentheses are the estimated standard deviations in the least significant digits. ^b See Figure 2 for the atom numbering scheme.

is the observation of centrosymmetric pairs of molecules with short internuclear distances as indicated in 6. In this case,



6

a P(1)...P(1)' distance of 3.345 Å is found for the symmetry-equivalent phosphorus, P(1)', at -x, -y, -z, and the P(1)...P(2)' distance in the molecule pair is 3.771 Å. The P(1)...P(1)' distance is thus somewhat less than the sum of van der Waals radii for phosphorus (3.60 Å).⁷ P(1)' and N(4)

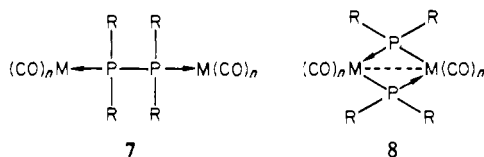
Table III. Bond Lengths (Å) and Bond Angles (Deg) in $P_2[MeNC(O)NMe]_2$ (4)^{a,b}

P(1)-P(2)	2.222 (2)	N(3)-C(3)	1.451 (8)
P(1)-N(1)	1.736 (4)	N(4)-C(5)	1.378 (7)
P(1)-N(4)	1.673 (4)	N(4)-C(4)	1.488 (7)
P(2)-N(3)	1.734 (5)	N(6)-C(5)	1.419 (7)
P(2)-N(6)	1.699 (5)	N(6)-C(6)	1.472 (7)
N(1)-C(2)	1.380 (8)	C(2)-O(2)	1.189 (8)
N(1)-C(1)	1.474 (7)	C(5)-O(5)	1.204 (6)
N(3)-C(2)	1.452 (8)		
P(2)-P(1)-N(1)	91.6 (2)	P(2)-N(3)-C(3)	120.0 (4)
P(2)-P(1)-N(4)	91.7 (2)	P(2)-N(6)-C(6)	119.7 (4)
N(1)-P(1)-N(4)	104.4 (2)	C(1)-N(1)-C(2)	115.8 (4)
P(1)-P(2)-N(3)	91.9 (2)	C(4)-N(4)-C(5)	113.9 (4)
P(1)-P(2)-N(6)	91.2 (2)	C(3)-N(3)-C(2)	118.4 (5)
N(3)-P(2)-N(6)	104.5 (2)	C(6)-N(6)-C(5)	117.1 (5)
P(1)-N(1)-C(2)	123.8 (4)	N(1)-C(2)-N(3)	110.7 (5)
P(1)-N(4)-C(5)	123.8 (4)	N(4)-C(5)-N(6)	111.1 (4)
P(2)-N(3)-C(2)	121.6 (4)	N(1)-C(2)-O(2)	128.3 (6)
P(2)-N(6)-C(5)	121.8 (4)	N(3)-C(2)-O(2)	120.9 (6)
P(1)-N(1)-C(1)	120.1 (4)	N(4)-C(5)-O(5)	126.8 (5)
P(1)-N(4)-C(4)	120.8 (4)	N(6)-C(5)-O(5)	122.1 (5)

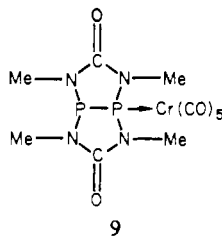
^a Numbers in parentheses are the estimated standard deviations in the least significant digits. ^b See Figure 3 for the atom numbering scheme.

take up axial positions in an incipient (ψ)-trigonal-bipyramidal geometry at P(1), and P(2), N(1), and a phosphorus lone pair adopt the equatorial positions, as evidenced by the following angles: P(1)'...P(1)-N(4) 164.5°, P(1)'...P(1)-N(1) 90.2°, P(1)'...P(1)-P(2) 82.7°. The formation of weak dimers also influences the pattern of bond lengths in each molecule of **4**. Thus, although the average P-N bond lengths at P(1) and P(2) differ by only ~0.01 Å (which is expected because the average bond angles are virtually identical), and P-N bond lengths differ on the average by ~0.05 Å in each of the five-membered rings, with P(1)-N(4) and P(2)-N(6) being significantly shorter than P(1)-N(1) and P(2)-N(3). Finally, it is interesting to note that a dimeric species like **6** has been suggested by McFarlane and McFarlane⁹ as one of the possible transition states for scrambling reactions of diphosphines,¹⁰ and this general type of association was postulated much earlier¹¹ to explain the relative thermal instability of $Me_2PP(CF_3)_2$.

Reactions of $P_2[MeNC(O)NMe]_2$ (4). The reactions of diphosphines with metal carbonyls have been investigated extensively⁴ and lead typically to complexes of type **7** or under



more vigorous conditions to phosphido-bridged species **8**. We have found that in equimolar stoichiometry **4** and $Cr(CO)_5$ -THF react to produce **9**. This complex was characterized by



(9) McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* 1972, 1189-1190.

(10) In a subsequent paper, it has been suggested that the scrambling reactions proceed via phosphinyl radicals, $R_1R_2P\cdot$. See: Harris, R. K.; Norval, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* 1979, 826-831.

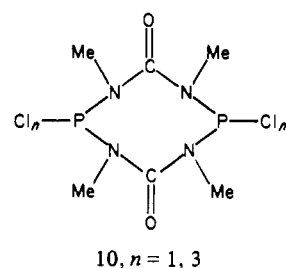
(11) Grant, L. R., Jr.; Burg, A. B. *J. Am. Chem. Soc.* 1962, 84, 1834-1837.

Table IV. Experimental Details of the X-ray Diffraction Studies of **3A** and **4**

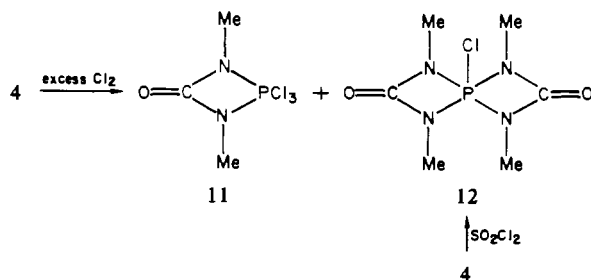
	$C_{18}H_{14}N_4O_3F_6P_2$ (3A)	$C_6H_{12}N_4O_2P_2$ (4)
Crystal Data		
fw	510.3	234.1
space group	$P\bar{1}$	$P2_1/n$
unit cell constants ($22 \pm 1^\circ C$)		
a , Å	10.780 (3)	6.577 (3)
b , Å	15.448 (6)	19.276 (6)
c , Å	6.588 (3)	8.531 (2)
α , deg	94.13 (7)	90
β , deg	95.73 (5)	92.64 (3)
γ , deg	98.01 (5)	90
Z	2	4
D_{calcd} , g cm ⁻³	1.58	1.44
Measurement of Intensity Data		
radiation	Cu K α	Cu K α
scan mode	$\theta-2\theta$	$\theta-2\theta$
scan speed, deg min ⁻¹	2.02-9.77	2.02-9.77
2θ angular range	$3.5 \leq 2\theta \leq 135^\circ$	$3.5 \leq 2\theta \leq 130^\circ$
reflectns measd	3605	1833
abs corr, cm ⁻¹	$\mu(Cu K\alpha) = 24.5$	$\mu(Cu K\alpha) = 34.0$
max transmissn	0.405	0.609
min transmissn	0.251	0.239
Structure Refinement		
I observn criterion	$I \geq 2.0\sigma(I)$	$I \geq 2.0\sigma(I)$
no. of reflectns	2922	982
k (scale factor)	2.8105	1.5779
g (weighting factor)	0.0002	0.0003
R	0.057	0.065
R_w	0.058	0.055

elemental analysis, and NMR, IR, and mass spectroscopy. Part of our reason for synthesizing **9** was to determine whether it exhibited fluxional behavior. However, there is no evidence for migration of the $Cr(CO)_5$ moiety up to 30 °C. In view of the results with the P-P(O) compound **3A**, this is not surprising because formation of a dimer like **5** is impossible for **9**.

One of the well-known reactions of diphosphines is halogenation to produce halophosphines or trihalophosphoranes, depending on the stoichiometry.⁴ It was therefore thought that chlorine cleavage of the P-P bond of **4** might lead to eight-membered ring compounds, **10**. However, treatment of **4** with



excess Cl_2 results in a mixture of **11** and **12**, while treatment



of **4** with an equimolar quantity of SO_2Cl_2 produces **12**. The

Table V. Atom Coordinates and Thermal Parameters ($\text{Å}^2 \times 10^3$) for 3A with Standard Deviations in Parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{11}^a	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.8503 (1)	1.1232 (1)	-0.0116 (1)	33 (0)	43 (0)	31 (0)	-2 (0)	3 (0)	4 (0)
P(2)	0.8308 (1)	0.9815 (1)	-0.0075 (1)	33 (0)	41 (0)	34 (0)	-4 (0)	4 (0)	4 (0)
O	0.9088 (2)	0.9206 (1)	-0.0934 (4)	40 (1)	45 (1)	47 (1)	-9 (1)	7 (1)	10 (1)
N(1)	0.6890 (2)	1.1105 (2)	-0.0867 (4)	32 (1)	47 (2)	39 (2)	-1 (1)	1 (1)	8 (1)
C(2)	0.6163 (3)	1.0285 (2)	-0.1497 (5)	35 (2)	57 (2)	36 (2)	-2 (2)	2 (2)	4 (2)
O(2)	0.5076 (2)	1.0183 (2)	-0.2248 (4)	35 (1)	76 (2)	58 (2)	3 (1)	-6 (1)	0 (1)
N(3)	0.6835 (3)	0.9602 (2)	-0.1181 (4)	33 (1)	45 (2)	44 (2)	-8 (1)	1 (1)	-1 (1)
N(4)	0.8637 (3)	1.1323 (2)	0.2521 (4)	41 (2)	40 (1)	32 (1)	-4 (1)	4 (1)	3 (1)
C(5)	0.8496 (3)	1.0586 (2)	0.3639 (5)	42 (2)	51 (2)	30 (2)	-3 (2)	4 (2)	2 (1)
O(5)	0.8570 (3)	1.0623 (2)	0.5501 (4)	87 (2)	61 (2)	31 (1)	-1 (1)	7 (1)	6 (1)
N(6)	0.8293 (3)	0.9805 (2)	0.2434 (4)	46 (2)	42 (2)	31 (1)	-1 (1)	2 (1)	1 (1)
C(11)	0.6365 (3)	1.1882 (2)	-0.1274 (6)	37 (2)	55 (2)	43 (2)	5 (2)	3 (2)	11 (2)
C(12)	0.6645 (4)	1.2593 (2)	0.0170 (6)	48 (2)	54 (2)	51 (2)	3 (2)	0 (2)	14 (2)
C(13)	0.6225 (4)	1.3377 (3)	-0.0222 (7)	60 (3)	54 (2)	70 (3)	-3 (2)	1 (2)	17 (2)
C(14)	0.5495 (5)	1.3448 (3)	-0.2015 (9)	80 (4)	71 (3)	92 (4)	14 (3)	-15 (3)	32 (3)
C(15)	0.5215 (5)	1.2741 (3)	-0.3439 (8)	89 (4)	75 (3)	73 (3)	6 (3)	-27 (3)	29 (3)
C(16)	0.5641 (4)	1.1956 (3)	-0.3096 (7)	59 (3)	69 (3)	54 (3)	7 (2)	-10 (2)	20 (2)
C(131)	0.6553 (6)	1.4120 (3)	0.1376 (10)	106 (5)	68 (4)	109 (5)	-11 (3)	-7 (4)	29 (3)
F(131)	0.6417 (6)	1.4894 (2)	0.0673 (7)	129 (4)	39 (2)	105 (3)	-2 (2)	9 (3)	26 (2)
F(132)	0.7773 (6)	1.4249 (4)	0.2020 (17)	123 (5)	81 (3)	223 (8)	-81 (4)	-93 (6)	38 (3)
F(133)	0.5824 (11)	1.4041 (5)	0.2860 (12)	276 (10)	122 (5)	107 (5)	-62 (4)	105 (6)	-66 (6)
C(3)	0.6205 (4)	0.8700 (2)	-0.1764 (7)	57 (2)	48 (2)	66 (3)	-12 (2)	-4 (2)	-10 (2)
C(6)	0.8147 (5)	0.8982 (3)	0.3446 (7)	83 (3)	50 (2)	53 (3)	12 (2)	4 (2)	-2 (2)
C(41)	0.9216 (3)	1.2142 (2)	0.3594 (5)	50 (2)	41 (2)	35 (2)	-7 (1)	2 (2)	9 (2)
C(42)	1.0296 (3)	1.2581 (2)	0.2944 (6)	52 (2)	42 (2)	61 (3)	-13 (2)	2 (2)	4 (2)
C(43)	1.0842 (4)	1.3387 (3)	0.3930 (8)	60 (3)	48 (2)	87 (3)	-15 (2)	-1 (2)	0 (2)
C(44)	1.0327 (6)	1.3755 (3)	0.5560 (8)	112 (4)	58 (3)	77 (4)	-33 (3)	0 (3)	4 (3)
C(45)	0.9257 (6)	1.3317 (3)	0.6186 (8)	121 (5)	69 (3)	61 (3)	-25 (2)	18 (3)	14 (3)
C(46)	0.8696 (4)	1.2508 (3)	0.5210 (6)	82 (3)	61 (2)	49 (2)	-15 (2)	17 (2)	10 (2)
C(431)	1.2004 (6)	1.3845 (4)	0.3234 (11)	97 (5)	64 (4)	165 (7)	-31 (4)	16 (5)	-25 (3)
F(431)	1.2937 (5)	1.4019 (6)	0.4764 (12)	70 (4)	225 (8)	214 (8)	-15 (7)	-25 (4)	-45 (4)
F(432)	1.1902 (16)	1.4630 (4)	0.2800 (33)	286 (16)	61 (4)	442 (25)	9 (7)	237 (17)	-31 (5)
F(433)	1.2359 (9)	1.3485 (5)	0.1564 (16)	142 (5)	93 (4)	214 (8)	-57 (5)	118 (6)	-55 (4)
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U, \text{Å}^2$	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U, \text{Å}^2$	
F(134)	0.5651 (17)	1.4595 (15)	0.1558 (37)	219 (9)	F(434)	1.2859 (13)	1.3337 (10)	0.2937 (26)	130 (6)
F(135)	0.7609 (18)	1.4630 (16)	0.1144 (39)	236 (13)	F(435)	1.2108 (29)	1.4707 (7)	0.3473 (44)	145 (8)
F(136)	0.6927 (15)	1.3943 (8)	0.3237 (15)	106 (4)	F(436)	1.1674 (18)	1.4047 (16)	0.1306 (22)	177 (7)

^a The form of the anisotropic temperature factors is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$.

mechanisms of formation of **11** and **12** are not known; however, it is plausible that **11** arises from cleavage of an eight-membered ring precursor, **10**, and that the spirocyclic species **12** arises from the same precursor via elision of PCl_3 . Compounds **11** and **12** have both been synthesized by different routes, and their characterization and properties will be the subject of a future publication.¹²

Experimental Section

Materials and General Procedures. The silyl-substituted urea, $[\text{Me}_2\text{SiN}(\text{Me})_2\text{CO}]_2$,¹³ and $\text{OP}_2[3\text{-CF}_3\text{C}_6\text{H}_4\text{NC}(\text{O})\text{NMe}_2]$ (**3A**)¹³ were prepared according to published methods. All reactions were carried out under a dry-nitrogen atmosphere with the necessary precautions being taken with air- and moisture-sensitive compounds. All solvents were dried and purified by conventional methods and handled under a dry-nitrogen atmosphere.

Spectroscopic Measurements. ¹H and ¹⁹F NMR spectra were recorded on Nicolet NT-200 and Varian EM-390 instruments operating at spectrometer frequencies of 200 and 84.96 MHz, respectively. ¹H and ¹⁹F chemical shifts were measured with respect to internal CH_2Cl_2 (δ 5.28 relative to Me_4Si) and external CCl_3F , respectively. The ³¹P NMR spectra were measured in the FT mode on a Bruker WH-90 instrument operating at a spectrometer frequency of 36.43 MHz. Chemical shifts are referenced externally to 85% H_3PO_4 .

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 157 spectrophotometer using NaCl plates. Mass spectra were recorded

on a Varian CH7 instrument operating at an ionizing voltage of 70 eV.

Preparation of $\text{P}_2[\text{MeNC}(\text{O})\text{NMe}_2]$ (4**).** A solution of 17.2 g (74.0 mmol) of $[\text{Me}_2\text{SiN}(\text{Me})_2\text{CO}]_2$ in 60 mL of CH_2Cl_2 was added dropwise to a stirred solution of 10.1 g (74.0 mmol) of PCl_3 in 30 mL of CH_2Cl_2 . The reaction was conducted in a 250-mL two-necked flask which was equipped with a reflux condenser, dropping funnel, and provision for the ingress and egress of dry N_2 . The flask became warm during the addition, following which the reaction mixture was refluxed for 1 h. Removal of solvent, Me_2SiCl_2 , and other volatiles in vacuo at 40 °C afforded a residue which was treated with 50 mL of CCl_4 . Following this, the residue was separated by filtration, treated three times with 5-mL portions of CCl_4 , and then sublimed in vacuo at 140–150 °C. One more sublimation (180–190 °C (760 torr)) resulted in a 13% yield (2.3 g) of pure **4**. Anal. Calcd for $\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2\text{P}_2$: C, 30.78; H, 5.16; N, 23.93; P, 26.46. Found: C, 30.7; H, 5.1; N, 23.9; P, 26.4. IR data: 2930 s, 1685 s, 1660 s, 1520 w, 1465 s, 1385 m, 1345 m, 1240 w, 1195 m, 1040 w, 980 s, sh, 970 s, 840 w, 770 m, 730 cm^{-1} . The mass spectrum exhibited a molecular ion (m/e 234, 30% relative intensity) and peaks corresponding to $\text{M} - \text{NCH}_3\text{CO}$ (177, 30%), $\text{P}_2\text{NCH}_3\text{CONCH}_3$ (148, 10%), PNCH_3CO (88, 20%), and PNCH_3 (60, 100%).

Preparation of **9, the $\text{Cr}(\text{CO})_5$ Complex of **4**.** A solution of 0.48 g (2.0 mmol) of **4** in 20 mL of tetrahydrofuran (THF) was added slowly via a dropping funnel to a stirred solution of 0.53 g (2.0 mmol) of $\text{Cr}(\text{CO})_5$ in 100 mL of THF which was contained in a two-necked flask of 250-mL capacity. Removal of the solvent afforded a white residue which was recrystallized from THF to produce white crystals of **9** in 70% yield (0.7 g). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{CrN}_4\text{O}_7\text{P}_2$: C, 31.00; H, 2.84; N, 13.15. Found: C, 30.9; H, 2.8; N, 13.2. IR data: 2950 s, 2070 m, 1985 s, 1970 s, 1950 s, 1930 s, 1700 s, 1470 s, 1435 m, 1415 w, 1385 m, 1335 s, 1270 w, 1235 m, 1195 w, 1035 w, 985 s, 975 s, sh, 840 m, 810 w, 770 m, 760 s, 735 s, 680 m, 660

(12) Roesky, H. W.; Djarrah, H., to be submitted for publication.

(13) Klebe, J. F.; Bush, J. B., Jr.; Lyons, J. E. *J. Am. Chem. Soc.* **1964**, *86*, 4400–4406.

Table VI. Atom Coordinates and Thermal Parameters ($\text{\AA}^2 \times 10^3$) for 4 with Standard Deviations in Parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{11}^a	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(2)	0.9760 (2)	0.4166 (1)	0.2597 (2)	52 (1)	52 (1)	50 (1)	6 (1)	10 (1)	4 (1)
P(1)	0.9963 (2)	0.4137 (1)	0.5202 (2)	35 (1)	58 (1)	51 (1)	-6 (1)	11 (1)	0 (1)
N(3)	1.2386 (7)	0.4185 (3)	0.2500 (6)	54 (3)	70 (4)	60 (3)	-1 (3)	30 (3)	-11 (3)
C(2)	1.3718 (10)	0.4125 (3)	0.3899 (7)	89 (5)	36 (3)	60 (4)	2 (4)	-7 (4)	-10 (4)
N(1)	1.2604 (6)	0.4118 (3)	0.5231 (5)	22 (3)	79 (4)	65 (3)	1 (3)	20 (2)	9 (3)
N(6)	0.9154 (6)	0.3310 (3)	0.2514 (5)	34 (3)	74 (4)	43 (3)	-6 (3)	7 (2)	1 (3)
C(5)	0.8812 (8)	0.2919 (3)	0.3887 (7)	40 (4)	32 (3)	69 (4)	-4 (3)	2 (3)	-7 (3)
N(4)	0.9277 (6)	0.3301 (2)	0.5221 (5)	35 (3)	62 (3)	42 (3)	5 (3)	-2 (2)	4 (3)
C(3)	1.3304 (10)	0.4262 (4)	0.0995 (7)	64 (4)	116 (6)	49 (4)	15 (5)	46 (4)	-2 (5)
O(2)	1.5517 (5)	0.4118 (3)	0.3809 (5)	37 (1)	112 (3)	111 (4)	5 (3)	26 (2)	-5 (3)
C(1)	1.3794 (9)	0.4157 (4)	0.6735 (6)	61 (4)	93 (5)	63 (4)	17 (4)	-29 (4)	-2 (5)
C(6)	0.8528 (10)	0.2992 (3)	0.0999 (7)	69 (4)	91 (5)	45 (4)	-12 (4)	7 (4)	-1 (4)
O(5)	0.8152 (6)	0.2337 (2)	0.3828 (4)	72 (3)	56 (3)	65 (3)	-6 (2)	2 (2)	-12 (2)
C(4)	0.8654 (10)	0.2965 (4)	0.6693 (6)	66 (5)	103 (6)	45 (4)	14 (4)	12 (4)	-9 (4)

^a The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$.

cm^{-1} . The mass spectrum exhibited a molecular ion (m/e 426, 15% relative intensity) and peaks corresponding to $M - \text{CO}$ (398, 2%), $M - 2\text{CO}$ (370, 1%), $M - 3\text{CO}$ (342, 4%), $M - 4\text{CO}$ (314, 38%), $M - 5\text{CO}$ (286, 100%), $\text{P}_2(\text{NCH}_3\text{CONCH}_3)_2$ (234, 11%), $\text{P}_2\text{NC}_2\text{H}_3\text{CONCH}_3\text{CO}$ (177, 11%), and PNCH_3 (60, 95%).

Reactions of 4 with Cl_2 and SO_2Cl_2 . The reaction of excess Cl_2 gas with 4 in CH_2Cl_2 solution resulted in 11 and 12. Compound 12 also resulted from the reaction of 4 with an equimolar quantity of SO_2Cl_2 in CH_2Cl_2 solution. Compounds 11 and 12 have been synthesized by different routes, and their characterizations and properties will be reported shortly.¹²

Collection of X-ray Crystallographic Data for 3A and 4. Experimental work was carried out on a Syntex P2₁ diffractometer with graphite-monochromated Cu K α radiation. Details of the intensity data collection and the structure refinement are given in Table IV. Unit cell constants were obtained by least-squares refinement of settings of 15 high-angle reflections $\pm(hkl)$. Intensity data were collected in the θ - 2θ mode to a maximum 2θ value of 135° for 3A and 130° for 4. Two control reflections were monitored every 48 reflections. No significant deviations in their intensities were observed. The net intensities of each reflection were given by $I = [P - (B_1 + B_2)]S$, where P is the total scan count, B_1 and B_2 are the stationary left and right background counts, respectively, each measured for half of the total scan time, and S is the scan rate. The standard deviation of the net intensity is then defined as

$$\sigma(I) = [P + (B_1 + B_2)]^{1/2}S$$

Reflections were scanned from 1.1° below the $K\alpha_1$ to 1.1° above the $K\alpha_2$ 2θ value. Absorption corrections were applied empirically on the basis of azimuthal scan data with ψ intervals of 20° for 20 strong reflections in various regions of reciprocal space. After reflections with $I < 2.0\sigma(I)$ had been treated as unobserved, data reduction yielded 2922 and 982 independent reflections for 3A and 4, respectively. The number of observable reflections (and hence the quality of the X-ray analysis) for 4 was limited by the small size of the best available crystal, namely, $0.32 \times 0.05 \times 0.04$ mm. The dimensions of the crystal of 3A were $0.25 \times 0.28 \times 0.71$ mm.

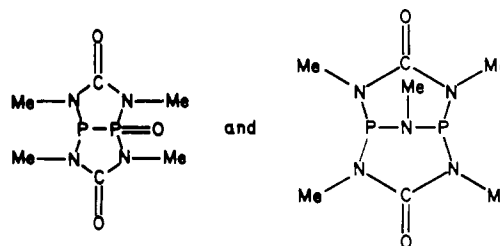
Structure Solution and Refinement for 3A and 4. Both structures were solved by direct methods using SHELX.¹⁴ Refinement was by full-matrix least squares with $\sum w\Delta^2$ being minimized. The CF_3 fluorines in 3A are disordered and display extremely pronounced thermal motions. It was found that these disorders could best be described in terms of two preferred orientations of the CF_3 groups related to one another by a rotation of $\sim 60^\circ$ about the C(13)-C(131) and C(43)-C(431) axes, respectively, and with site occupation factors of 0.6667 for the first [F(131)-F(133) and F(431)-F(433)] and 0.3333 for the second preferred orientation [F(134)-F(136) and F(434)-F(436)]. The fluorine atoms of the first preferred orientation were refined anisotropically, those of the second isotropically. Inspection of the thermal motions indicate, however, that there is some degree

of free rotation between these two orientations. The benzene hydrogens in 3A were assigned individual isotropic temperature factors and allowed to ride on the corresponding carbon atoms with $d(\text{C}-\text{H}) = 1.08$ Å and equal H-C-C angles. Methyl protons in both 3A and 4 were refined rigidly with $d(\text{C}-\text{H}) = 1.08$ Å, tetrahedral bond angles, and group isotropic temperature factors. Weighting schemes for 3A and 4 were given by $w = k(\sigma^2(F_o) + gF_o^2)^{-1}$. The scattering factors for the nonhydrogen atoms were taken from Cromer et al.¹⁵ and for the hydrogen atoms from Stewart et al.¹⁶ Computations were performed on a PDP 10 computer with the use of SHELX (G. M. Sheldrick), ORTEP¹⁷ (C. K. Johnson), and locally developed programs.

Atom coordinates and thermal parameters for 3A and 4 are presented in Tables V and VI, and tabulations of observed and calculated structure factor amplitudes are available.

Acknowledgment. We are grateful to the Deutschen Forschungsgemeinschaft, dem Fonds der Chemischen Industrie, Hoechst AG, the National Science Foundation (Grant CHE 7910155), and the Robert A. Welch Foundation for generous financial support.

Noted Added in Proof. Since the submittal of this manuscript it has been found that the reaction of $[(\text{Me}_3\text{Si})(\text{Me})\text{N}]_2\text{CO}$ with PCl_3 results in the production of



if the order of addition of reagents is reversed. These new compounds have been characterized by elemental analysis, NMR, IR, and mass spectroscopy. This additional work was performed by D. Amirzadeh-Asl and will be the subject of a future publication.

Registry No. 3A, 77507-68-7; 3D, 74393-06-9; 4, 77507-69-8; 9, 77507-85-8; 11, 3576-20-3; 12, 77507-70-1; $[\text{Me}_3\text{SiN}(\text{Me})_2]_2\text{CO}$, 10218-17-4; PCl_3 , 7719-12-2; $\text{Cr}(\text{CO})_5\text{THF}$, 15038-41-2; Cl_2 , 7782-50-5; SO_2Cl_2 , 7791-25-5; 2-chloro-1,3,5-trimethyl-1,3,5-triazaphosphorin-4,6-dione, 77507-71-2.

Supplementary Material Available: Listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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