A New, Convenient Synthesis of the Linear Phosphazene Salt [Cl$_3$P=N=PCl$_3$]Cl: Preparation of Higher Linear Homologs [Cl$_3$P=N-(PCl$_2$=N)$_x$=PCl$_3$]Cl (x = 1 - 3) and the 16-membered Macrocycle [NCCl(NPCl$_2$)$_3$]$_2$

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Supporting Information

Experimental Section

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen or argon (Air Products) using common Schlenk techniques or an inert atmosphere glove box (M-Braun). Solvents were dried and collected using a Grubbs-type solvent purification system manufactured by M-Braun.[1] ^{1}H and ^{31}P{^{1}H} NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1 and 121.5 MHz) and were referenced either to protic impurities in the solvent (^{1}H) or externally to 85 % H_3PO_4 (^{31}P{^{1}H}) in CDCl$_3$, CD$_2$Cl$_2$ or D$_2$O. ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were obtained on a Varian Unity 400 spectrometer (100.5 and 79.4 MHz) and were both referenced externally to SiMe$_4$ in CDCl$_3$. Mass spectra were obtained with the use of a VG-250S mass spectrometer using a 70 eV electron impact ionization source. Melting points (uncorrected) were obtained in 0.5 mm (o.d.) glass capillaries which were flame sealed under nitrogen. Elemental analyses were performed at the University of Toronto using a Perkin-Elmer 2400 Series CHN Analyzer. Phosphorus pentachloride and 4-dimethylaminopyridine (DMAP) and bis(trimethylsilyl)carbodiimide were obtained from Aldrich and used as received. As a precautionary measure we note that DMAP is a toxic reagent and one should consult MSDS before use. Cl$_3$P=NSiMe$_3$ (**1**)[2] and [Cl$_3$P=N=PCl$_3$]PCl$_6$ (**11**)[3] were prepared according to literature procedures.

X-ray Crystallographic Structure Determination of 5, 6 and 8. Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A combination of 1° ϕ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[4] The structures were solved and refined with the SHELXTL-PC v6.12 software package.[5] Refinement was by full-matrix least squares on F^2 using data (including negative intensities) with hydrogen atoms bonded to carbon atoms included in calculated positions and treated as riding atoms. Compound **6** crystallized with 0.5 mole equiv. of CH$_2$Cl$_2$ in the lattice. The severity of the disorder within the solvent molecules precluded adequate modeling, therefore the refinement was conducted with the exclusion of CH$_2$Cl$_2$ (using the "Squeeze" option in Platon).[6] However, the density of the crystal was calculated based on the empirical formula **6•0.5 CH$_2$Cl$_2$**.

New Preparation of [Cl$_3$P=N=PCl$_3$]Cl, (1). A solution of Cl$_3$P=NSiMe$_3$ (4.38 g, 19.5 mmol) in 10 mL of CH$_2$Cl$_2$ was added dropwise to a suspension of PCl$_5$ (8.01 g, 38.5 mmol). A yellow suspension was observed after 2.5 h and the ^{31}P NMR spectrum of the reaction mixture was consistent with the formation of [Cl$_3$P=N=PCl$_3$]PCl$_6$ (δ = 21 (s) and -296 (s) ppm for [Cl$_3$P=N=PCl$_3$]$^+$ and PCl$_6^-$, respectively). DMAP was then added portionwise (2.39 g, 19.6 mmol) to the suspension to give a bright yellow solution over a white precipitate. The white solid was isolated by filtration and washed with CH$_2$Cl$_2$ (5 × 50 mL) until the washings were colorless. Pure **1** was recovered after prolonged drying under dynamic vacuum (4.79 g, 76 %). The filtrate was cooled to –30 °C to produce large yellow needles (6.07 g, 95 %) that were identified (*vide supra*) as Cl$_5$P•DMAP (**4**).
^{31}P NMR (Cl$_2$CH-CHCl$_2$): δ = 19.4 ppm (s) [lit., in Cl$_2$CH-CHCl$_2$: δ = 18.4 ppm (s)[7]]. Anal. Calcd. for Cl$_7$NP$_2$ (324.0): %N: 4.32. Found: %N: 3.92.

Preparation of DMAP•PCl$_5$ (4) from DMAP and PCl$_5$. DMAP (0.31 g, 2.5 mmol) was added portionwise to a suspension of PCl$_5$ (0.52 g, 2.5 mmol) in 10 mL of CH$_2$Cl$_2$. A bright yellow suspension was obtained and the reaction was stirred for 2 h. Removal of the volatiles gave a yellow solid and recrystalliation of this material from CH$_2$Cl$_2$ (-30 °C) gave large yellow needles of **4** within 24 h (0.74 g, 90 %).
^{31}P NMR (CDCl$_3$): δ = -237.8 ppm (s). ^{1}H NMR (CDCl$_3$): δ = 3.33 (s, 6H, NMe$_2$), 6.57 (dd, 2H, HC$_{aryl}$, J = 2.4 and 8.3 Hz) and 9.50 ppm (dd, 2H, J = 8.1 and 17.7 Hz, HC$_{aryl}$). ^{13}C{^{1}H} NMR

(CDCl$_3$): δ = 40.2 (s, NMe$_2$), 102.6 (d, J_{CP} = 8.1 Hz, HC$_{aryl}$) and 143.2 ppm (d, J_{CP} = 7.4 Hz, HC$_{aryl}$). mp (°C): 164.5-165.5. Anal. Calcd. for C$_7$H$_{10}$Cl$_5$N$_2$P (330.4): %C: 25.45; %H: 3.05; %N: 8.48. Found: %C 25.61; %H: 3.25; %N: 8.33.

Preparation of [Cl$_3$P=N-PCl$_2$=N=PCl$_3$]Cl (5). To a white suspension of **1** (0.49 g, 1.5 mmol) in 5 mL of CH$_2$Cl$_2$ was added dropwise a 1 mL solution of Cl$_3$P=NSiMe$_3$ (0.34 g, 1.5 mmol). A clear, colorless solution was observed within 20 min and the reaction was stirred for a further 2 h. Hexanes (1 mL) were carefully layered on top of the reaction mixture and subsequent cooling to -30 °C produced large colorless plates of **5•CH$_2$Cl$_2$** (0.47 g, 59 %).
^{31}P NMR (CDCl$_3$): δ = 13.8 (d, Cl$_3$*P*N-, $^2J_{PP}$ = 40.1 Hz) and −11.5 ppm (t, -N*P*Cl$_2$N-, $^2J_{PP}$ = 40.1 Hz); 2:1 ratio. mp (°C): 110-112. Anal. Calcd. for **5•CH$_2$Cl$_2$**, CH$_2$Cl$_{11}$N$_2$P$_3$ (524.9): %C: 2.29; %H: 0.38; %N: 5.34. Found: %C: 1.76; %H: 0.30; %N: 5.37.

Preparation of [Cl$_3$P=N-PCl$_2$=N-PCl$_2$=N=PCl$_3$]Cl (6). To a white suspension of **1** (0.19 g, 0.59 mmol) in 3 mL of CH$_2$Cl$_2$ was added dropwise a 1 mL solution of Cl$_3$P=NSiMe$_3$ (0.27 g, 1.2 mmol). A clear, colorless solution was formed within 20 min and the reaction was stirred for a further 2 h. Hexanes (1 mL) were carefully layered on top of the reaction mixture and subsequent cooling to −30 °C produced large colorless needles of **6•0.5CH$_2$Cl$_2$** (0.15 g, 42 %).
^{31}P NMR (CDCl$_3$): δ = 10.9 (br, Cl$_3$*P*N-) and -13.0 ppm (br, -N*P*Cl$_2$N-); 1:1 ratio. mp (°C): 140-143. Anal. Calcd. for **6•0.5 CH$_2$Cl$_2$**, C$_{0.5}$HCl$_{12}$N$_3$P$_4$ (598.4): %C: 1.00; %H: 0.17; %N: 7.02. Found: %C: 1.33; %H: 0.21; %N: 6.82.

Preparation of [Cl$_3$P=N-PCl$_2$=N-PCl$_2$-N=PCl$_2$=N=PCl$_3$]Cl (7). To a white suspension of **1** (0.22 g, 0.68 mmol) in 5 mL of CH$_2$Cl$_2$ was added dropwise a 1 mL solution of Cl$_3$P=NSiMe$_3$ (0.46 g, 2.1 mmol). A clear, colorless solution was observed within 5 min and the reaction was stirred for 20 h. The volatiles were removed, and the resulting white oily residue was dissolved in a 1:1 CH$_2$Cl$_2$/hexanes mixture (3 mL) and cooled to -30 °C. An oily layer then formed at the bottom of the vial. Decanting the supernatant provided **7** as a white oil upon removal of the volatiles (0.24 g, 55 %). Despite numerous attempts to purify this material, residual **6** (*ca.* 5 %) was always present. The reported yield is based upon the assumption that **7** is unsolvated, and as such should be regarded as an estimate.
^{31}P{^{1}H} NMR (CDCl$_3$): δ = 9.0 (m, Cl$_3$*P*N-) and -14.5 ppm (m, -N*P*Cl$_2$N-); 2:3 ratio. Due to the presence of extraneous **6**, elemental analysis was not performed.

Synthesis of [NCCl(NPCl$_2$)$_3$]$_2$ (8). To a solution of **5•CH$_2$Cl$_2$** (0.38 g, 0.73 mmol) in 3 mL of CH$_2$Cl$_2$ was added dropwise a solution of Me$_3$SiN=C=NSiMe$_3$ (0.13 g, 0.71 mmol) in 1 mL of CH$_2$Cl$_2$. The reaction was stirred for two days to give a mixture of two products (A and B) in approximately equal amounts. Compound A gave a doublet at -2.7 ppm and a triplet at −17.4 ppm ($^2J_{PP}$ = 29.2 Hz), while compound B displayed similar resonances at −4.9 (d) and −17.0 ppm (t, $^2J_{PP}$ = 41.3 Hz). Layering of hexanes (0.5 mL) onto the reaction mixture followed by cooling to −30 °C for 3 weeks produced large colorless blocks of compound A, which were identified as the 16-membered heterocycle **8** (70 mg, 24 %). Compound B is tentatively assigned as the related 8-membered heterocycle [NCCl(NPCl$_2$)$_3$] (**9**)
Data for **8**: ^{31}P NMR (CDCl$_3$): -2.7 (d, $^2J_{PP}$ = 29.2 Hz, CCl-N=*P*Cl$_2$-) and −17.4 (t, $^2J_{PP}$ = 29.2 Hz, PCl$_2$=N-*P*Cl$_2$=N-PCl$_2$); 2:1 ratio. EI-MS (70 eV, *m/z*, %): 783 [M$^+$ - Cl, 26, correct isotope distribution for 13 Cl atoms], 711 [M$^+$ - 3 Cl, 5], 373 [{NCCl(NPCl$_2$)$_3$} - Cl, 100]. mp (°C): 97-98. Anal. Calcd. for C$_2$Cl$_{14}$N$_8$P$_6$ (818.3): %C: 2.94; %N: 13.69. Found: %C: 3.13; %N: 13.10.

References:
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Table 1. Crystal data and structure refinement for **5•CH₂Cl₂**

Identification code	k03156
Empirical formula	C H2 Cl11 N2 P3
Formula weight	524.91
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.6850(4) Å α= 90°.
	b = 12.6600(5) Å β= 96.760(2)°.
	c = 12.9850(3) Å γ = 90°.
Volume	1744.30(10) Å^3
Z	4
Density (calculated)	1.999 Mg/m^3
Absorption coefficient	2.004 mm^{-1}
F(000)	1016
Crystal size	0.35 x 0.30 x 0.10 mm^3
Theta range for data collection	2.84 to 27.49°.
Index ranges	-13<=h<=13, -16<=k<=16, -14<=l<=16
Reflections collected	15564
Independent reflections	3995 [R(int) = 0.0547]
Completeness to theta = 27.49°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.850 and 0.649
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3995 / 0 / 155
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0748
R indices (all data)	R1 = 0.0527, wR2 = 0.0826
Extinction coefficient	0.0020(3)
Largest diff. peak and hole	0.560 and -0.486 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for **5·CH₂Cl₂**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(9)	2023(1)	4331(1)	1504(1)	25(1)
Cl(1)	10484(1)	3014(1)	5612(1)	57(1)
Cl(2)	10489(1)	3592(1)	3265(1)	31(1)
Cl(3)	8889(1)	1667(1)	3910(1)	41(1)
Cl(4)	7298(1)	4374(1)	6250(1)	38(1)
Cl(5)	6186(1)	5259(1)	4084(1)	36(1)
Cl(6)	3923(1)	1859(1)	5165(1)	34(1)
Cl(7)	3936(1)	3064(1)	3041(1)	31(1)
Cl(8)	5659(1)	1048(1)	3570(1)	39(1)
P(1)	9401(1)	3115(1)	4288(1)	23(1)
P(2)	7009(1)	3992(1)	4766(1)	22(1)
P(3)	5031(1)	2348(1)	4154(1)	22(1)
N(1)	8298(2)	3892(2)	4321(2)	34(1)
N(2)	6109(3)	3039(2)	4657(2)	40(1)
C(1S)	8470(3)	4801(3)	1182(2)	34(1)
Cl(10)	7537(1)	3689(1)	1422(1)	52(1)
Cl(11)	8235(1)	5838(1)	2043(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for **5•CH₂Cl₂**.

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Cl(1)-P(1)	1.9611(11)
Cl(2)-P(1)	1.9610(10)
Cl(3)-P(1)	1.9600(11)
Cl(4)-P(2)	1.9752(10)
Cl(5)-P(2)	1.9869(10)
Cl(6)-P(3)	1.9678(10)
Cl(7)-P(3)	1.9703(10)
Cl(8)-P(3)	1.9633(10)
P(1)-N(1)	1.538(3)
P(2)-N(2)	1.538(3)
P(2)-N(1)	1.561(2)
P(3)-N(2)	1.531(3)
C(1S)-Cl(11)	1.762(3)
C(1S)-Cl(10)	1.775(3)
N(1)-P(1)-Cl(3)	114.40(12)
N(1)-P(1)-Cl(1)	113.07(11)
Cl(3)-P(1)-Cl(1)	106.09(6)
N(1)-P(1)-Cl(2)	109.82(10)
Cl(3)-P(1)-Cl(2)	106.76(5)
Cl(1)-P(1)-Cl(2)	106.18(5)
N(2)-P(2)-N(1)	118.16(16)
N(2)-P(2)-Cl(4)	107.81(12)
N(1)-P(2)-Cl(4)	109.72(11)
N(2)-P(2)-Cl(5)	110.67(11)
N(1)-P(2)-Cl(5)	105.30(10)
Cl(4)-P(2)-Cl(5)	104.33(5)
N(2)-P(3)-Cl(8)	111.72(12)
N(2)-P(3)-Cl(6)	112.10(12)
Cl(8)-P(3)-Cl(6)	104.73(5)
N(2)-P(3)-Cl(7)	113.70(11)
Cl(8)-P(3)-Cl(7)	107.63(5)
Cl(6)-P(3)-Cl(7)	106.40(4)
P(1)-N(1)-P(2)	140.73(18)

P(3)-N(2)-P(2)	156.7(2)
Cl(11)-C(1S)-Cl(10)	110.77(17)

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **5•CH₂Cl₂**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(9)	27(1)	25(1)	23(1)	3(1)	7(1)	1(1)
Cl(1)	42(1)	86(1)	39(1)	21(1)	-12(1)	-10(1)
Cl(2)	25(1)	33(1)	37(1)	6(1)	13(1)	0(1)
Cl(3)	41(1)	29(1)	58(1)	-9(1)	26(1)	-9(1)
Cl(4)	44(1)	45(1)	26(1)	-11(1)	7(1)	1(1)
Cl(5)	35(1)	29(1)	48(1)	12(1)	16(1)	11(1)
Cl(6)	33(1)	42(1)	28(1)	5(1)	11(1)	1(1)
Cl(7)	28(1)	35(1)	28(1)	7(1)	-2(1)	0(1)
Cl(8)	41(1)	32(1)	45(1)	-7(1)	14(1)	7(1)
P(1)	20(1)	25(1)	25(1)	2(1)	5(1)	1(1)
P(2)	21(1)	21(1)	24(1)	-1(1)	6(1)	1(1)
P(3)	20(1)	22(1)	24(1)	0(1)	3(1)	-1(1)
N(1)	31(1)	35(2)	38(1)	8(1)	17(1)	10(1)
N(2)	36(2)	27(2)	51(2)	7(1)	-15(1)	-9(1)
C(1S)	38(2)	36(2)	27(2)	2(1)	4(1)	0(1)
Cl(10)	59(1)	51(1)	44(1)	-6(1)	1(1)	-21(1)
Cl(11)	46(1)	41(1)	39(1)	-7(1)	10(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2x 10 ^{3}) for **5•CH₂Cl₂**.

	x	y	z	U(eq)
H(1SA)	9371	4598	1266	41
H(1SB)	8245	5044	459	41

Table 6. Crystal data and structure refinement for **6•0.5 CH₂Cl₂**.

Identification code	k03192a
Empirical formula	C0.50 H Cl12 N3 P4
Formula weight	598.32
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2/c

Unit cell dimensions

$a = 14.9781(6)$ Å	$\alpha = 90°$.
$b = 11.2624(8)$ Å	$\beta = 115.594(3)°$.
$c = 14.9417(10)$ Å	$\gamma = 90°$.

Volume	2273.2(2) Å³
Z	4
Density (calculated)	1.748 Mg/m³
Absorption coefficient	1.732 mm⁻¹
F(000)	1156
Crystal size	0.12 x 0.12 x 0.08 mm³
Theta range for data collection	3.96 to 27.53°.
Index ranges	-19<=h<=19, -13<=k<=14, -18<=l<=19
Reflections collected	19522
Independent reflections	5206 [R(int) = 0.1168]
Completeness to theta = 25.00°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.930 and 0.751
Refinement method	Full-matrix least-squares on F²
Data / restraints / parameters	5206 / 0 / 164
Goodness-of-fit on F²	1.062
Final R indices [I>2sigma(I)]	R1 = 0.1090, wR2 = 0.2732
R indices (all data)	R1 = 0.1607, wR2 = 0.2917
Extinction coefficient	0.0037(8)
Largest diff. peak and hole	1.146 and -0.842 e.Å⁻³

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for **6•0.5 CH$_2$Cl$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	1722(2)	4290(3)	5791(2)	43(1)
Cl(2)	-283(2)	3383(3)	5809(2)	44(1)
Cl(3)	1739(2)	3189(3)	7736(2)	44(1)
Cl(4)	1291(3)	-619(3)	5337(3)	58(1)
Cl(5)	2989(3)	463(4)	7211(3)	59(1)
Cl(6)	4650(3)	926(4)	6082(3)	60(1)
Cl(7)	3121(3)	-839(3)	4567(3)	49(1)
Cl(8)	3159(2)	2965(3)	2327(2)	42(1)
Cl(9)	3168(2)	4119(3)	4265(2)	42(1)
Cl(10)	5116(2)	3030(3)	4304(2)	43(1)
P(1)	1137(2)	3026(3)	6286(2)	33(1)
P(2)	1992(2)	890(3)	5841(2)	34(1)
P(3)	3334(2)	870(3)	4910(2)	36(1)
P(4)	3671(2)	2759(3)	3772(2)	33(1)
N(1)	1212(7)	1750(9)	5914(8)	38(2)
N(2)	2498(7)	1364(8)	5187(7)	33(2)
N(3)	3397(7)	1507(9)	4014(8)	37(2)
Cl(11)	2608(2)	6406(3)	5073(2)	34(1)

Table 8. Bond lengths [Å] and angles [°] for **6•0.5 CH₂Cl₂**

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Cl(1)-P(1)	1.976(4)
Cl(2)-P(1)	1.971(4)
Cl(3)-P(1)	1.963(4)
Cl(4)-P(2)	1.968(5)
Cl(5)-P(2)	2.002(5)
Cl(6)-P(3)	1.994(5)
Cl(7)-P(3)	1.981(5)
Cl(8)-P(4)	1.967(4)
Cl(9)-P(4)	1.984(4)
Cl(10)-P(4)	1.980(4)
P(1)-N(1)	1.562(11)
P(2)-N(1)	1.557(10)
P(2)-N(2)	1.567(10)
P(3)-N(3)	1.558(11)
P(3)-N(2)	1.580(9)
P(4)-N(3)	1.554(10)
N(1)-P(1)-Cl(3)	114.2(4)
N(1)-P(1)-Cl(2)	106.9(4)
Cl(3)-P(1)-Cl(2)	106.85(19)
N(1)-P(1)-Cl(1)	114.7(4)
Cl(3)-P(1)-Cl(1)	106.2(2)
Cl(2)-P(1)-Cl(1)	107.6(2)
N(1)-P(2)-N(2)	114.2(6)
N(1)-P(2)-Cl(4)	105.8(4)
N(2)-P(2)-Cl(4)	112.2(4)
N(1)-P(2)-Cl(5)	109.2(4)
N(2)-P(2)-Cl(5)	111.8(4)
Cl(4)-P(2)-Cl(5)	102.9(2)
N(3)-P(3)-N(2)	114.3(5)
N(3)-P(3)-Cl(7)	106.8(4)
N(2)-P(3)-Cl(7)	110.7(4)
N(3)-P(3)-Cl(6)	109.6(4)
N(2)-P(3)-Cl(6)	110.7(4)

Cl(7)-P(3)-Cl(6)	104.2(2)
N(3)-P(4)-Cl(8)	110.2(4)
N(3)-P(4)-Cl(10)	113.5(4)
Cl(8)-P(4)-Cl(10)	105.28(19)
N(3)-P(4)-Cl(9)	115.6(4)
Cl(8)-P(4)-Cl(9)	106.6(2)
Cl(10)-P(4)-Cl(9)	104.8(2)
P(2)-N(1)-P(1)	140.2(7)
P(2)-N(2)-P(3)	134.0(7)
P(4)-N(3)-P(3)	137.6(7)

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Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters (Å^2x 10^3) for **6•0.5 CH₂Cl₂**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	44(2)	41(2)	46(2)	10(1)	22(1)	-3(1)
Cl(2)	34(2)	47(2)	51(2)	3(1)	19(1)	3(1)
Cl(3)	47(2)	51(2)	34(2)	1(1)	18(1)	2(1)
Cl(4)	64(2)	42(2)	83(3)	-13(2)	45(2)	-15(2)
Cl(5)	53(2)	80(3)	42(2)	19(2)	18(2)	12(2)
Cl(6)	39(2)	89(3)	50(2)	5(2)	17(2)	-4(2)
Cl(7)	64(2)	30(2)	70(2)	0(2)	45(2)	2(2)
Cl(8)	51(2)	43(2)	34(2)	5(1)	19(1)	2(1)
Cl(9)	50(2)	36(2)	49(2)	-3(1)	29(2)	4(1)
Cl(10)	34(2)	46(2)	49(2)	6(1)	19(1)	0(1)
P(1)	33(2)	36(2)	34(2)	2(1)	17(1)	3(1)
P(2)	39(2)	32(2)	34(2)	1(1)	19(1)	-1(1)
P(3)	34(2)	34(2)	40(2)	1(1)	17(1)	1(1)
P(4)	37(2)	30(2)	37(2)	2(1)	20(1)	1(1)
N(1)	38(5)	39(6)	39(6)	1(5)	17(4)	13(4)
N(2)	44(6)	22(5)	43(6)	0(4)	28(5)	5(4)
N(3)	39(5)	28(5)	48(6)	-3(4)	23(5)	-3(4)
Cl(11)	36(2)	32(2)	39(2)	-4(1)	21(1)	-2(1)

Table 10. Crystal data and structure refinement for **8**

Identification code	k03181a
Empirical formula	C2 Cl14 N8 P6
Formula weight	818.22
Temperature	150(2) K
Wavelength	0.71073 ≈
Crystal system	Monoclinic
Space group	P 21/c

Unit cell dimensions		
	a = 10.5679(2) Å	α = 90°.
	b = 12.7427(2) Å	β = 111.1100(10)°.
	c = 10.3853(2) Å	γ = 90°.

Volume	1304.67(4) Å^3
Z	2
Density (calculated)	2.083 Mg/m^3
Absorption coefficient	1.860 mm^{-1}
F(000)	792
Crystal size	0.30 x 0.28 x 0.24 mm^3
Theta range for data collection	2.61 to 27.48°.
Index ranges	-12<=h<=13, -16<=k<=16, -13<=l<=13
Reflections collected	9215
Independent reflections	2978 [R(int) = 0.0266]
Completeness to theta = 27.48°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.641 and 0.557
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2978 / 0 / 137
Goodness-of-fit on F^2	1.099
Final R indices [I>2sigma(I)]	R1 = 0.0252, wR2 = 0.0568
R indices (all data)	R1 = 0.0300, wR2 = 0.0591
Extinction coefficient	0.0043(7)
Largest diff. peak and hole	0.362 and -0.403 e.Å^{-3}

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	6080(1)	-3497(1)	19(1)	32(1)
Cl(2)	5359(1)	-1497(1)	1359(1)	27(1)
Cl(3)	8543(1)	-2088(1)	-1494(1)	35(1)
Cl(4)	7602(1)	248(1)	-1804(1)	33(1)
Cl(5)	9706(1)	-333(1)	3350(1)	29(1)
Cl(6)	7001(1)	950(1)	3895(1)	31(1)
Cl(7)	9052(1)	2352(1)	3117(1)	30(1)
P(1)	5254(1)	-2072(1)	-467(1)	17(1)
P(2)	7600(1)	-1045(1)	-736(1)	19(1)
P(3)	7390(1)	1497(1)	2267(1)	17(1)
N(1)	6084(2)	-1365(1)	-1104(2)	21(1)
N(2)	8598(2)	-953(1)	849(2)	23(1)
N(3)	7615(2)	556(1)	1364(2)	20(1)
N(4)	6258(2)	2276(1)	1411(2)	20(1)
C(1)	8493(2)	-213(2)	1671(2)	20(1)

Table 13. Bond lengths [Å] and angles [°] for **8**.

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Cl(1)-P(1)	1.9990(7)
Cl(2)-P(1)	1.9987(7)
Cl(3)-P(2)	1.9863(7)
Cl(4)-P(2)	1.9861(7)
Cl(5)-C(1)	1.7602(19)
Cl(6)-P(3)	2.0038(7)
Cl(7)-P(3)	1.9827(7)
P(1)-N(1)	1.5612(17)
P(1)-N(4)#1	1.5664(16)
P(2)-N(1)	1.5612(17)
P(2)-N(2)	1.6078(16)
P(3)-N(4)	1.5630(16)
P(3)-N(3)	1.5915(16)
N(2)-C(1)	1.303(3)
N(3)-C(1)	1.307(2)
N(4)-P(1)#1	1.5664(16)
N(1)-P(1)-N(4)#1	115.65(9)
N(1)-P(1)-Cl(2)	110.02(7)
N(4)#1-P(1)-Cl(2)	110.48(7)
N(1)-P(1)-Cl(1)	111.79(7)
N(4)#1-P(1)-Cl(1)	105.15(6)
Cl(2)-P(1)-Cl(1)	102.92(3)
N(1)-P(2)-N(2)	120.42(9)
N(1)-P(2)-Cl(4)	106.68(7)
N(2)-P(2)-Cl(4)	112.29(7)
N(1)-P(2)-Cl(3)	110.22(7)
N(2)-P(2)-Cl(3)	102.53(6)
Cl(4)-P(2)-Cl(3)	103.40(3)
N(4)-P(3)-N(3)	112.96(9)
N(4)-P(3)-Cl(7)	106.15(6)
N(3)-P(3)-Cl(7)	112.36(6)
N(4)-P(3)-Cl(6)	110.67(7)
N(3)-P(3)-Cl(6)	110.75(7)

Cl(7)-P(3)-Cl(6)	103.48(3)
P(1)-N(1)-P(2)	136.92(11)
C(1)-N(2)-P(2)	122.98(14)
C(1)-N(3)-P(3)	131.65(14)
P(3)-N(4)-P(1)#1	130.54(11)
N(2)-C(1)-N(3)	127.10(17)
N(2)-C(1)-Cl(5)	112.52(14)
N(3)-C(1)-Cl(5)	120.39(14)

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table 14. Anisotropic displacement parameters $(Å^2 x 10^3)$ for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	39(1)	22(1)	31(1)	5(1)	9(1)	12(1)
Cl(2)	35(1)	31(1)	18(1)	-3(1)	11(1)	2(1)
Cl(3)	27(1)	46(1)	32(1)	-18(1)	9(1)	9(1)
Cl(4)	40(1)	32(1)	32(1)	2(1)	19(1)	-8(1)
Cl(5)	28(1)	31(1)	19(1)	-5(1)	-1(1)	8(1)
Cl(6)	35(1)	39(1)	25(1)	8(1)	16(1)	6(1)
Cl(7)	19(1)	26(1)	42(1)	-12(1)	7(1)	-6(1)
P(1)	19(1)	16(1)	16(1)	1(1)	6(1)	3(1)
P(2)	17(1)	22(1)	18(1)	-5(1)	6(1)	1(1)
P(3)	16(1)	16(1)	18(1)	-3(1)	6(1)	-2(1)
N(1)	18(1)	26(1)	19(1)	2(1)	5(1)	0(1)
N(2)	19(1)	24(1)	22(1)	-6(1)	3(1)	4(1)
N(3)	21(1)	19(1)	18(1)	-4(1)	4(1)	0(1)
N(4)	21(1)	16(1)	24(1)	-1(1)	9(1)	0(1)
C(1)	17(1)	22(1)	18(1)	-3(1)	4(1)	0(1)