Synthesis of Molecular Precursors to Carbon−Nitrogen−Phosphorus Polymeric Systems

Jeff McMurran, J. Kouvetakis,* and David C. Nesting

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

John L. Hubbard

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

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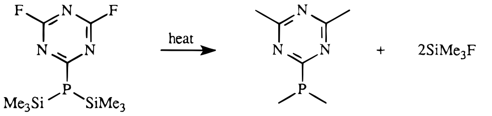
The synthesis, single-crystal X-ray structure, and decomposition reactions of new molecular precursors to amorphous C_3N_3P, a material analogous to C_3N_4, are described. These precursors, $F_2(C_3N_3)P(SiMe_3)_2$ and $Cl_2(C_3N_3)P(SiMe_3)_2$, are prepared via reactions of $C_3N_3X_3$ (X = F, Cl) with $P(SiMe_3)_3$ and decompose at 200−400 °C via complete elimination of stable $SiMe_3X$ (X = F, Cl) byproducts to produce thin films and bulk material of composition C_3N_3P. This material reacts with oxygen to form a novel C_3N_3PO polymer. C_3N_3P and C_3N_3PO represent promising precursors for high-pressure synthesis of three-dimensionally bonded structures that are expected to be hard, strong, and refractory.

Introduction

Recently we reported synthetic routes to stoichiometric carbon nitride involving the thermolysis of molecular precursors such as $X_2(C_3N_3)N(SnMe_3)_2$ and $X_2(C_3N_3)N(SiMe_3)_2$ (X = F,Cl).[1,2] These precursors decompose at 300−400 °C via elimination of stable $SnMe_3X$ and $SiMe_3X$ species to produce thin films and powder materials of composition C_3N_4, the highest nitrogen content observed in bulk C−N solids. These materials are primarily sp^2 hybridized and have a two-dimensional structure for which, according to spectroscopic studies, the $(CN)_3N$ framework of the molecule is both the compositional and structural building block. The films and powders are currently utilized as precursors for the high-pressure synthesis of tetrahedral C_3N_4, which is predicted to be isostructural to Si_3N_4 and may have a hardness similar to that of diamond.[3−6] The synthesis of related materials such as $C_3N_{4-x}P_x$ in which nitrogen atoms are substituted by phosphorus are of immediate interest because the synthetic pathway, the structural units, and physical properties are expected to be similar to those of C_3N_4.[7,8] Moreover, the phosphorus atom may promote 3-dimensionality in these materials, especially at high pressures, because of the propensity to form PN_4 tetrahedra.

Our approach to P-substituted analogues of carbon nitrides is similar to that employed for the synthesis of C_3N_4. Volatile single-source precursors with composition $F_2(C_3N_3)P(SiMe_3)_2$ (**1**) and $Cl_2(C_3N_3)P(SiMe_3)_2$ (**2**) are initially prepared. These clearly incorporate the stoichiometry of the desired product, C_3N_3P, which is obtained from the thermal decomposition of the precursor via elimination of the extremely stable $SiMe_3F$ and $SiMe_3Cl$ byproducts as shown below for **1** (eq 1). The



(1)

stoichiometric analogue of an extended solid with composition C_3N_3P is the molecular phosphorus tricyanide $P(CN)_3$.[9] However **1** and **2** possess the structural building block that is necessary to construct the desired solid-state system in which C_3N_3 rings are linked by P atoms in a sheetlike polymeric structure.

In this paper we report the synthesis and structural characterization of compounds **1** and **2** and their decomposition reactions to produce a C_3N_3P solid which in the presence of oxygen forms a novel quaternary material of composition C_3N_3PO.

Results and Discussion

Compounds $F_2(C_3N_3)P(SiMe_3)_2$ (**1**) and $Cl_2(C_3N_3P(SiMe_3)_2$ (**2**) were prepared by the reaction of tris(trimethylsilyl)phosphine[10] with 2,4,6-trifluoro-1,3,5-triazine and 2,4,6-trichloro-1,3,5-triazine respectively (eq 2)

Compound **1** is highly air sensitive and in its pure form is a colorless solid that sublimes readily at 40 °C

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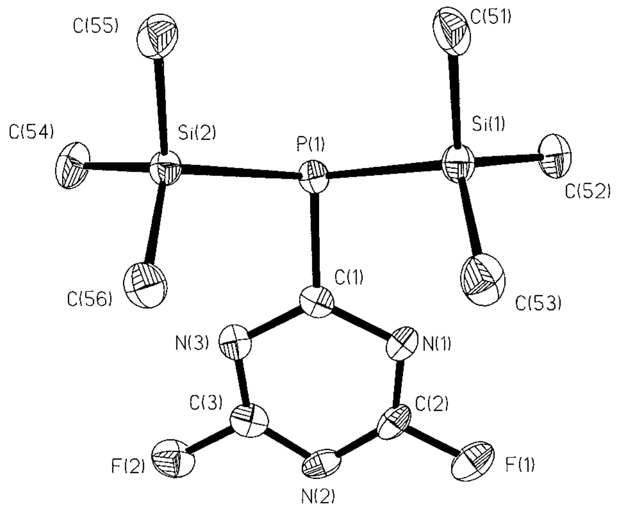
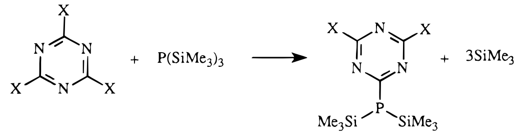


Figure 1. Thermal ellipsoid plot (30% probability) of one of the four independent molecules in the crystal of **1**.



(2)

X= Cl, F

1 X=F

2 X=Cl

and 10^{-3} Torr and melts sharply at 50 °C. Infrared and mass spectroscopic data as well as elemental analysis results are consistent with the $F_2(C_3N_3)P(SiMe_3)_2$ molecular composition. The infrared spectrum reveals weak bands at 2970 and 2900 cm^{-1} corresponding to the symmetric and asymmetric C−H stretches of the $SiMe_3$ ligand and the strong absorption of the aromatic ring are found at 1600 cm^{-1}. Mass spectrometric analysis reveals the molecular ion (M^+) at 293 amu and ($M^+ - CH_3$) as the most intense peak at 278 amu. Additional evidence for the six-membered ring structure is provided by the ^{13}C NMR spectrum, that shows the two nonequivalent ring carbons at 169.6 and 203.05 ppm, respectively, in the intensity ratio of 2:1. The resonances corresponding to the three ring carbons show splitting patterns consistent with the proposed monosubstituted ring structure of the molecule. In addition, the ^{13}C NMR spectrum shows the resonance corresponding to the methyl carbons of the $SiMe_3$ groups at 1.80 ppm. To confirm the structure and composition, we performed a single-crystal structure determination to further characterize the compound.

Compound **1** crystallizes by slow sublimation to form transparent crystals that were used for a single-crystal X-ray structure determination of the material (Tables 1, 2). As shown in Figure 1 the $(CN)_3P$ framework of the molecule is essentially planar; however, the $(CN)_3$ ring is significantly distorted from a regular hexagon. The C1−N1−C2 angle is 112.3° (4) whereas the opposite N2−C3−N3 is 132.0° (5). The C−N bond lengths appear to be within a range of a typical double bond (1.31−1.35 Å), whereas the C−P bond length is substantially longer (1.81 Å) but still within the range of a typical C−P bond.

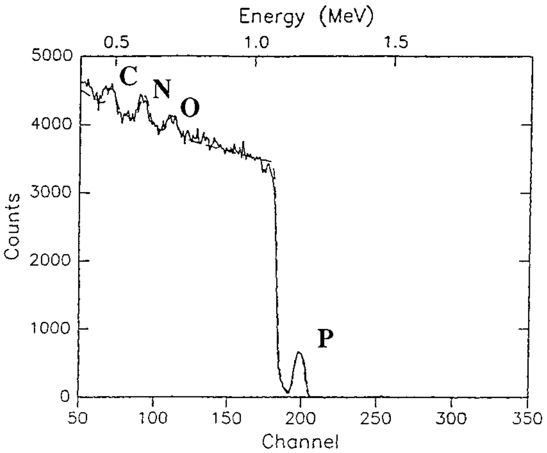


Figure 2. The 2.0 MeV Rutherford backscattering spectrum (RBS) of C−N−P−O material deposited on (100) Si at 350 °C via decomposition of compound **1**. Simulation of the composition using the program RUMP as indicated by the dotted line indicates a composition of C_3N_3PO.

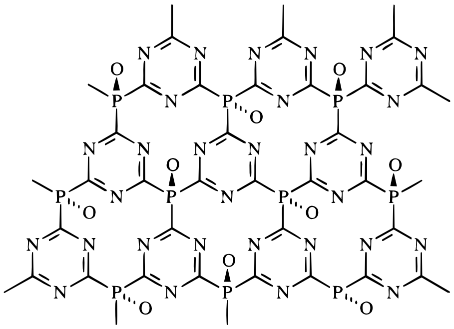


Figure 3. Plausible polymeric structure for C_3N_3PO.

The thermal decomposition of compound **1** was initially carried out in a low-pressure (base pressure 10^{-7} Torr) chemical vapor deposition reactor at 325−375 °C and 10^{-2} Torr to yield thin-film materials on (100)Si via elimination of $SiMe_3F$. Two equivalents of $SiMe_3F$ were eliminated and identified by FTIR and vapor pressure measurements. The films were characterized by Rutherford backscattering spectroscopy (RBS) revealing that carbon, nitrogen, and phosphorus are present in the ratio of 3:3:1, respectively, and that the films were completely free of silicon and fluorine impurities. However, some oxygen contamination was detected in the as-deposited samples. These samples oxidize further in air to eventually yield a material with composition C_3N_3PO. The oxidized material did not degrade further and remained coherent and remarkably adherent to the substrate. Figure 2 shows the RBS spectrum of a thin film with composition C_3N_3PO on Si. To examine the stability of the materials, additional films were grown in which the carrier gas contained 0.1 at. % oxygen. The RBS analysis yielded the same stoichiometry as the previous samples grown without oxygen. Materials exposed to air for extended periods of time and materials deposited in the presence of small oxygen partial pressures always had a composition of approximately C_3N_3PO, indicating that the P atom is likely to be in a bonding environment that consists of three carbons and one oxygen atom as shown in the hypothetical structure in Figure 3. This polymeric material is thermally stable up to 800 °C under high vacuum and is amorphous, as shown by X-ray diffraction.

Decomposition reactions of compound **1** were also carried out in a sealed stainless steel tube reactor for

Table 1. Structure Determination Summary for $C_3N_3F_2P(SiMe_3)_2$ (1) and $C_3N_3Cl_2P(SiMe_3)_2$ (2)

empircal formula	$C_9H_{18}N_3F_2PSi_2$	$C_9H_{18}N_3PSi_2Cl_2$
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	12.319(4)	15.630(5)
b (Å)	15.318(4)	12.538(4)
c (Å)	19.220(7)	18.400(6)
α (deg)	113.32(2)	
β (deg)	108.14(2)	108.51(3)
γ (deg)	90.15(2)	
V (Å$^{3)}$	3131.9(16)	3419(2)
Z	8	8
color; habit	colorless; prisms	colorless; rods
formula weight	293.4 amu	326.4 amu
D_{calc} (g/cm^3)	1.245	1.27
crystal size (mm)	0.2 × 0.3 × 0.5	0.25 × 0.30 × 0.35
temp (K)	173	173
2θ range (deg)	3.5−45	3−45
scan type	q	$2\theta-\theta$
scan speed (deg/min)	3.00−15.00 °/ min in ω	3.00−15.00 °/ min in ω
scan range (deg)	1.20 plus $k\alpha$ separation	1.20 plus $k\alpha$ separation
reflns collected	8665	4818
independent reflns	8422	4564
observed reflns	5823 [$F > 3\sigma(F)$]	2913 [$F > 3\sigma(F)$]
weighting scheme	$\omega^{-1} = \sigma^2F + 0.0015\ F^2$	$\omega^{-1} = \sigma^2F + 0.005\ F^2$
number of parameters	613	307
R	0.0484	0.0544
WR	0.0607	0.0523
goodness of fit	1.10	1.31
largest diff peak (e$^-$/Å^3)	0.68	0.37
μ (mm^{-1})	0.34	0.6

the purpose of obtaining bulk powder for high-pressure experiments. These decompositions were carried out at 180−200 °C and produced 2 equiv of volatile $SiMe_3F$. The remaining residue analyzed for C, N, and P in an approximate 3:3:1 ratio, respectively. The analysis also revealed that the hydrogen content was less than 0.5%, which is indicative of complete elimination of the $SiMe_3$ groups. These bulk polymeric materials are amorphous and stable up to 800 °C. We intend to carry out multianvil and diamond anvil cell high-pressure experiments in order to transform this material to three-dimensional highly cross-linked and crystalline structures that are expected to be strong and hard.

In a synthesis similar to that of **1** the reaction of 2,4,6-trichloro-1,3,5-triazene and tris(trimethylsilyl)phosphine yielded **2** as a colorless air-sensitive solid. This compound was also characterized using GC/MS, FTIR, NMR, and single-crystal X-ray diffraction. The mass spectrum showed a parent (M^+) at 325 amu and ($M^+ - CH_3$) as the strongest peak at 310 amu. The ^{13}C NMR spectrum indicated a monosubstituted ring structure with the presence of two nonequivalent ring carbon environments at 168.5 (doublet) and 197.1 (doublet) ppm in the ratio of 2:1, respectively, and the $SiMe_3$ carbons at 0.949 ppm. The FTIR spectra of **2** are consistent with the aromatic ring structure with absorptions corresponding to the aromatic modes at 1521 cm^{-1} and also indicated the presence of the $SiMe_3$ group by the characteristic vibrational modes such as CH_3 asymmetric and symmetric stretches at 2958 and 2890 cm^{-1}, asymmetric and symmetric deformations at 1458 and 1250 cm^{-1}, as well as asymmetric and symmetric rocking modes at 845 and 760 cm^{-1}.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1 Averaged over the Four Independent Molecules and Numbered as in the First Molecule

C(1)−N(1)	1.31(1)	P(1)−Si(1)	2.256(5)
C(1)−N(3)	1.36(2)	P(1)−Si(2)	2.272(5)
C(1)−P(1)	1.81(1)	Si(1)−C(51)	1.86(2)
C(2)−N(1)	1.30(2)	Si(1)−C(52)	1.86(2)
C(2)−N(2)	1.32(2)	Si(1)−C(53)	1.86(1)
C(2)−F(1)	1.33(1)	Si(2)−C(54)	1.86(1)
C(3)−N(2)	1.31(1)	Si(2)−C(55)	1.86(2)
C(3)−N(3)	1.30(2)	Si(2)−C(56)	1.86(2)
C(3)−F(2)	1.34(2)		
N(1)−C(1)-N(3)	123.4(8)	Si(1)−P(1)-Si(2)	112.6(3)
N(1)−C(1)-P(1)	118.4(8)	C(1)−P(1)-Si(2)	101.1(4)
N(3)−C(1)-P(1)	117.1(6)	C(1)−P(1)-Si(1)	101.9(4)
N(1)−C(2)-N(2)	130.7(8)	C(1)−N(3)-C(3)	112.6(7)
N(2)−C(3)-N(3)	130.5 (8)	C(2)−N(2)-C(3)	109.4(8)
C(1)−N(1)-C(2)	113.1(7)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2 Averaged over Both Independent Molecules and Labeled as the First Molecule

P(1)−Si(1)	2.248(4)	N(1)−C(1)	1.35(1)
P(1)−Si(2)	2.274(4)	N(1)−C(2)	1.30(1)
P(1)−C(1)	1.812 (9)	N(2)−C(2)	1.33(1)
Cl(1)−C(2)	1.73(1)	N(2)−C(3)	1.32(1)
Cl(2)−C(3)	1.73(1)	N(3)−C(1)	1.34(1)
Si(1)−C(4)	1.86(1)	N(3)−C(3)	1.32(1)
Si(1)−C(5)	1.86(1)	Si(2)−C(9)	1.85(1)
Si(1)−C(6)	1.86(1)	Si(2)−C(8)	1.85(1)
Si(2)−C(7)	1.86(1)		
Si(1)−P(1)-Si(2)	112.3(6)	N(2)−C(3)-N(3)	129.1(10)
Si(1)−P(1)-C(1)	101.7(9)	N(1)−C(2)-N(2)	128.9(10)
Si(2)−P(1)-C(1)	102.4(9)	N(1)−C(1)-N(3)	123.2(8)
C(1)−N(1)-C(2)	114.4(8)	P(1)−C(1)-N(3)	118.6(7)
C(2)−N(2)-C(3)	110.6(7)	P(1)−C(1)-N(1)	118.1(7)
C(1)−N(3)-C(3)	113.8(9)		

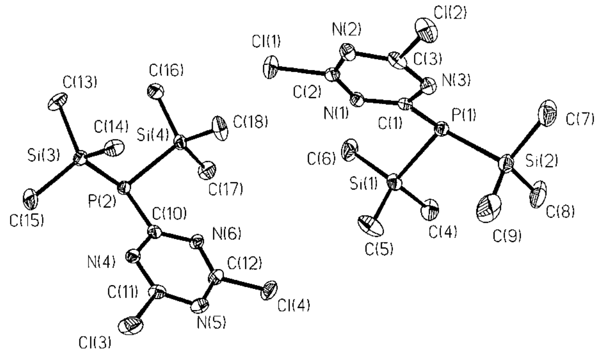


Figure 4. Thermal ellipsoid plot (30% probability) of the asymmetric unit of compound **2**. The closest nonbonded contacts are 2.81 Å between Cl (3a) and C (7b).

A single-crystal X-ray structure determination of **2** was performed to further characterize the molecule (Tables 1 and 3). The structural features (i.e., C−N, C−P bond angles and bond lengths) of **2** were very similar with those of **1** as shown in Figure 4. Details of the structure analysis are presented in the Experimental Section. The decomposition of compound **2** was also carried out in the low-pressure chemical vapor deposition reactor at 425 °C via complete elimination of $SiMe_3Cl$. The RBS analysis revealed that the composition of the thin films, which were exposed to air, was essentially C_3N_3PO. This material was also amorphous and stable up to 800 °C.

Summary

We have demonstrated the synthesis and characterization of new molecular precursors $F_2(C_3N_3)P(SiMe_3)_2$ (**1**) and $Cl_2(C_3N_3)P(SiMe_3)_2$ (**2**), which are analogous to previously reported $X_2(C_3N_3)N(SiMe_3)_2$ (X = Cl, F) precursors of stoichiometric C_3N_4. Compounds **1** and **2** decompose at 200−350 °C via loss of $SiMe_3X$ to produce thin films and powders of composition C_3N_3P, but in the presence of oxygen a new polymeric material with a composition of approximately C_3N_3PO is formed. In forming new materials with three-dimensional bonding, it will be important to prepare the high-pressure samples in an inert atmosphere. It is anticipated that the propensity of phosphorus to form more than three bonds will provide a driving force in the high-pressure reactions to attain three-dimensional materials.

Experimental Section

General Procedures. Reactions were performed under prepurified nitrogen with standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl prior to use. ^{1}H NMR (300 MHz) and ^{13}C NMR (125.7 MHz) spectra were collected on a Varian Gemini 300 spectrometer and were referenced to the solvent resonances (^{31}P spectra were referenced to 85% H_3PO_4). FTIR spectra were recorded on a Nicolet Magna-IR spectrometer either in Nujol mull or in a 10-cm gas cell with KBr windows. Elemental analyses were performed by Galbraith laboratories (Knoxville, TN) and at Goldwater Science Laboratories at ASU. Electron ionization mass spectra were collected on a Varian Saturn 4D spectrometer. The reagents 2,4,6-trichloro-1,3,5-triazine (Aldrich) and the 2,4,6-trifluoro-1,3,5-triazine (Alfa Chemicals) were used as received. Tris(trimethylsilyl)phosphine was synthesized by a procedure described in ref 10.

Synthesis of $F_2(C_3N_3)P(SiMe_3)_2$ (1). To a solution of $C_3N_3F_3$ (1.6 g, 11.8 mmol) in diethyl ether (30 mL) was added a 40-mL etheral solution of $P(SiMe)_3$ (2.96 g, 11.85 mmol) at −20 °C. The brown solution was slowly allowed to reach ambient temperature and stirred for 2−3 h. The solvent was removed in vacuo, and the remaining solid was sublimed at 45 °C to produce a colorless crystalline solid (3.16 g, 91% yield), mp 50 °C. IR (Nujol) 1600 (s), 1506 (s),1431 (m), 1289 (m), 1254 (m) 1060 (m), 930 (w) 851 (vs), 758 (w), 700 (w), 638 (w), 470 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C: δ 0.233 [9H, d ^4J(PH) = 6.8 Hz]. ^{31}P NMR ($CDCl_3$, 25 °C) δ 94.22. ^{13}C NMR ($CDCl_3$, 25 °C) δ 1.79 [d, ^3J(C−P) = 48 Hz], 169.75 [ddd, ^1J(C−F) = 930 Hz, ^3J(CF) = 70 Hz, ^3J(C−P) = 27 Hz], 203.06 [^1J(CP) = 38.8 Hz, ^3J(CF) = 42 Hz]. GC/MS (*m/e*) 293 (M^+), 293 (M^+ − Me), 220 (M^+ − $SiMe_3$), 201 (M^+ − $SiMe_3$-F). Anal. Calcd for $F_2(C_3N_3)P(SiMe_3)_2$: C, 36.89; H, 6.14; N, 14.33. Found: C, 36.08; H, 6.00; N, 14.21.

Synthesis of $Cl_2(C_3N_3)P(SiMe_3)_2$ (2). To a solution of $C_3N_3Cl_3$ (1.0 g, 5.428 mmol) in diethyl ether (30 mL) was added a 25-mL etheral solution of $P(SiMe)_3$ (1.35 g, 5.428 mmol) at −20 °C. The solution was allowed to reach ambient temperature and stirred for 20 h, during which time the solution turned dark brown. The solvent was removed in vacuo and the remaining light brown residue was sublimed at 40 °C and 10^{-3} Torr to yield a colorless crystalline solid (1.4 g, 73% yield), mp 58 °C. IR (KBr) 2958 (w), 2889 (w), 1521 (s), 1458 (s), 1250 (s), 1135 (w), 1065 (w), 844 (s), 760 (m), 764 (m), 698 (w), 630 (w), 443 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C) δ 0.408 (9H, d ^4J(PH) = 3.2 Hz). ^{31}P NMR ($CDCl_3$, 25 °C) δ 96.58. ^{13}C NMR ($CDCl_3$) δ 0.949 [d, ^3J(PC) = 38 Hz], 168.5 [d, ^3J(PC) = 16 Hz], 197.1 [d, ^1J(PC) = 32 Hz]. GC/MS (*m/e*) 325 (M^+), 310 (M^+ − Me), 252 (M^+ − $SiMe_3$), 217 (M^+ − $SiMe_3$−Cl). Elemental anal. calcd: C, 33.25; H, 5.53; N, 12.92; P, 9.53. Found: C, 32.42; H, 5.41; N, 13.33; P, 9.62.

Structure of $F_2(C_3N_3)P(SiMe_3)_2$ (1). Air- and moisture-sensitive crystals of $F_2(C_3N_3)P(SiMe_3)_2$ were mounted under N_2 in a mixture of octane and beeswax. A suitable specimen was mounted vertically in a 0.3-mm X-ray capillary and immediately centered optically on a Siemens P4 autodiffractometer equipped with the LT-2a temperature controller preset at −100 °C. A random search quickly located 25 reflections with $15° < 2\theta < 30°$. Autocentering of these reflections revealed a primitive triclinic cell. The entire hemisphere of the data was collected out to $2\theta = 45°$. The data were corrected for minor absorption by the empirical ψ-scan method. Structure solution was performed by use of direct methods. Subsequent cycles of refinement and difference maps led to the location of all the non-hydrogen atoms in each of the four independent molecules of the asymmetric unit; all non-hydrogen atoms were modeled anisotropically, and the H atoms were positioned in a riding model with fixed C−H distances and isotropic thermal parameters. Convergence led to final R/R_w values of 0.0484/0.0607 with 5823 data ($F > 4\sigma F$) and 613 parameters. All data reduction, solution and refinement calculations utilized the SHELTEXT Plus package of programs available from Siemens Analytical X-ray, Madison, WI.

Structure of $Cl_2(C_3N_3)P(SiMe_3)_2$ (2). A suitable specimen sealed in an X-ray capillary tube was mounted on the Siemens P4 autodiffractometer, and a random search located 25 reflections with $15° < 2\theta < 30°$. Autocentering of these reflections revealed a primitive monoclinic cell. One-half of the hemisphere of the data was collected out to $2\theta = 45°$. Analysis of the systematic absences showed an unambiguous assignment of $P2_1/n$, an alternate setting of $P2_1/c$ (No. 14). The absorption profile determined by empirical ψ scans did not show any significant absorption (variation less than 3%). Structure solution was performed by use of direct methods. Subsequent cycles of refinement and difference maps led to the location of all the non-hydrogen atoms of two independent molecules of the asymmetric unit; all non-hydrogen atoms were modeled anisotropically and the H atoms were positioned in a riding model with fixed C−H distances and isotropic thermal parameters. Convergence led to final R/R_w values of 0.0544/0.0523 with 2913 data ($F > 3\sigma F$) and 307 parameters.

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Supporting Information Available: Experimental details and tables of structure determination information and atomic coordinates (21 pages); tables of structure factors (25 pages). Ordering information is given on any current masthead page.

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