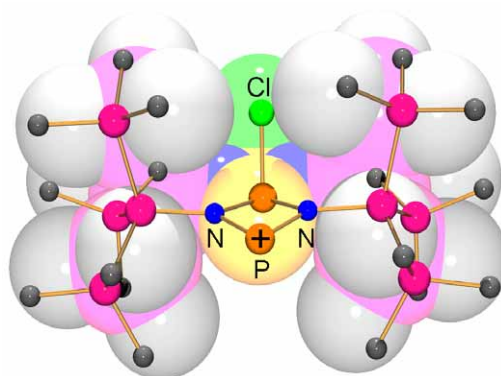


Hypersilylated Cyclodiphosphadiazanes and Cyclodiphosphadiazanium Salts

René Kuzora, Axel Schulz, Alexander Villinger and Ronald Wustrack*



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1. Experimental

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,^[1] dried over P₄O₁₀ and freshly distilled prior to use. *N*-hexane was dried over Na/Benzophenone/Tetraglyme and freshly distilled prior to use. THF was dried over Na/Benzophenone and freshly distilled prior to use. Toluene was dried over Na/K/Benzophenone and freshly distilled prior to use. Tris-(trimethylsilyl)silyl-amine was prepared according to a literature procedure.^[2] Triethylamine (98%, Merck) and PCl₃ (99.9%, Acros) were freshly distilled prior to use. GaCl₃ (99.999%, Sigma-Aldrich), Silvertriflourmethanesulfonate (98%, Fluka) and *n*-BuLi (2.5M, Acros) were used as recieved.

NMR: ³¹P{¹H}, ²⁹Si-INEPT, ¹⁹F{¹H}, ¹³C{¹H}, ¹³C-DEPT and ¹H-NMR spectra were obtained on a Bruker AVANCE 300, 400 or 500 spectrometer and were referenced internally to the deuterated solvent (¹³C, CD₂Cl₂: δ_{reference} = 54 ppm, C₆D₆: δ_{reference} = 128 ppm) or to protic impurities in the deuterated solvent (¹H, CDHCl₂: δ_{reference} = 5.31 ppm, C₆D₅H: δ_{reference} = 7.16 ppm). C₆D₆ was dried over Na/benzophenone, CD₂Cl₂ was dried as depicted above for the undeuterated solvent.

IR: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device or Nicolet 380 FTIR with Smart Orbit ATR module.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064nm).

MS: Finnigan MAT 95-XP from Thermo Electron.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

DSC: DSC 823e from Mettler-Toledo, Heating-rate 20 °C/min.

2. Structure elucidation

X-ray Structure Determination: X-ray quality crystals of **5**, **6** and **7** were selected in Fomblin-YR1800 oil (Alfa Aesar) at ambient temperatures, X-ray quality crystals of **4** and **8** were selected in Galden-HT230 oil (Solvay Solexis) at 200 K. All samples were cooled to 173(2) K during measurement. The data were collected on a Bruker-Nonius Apex X8 CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$). The structures were solved by direct methods (*SHELXS-97*)^[3] and refined by full-matrix least squares procedures (*SHELXL-97*).^[4] Semi-empirical absorption corrections were applied (SADABS).^[5] All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

The P(SO₃CF₃)-Fragment in molecule **6** was disordered and was split in two parts. The occupancy of each part was refined freely (0.833(2)/0.167(2)). The N₂P₂Cl⁺-unit in **7** was disordered. The position of the P-atoms and the Cl-atom was split in two parts. The occupancy of each part was refined freely (0.853(8)/ 0.147(8)). The Dichloromethane molecule in **7** was disordered. The position of the Cl-atoms was split in two parts. The occupancy of each part was refined freely (0.57(10)/ 0.43(10)).

Several samples of **5** have been measured, which all gave the same result. **5** crystallizes in the cubic spacegroup P2₁3 ($a = 15.8101(2)$ Å, $V = 3951.88(9)$ Å³) with four molecules in the unit cell. The molecules lie along the crystallographic three-fold axis and are found to be disordered over two positions, which results in a heavy disorder which could not be modelled satisfactorily.

Table S1. Crystallographic Details of **4**, **6** and **7**

	4	6	7
Chem. Formula	C ₉ H ₂₈ Cl ₂ NPSi ₄	C ₁₉ H ₅₄ ClF ₃ N ₂ O ₃ P ₂ SSi ₈	C ₁₉ H ₅₆ Cl ₇ GaN ₂ P ₂ Si
Form. Wght. [g mol ⁻¹]	364.55	769.81	917.19
Colour	Colourless	Colourless	Red
Cryst. system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /c	P2 ₁ /c
<i>a</i> [Å]	15.513(3)	18.508(4)	14.5675(16)
<i>b</i> [Å]	9.906(2)	13.008(3)	12.0572(16)
<i>c</i> [Å]	27.600(6)	18.329(4)	27.204(4)
α [°]	90.00	90.00	90.00
β [°]	90.80(3)	108.40(3)	101.975(3)
γ [°]	90.00	90.00	90.00
<i>V</i> [Å ³]	4240.9(15)	4187.2(15)	4674.2(11)
<i>Z</i>	8	4	4
$\rho_{\text{calc.}}$ [g cm ⁻³]	1.142	1.221	1.303
μ [mm ⁻¹]	0.594	0.483	1.278
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173 (2)	173 (2)	173 (2)
Measured reflections	27606	70840	37008
Independent reflections	6166	12191	8045
Reflections with $I > 2\sigma(I)$	4528	10111	6624
<i>R</i> _{int.}	0.0265	0.0242	0.0471
<i>F</i> (000)	1552	1632	1904
<i>R</i> ₁ (R [$F^2 > 2\sigma(F^2)$])	0.0399	0.0494	0.0849
w <i>R</i> ₂ (F^2)	0.1048	0.1371	0.2428
GooF	1.044	1.047	1.032
Parameters	167	434	418
CCDC #			

Table S2. Crystallographic Details of tris(trimethylsilyl)chlorosilane.

	tris(trimethylsilyl)chlorosilane (8)
Chem. Formula	C ₉ H ₂₇ ClSi ₄
Form. Wght. [g mol ⁻¹]	283.12
Colour	Colourless
Cryst. system	Cubic
Space group	Pa-3
<i>a</i> [Å]	15.467(3)
<i>b</i> [Å]	15.467(3)
<i>c</i> [Å]	15.467(3)
<i>α</i> [°]	90.00
<i>β</i> [°]	90.00
<i>γ</i> [°]	90.00
<i>V</i> [Å ³]	3700.3(12)
<i>Z</i>	8
<i>ρ</i> _{calc.} [g cm ⁻³]	1.016
<i>μ</i> [mm ⁻¹]	0.441
<i>λ</i> _{MoKα} [Å]	0.71073
<i>T</i> [K]	173 (2)
Measured reflections	7244
Independent reflections	1628
Reflections with <i>I</i> > 2σ(<i>I</i>)	1198
<i>R</i> _{int.}	0.0311
<i>F</i> (000)	1232
<i>R</i> ₁ (R [<i>F</i> ² > 2σ(<i>F</i> ²)])	0.0349
<i>wR</i> ₂ (<i>F</i> ²)	0.0903
GooF	1.026
Parameters	46
CCDC #	

Scheme S1. Numbering scheme of **4**.

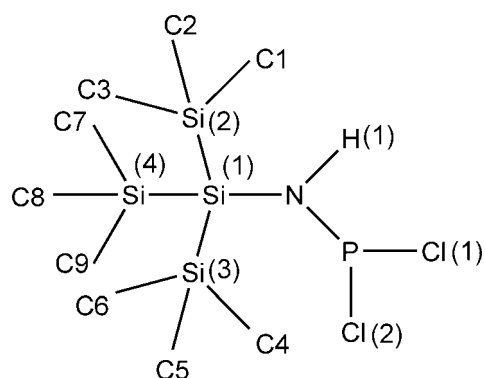


Table S3. Selected bond lengths (Å), angles and torsion angles (°) of **4**.

N—P	1.6223 (16)	N—P—Cl2	102.36 (8)
N—Si1	1.7888 (16)	N—P—Cl1	103.07 (7)
N—H1	0.69 (2)	Cl2—P—Cl1	95.97 (4)
P—Cl1	2.1008 (9)	N—Si1—Si2	106.91 (7)
P—Cl2	2.0765 (10)	N—Si1—Si4	105.47 (6)
Si1—Si2	2.3489 (7)	Si2—Si1—Si4	111.11 (3)
Si1—Si3	2.3583 (8)	N—Si1—Si3	110.09 (6)
Si1—Si4	2.3497 (9)	Si2—Si1—Si3	110.91 (3)
Si2—C1	1.870 (2)	Si4—Si1—Si3	112.08 (2)
Si2—C2	1.865 (2)	Si1—N—P—Cl2	-135.02 (12)
Si2—C3	1.872 (2)	Si1—N—P—Cl1	125.77 (12)
Si3—C4	1.865 (2)	P—N—Si1—Si2	-115.89 (13)
Si3—C5	1.876 (2)	P—N—Si1—Si4	125.77 (12)
Si3—C6	1.869 (2)	P—N—Si1—Si3	4.67 (16)
Si4—C7	1.863 (2)	N—Si1—Si2—C2	46.43 (11)
Si4—C8	1.859 (2)	N—Si1—Si2—C1	167.46 (11)
Si4—C9	1.859 (3)	N—Si1—Si3—C6	54.07 (11)
P—N—Si1	125.98 (10)	N—Si1—Si3—C5	172.15 (10)
P—N—H1	119.0 (19)	N—Si1—Si4—C9	-74.89 (16)
Si1—N—H1	114.7 (19)	N—Si1—Si4—C8	45.19 (12)

Scheme S2. Numbering scheme of **6**.

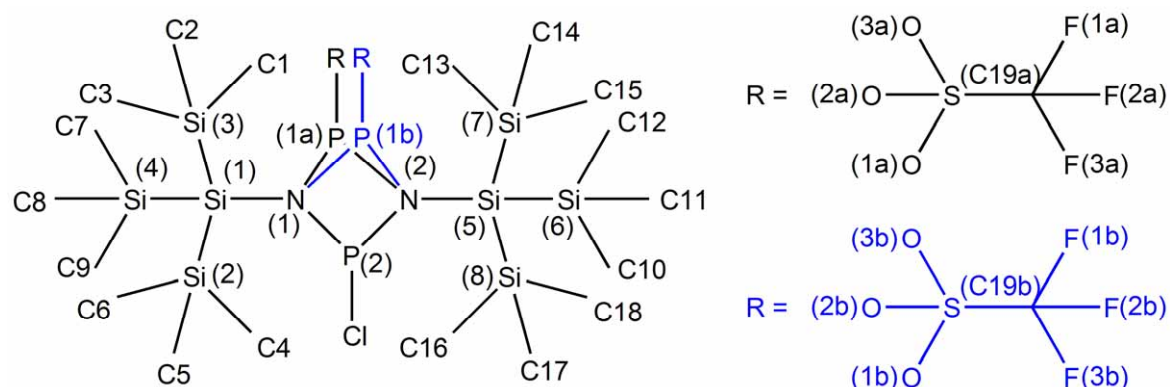


Table S4. Selected bond lengths (Å), angles and torsion angles (°) of **6**.

P1A—N2	1.689 (2)	O3B—S1B—C19B	105.9 (13)
P1A—N1	1.698 (2)	O2B—S1B—C19B	98.2 (14)
P1A—O1A	1.795 (3)	O1B—S1B—C19B	100.2 (10)
P1A—P2	2.4951 (14)	S1B—O1B—P1B	135.7 (9)
S1A—O3A	1.414 (2)	F3B—C19B—F1B	114 (3)
S1A—O2A	1.423 (2)	F3B—C19B—F2B	91 (2)
S1A—O1A	1.543 (2)	F1B—C19B—F2B	109 (2)
S1A—C19A	1.822 (5)	F3B—C19B—S1B	117.2 (16)
C19A—F2A	1.314 (5)	F1B—C19B—S1B	115 (2)
C19A—F3A	1.319 (6)	F2B—C19B—S1B	108 (2)
C19A—F1A	1.325 (4)	N1—P2—N2	85.17 (8)
P1B—N1	1.688 (7)	N1—P2—Cl	102.98 (7)
P1B—O1B	1.760 (12)	N2—P2—Cl	105.43 (8)
P1B—N2	1.778 (7)	N1—P2—P1A	42.75 (6)
P1B—P2	2.503 (7)	N2—P2—P1A	42.42 (6)
S1B—O3B	1.409 (17)	Cl—P2—P1A	109.47 (5)
S1B—O2B	1.434 (15)	N1—P2—P1B	42.19 (16)
S1B—O1B	1.447 (13)	N2—P2—P1B	45.24 (16)
S1B—C19B	1.75 (2)	Cl—P2—P1B	120.37 (14)

C19B—F3B	1.28 (3)	P1B—N1—P2	95.1 (2)
C19B—F1B	1.35 (3)	P1A—N1—P2	94.34 (9)
C19B—F2B	1.44 (4)	P1B—N1—Si1	126.9 (2)
P2—N1	1.7037 (17)	P1A—N1—Si1	134.38 (11)
P2—N2	1.7075 (17)	P2—N1—Si1	128.98 (10)
P2—Cl	2.0916 (10)	P1A—N2—P2	94.56 (9)
N1—Si1	1.7980 (17)	P2—N2—P1B	91.8 (2)
N2—Si5	1.8124 (17)	P1A—N2—Si5	132.22 (11)
Si1—Si2	2.3568 (12)	P2—N2—Si5	125.26 (10)
Si1—Si3	2.3595 (9)	P1B—N2—Si5	124.9 (2)
Si1—Si4	2.3647 (9)	N1—Si1—Si2	109.66 (7)
Si5—Si6	2.3532 (9)	N1—Si1—Si3	105.93 (6)
Si5—Si8	2.3536 (11)	Si2—Si1—Si3	109.48 (3)
Si5—Si7	2.3629 (9)	N1—Si1—Si4	110.56 (6)
N2—P1A—N1	85.93 (10)	Si2—Si1—Si4	109.02 (3)
N2—P1A—O1A	102.11 (12)	Si3—Si1—Si4	112.14 (4)
N1—P1A—O1A	98.49 (11)	N2—P1A—O1A—S1A	104.26 (19)
N2—P1A—P2	43.01 (6)	N1—P1A—O1A—S1A	-168.12 (17)
N1—P1A—P2	42.91 (6)	N1—P1B—O1B—S1B	49.2 (12)
O1A—P1A—P2	104.14 (9)	N2—P1B—O1B—S1B	-35.1 (12)
O3A—S1A—O2A	121.24 (16)	P2—P1B—O1B—S1B	7.5 (13)
O3A—S1A—O1A	110.65 (17)	N2—P1A—P2—N1	179.98 (14)
O2A—S1A—O1A	111.23 (15)	O1A—P1A—P2—N1	87.28 (13)
O3A—S1A—C19A	104.94 (16)	N1—P1A—P2—N2	-179.98 (14)
O2A—S1A—C19A	105.76 (18)	O1A—P1A—P2—N2	-92.70 (13)
O1A—S1A—C19A	100.59 (14)	N2—P1A—P2—Cl	91.79 (10)
S1A—O1A—P1A	125.00 (15)	N1—P1A—P2—Cl	-88.19 (10)
F2A—C19A—F3A	107.9 (4)	N2—P1B—P2—N1	156.6 (3)
F2A—C19A—F1A	109.3 (4)	O1B—P1B—N1—P2	-113.4 (5)
F3A—C19A—F1A	108.4 (3)	N2—P1B—N1—P2	-15.8 (2)
F2A—C19A—S1A	111.9 (2)	N2—P1A—N1—P2	-0.01 (9)

F3A—C19A—S1A	111.5 (3)	N2—P1A—N1—Si1	-163.16 (16)
F1A—C19A—S1A	107.7 (3)	N2—P2—N1—P1B	16.5 (2)
N1—P1B—O1B	96.7 (5)	Cl—P2—N1—P1B	121.2 (2)
N1—P1B—N2	83.5 (3)	N2—P2—N1—P1A	0.01 (9)
N1—P1A—O1A	98.49 (11)	Cl—P2—N1—P1A	104.75 (8)
O1B—P1B—N2	98.2 (5)	N2—P2—N1—Si1	164.56 (14)
N1—P1B—P2	42.69 (16)	Cl—P2—N1—Si1	-90.70 (13)
O1B—P1B—P2	110.7 (5)	N1—P1A—N2—P2	0.01 (9)
N2—P1B—P2	42.99 (15)	N1—P2—N2—P1A	-0.01 (9)
O3B—S1B—O2B	122.5 (12)	Cl—P2—N2—P1A	-102.16 (8)
O3B—S1B—O1B	113.0 (9)	N1—P2—N2—P1B	-15.6 (2)
O2B—S1B—O1B	112.9 (8)	Cl—P2—N2—P1B	-117.7 (2)

Scheme S3. Numbering scheme of 7.

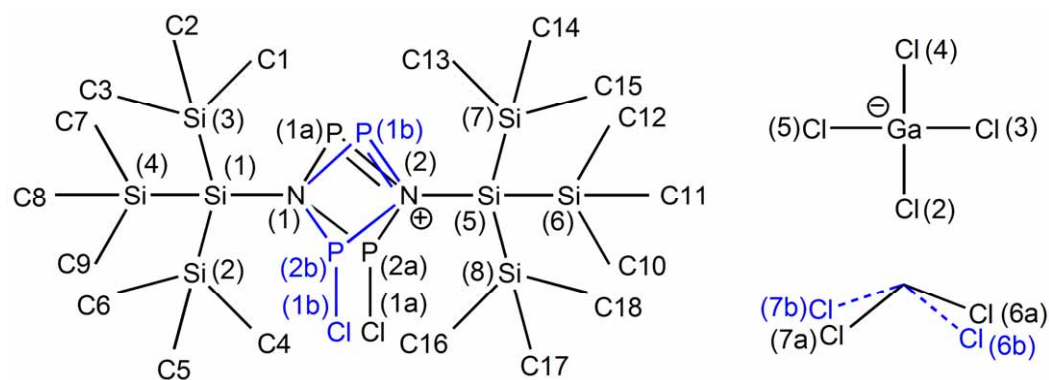


Table S5. Selected bond lengths (Å), angles and torsion angles (°) of 7.

Ga—Cl4	2.168 (3)	P1A—N1—Si1	134.0 (4)
Ga—Cl5	2.171 (3)	P2A—N1—Si1	132.7 (4)
Ga—Cl2	2.173 (3)	P2B—N1—Si1	128.5 (8)
Ga—Cl3	2.175 (3)	P1A—N2—P2A	92.7 (4)
Cl2—P1B	2.56 (5)	P1B—N2—P2B	90.8 (14)
P1A—N1	1.648 (7)	P1B—N2—Si5	142.2 (12)
P1A—N2	1.653 (8)	P1A—N2—Si5	134.2 (5)
P1A—P2A	2.449 (4)	P2A—N2—Si5	132.8 (4)
P2A—N2	1.732 (7)	P2B—N2—Si5	126.4 (7)
P2A—N1	1.737 (7)	N1—Si1—Si4	110.3 (2)
P2A—Cl1A	2.039 (4)	N1—Si1—Si2	106.7 (2)
P1B—N2	1.53 (3)	Si4—Si1—Si2	113.23 (12)
P1B—N1	1.54 (3)	N1—Si1—Si3	105.4 (2)
P1B—P2B	2.37 (4)	Si4—Si1—Si3	110.21 (12)
P2B—N1	1.78 (2)	Si2—Si1—Si3	110.60 (12)
P2B—N2	1.79 (2)	N2—Si5—Si6	107.0 (2)
P2B—Cl1B	2.03 (6)	N2—Si5—Si7	108.5 (3)
N1—Si1	1.837 (7)	N2—P1B—N1—P2B	4(3)
N2—Si5	1.833 (7)	Cl2—P1B—N1—P2B	138 (2)
Si1—Si4	2.363 (3)	N2—P1B—N1—Si1	177.4 (7)

Si1—Si2	2.363 (3)	Cl2—P1B—N1—Si1	-49 (4)
Si1—Si3	2.369 (3)	N2—P1A—N1—P2A	-12.1 (4)
Si5—Si6	2.362 (3)	N2—P1A—N1—Si1	176.8 (6)
Si5—Si7	2.362 (3)	N2—P2A—N1—P1A	11.6 (4)
Si5—Si8	2.366 (3)	Cl1A—P2A—N1—P1A	112.1 (3)
Cl4—Ga—Cl5	109.51 (15)	N2—P2A—N1—Si1	-177.1 (6)
Cl4—Ga—Cl2	109.35 (14)	Cl1A—P2A—N1—Si1	-76.5 (6)
Cl5—Ga—Cl2	109.68 (15)	Cl1B—P2B—N1—P1B	-107 (3)
Cl4—Ga—Cl3	109.47 (14)	N2—P2B—N1—Si1	-178.1 (6)
Cl5—Ga—Cl3	110.85 (16)	Cl1B—P2B—N1—Si1	79 (2)
Cl2—Ga—Cl3	107.96 (14)	Cl2—P1B—N2—P2B	-136 (2)
Ga—Cl2—P1B	139.1 (9)	N1—P1B—N2—Si5	-175.0 (8)
N1—P1A—N2	88.8 (4)	Cl2—P1B—N2—Si5	53 (5)
N2—P2A—N1	83.5 (3)	N1—P1A—N2—P2A	12.1 (4)
N2—P2A—Cl1A	101.5 (3)	N1—P1A—N2—Si5	-173.3 (6)
N1—P2A—Cl1A	100.4 (3)	N1—P2A—N2—P1A	-11.5 (4)
N2—P1B—N1	98 (2)	Cl1A—P2A—N2—P1A	-110.9 (3)
N2—P1B—Cl2	122 (2)	N1—P2A—N2—Si5	173.7 (6)
N1—P1B—Cl2	119 (3)	Cl1A—P2A—N2—Si5	74.4 (6)
N1—P2B—N2	80.7 (9)	P1A—P2A—N2—Si5	-174.7 (8)
N1—P2B—Cl1B	105 (3)	N1—P2B—N2—P1B	4(2)
N2—P2B—Cl1B	105 (2)	Cl1B—P2B—N2—P1B	107 (4)
Cl1B—P2B—P1B	112 (4)	N1—P2B—N2—Si5	176.7 (6)
P1A—N1—P2A	92.6 (4)	Cl1B—P2B—N2—Si5	-80 (3)
P1B—N1—Si1	140.4 (13)	P1B—P2B—N2—Si5	173 (2)

Scheme S4. Numbering scheme of tris(trimethylsilyl)chlorosilane.

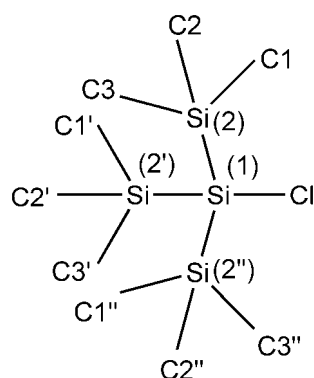
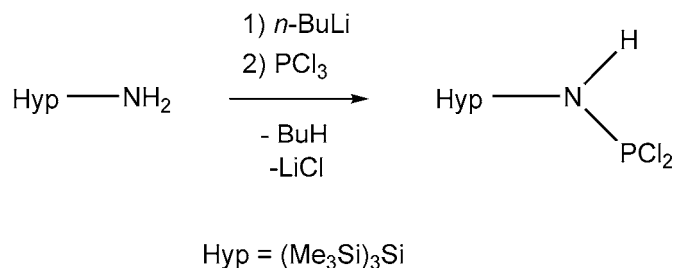


Table S6. Selected bond lengths (Å), angles and torsion angles (°) of tris(trimethylsilyl)chlorosilane.

Si1—Cl	2.1248 (9)	C1—Si2—Si1	110.54 (8)
Si1—Si2 ⁱ	2.3406 (6)	C3—Si2—Si1	110.36 (7)
Si1—Si2	2.3406 (6)	C2—Si2—Si1	109.17 (7)
Si1—Si2 ⁱⁱ	2.3406 (6)	Cl—Si1—Si2—C1	-60.46 (10)
Si2—C1	1.860 (2)	Si2 ⁱ —Si1—Si2—C1	54.39 (11)
Si2—C3	1.862 (2)	Si2 ⁱⁱ —Si1—Si2—C1	-175.31 (10)
Si2—C2	1.8663 (18)	Cl—Si1—Si2—C3	57.48 (9)
Cl—Si1—Si2	105.508 (18)	Si2 ⁱ —Si1—Si2—C3	172.32 (9)
Si2 ⁱ —Si1—Si2	113.127 (15)	Si2 ⁱⁱ —Si1—Si2—C3	-57.37 (10)
C1—Si2—C3	106.81 (14)	Cl—Si1—Si2—C2	178.69 (8)
C1—Si2—C2	109.77 (11)	Si2 ⁱ —Si1—Si2—C2	-66.46 (8)
C3—Si2—C2	110.17 (10)	Si2 ⁱⁱ —Si1—Si2—C2	63.84 (8)

Symmetry codes: (i) z, x, y ; (ii) y, z, x .

3. Synthesis of *N*-tris(trimethylsilyl)silyl-aminodichlorophosphine (**4**)

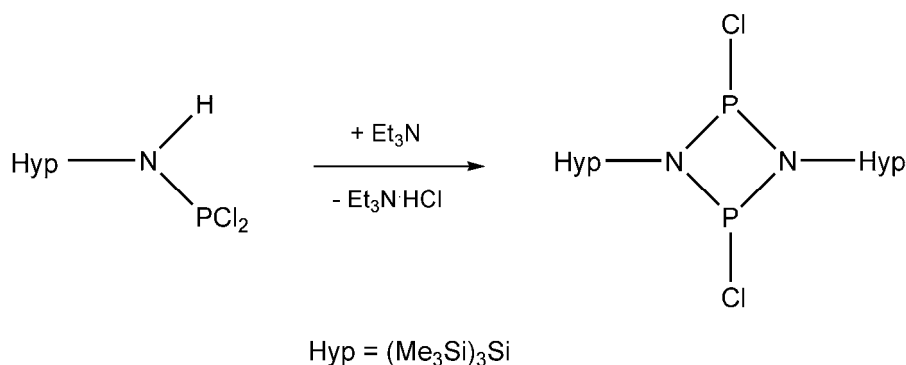


To a stirred solution of Tris(trimethylsilyl)silyl-amine (1,737 g, 6.6 mmol) in *n*-hexane (25 mL), *n*-BuLi (2.24 M, 2.94 mL, 6.6 mmol) was added dropwise at 0 °C over a period of 20 minutes. The resulting colourless solution is warmed to ambient temperatures and stirred for 45 minutes at 25 °C and was then added dropwise to a solution of PCl₃ (1.88 g, 13.75 mmol) in *n*-hexane (25 mL) at -50 °C over a period of 30 minutes. The resulting colourless suspension was stirred for 10 minutes at 0 °C and was then filtered (F4), resulting in a colourless solution. Removal of solvent in vacuo yields 1.68 g (4.6 mmol, 70%) of **4** as colourless, ceraceous solid.

Mp 220 °C (dec.). Anal. calc. % (found): C 29.65 (29.88), H 7.74 (7.46), N 3.84 (3.69), ³¹P{¹H}-NMR (25 °C, C₆D₆, 202.5 MHz): δ = 180.3. ²⁹Si-NMR (25 °C, C₆D₆, 99.4 MHz): δ = -34.1 (m, ²J(²⁹Si-³¹P) = 22 Hz, Si(Si(CH₃)₃)₃), -13.9 (m, ³J(²⁹Si-³¹P) = 1,6 Hz, Si(Si(CH₃)₃)₃). ¹H-NMR (25 °C, C₆D₆, 500.13 MHz): δ = 0.14 (s, 27 H, ⁵J(¹H-³¹P) = 0.5 Hz, Si(Si(CH₃)₃)₃). ¹³C{¹H}-NMR (25 °C, C₆D₆, 125.8 MHz): δ = 0.11 (s, ⁴J(¹³C-³¹P) = 2.7 Hz, Si(Si(CH₃)₃)₃). IR (ATR, 25 °C, 32 scans, cm⁻¹): = 3334 (w), 2950 (m), 2894 (w), 1440 (w), 1398 (w), 1311 (w), 1245 (s), 1179 (w), 1048 (w), 931 (m), 825 (vs), 744 (m), 689 (s) 621 (s). MS (EI, 70eV); *m/z* (%): 36(13), 38(5), 43(6), 45(12), 49(5), 69(7), 73(100) [Si(CH₃)₃]⁺, 74(10), 75(7), 84(6), 86(5), 93(9), 100(9), 116(6), 117(14), 118(5), 119(6), 129(6), 130(12), 131(19), 132(15), 146(9), 147(20), 159(8), 163(5), 166(5), 174(17), 175(5), 204(13), 208(5), 262(24) [NH-Si(Si(CH₃)₃)₃]⁺, 263(8), 264(5), 267(5), 306(7), 208(5), 364(7) [M+H]⁺, 366(6).

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated *n*-hexane solution of **4** to -80 °C.

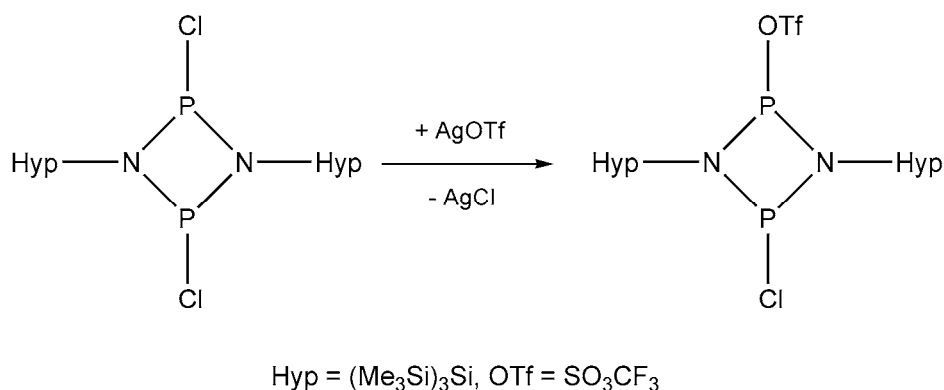
Synthesis of 1,3-dichloro-2,4-bis-tris(trimethylsilyl)silyl-cyclo-diphosphazane (5)



To a stirred solution of *N*-tris(trimethylsilyl)silyl-aminodichlorophosphine (**4**) (4.19 g, 11.5 mmol) in *n*-hexane (40 mL) triethylamine (3.5 mL, 25.0 mmol) was added dropwise at 0 °C over a period of 10 minutes. The resulting colourless suspension is then warmed to ambient temperatures over a period of 30 minutes. The colourless suspension was then filtered (F4), resulting in a colourless, clear solution. Removal of solvent and excess triethylamine *in vacuo* yields a pale yellow solid. Recrystallization from *n*-hexane yields 6.0 g (9.2 mmol, 80 %) of **5** as a colourless, crystalline solid.

Mp 271 °C (dec.). Anal. calc. % (found): C 32.95 (32.72), H 8.29 (8.37), N 4.27 (4.09). ³¹P{¹H}-NMR (25 °C, C₆D₆, 202.5 MHz): δ = 257.0. ²⁹Si-NMR (25 °C, C₆D₆, 99.4 MHz): δ = -35.6 (m, Si(Si(CH₃)₃)₃), -13.5 (m, ³J(²⁹Si-³¹P) = 1.3 Hz, Si(Si(CH₃)₃)₃). ¹H-NMR (25 °C, C₆D₆, 500.13 MHz): δ = 0.34 (s, 54 H, Si(Si(CH₃)₃)₃). ¹³C{¹H}-NMR (25 °C, C₆D₆, 125.8 MHz): δ = 1.14 (s, Si(Si(CH₃)₃)₃). IR (ATR, 25 °C, 32 scans, cm⁻¹): = 2948 (m), 2891 (w) 1440 (w), 1397 (w), 1311 (w), 1257 (m), 1243 (s), 1052 (w), 934 (m), 910 (s), 820 (vs), 745 (s), 687 (s) 621 (s). Raman (200 mW, 25 °C, 201 scans, cm⁻¹): = 2950 (5), 2892 (10), 691 (1), 630 (5). MS (EI, 70eV); *m/z* (%): 45(5), 73(100) [Si(CH₃)₃]⁺, 74(6), 100(15), 130(21), 131(13), 173(5), 204(22), 245(12), 275(8), 292(12), 295(16), 297(7), 581(11) [M-Si(CH₃)₃]⁺, 583(11), 641(2) [M-CH₃]⁺.

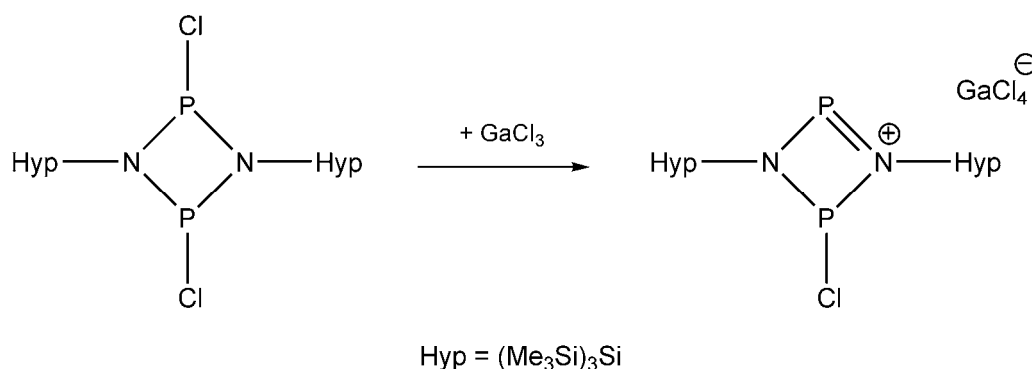
Synthesis of 1-chloro-3-trifluoromethanesulfonato-2,4-bis-tris(trimethylsilyl)silyl-*cyclo*-diphosphadiazane (6)



To a stirred solution of 1,3-dichloro-2,4-bis-tris(trimethylsilyl)silyl-*cyclo*-diphosphadiazane (**5**) (0.656 g, 1.0 mmol) in toluene (10 mL), silvertrifluoromethanesulfonate (0.28 g, 1.1 mmol) in toluene (5 mL), was added dropwise at $-30\text{ }^{\circ}\text{C}$ over a period of 10 minutes. The resulting colourless suspension is then warmed to ambient temperatures over a period of 30 minutes in the dark and was then filtered (F4), resulting in a colourless solution. After removal of solvent *in vacuo* *n*-hexane (10 mL) is added. The resulting colourless suspension was then filtered (F4) a second time, resulting in a colourless solution. Removal of solvent *in vacuo* yields a colourless solid. Recrystallization from *n*-hexane yields 0.46 g (0.6 mmol, 60%) of **6** as a colourless, crystalline solid.

Mp $106\text{ }^{\circ}\text{C}$ (dec.). Anal. calc. % (found): C 29.65 (30.16), H 7.07 (7.37), N 3.64 (3.47). $^{31}\text{P}\{^1\text{H}\}$ -NMR (25 $^{\circ}\text{C}$, C₆D₆, 121.5 MHz): $\delta = 256.9$ (d, $^3J(^{31}\text{P}-^{31}\text{P}) = 116\text{ Hz}$) 258.8 (d, $^3J(^{31}\text{P}-^{31}\text{P}) = 116\text{ Hz}$). ^{29}Si -NMR (25 $^{\circ}\text{C}$, C₆D₆, 99.4 MHz): $\delta = -30.7$ (m, Si(Si(CH₃)₃)₃), -13.1 (m, $^3J(^{29}\text{Si}-^{31}\text{P}) = 1,2\text{ Hz}$, Si(Si(CH₃)₃)₃). ^1H -NMR (25 $^{\circ}\text{C}$, C₆D₆, 500.13 MHz): $\delta = 0.31$ (s, 54 H, Si(Si(CH₃)₃)₃). $^{13}\text{C}\{^1\text{H}\}$ -NMR (25 $^{\circ}\text{C}$, C₆D₆, 125.8 MHz): 1.09 (s, Si(Si(CH₃)₃)₃), 119.3 (q, $^1J(^{13}\text{C}-^{19}\text{F}) = 320.7\text{ Hz}$, CF₃). ^{19}F -NMR (25 $^{\circ}\text{C}$, C₆D₆, 282.4 MHz): -76.1 . IR (ATR, 25 $^{\circ}\text{C}$, 32 scans, cm^{-1}): = 2950 (m), 2895 (w) 1383 (m), 1311 (w), 1245 (s), 1199 (s), 1143 (m), 1022 (w), 975 (m), 936 (w), 904 (m), 818 (vs), 747 (s), 689 (s). Raman (200 mW, 25 $^{\circ}\text{C}$, 112 scans, cm^{-1}): = 3490 (1), 2953 (5), 2895 (10), 690 (1), 629 (3), 169 (2). MS (FAB⁺, Cs, 20keV, *p*-NBA matrix): 73 [Si(CH₃)₃]⁺, 292 [PN-Si(Si(CH₃)₃)₃]⁺, 621 [M-OTf+2H]⁺, 736 [M-Cl+3H]⁺. Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated dichloromethane solution of **6** to $-40\text{ }^{\circ}\text{C}$.

Synthesis of 2-chloro-3,4-bis-tris(trimethylsilyl)silyl-cyclo-diphosphadiazenium-tetrachloridogallate (7)



To a stirred solution of 1,3-dichloro-2,4-bis-tris(trimethylsilyl)silyl-cyclo-diphosphadiazenane (**5**) (0.656 g, 1.0 mmol) in CH₂Cl₂ (5 mL), GaCl₃ (0.176 g, 1.0 mmol) in CH₂Cl₂ (5 mL), was added dropwise at -78 °C over a period of 5 minutes. The resulting dark red solution is warmed to -30 °C. Removal of solvent *in vacuo* at -30 °C yields 0.810 g (0.97 mmol, 97%) **7** as a microcrystalline solid.

Mp 54 °C; 151 °C (dec.). Anal. calc. % (found): C 25.98 (26.57), H 6.54 (6.27), N 3.37 (2.99). ³¹P{¹H}-NMR (25 °C, C₆D₆, 161.9 MHz): δ = 238.1 (d, ³J(³¹P-³¹P) = 68Hz, N-P-Cl), 405.4 (d, ³J(³¹P-³¹P) = 68Hz, N⁺=P). ²⁹Si-NMR (25 °C, C₆D₆, 99.4 MHz): δ = -20.2 (m, Si(Si(CH₃)₃)₃), -12.1 (m, ³J(²⁹Si-³¹P) = 1.3 Hz, Si(Si(CH₃)₃)₃). ¹H-NMR (25 °C, C₆D₆, 500.13 MHz): δ = 0.33 (s, 54 H, Si(Si(CH₃)₃)₃). ¹³C{¹H}-NMR (25 °C, C₆D₆, 125.8 MHz): δ = 0.51 (s, Si(Si(CH₃)₃)₃). IR (ATR, 25 °C, 32 scans, cm⁻¹): = 2950 (m), 2894 (w), 1400 (w), 1312 (w), 1246 (m), 1151 (m), 1090 (w), 1026 (w), 979 (m), 826 (vs), 744 (m), 689 (m), 621 (m), 534 (w). MS (EI, 70eV, M = [Si(Si(CH₃)₃)₃]₂N₂P₂Cl⁺); *m/z* (%): 45(14), 73(100) [Si(CH₃)₃]⁺, 74(18), 93(13), 100(39), 130(65), 131(50), 147(20), 159(18), 173(21), 174(43), 188(15), 204(70), 205(17), 245(41) [Si(Si(CH₃)₃)₃-2H], 261(19), 275(28), 292(28) [PN-Si(Si(CH₃)₃)₃], 295(41), 297(18), 319(16), 459(41), 460(15), 461(23), 563(15), 581(17) [M-Si(CH₃)₃+Cl]⁺, 583(17), 621(17) [M+2H]⁺.

Crystals suitable for X-ray crystallographic analysis were obtained, by cooling a saturated dichloromethane solution of **7** to -80 °C.

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