Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Diatomic PN – Trapped in a *Cyclo*-Tetraphosphazene

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This file includes:

1. Experimental

General Information. All manipulations were carried under oxygen- and moisture free conditions using standard Schlenk and Drybox techniques.

Dichloromethane was purified according to a literature procedure[1], dried over P_4O_{10}, stored over CaH_2 and was freshly distilled prior to use, as was C_6H_5F. Toluene and benzene were dried over Na/benzophenone and freshly distilled prior to use. *N*-hexane was dried over Na/Benzophenone/Tetraglyme and freshly distilled prior to use. *N*,*N*-bis(trimethylsilyl)amiodichlorophosphane[1], silver trifluoromethylsulfonate AgOTf[2] and $W(CO)_3(C_2H_5CN)_3$[3] have been reported previously and were prepared according to a modified literature procedure. 2,3-dimethyl-1,3-butadiene (98 %, Aldrich) and 1,3-*cyclo*-hexadiene (*stabilized for synthesis*, Merck) were stirred over $NaBH_4$ for 24 h and stored over mole sieves. $Mo(CO)_6$ (pract., Fluka) was freshly sublimed prior to use.

NMR: $^{31}P\{^1H\}$-, ^{29}Si INEPT-, 19F$\{^1H\}$-, $^{13}C\{^1H\}$- and ^1H-NMR spectra were recorded on BRUKER spectrometers AVANCE 250, AVANCE 300 and AVANCE 500, respectively. The ^1H- and ^{13}C-NMR chemical shifts were referenced to the solvent signals ($CDHCl_2$: δ (^1H) = 5.31; δ (^{13}C) = 54.0). The ^{19}F, ^{29}Si-NMR and ^{31}P-NMR chemical shifts are referred to $CFCl_3$, TMS and H_3PO_4 (85%) respectively. CD_2Cl_2 was dried over P_4O_{10} and was degased prior to use.

CHN analysis: Analysator Flash EA 1112 from Thermo Quest.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR module.

RAMAN: LabRAM HR 800 Horiba Jobin YVON equipped with a High Stability BX40 Microscope (Focus 1 µm) or an Olympus Mplan 50xNA 0.70 lens, the laser is variable and was chosen prior to the measurement (Wavelength Laser (x.x aperture), number of accumulations@accumulation time).

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 5°C/min) was used.

MS: Finnigan MAT 95-XP from Thermo Electron was used.

2. Structure elucidation

X-ray Structure Determination: X-ray quality crystals of **5**, **5b**, **7**, **8**, **9**, **5·Mo**, **5·W$_2$** and **Mo(CO)$_3$(C$_2$H$_5$CN)$_3$** were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The data was collected on a Bruker Kappa Apex-II CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073). The structures were solved by direct methods (*SHELXS-97*)[4] and refined by full-matrix least squares procedures (*SHELXL-97*).[5] Semi-empirical absorption corrections were applied (*SADABS*).[6] All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Both CH_2Cl_2 molecules in **5_1** were found to be disordered and were split in two parts, respectively. The occupation of each part was refined freely (0.918(2)/0.082(2)//0.58(2)/0.42(2)).

A C_6H_8 moiety in one of the cations, along with an anion in **8** were found to be disordered and were split in two parts, respectively. The occupation of each part was refined freely (0.796(5)/0.204(5)//0.65(2)/0.35(2)).

The cation in **9** was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.896(3)/0.104(3))

One of the toluene molecules in **5·Mo_2** was found to be disordered and was split in three parts. The occupation of each part was refined freely (0.328(7)/0.340(7)/0.233(5))

Table S1. Crystallographic Details of **5_1**, **5_2** and **5b**.

Compound	**5_1**	**5_2**	**5b**
Chem. Formula	$C_{26}H_{44}N_4P_4Cl_4$	$C_{25}H_{42}N_4P_4Cl_2$	$C_{30}H_{50}N_5P_5$
Form. Wght. [g mol^{-1}]	678.33	593.41	635.60
Colour	Colourless	Colourless	Colourless
Cryst. system	triclinic	monoclinic	monoclinic
Space group	*P*-1	*C*2/c	$P2_1$
a [Å]	11.5705(5)	18.4786(14)	5.817(2)
b [Å]	12.2221(3)	10.3968(7)	20.654(7)
c [Å]	13.6923(3)	16.6760(12)	14.186(5)
α [°]	111.408(1)	90	90
β [°]	105.640(1)	109.266(3)	90.25(2)
γ [°]	97.431(1)	90	90
V [Å^3]	1679.02(9)	3024.3(4)	1704.2(1)
Z	2	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.342	1.303	1.239
μ [mm^{-1}]	0.57	0.45	0.30
T [K]	173(2)	173(2)	173(2)
Measured reflections	48693	11916	9224
Independent reflections	8903	2669	3961
Reflections with $I > 2\sigma(I)$	6414	1440	1767
R_{int}	0.051	0.113	0.143
F(000)	712	1256	680
$R_1(R[F^2>2\sigma(F^2)])$	0.043	0.056	0.035
wR_2 (F^2)	0.1184	0.1231	0.4032
GooF	1.014	1.002	1.086
Parameters	380	163	172

Table S2. Crystallographic Details of **9**, **10** and **11.**

Compound	**7**	**8**	**9**
Chem. Formula	$C_{16}H_{29}NPSiF_3O_3S$	$C_{15}H_{25}NPSiF_3O_3S$	$C_{13}H_{25}F_3NO_4SCl_2$
Form. Wght. [g mol^{-1}]	431.52	427.49	462.28
Colour	Colourless	Colourless	Colourless
Cryst. system	triclinic	Monoclinic	Orthorhombic
Space group	*P*-1	*P*2$_1$/n	*Pna*2$_1$
a [Å]	11.1833(3)	8.7479(3)	17.3330(14)
b [Å]	16.4208(4)	10.5358(4)	8.3372(6)
c [Å]	19.4337(5)	42.671(1)	14.4037(10)
α [°]	67.276(1)	90	90
β [°]	82.190(1)	93.724(2)	90
γ [°]	83.22381)	90	90
V [Å^3]	3252.8(1)	3924.5	2081.5(3)
Z	6	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.322	1.255	1.475
μ [mm^{-1}]	0.32	0.35	0.53
T [K]	173(2)	173(2)	173(2)
Measured reflections	54016	48811	14093
Independent reflections	15669	9008	4994
Reflections with $I > 2\sigma(I)$	8972	5097	3252
R_{int}	0.061	0.089	0.062
F(000)	1368	1792	960
R_1(R[F^2>2σ(F^2)])	0.052	0.055	0.053
wR_2 (F^2)	0.1225	0.1360	0.1300
GooF	1.014	1.016	0.967
Parameters	724	561	299

Table S3. Crystallographic Details of **5·Mo_1, 5·Mo_2** and **5·W$_2$(CO)$_7$**.

Compound	**5·Mo(CO)$_3$_1**	**5·Mo(CO)$_3$_2**	**5·W$_2$(CO)$_7$**
Chem. Formula	$C_{27}H_{40}N_4P_4MoO_3$	$C_{27}H_{40}N_4P_4MoO_3*1.4(C_7H_8)$	$C_{31}H_{40}N_4P_4W_2O_7$
Form. Wght. [g mol^{-1}]	688.45	817.50	1072.25
Colour	Yellow	Colourless	Colourless
Cryst. system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
a [Å]	9.0715(4)	9.1199(3)	20.4707(8)
b [Å]	18.1902(6)	13.8435(5)	20.2868(7)
c [Å]	18.4948(7)	17.1181(7)	18.9919(6)
α [°]	90	70.892(2)	90
β [°]	94.483(2)	88.485(2)	110.519(2)
γ [°]	90	89.599(2)	90
V [Å^3]	3042.5(2)	2041.4(1)	7386.7(5)
Z	4	2	8
$\rho_{calc.}$ [g cm^{-3}]	1.503	1.330	1.928
μ [mm^{-1}]	0.68	1.48	6.45
T [K]	173(2)	173(2)	173(2)
Measured reflections	39864	60358	132908
Independent reflections	7327	12924	26725
Reflections with $I > 2\sigma(I)$	4492	9108	15113
R_{int}	0.107	0.056	0.095
$F(000)$	1424	852	4144
$R_1(R[F^2>2\sigma(F^2)])$	0.052	0.046	0.048
wR_2 (F^2)	0.1104	0.1217	0.1003
GooF	1.013	1.034	1.013
Parameters	360	425	881

Table S4. Crystallographic Details of **X**.

Compound	**X**
Chem. Formula	$C_{12}H_{15}N_3MoO_3$
Form. Wght. [g mol^{-1}]	345.21
Colour	Colourless
Cryst. system	Monoclinic
Space group	$P2_1/m$
a [Å]	5.9362(2)
b [Å]	13.8472(5)
c [Å]	9.4000(3)
α [°]	90
β [°]	97.888(2)
γ [°]	90
V [Å^3]	765.37(5)
Z	2
$\rho_{\mathrm{calc.}}$ [g cm^{-3}]	1.498
μ [mm^{-1}]	0.86
T [K]	173(2)
Measured reflections	14262
Independent reflections	2862
Reflections with $I > 2\sigma(I)$	2611
R_{int}	0.041
F(000)	348
R_1(R[F^2>2σ(F^2)])	0.023
wR_2 (F^2)	0.0478
GooF	1.059
Parameters	99

Scheme S1. Numbering scheme of Tetraphatetrazen (**5_1**).

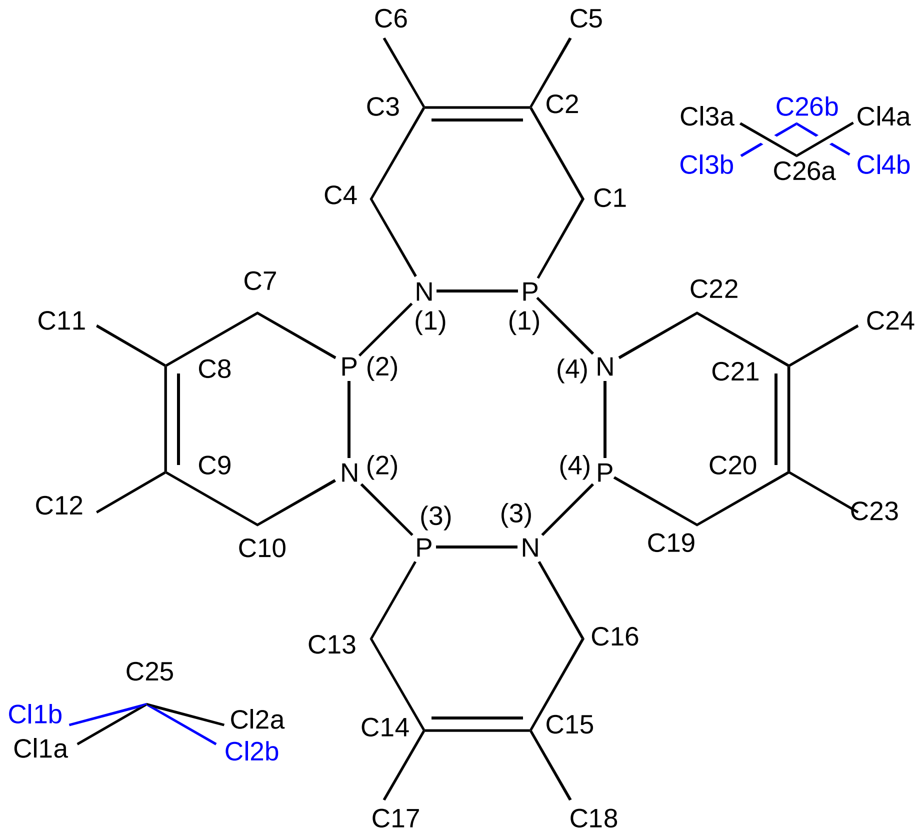

Table S4. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **5_1**.

P1—N1	1.7146 (16)	**C1—C2**	1.509 (3)
P1—N4	1.7297 (16)	**C2—C3**	1.334 (3)
P1—C1	1.835 (2)	**C2—C5**	1.507 (3)
P2—N2	1.7111 (16)	**C3—C6**	1.504 (3)
P2—N1	1.7262 (16)	**C3—C4**	1.505 (3)
P2—C7	1.836 (2)	**C7—C8**	1.507 (3)
P3—N3	1.7122 (16)	**C8—C9**	1.333 (3)
P3—N2	1.7228 (17)	**C8—C11**	1.511 (3)
P3—C13	1.830 (2)	**C9—C10**	1.506 (3)
P4—N4	1.7101 (16)	**C9—C12**	1.511 (3)
P4—N3	1.7232 (16)	**C13—C14**	1.514 (3)
P4—C19	1.832 (2)	**C14—C15**	1.328 (3)

N1—C4	1.470 (2)	**C14—C17**	1.508 (3)
N2—C10	1.469 (2)	**C15—C16**	1.507 (3)
N3—C16	1.472 (2)	**C15—C18**	1.511 (3)
N4—C22	1.473 (2)	**C19—C20**	1.513 (3)
C20—C21	1.332 (3)	**C21—C22**	1.508 (3)
C20—C23	1.507 (3)	**C21—C24**	1.513 (3)
C25—Cl1B	1.711 (11)	**C26A—Cl3A**	1.733 (8)
C25—Cl2B	1.74 (2)	**C26A—Cl4A**	1.737 (15)
C25—Cl2A	1.753 (3)	**C26B—Cl3B**	1.734 (9)
C25—Cl1A	1.759 (3)	**C26B—Cl4B**	1.737 (15)
N1—P1—N4	108.77 (8)	**C4—N1—P1**	123.24 (12)
N1—P1—C1	98.72 (8)	**C4—N1—P2**	122.71 (12)
N4—P1—C1	101.29 (8)	**P1—N1—P2**	111.10 (9)
N2—P2—N1	108.65 (8)	**C10—N2—P2**	122.85 (13)
N2—P2—C7	98.58 (9)	**C10—N2—P3**	122.94 (13)
N1—P2—C7	101.44 (8)	**P2—N2—P3**	110.96 (9)
N3—P3—N2	108.49 (8)	**C16—N3—P3**	123.14 (12)
N3—P3—C13	98.79 (8)	**C16—N3—P4**	123.02 (12)
N2—P3—C13	102.46 (9)	**P3—N3—P4**	111.39 (9)
N4—P4—N3	109.07 (8)	**C22—N4—P4**	123.60 (13)
N4—P4—C19	98.59 (9)	**C22—N4—P1**	122.77 (13)
N3—P4—C19	101.79 (9)	**P4—N4—P1**	111.06 (9)
C3—C2—C5	123.09 (19)	**C2—C3—C6**	123.89 (18)
C3—C2—C1	123.67 (17)	**C2—C3—C4**	125.15 (18)
C5—C2—C1	113.24 (17)	**C6—C3—C4**	110.96 (17)
C1—P1—N1—C4	40.21 (16)	**C1—C2—C3—C6**	−179.64 (18)
N2—P2—N1—P1	−96.76 (10)	**C7—P2—N1—C4**	−38.86 (16)

Scheme S2. Numbering scheme of Tetraphatetrazen (**5_2**).

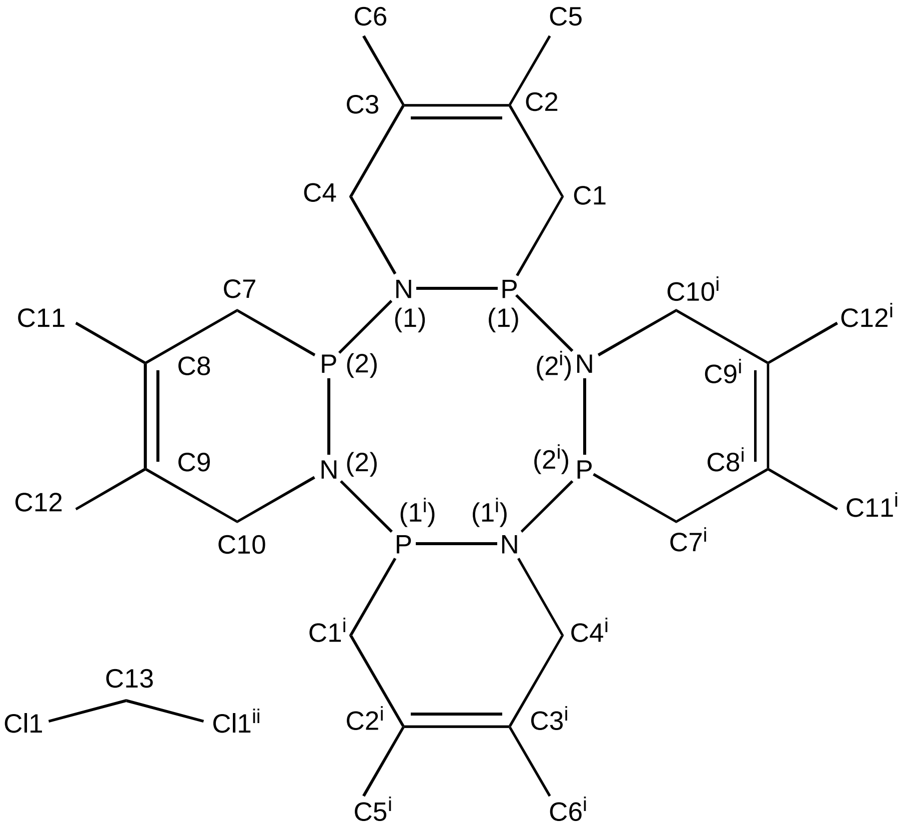

Table S5. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **5_2**.

P1—N1	1.709 (3)	**C2—C3**	1.332 (6)
P1—N2i	1.719 (3)	**C2—C5**	1.507 (6)
P1—C1	1.848 (4)	**C3—C4**	1.494 (6)
P2—N2	1.717 (3)	**C3—C6**	1.526 (5)
P2—N1	1.732 (3)	**C7—C8**	1.517 (5)
P2—C7	1.827 (4)	**C8—C9**	1.323 (5)
N1—C4	1.477 (5)	**C8—C11**	1.516 (5)
N2—C10	1.476 (5)	**C9—C10**	1.506 (5)
N2—P1i	1.719 (3)	**C9—C12**	1.512 (5)
C1—C2	1.508 (5)	**C13—Cl1ii**	1.756 (4)
Cl1—C13	1.756 (4)	**C3—C2—C5**	124.1 (4)
N1—P1—N2i	108.40 (16)	**C3—C2—C1**	122.9 (4)

N1—P1—C1	99.89 (17)	**C5—C2—C1**	113.0 (4)
N2i—P1—C1	100.81 (17)	**C2—C3—C4**	126.4 (4)
N2—P2—N1	107.94 (16)	**C2—C3—C6**	122.5 (4)
N2—P2—C7	97.54 (17)	**C4—C3—C6**	111.1 (4)
N1—P2—C7	102.21 (18)	**C10—N2—P2**	121.6 (3)
C4—N1—P1	124.1 (3)	**C10—N2—P1i**	121.5 (2)
C4—N1—P2	122.9 (3)	**P2—N2—P1i**	113.81 (18)
P1—N1—P2	110.48 (17)	**C1—C2—C3—C6**	178.8 (4)
C1—P1—N1—C4	33.3 (3)	**C7—P2—N1—C4**	−27.8 (3)
N2—P2—N1—P1	−88.1 (2)		

Symmetry codes: (i) −x+1, y, −z+1/2; (ii) −x+2, y, −z+1/2.

Scheme S3. Numbering scheme of **5b**.

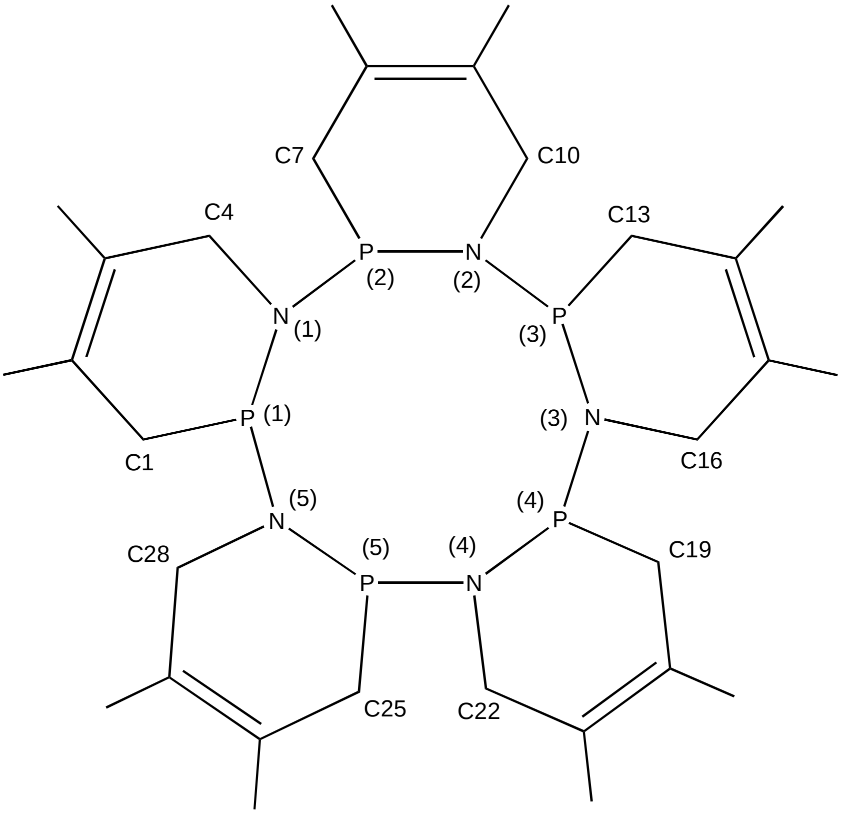

Table S6. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **5b**.

P1—N5	1.692 (17)	**P1—C1**	1.86 (2)
P1—N1	1.699 (17)	**P2—C7**	1.82 (2)
P2—N1	1.680 (18)	**P3—C13**	1.84 (2)
P2—N2	1.699 (17)	**P4—C19**	1.80 (2)
P3—N2	1.692 (18)	**P5—C25**	1.86 (2)
P3—N3	1.703 (18)	**N1—C4**	1.47 (3)
P4—N3	1.680 (18)	**N2—C10**	1.45 (3)
P4—N4	1.704 (19)	**N3—C16**	1.46 (2)
P5—N4	1.691 (18)	**N4—C22**	1.48 (3)
P5—N5	1.73 (2)	**N5—C28**	1.45 (3)

Scheme S4. Numbering scheme of $\mathbf{[Me_3SiN(C_6H_{10})P(C_6H_{10})][O_3SCF_3]}$ (**7**).

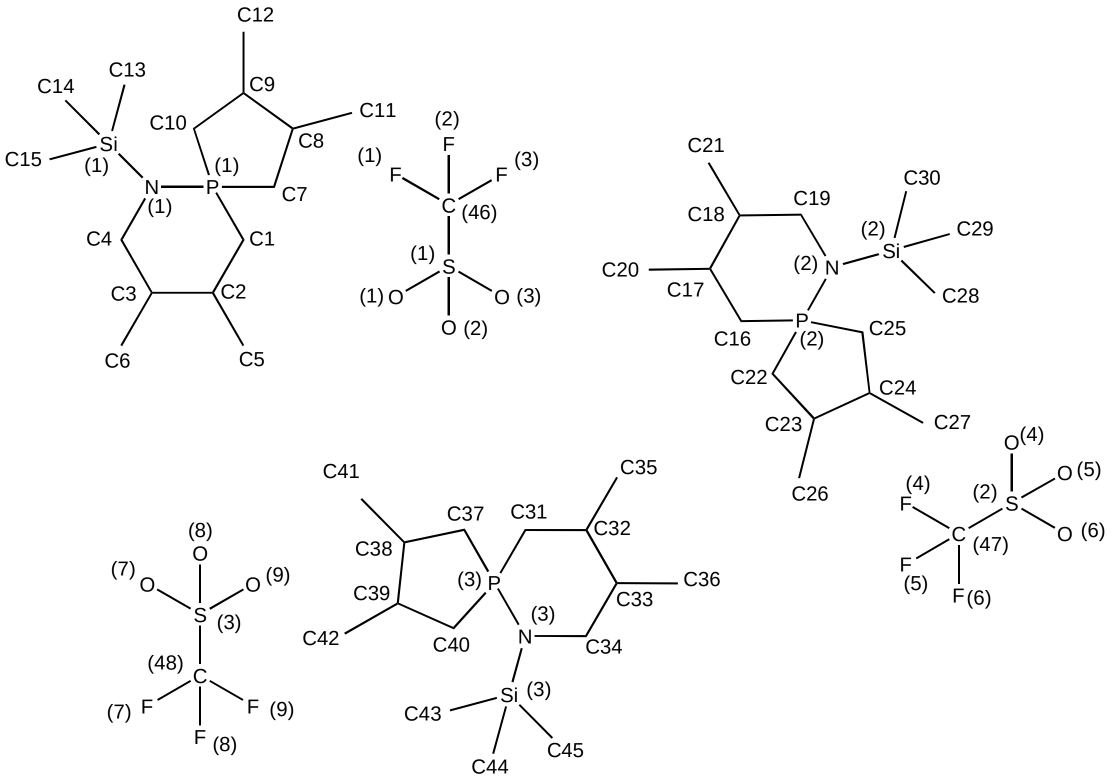

Table S7. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **7**.

C1—P1	1.773 (3)	**C15—Si1**	1.855 (3)
C4—N1	1.504 (3)	**C16—F2**	1.321 (3)
N1—P1	1.634 (2)	**C16—F1**	1.328 (3)
C1—C2	1.518 (3)	**C16—F3**	1.330 (3)
C2—C3	1.331 (3)	**O1—S1**	1.422 (2)
C2—C5	1.492 (3)	**O2—S1**	1.428 (2)
C3—C6	1.497 (4)	**O3—S1**	1.421 (2)
C3—C4	1.508 (3)	**C16—S1**	1.811 (3)
N1—Si1	1.769 (2)	**C7—P1**	1.801 (3)
Si1—C13	1.853 (3)	**C10—P1**	1.797 (3)
C14—Si1	1.833 (3)	**C8—C9**	1.322 (4)
C7—C8	1.498 (4)	**C17—P2**	1.782 (3)
N2—P2	1.630 (2)	**N2—Si2**	1.767 (2)

C17—C18	1.522 (3)	**C23—C24**	1.509 (3)
C18—C19	1.328 (3)	**C24—C25**	1.334 (3)
C18—C21	1.491 (3)	**C24—C27**	1.514 (4)
C19—C22	1.501 (3)	**C25—C28**	1.505 (4)
C19—C20	1.508 (3)	**C25—C26**	1.512 (3)
C23—P2	1.805 (2)	**C26—P2**	1.798 (3)
Si2—C29	1.851 (3)	**C32—F6**	1.328 (3)
C30—Si2	1.853 (3)	**C32—F5**	1.333 (3)
C31—Si2	1.843 (3)	**C32—F4**	1.334 (3)
O4—S2	1.4337 (19)	**C32—S2**	1.817 (3)
O5—S2	1.435 (2)	**O6—S2**	1.4304 (19)
C33—P3	1.781 (3)	**C36—N3**	1.515 (3)
N3—P3	1.632 (2)	**N3—Si3**	1.765 (2)
C33—C34	1.512 (3)	**C39—P3**	1.790 (3)
C34—C35	1.330 (3)	**C39—C40**	1.509 (3)
C34—C37	1.505 (3)	**C40—C41**	1.330 (3)
C35—C38	1.500 (3)	**C40—C43**	1.502 (3)
C35—C36	1.517 (3)	**C41—C44**	1.496 (3)
C36—N3	1.515 (3)	**C41—C42**	1.517 (4)
C45—Si3	1.854 (3)	**C42—P3**	1.804 (2)
Si3—C46	1.852 (3)	**O7—S3**	1.4316 (19)
C47—Si3	1.849 (3)	**O8—S3**	1.4420 (19)
C48—F9	1.324 (3)	**O9—S3**	1.4309 (19)
C48—F8	1.325 (3)	**C48—S3**	1.818 (3)
C48—F7	1.325 (3)	**N1—Si1—C14**	109.34 (13)
O3—S1—O1	115.08 (14)	**N1—Si1—C13**	108.43 (13)
O3—S1—O2	116.49 (15)	**C14—Si1—C13**	111.13 (15)
O1—S1—O2	113.53 (14)	**C4—N1—P1**	115.06 (17)
N1—P1—C1	104.99 (11)	**C4—N1—Si1**	116.38 (16)
N1—P1—C10	116.24 (12)	**P1—N1—Si1**	127.82 (13)

C1—P1—C10	110.37 (13)	**F2—C16—F1**	106.9 (3)
N1—P1—C7	117.46 (12)	**F2—C16—F3**	106.9 (3)
C1—P1—C7	110.98 (13)	**F1—C16—F3**	107.3 (2)
C10—P1—C7	96.80 (12)	**C9—C8—C7**	117.0 (2)
C3—C2—C5	126.9 (2)	**C9—C8—C11**	126.7 (3)
C3—C2—C1	117.4 (2)	**C7—C8—C11**	116.3 (2)
C5—C2—C1	115.7 (2)	**P1—C1—C2—C5**	129.2 (2)
C2—C3—C4—N1	51.4 (3)	**P1—C7—C8—C9**	6.8 (3)
C5—C2—C3—C4	−179.7 (2)	**C11—C8—C9—C10**	177.4 (3)
Si1—N1—P1—C7	59.5 (2)	**C4—N1—P1—C10**	115.27 (19)
C4—N1—P1—C1	−7.0 (2)	**C2—C1—P1—N1**	51.2 (2)

Scheme S5. Numbering scheme of **[$Me_3SiN(C_6H_8)P(C_6H_8)$][O_3SCF_3] (8)**.

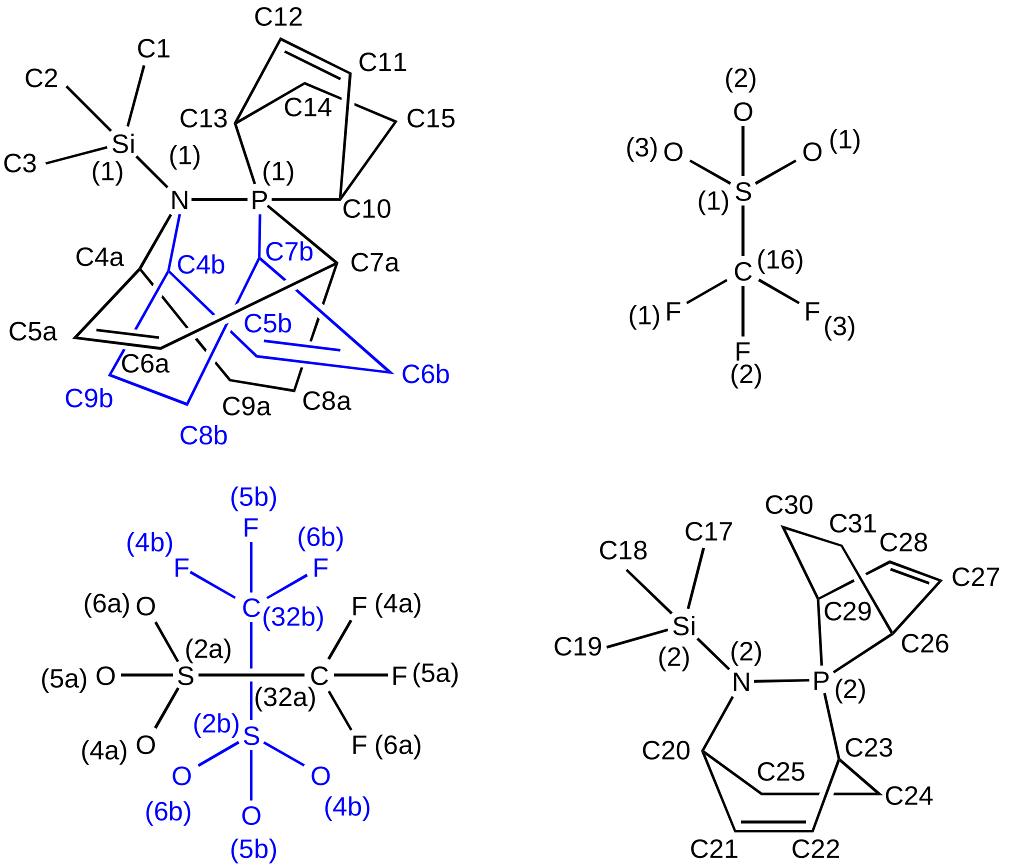

Table S8. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **8**.

P1—N1	1.625 (2)	**Si1—C3**	1.844 (3)
P1—C4A	1.806 (9)	**Si1—C1**	1.851 (4)
P1—C13	1.825 (3)	**Si1—C2**	1.855 (4)
P1—C10	1.829 (3)	**C4A—C5A**	1.500 (9)
P1—C4B	1.83 (4)	**C4A—C9A**	1.577 (8)
N1—C7B	1.49 (2)	**C5A—C6A**	1.309 (7)
N1—C7A	1.588 (5)	**C6A—C7A**	1.487 (6)
N1—Si1	1.779 (2)	**C7A—C8A**	1.528 (6)
C4B—C5B	1.44 (3)	**C8A—C9A**	1.511 (7)
C5B—C6B	1.32 (3)	**C6B—C7B**	1.59 (3)
C7B—C8B	1.50 (3)	**C8B—C9B**	1.43 (3)

C10—C11	1.507 (5)	**C12—C13**	1.470 (5)
C10—C15	1.537 (5)	**C13—C14**	1.538 (4)
C11—C12	1.339 (5)	**C14—C15**	1.544 (4)
S1—O1	1.429 (2)	**S1—C16**	1.797 (4)
S1—O2	1.431 (2)	**C16—F1**	1.306 (4)
S1—O3	1.439 (3)	**C16—F3**	1.337 (4)
P2—N2	1.643 (2)	**C16—F2**	1.350 (4)
P2—C23	1.812 (3)	**N2—C20**	1.539 (3)
P2—C26	1.824 (3)	**N2—Si2**	1.790 (2)
P2—C29	1.833 (3)	**Si2—C19**	1.850 (3)
Si2—C17	1.856 (3)	**Si2—C18**	1.854 (3)
C20—C21	1.499 (4)	**C21—C22**	1.328 (4)
C20—C25	1.515 (4)	**C22—C23**	1.500 (5)
C23—C24	1.548 (4)	**C24—C25**	1.499 (4)
C26—C27	1.538 (5)	**C28—C29**	1.478 (4)
C26—C31	1.542 (4)	**C29—C30**	1.544 (4)
C27—C28	1.298 (5)	**C30—C31**	1.551 (4)
S2A—O4A	1.394 (8)	**S2B—O5B**	1.395 (15)
S2A—O5A	1.420 (9)	**S2B—O4B**	1.420 (16)
S2A—O6A	1.426 (8)	**S2B—O6B**	1.429 (15)
S2A—C32A	1.802 (7)	**S2B—C32B**	1.793 (12)
C32A—F4A	1.339 (5)	**C32B—F4B**	1.272 (19)
C32A—F6A	1.318 (13)	**C32B—F6B**	1.32 (2)
C32A—F5A	1.338 (15)	**C32B—F5B**	1.34 (2)
N2—P2—C23	101.82 (13)	**C20—N2—P2**	110.36 (16)
N2—P2—C26	121.58 (13)	**C20—N2—Si2**	116.85 (16)
C23—P2—C26	117.39 (15)	**P2—N2—Si2**	129.53 (13)
N2—P2—C29	120.08 (13)	**N2—Si2—C19**	110.41 (12)
C23—P2—C29	112.69 (15)	**N2—Si2—C18**	107.92 (13)
C26—P2—C29	83.65 (15)	**C19—Si2—C18**	106.93 (15)

O1—S1—O2	114.25 (16)	**F1—C16—F3**	108.4 (3)
O1—S1—O3	115.38 (15)	**F1—C16—F2**	106.0 (3)
O2—S1—O3	116.52 (15)	**F3—C16—F2**	107.1 (3)
C23—P2—N2—C20	14.4 (2)	**C26—P2—N2—C20**	147.32 (18)
C23—P2—N2—Si2	−144.14 (18)	**P2—N2—C20—C21**	45.1 (3)
C29—P2—N2—Si2	90.64 (19)	**C21—C22—C23—C24**	−54.4 (4)
C31—C26—C27—C28	61.5 (4)	**C29—P2—C26—C27**	53.4 (2)
C29—P2—C26—C31	−54.0 (2)	**N2—P2—C29—C28**	−177.77 (2)

Symmetry codes: (i) –x, -y, -z.

Scheme S6. Numbering scheme of **[PN(C_6H_{10})]$_4$•(Mo(CO)$_3$** (**5•Mo_1**).

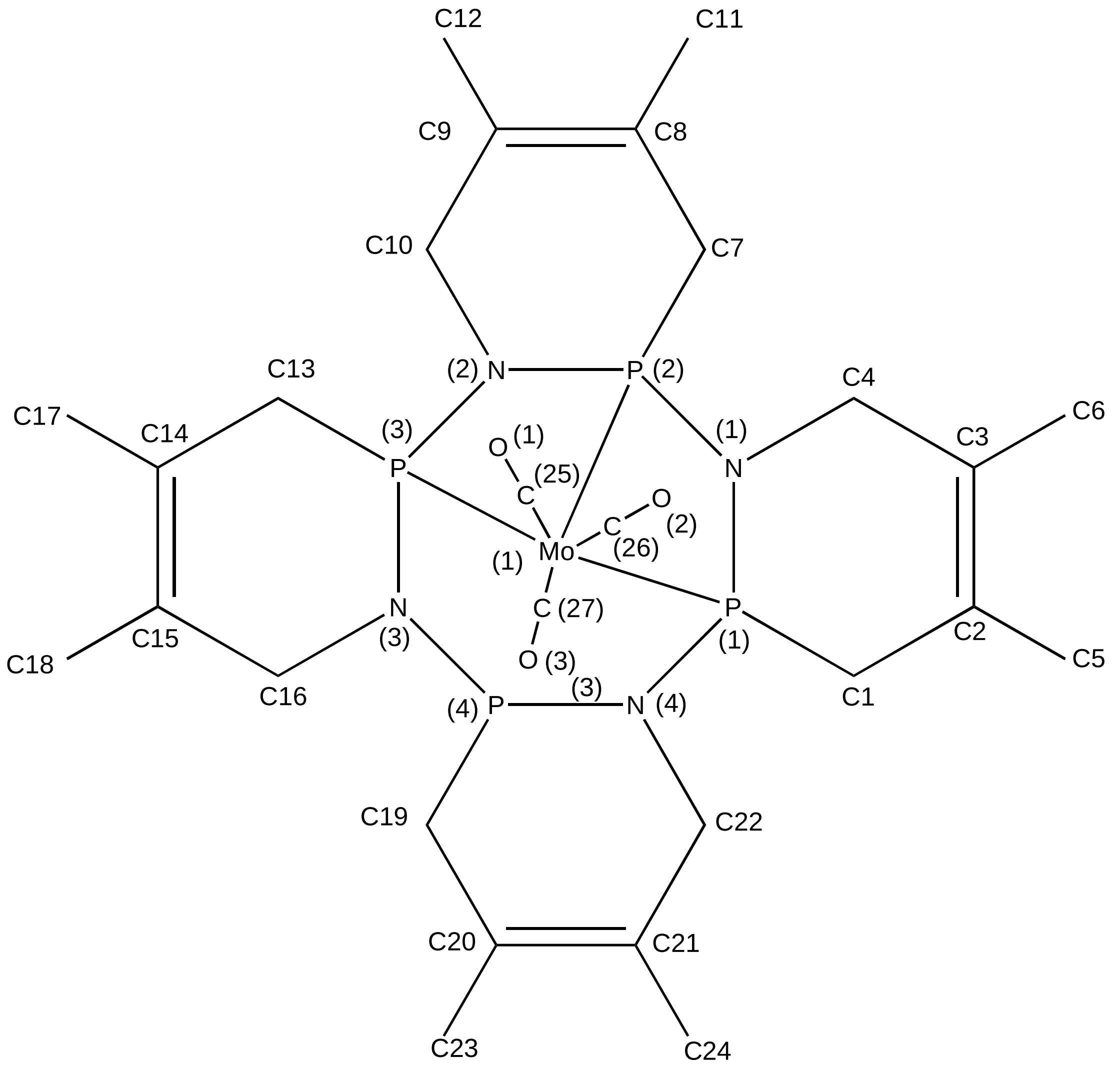

Table S9. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **5•Mo_1**.

Mo1—C25	1.960 (5)	**P1—P2**	2.6644 (16)
Mo1—C26	1.942 (5)	**P2—N2**	1.681 (3)
Mo1—C27	1.949 (5)	**P2—N3**	1.709 (3)
Mo1—P1	2.4690 (12)	**P2—C7**	1.814 (4)
Mo1—P2	2.4557 (12)	**P2—P3**	2.6385 (16)
Mo1—P3	2.4970 (12)	**P3—N4**	1.681 (3)
Mo1—P1	2.5275 (6)	**P3—N3**	1.703 (3)
P1—N1	1.674 (3)	**P3—C13**	1.820 (4)

P1—N2	1.719 (4)	**P4—N4**	1.727 (3)
P1—C1	1.814 (4)	**P4—N1**	1.749 (4)
O3—C3	1.152 (3)	**P4—C19**	1.850 (4)
N1—C4	1.477 (5)	**O1—C25**	1.165 (5)
N2—C10	1.462 (5)	**O2—C26**	1.174 (6)
N3—C16	1.462 (5)	**O3—C27**	1.163 (5)
N4—C22	1.490 (5)	**O1—C25**	1.165 (5)
C1—C2	1.507 (6)	**C19—C20**	1.516 (6)
C2—C3	1.333 (6)	**C20—C21**	1.329 (6)
C3—C4	1.512 (6)	**C21—C22**	1.515 (6)
C2—C5	1.504 (6)	**C20—C23**	1.507 (6)
C3—C6	1.492 (6)	**C21—C24**	1.500 (6)
C26—Mo1—C27	89.2 (2)	**C27—Mo1—P2**	98.61 (15)
C26—Mo1—C25	92.0 (2)	**C25—Mo1—P2**	159.49 (13)
C27—Mo1—C25	95.81 (19)	**C26—Mo1—P1**	90.34 (14)
N1—P1—N2	109.98 (18)	**N2—P2—N3**	111.21 (17)
N1—P1—C1	100.88 (19)	**N2—P2—C7**	100.49 (19)
N2—P1—C1	104.64 (19)	**N3—P2—C7**	106.82 (19)
N4—P3—N3	108.64 (18)	**N4—P4—N1**	106.66 (17)
N4—P3—C13	104.93 (19)	**N4—P4—C19**	95.75 (18)
N3—P3—C13	98.37 (19)	**N1—P4—C19**	100.55 (18)
C4—N1—P1	121.0 (3)	**C10—N2—P2**	125.0 (3)
C4—N1—P4	125.1 (3)	**C10—N2—P1**	130.1 (3)
P1—N1—P4	112.77 (19)	**P2—N2—P1**	103.20 (19)
C16—N3—P3	123.3 (3)	**C22—N4—P3**	124.4 (3)
C16—N3—P2	133.0 (3)	**C22—N4—P4**	119.9 (3)
P3—N3—P2	101.32 (18)	**P3—N4—P4**	115.65 (19)
P2—P3—N4—P4	78.4 (2)	**N1—P4—N4—C22**	101.7 (3)
P4—C19—C20—C21	57.7 (5)	**P1—P2—P3—C13**	176.7 (2)
P1—C1—C2—C5	160.4 (3)	**P2—C7—C8—C11**	−177.3 (3)

P3—C13—C14—C17	167.5 (3)		

Scheme S7. Numbering scheme of **[PN(C_6H_{10})]$_4$·(Mo(CO)$_3$ (5·Mo_2**)

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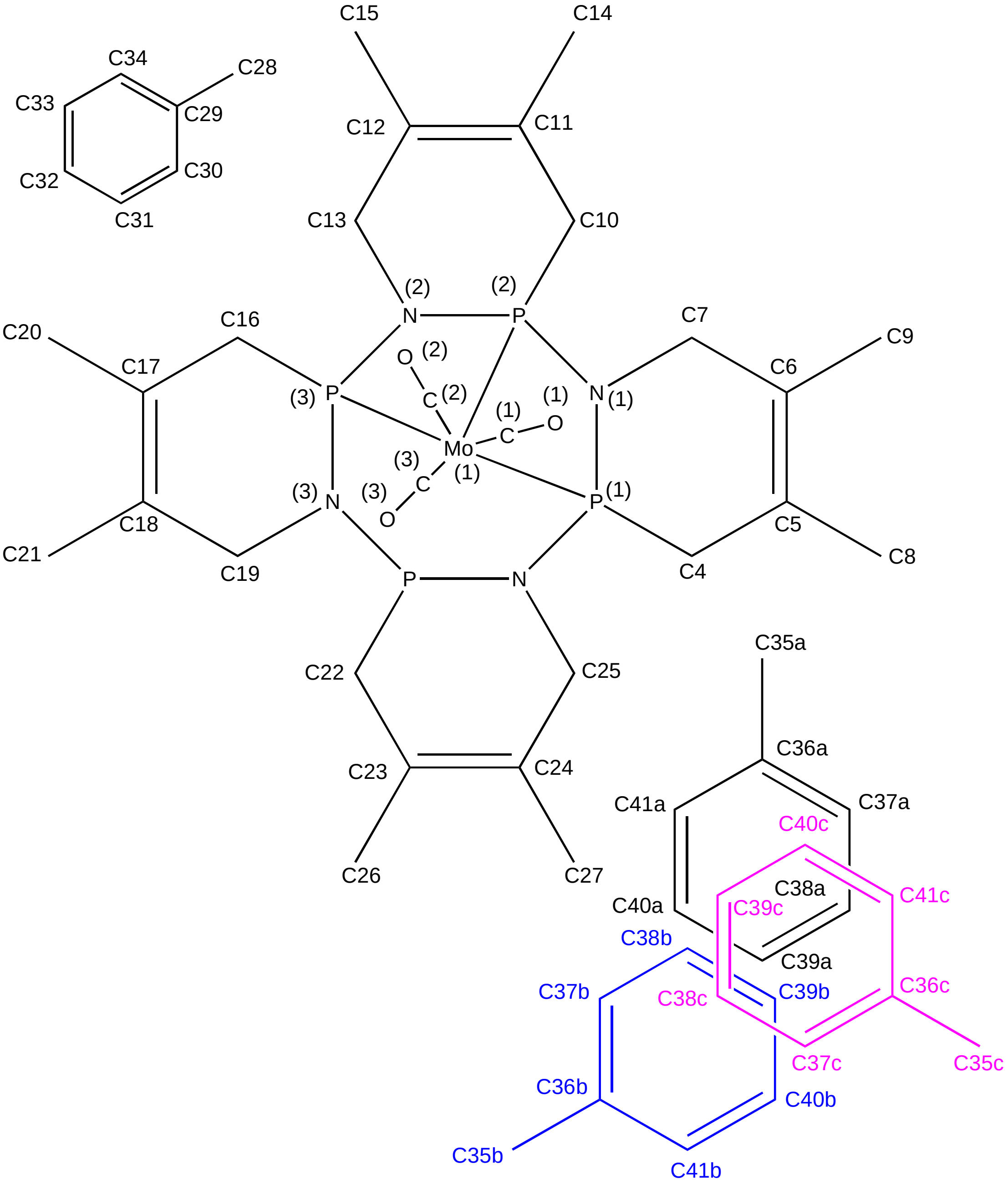

Table S10. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **5·Mo_2**.

Mo1—C1	1.985 (3)	**P1—N4**	1.685 (2)
Mo1—C2	1.972 (3)	**P1—N1**	1.7019 (19)
Mo1—C3	1.975 (3)	**P1—C4**	1.816 (2)

Mo1—P1	2.5275 (6)	**P1—P2**	2.6493 (8)
Mo1—P2	2.4778 (6)	**P2—N2**	1.690 (2)
Mo1—P3	2.4973 (6)	**P2—N1**	1.705 (2)
Mo1—P1	2.5275 (6)	**P2—C10**	1.805 (2)
P1—P2	2.6493 (8)	**P2—P3**	2.6823 (9)
O1—C2	1.155 (3)	**P3—N3**	1.679 (2)
O2—C1	1.155 (3)	**P3—N2**	1.718 (2)
O3—C3	1.152 (3)	**P3—C16**	1.800 (3)
N1—C7	1.460 (3)	**P4—N4**	1.718 (2)
N2—C13	1.463 (3)	**P4—N3**	1.744 (2)
N3—C19	1.473 (3)	**P4—C22**	1.855 (3)
N4—C25	1.490 (3)	**C22—C23**	1.514 (4)
C4—C5	1.517 (3)	**C23—C24**	1.332 (4)
C5—C6	1.339 (3)	**C23—C26**	1.497 (4)
C5—C8	1.506 (4)	**C24—C27**	1.502 (4)
C6—C7	1.498 (3)	**C24—C25**	1.511 (4)
C6—C9	1.509 (3)	**C2—Mo1—P2**	101.25 (7)
C2—Mo1—C3	89.63 (11)	**C3—Mo1—P2**	102.82 (8)
C2—Mo1—C1	92.40 (10)	**C1—Mo1—P2**	159.98 (7)
C3—Mo1—C1	91.74 (10)	**N2—P2—N1**	112.06 (10)
N4—P1—N1	109.19 (9)	**N2—P2—C10**	100.04 (10)
N4—P1—C4	105.03 (11)	**N1—P2—C10**	104.63 (11)
N1—P1—C4	98.72 (10)	**N4—P4—N3**	105.91 (10)
N3—P3—N2	109.96 (10)	**N4—P4—C22**	96.07 (11)
N3—P3—C16	100.03 (11)	**N3—P4—C22**	101.02 (11)
N2—P3—C16	104.03 (11)	**C13—N2—P2**	123.98 (17)
C7—N1—P1	124.12 (16)	**C13—N2—P3**	128.87 (17)
C7—N1—P2	131.45 (15)	**P2—N2—P3**	103.84 (10)
P1—N1—P2	102.09 (10)	**C25—N4—P1**	123.47 (17)
C19—N3—P3	122.16 (16)	**C25—N4—P4**	120.67 (16)

C19—N3—P4	125.28 (15)	**P1—N4—P4**	115.66 (10)
P3—N3—P4	111.50 (11)	**O1—C2—Mo1**	177.6 (2)
O2—C1—Mo1	178.7 (2)	**O3—C3—Mo1**	178.9 (3)
P4—C22—C23—C26	123.6 (2)	**P1—C4—C5—C8**	−168.0 (2)
P2—C10—C11—C14	−164.9 (2)	**P3—C16—C17—C20**	−152.1 (2)

Symmetry code: (i) −x, −y+1, −z+2.

Scheme S8. Numbering scheme of ***N*,*N*-bis(trimethylsilyl)aminochlorostibenium hexachloro-µ-[*N*,*N*-bis(trimethylsilyl)amino]-digallate** (5·W_2)

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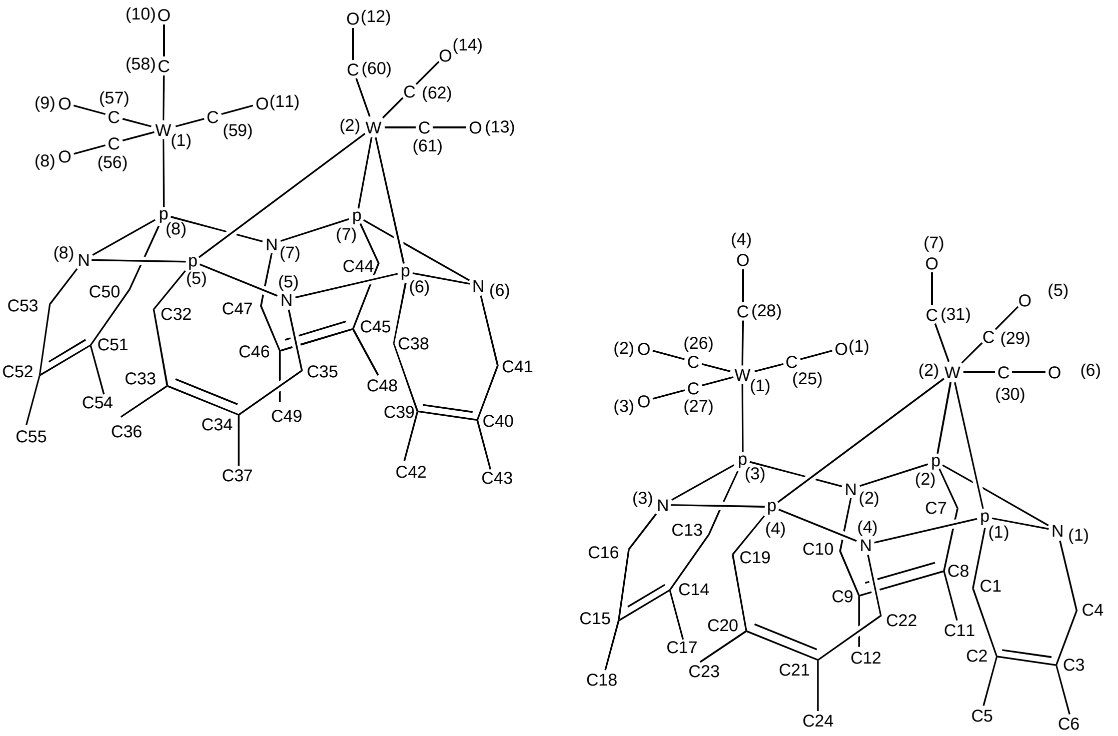

Table S11. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **5•W_2(CO)$_7$**.

W1—C26	1.939 (6)	**W2—C30**	1.940 (6)
W1—C27	1.994 (6)	**W2—C29**	1.981 (6)
W1—C25	2.021 (6)	**W2—C31**	1.999 (6)
W1—C28	2.021 (6)	**W2—P1**	2.4322 (13)
W1—P3	2.4568 (13)	**W2—P2**	2.4818 (13)
W1—W2	3.0984 (3)	**W2—P4**	2.5340 (14)
P1—N4	1.671 (5)	**P3—N3**	1.703 (4)
P1—N1	1.674 (4)	**P3—N2**	1.727 (4)
P1—C1	1.789 (5)	**P3—C13**	1.828 (5)
P1—P4	2.606 (2)	**P4—N3**	1.693 (4)
P1—P2	2.6149 (19)	**P4—N4**	1.694 (4)
P2—N2	1.687 (4)	**P4—C19**	1.812 (5)
P2—N1	1.698 (4)	**N1—C4**	1.474 (6)

P2—C7	1.803 (6)	**N2—C10**	1.465 (6)
O1—C25	1.141 (7)	**N3—C16**	1.475 (7)
O2—C26	1.169 (6)	**N4—C22**	1.458 (7)
O3—C27	1.164 (6)	**C1—C2**	1.511 (7)
O4—C28	1.155 (7)	**C2—C3**	1.332 (7)
O5—C29	1.159 (6)	**C2—C5**	1.502 (8)
O6—C30	1.178 (7)	**C3—C4**	1.495 (8)
O7—C31	1.178 (7)	**W4—C62**	1.934 (7)
C3—C6	1.519 (7)	**W4—C61**	1.990 (7)
W3—C57	1.929 (6)	**W4—C60**	2.010 (6)
W3—C58	2.007 (6)	**W4—P6**	2.4187 (14)
W3—C59	2.008 (7)	**W4—P7**	2.4969 (15)
W3—C56	2.013 (7)	**W4—P5**	2.5261 (13)
W3—P8	2.4548 (13)	**P7—N7**	1.691 (4)
W3—W4	3.0805 (3)	**P7—N8**	1.704 (4)
P5—N5	1.678 (4)	**P7—C47**	1.798 (5)
P5—N6	1.704 (4)	**P8—N8**	1.710 (4)
P5—C35	1.801 (5)	**P8—N5**	1.721 (4)
P5—P6	2.6093 (19)	**P8—C50**	1.826 (5)
P6—N6	1.670 (4)	**N5—C32**	1.470 (6)
P6—N7	1.676 (5)	**N6—C38**	1.469 (6)
P6—C41	1.789 (5)	**N7—C44**	1.473 (7)
P6—P7	2.601 (2)	**N8—C53**	1.466 (7)
Cl4—Ga1—Cl3	108.49 (4)	**O12—C60**	1.167 (7)
Si4—N2—Si3	113.04 (13)	**O13—C61**	1.158 (7)
O8—C56	1.148 (7)	**O14—C62**	1.192 (7)
O9—C57	1.180 (7)	**C25—W1—C28**	171.9 (2)
O10—C58	1.146 (6)	**C30—W2—C29**	87.8 (3)
O11—C59	1.154 (7)	**C30—W2—C31**	81.0 (3)
C26—W1—C27	95.0 (2)	**C29—W2—C31**	97.7 (2)

C26—W1—C25	84.9 (2)	**N2—P2—N1**	113.1 (2)
C27—W1—C25	87.3 (2)	**N2—P2—C7**	98.9 (2)
N4—P1—N1	111.2 (2)	**N1—P2—C7**	104.3 (2)
N4—P1—C1	107.6 (3)	**N3—P4—N4**	110.0 (2)
N1—P1—C1	102.7 (2)	**N3—P4—C19**	107.3 (3)
N3—P3—N2	107.3 (2)	**N4—P4—C19**	98.1 (2)
N3—P3—C13	97.6 (2)	**C10—N2—P2**	120.6 (3)
N2—P3—C13	103.0 (2)	**C10—N2—P3**	124.8 (4)
C4—N1—P1	123.9 (4)	**P2—N2—P3**	113.5 (2)
C4—N1—P2	133.1 (4)	**C22—N4—P1**	133.0 (4)
P1—N1—P2	101.7 (2)	**C22—N4—P4**	125.0 (4)
C16—N3—P4	123.7 (4)	**P1—N4—P4**	101.5 (2)
C16—N3—P3	124.0 (4)	**O12—C60—W4**	161.8 (6)
P4—N3—P3	112.3 (2)	**P4—W2—P2—C7**	175.2 (3)
O7—C31—W2	163.3 (6)	**P2—C7—C8—C11**	−149.8 (5)
W1—W2—P2—C7	92.2 (3)	**P4—C19—C20—C23**	−166.6 (4)
P1—C1—C2—C5	−158.7 (4)	**P3—C13—C14—C17**	−139.9 (5)

Scheme 9. Numbering scheme of **bis-[*N*,*N*-bis(trimethylsilyl)amino](trifalto)-stibane** (**11**)

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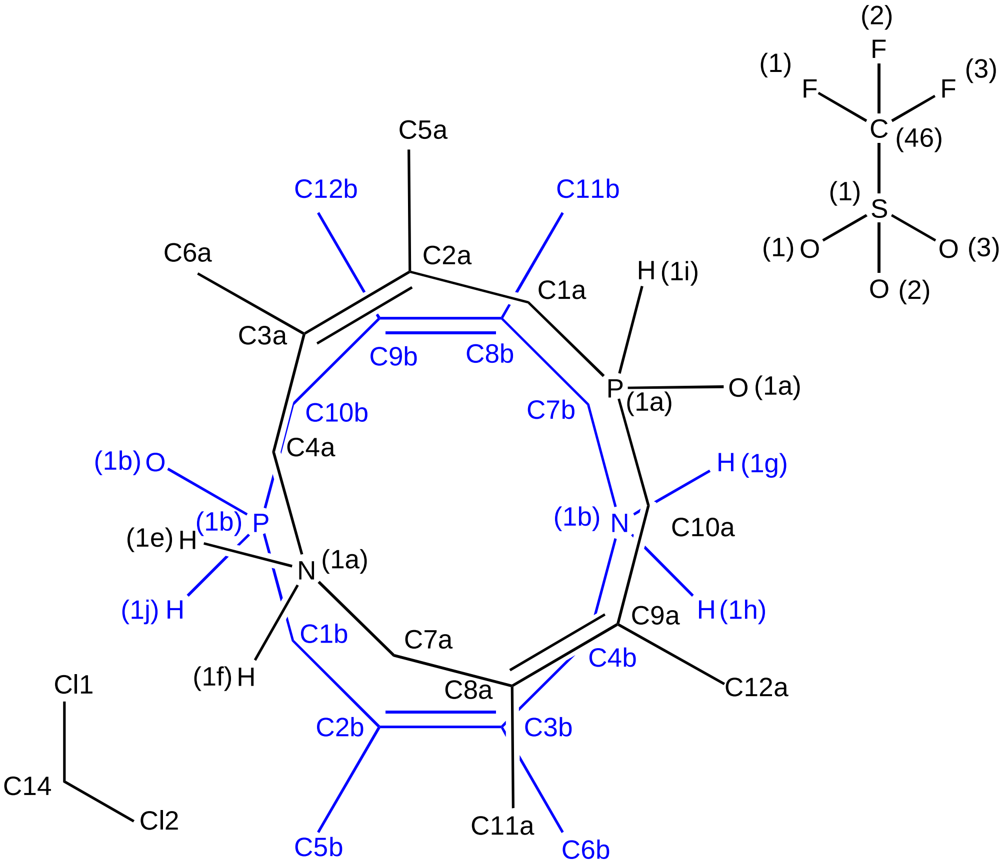


Table S12. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **11**.

P1A—O1A	1.500 (3)	**C1A—C2A**	1.514 (6)
P1A—C1A	1.795 (5)	**C2A—C3A**	1.334 (6)
P1A—C7A	1.795 (4)	**C2A—C5A**	1.528 (6)
P1A—H1I	1.30 (5)	**C3A—C4A**	1.485 (6)
N1A—C10A	1.497 (6)	**C3A—C6A**	1.518 (6)
N1A—C4A	1.509 (6)	**C7A—C8A**	1.515 (5)
N1A—H1E	0.92 (3)	**C8A—C9A**	1.327 (6)
N1A—H1F	0.91 (4)	**C8A—C11A**	1.506 (6)
C9A—C12A	1.513 (5)	**C9A—C10A**	1.501 (6)
P1B—O1B	1.513 (10)	**C1B—C2B**	1.512 (11)

P1B—C7B	1.787 (10)	**C2B—C3B**	1.333 (10)
P1B—C1B	1.793 (11)	**C2B—C5B**	1.533 (11)
P1B—H1J	1.2971	**C3B—C4B**	1.486 (11)
N1B—C10B	1.499 (12)	**C3B—C6B**	1.524 (11)
N1B—C4B	1.506 (11)	**C7B—C8B**	1.513 (11)
N1B—H1G	0.9200	**C8B—C9B**	1.326 (10)
N1B—C10B	1.499 (12)	**C8B—C11B**	1.508 (11)
C9B—C12B	1.513 (11)	**C9B—C10B**	1.506 (11)
S1—O2	1.397 (4)	**Cl1—C14**	1.745 (6)
S1—O4	1.420 (3)	**Cl2—C14**	1.751 (6)
S1—O3	1.425 (3)	**F2—C13**	1.305 (6)
S1—C13	1.798 (5)	**F3—C13**	1.335 (5)
F1—C13	1.310 (6)	**C10A—N1A—C4A**	114.3 (4)
O1A—P1A—C1A	112.5 (2)	**C10A—N1A—H1E**	108 (3)
O1A—P1A—C7A	115.3 (2)	**C4A—N1A—H1E**	110 (3)
C1A—P1A—C7A	106.3 (2)	**C10A—N1A—H1F**	111 (3)
O1A—P1A—H1I	117 (2)	**C4A—N1A—H1F**	115 (4)
C1A—P1A—H1I	103 (2)	**H1E—N1A—H1F**	96 (5)
C7A—P1A—H1I	102 (2)	**C9A—C8A—C11A**	121.8 (4)
C3A—C2A—C1A	124.5 (4)	**C9A—C8A—C7A**	124.2 (4)
C3A—C2A—C5A	122.4 (4)	**C11A—C8A—C7A**	114.1 (4)
C1A—C2A—C5A	113.1 (4)	**C7A—P1A—C1A—C2A**	−64.4 (4)
O1A—P1A—C1A—C2A	168.5 (3)	**P1A—C1A—C2A—C3A**	114.8 (5)
C1A—C2A—C3A—C4A	0.4 (8)	**O1A—P1A—C7A—C8A**	64.1 (4)
P1A—C7A—C8A—C9A	111.7 (4)	**C1A—P1A—C7A—C8A**	−61.3 (4)

Scheme 10. Numbering scheme of Tricarbonyltris(propionitrile)molybdenum(0) (**X**)

.

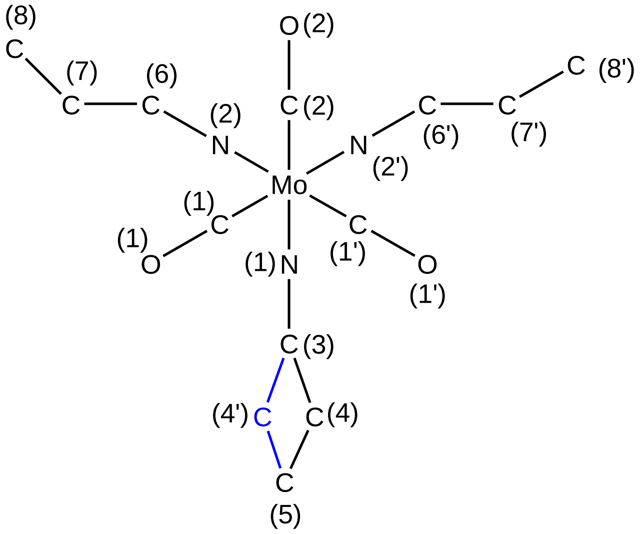


Table S13. Selected bond lenghts (Å) angles (°) and torsion angles (°) of **X**.

Mo1—C2	1.9307 (19)	**N2—C6**	1.1414 (16)
Mo1—C1i	1.9315 (13)	**O1—C1**	1.1719 (16)
Mo1—C1	1.9315 (13)	**O2—C2**	1.171 (2)
Mo1—N1	2.2185 (16)	**C3—C4**	1.465 (4)
Mo1—N2	2.2206 (11)	**C4—C5**	1.526 (4)
Mo1—N2i	2.2205 (11)	**C6—C7**	1.4620 (18)
N1—C3	1.140 (2)	**C7—C8**	1.510 (2)
C2—Mo1—C1i	89.16 (5)	**C3—N1—Mo1**	179.43 (15)
C2—Mo1—C1	89.16 (5)	**C6—N2—Mo1**	177.01 (11)
C1i—Mo1—C1	87.08 (7)	**O1—C1—Mo1**	179.07 (11)
C3—C4—C5	112.42 (19)	**O2—C2—Mo1**	179.91 (16)

Symmetry code: (i) x, −y+1/2, z.

3. Synthesis

3.1. Synthesis of *cyclo*-tetraphosphazane $[PN(C_6H_{10})]_4$ (5)

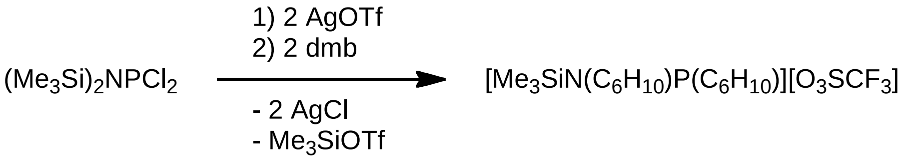
$$(Me_3Si)_2NPCl_2 \xrightarrow[\substack{C_7H_8,\ 115°C,\ 4.5\ h \\ -2\ Me_3SiCl}]{2.44\ dmb} 0.25\ [PN(C_6H_{10})]_4$$

$(Me_3Si)_2NPCl_2$ (0.821 g, 3.3 mmol) and 2,3-dimethyl-1,3-butadiene (0.662 g, 8.06 mmol) are combined in 10 ml toluene and the mixture is degased properly by three freeze-pump-thaw cycles. Afterwards the flask is placed in an oil bath and is refluxed *in vacuo* at 115°C over a period of 4.5 h. The resulting white suspension is slowly cooled to room temperature and polymers are removed by filtration. Afterwards the solvent is removed from the filtrate *in vacuo* and the residual oily liquid is redissolved in CH_2Cl_2, yielding after concentration to 0.2 ml and placement in the freezer for 12 h (−40 °C) colourless crystals of $[PN(C_6H_{10})]_4$ (0.112 g, 0.18 mmol, 22%). Taking on the residual oily liquid in C_6H_5F resulted in the deposition of colorless blocks of **5** together with small plates of $[P_5N_5(dmb)_5]$ (**5b**).

Mp. 70 °C (dec). **Anal**. calc. % (found) $[PN(C_6H_{10})]_4 \cdot CH_2Cl_2$: C 50.60 (50.74); H 7.13 (7.27); N 9.44 (10.10). **^{1}H NMR** (25 °C, CD_2Cl_2, 250.13 MHz): 1.54 (*s*, 12H, C*H*$_3$), 1.73 (*s*, 12H, C*H*$_3$), 1.74 (*m*, $J(^{13}C\text{-}^1H)$ = 119.16 Hz, 8H, PC*H*$_2$), 3.59 (*m*, 8H, NC*H*$_2$); **^{13}C{^{1}H} NMR** (25 °C, CD_2Cl_2, 62.90 MHz): 18.2 (*s*, CH_3) 20.9 (s, *C*H$_3$) 32.1 (*m*, P*C*H$_2$), 51.1 (*m*, N*C*H$_2$), 122.0 (*s*, C_{vinyl}) 125.3 (*s*, C_{vinyl}); **^{31}P NMR** (25 °C, CD_2Cl_2, 101.27 MHz): (**5**) 69.65 (*s*), (**5b**) 71.6 (*s*). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2978 (w), 2906 (m), 2855 (m), 2821 (m), 1436 (m), 1393 (w), 1382 (m), 1361 (w), 1275 (m), 1250 (m), 1218 (m), 1166 (m), 1135 (m), 1091 (m), 1044 (m), 956 (m), 920 (m), 862 (s), 839 (s), 805 (m), 778 (s), 751 (s), 724 (s), 695 (m), 645 (s), 563 (m). **RAMAN**: 2907 (7), 2865 (5), 2832 (1), 2797 (1), 1695 (5), 1442 (4), 1397 (6), 1277 (4), 1260 (4), 1166 (1), 1138 (1) 1104 (1), 962 (1), 780 (1), 758 (3), 696 (3), 642 (10), 566 (4), 495 (5), 423 (3), 368 (4), 321 (3), 288 (4), 264 (3), 248 (3). **MS** (CI, isobutane, m/z, > 10 %): $\{[PN(C_6H_{10})]_4+H\}^+$ 509 (15.8), $\{[PN(C_6H_{10})]_2+H\}^+$ 255, $\{[PN(C_6H_{10})]+H\}^+$ 128 (52.2); (ESI-TOF, m/z): $\{[PN(C_6H_{10})]_4+H\}^+$ 509.22, $\{[PN(C_6H_{10})]_5+H\}^+$ 636.28.

Crystals suitable for X-ray crystallographic analysis were obtained from a saturated CH_2Cl_2 solution solution of **5** at −40 °C.

3.2. Synthesis of [$Me_3SiN(dmb)P(dmb)$][CF_3SO_3] (7)



$$(Me_3Si)_2NPCl_2 \xrightarrow[\substack{-\ 2\ AgCl \\ -\ Me_3SiOTf}]{\substack{1)\ 2\ AgOTf \\ 2)\ 2\ dmb}} [Me_3SiN(C_6H_{10})P(C_6H_{10})][O_3SCF_3]$$

$(Me_3Si)_2NPCl_2$ (0.269 g, 1.05 mmol) in CH_2Cl_2 (3 ml) is combined with dmb (0.170 g, 2.1 mmol) and added to a slurry of AgOTf (0.523 g, 2.1 mmol) in CH_2Cl_2 (3 ml) at −80 °C. The greyish suspension is allowed to slowly warm to room temperature and is further stirred for one hour. Afterwards the solvent is removed *in vacuo* and the residual off-white solids are extracted with CH_2Cl_2 (5 ml). Removal of the solvents and washing of the crude material with minimal amounts of n-hexane yields [$Me_3SiN(dmb)P(dmb)$][CF_3SO_3] (**7**) as a white powder (0.325 g, 0.75 mmol, 72 %).

When a CH_2Cl_2 of **7** was placed in the freezer at −24 °C for 72 h the formation of small colorless needles was observed. These needles were crystallographically analysed to be the hydrolysis product of **9** [$(O)PH(dmb)_2NH_2$][CF_3SO_3] (**9**). Crystals of **9** decompose rapidly at room temperature.

Mp. 58 °C (dec). **^{1}H NMR** (25 °C, CD_2Cl_2, 500.13 MHz): 0.31 (*s*, $J(^{29}Si\text{-}^{1}H)$ = 6.59 Hz, $J(^{13}C\text{-}^{1}H)$ = 120.02 Hz, 9H, $Si(CH_3)_3$), 1.79 (*m*, 3 $C\boldsymbol{H_3}$), 1.91 (*s*, $C\boldsymbol{H_3}$), 2.76-2.97 (*m*, 4H, $PC\boldsymbol{H_2}$), 3.00 (d, $J(^{31}P\text{-}^{1}H)$ = 12.8 Hz, 2H, $PC\boldsymbol{H_2}$), 3.58 (d, $J(^{31}P\text{-}^{1}H)$ = 18.00 Hz, 2H, $NC\boldsymbol{H_2}$); **^{13}C{^{1}H} NMR** (25 °C, CD_2Cl_2, 125.76 MHz): 0.16 (*s*, $Si(CH_3)_3$) 16.5 (*d*, $J(^{31}P\text{-}^{13}C)$ = 14.50 Hz, 2 CH_3) 18.7 (*d*, $J(^{31}P\text{-}^{13}C)$ = 1.99 Hz, CH_3), 21.0 (*d*, $J(^{31}P\text{-}^{13}C)$ = 6.47 Hz, CH_3), 27.2 (*d*, $J(^{31}P\text{-}^{13}C)$ = 56.01 Hz, PCH_2), 36.6 (*d*, $J(^{31}P\text{-}^{13}C)$ = 60.47 Hz, 2 PCH_2), 50.0 (*d*, $J(^{31}P\text{-}^{13}C)$ = 3.56 Hz, NCH_2), 122.0 (*d*, $J(^{31}P\text{-}^{13}C)$ = 10.84 Hz, C_{vinyl}), 128.6 (*d*, $J(^{31}P\text{-}^{13}C)$ = 10.93 Hz, 2 C_{vinyl}), 134.15 (*d*, $J(^{31}P\text{-}^{13}C)$ = 14.73 Hz, C_{vinyl}); **^{19}F NMR** (25 °C, CD_2Cl_2, 282.40 MHz): −78.8 (*s*, CF_3SO_3); **^{29}Si NMR** (25 °C, CD_2Cl_2, 59.63 MHz): 7.7 (*m*, $Si(CH3)_3$). **^{31}P NMR** (25 °C, CD_2Cl_2, 202.46 MHz): 59.9 (*s*). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2954 (w), 2920 (w), 2864 (w), 1444 (w), 1418 (w), 1395 (w), 1255 (s), 1221 (s), 1188 (m), 1149 (s), 1113 (m), 1054 (m), 1028 (s), 978 (m), 904 (m), 841 (s), 802 (m), 755 (m), 711 (m), 695 (m), 666 (m), 634 (s), 572 (m).

Crystals suitable for X-ray crystallographic analysis were obtained from a saturated toluene solution of **7** at 25°C.

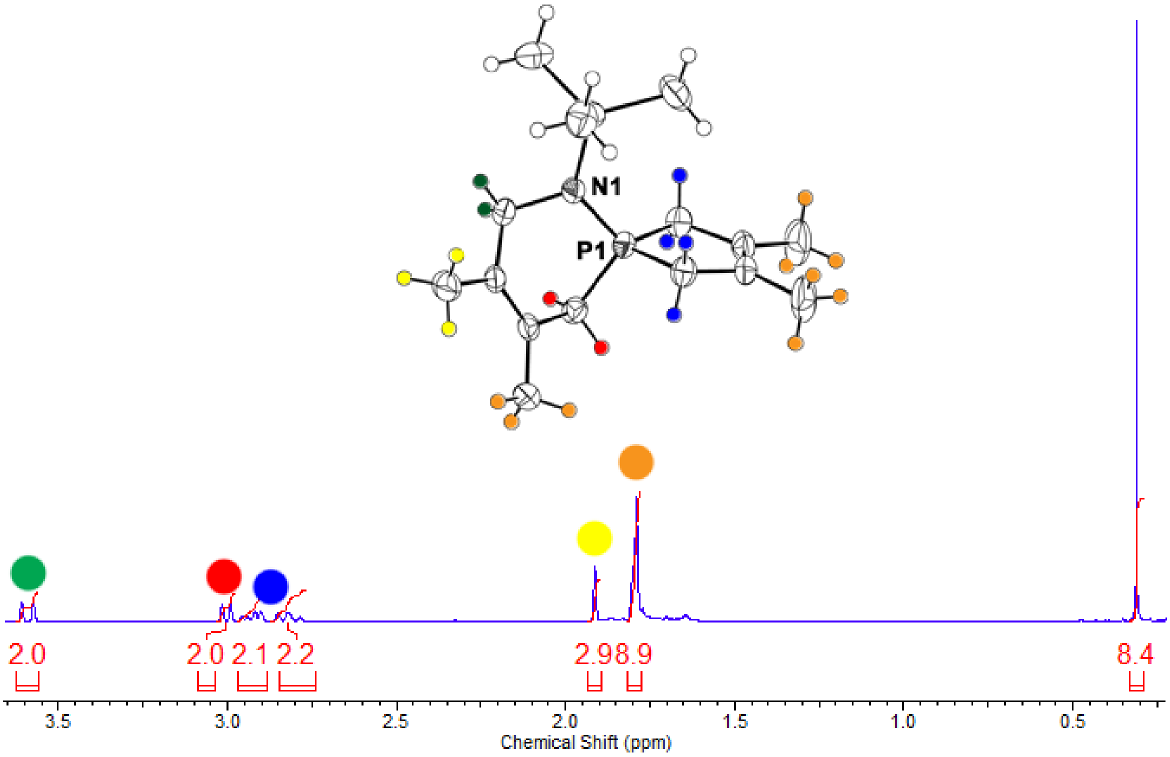


Figure S1. ^{1}H NMR spectrum of **7**$^{+}$. Distinguishable protons are highlighted.

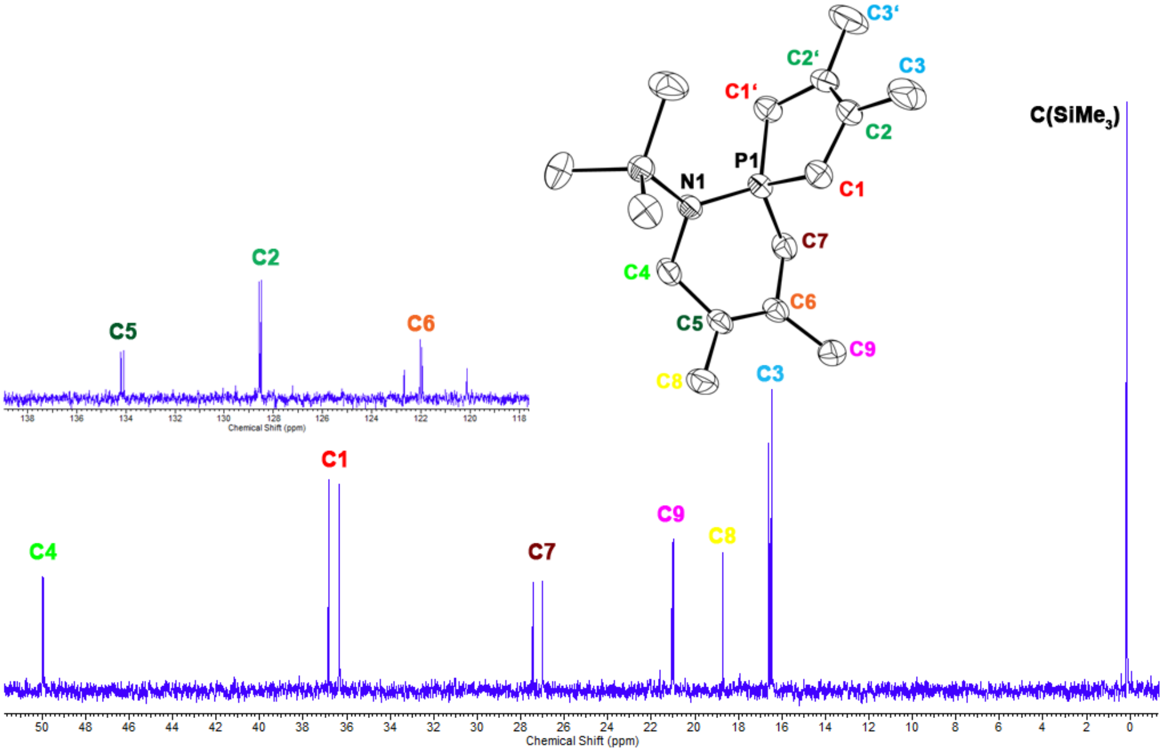


Figure S2. ^{13}C NMR spectrum of **7**$^{+}$.

3.3. Synthesis of $Me_3SiN(chd)P(chd)$ (8)

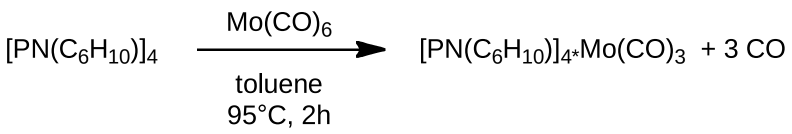
$$(Me_3Si)_2NPCl_2 \xrightarrow[\substack{\text{- 2 AgCl} \\ \text{- } Me_3SiOTf}]{\substack{\text{1) 2 AgOTf} \\ \text{2) 2 dmb}}} [Me_3SiN(C_6H_{10})P(C_6H_{10})][O_3SCF_3]$$

$(Me_3Si)_2NPCl_2$ (0.269 g, 1.05 mmol) in CH_2Cl_2 (3 ml) is combined with chd (0.166 g, 2.1 mmol) and added to a slurry of AgOTf (0.527 g, 2.1 mmol) in CH_2Cl_2 (3 ml) at −80 °C. The greyish suspension is allowed to slowly warm to room temperature and is further stirred for one hour. Afterwards the solvent is removed *in vacuo* and the residual off-white solids are extracted with CH_2Cl_2 (5 ml). Removal of the solvents and washing of the crude material with minimal amounts of *n*-hexane yields $[Me_3SiN(chd)P(chd)][CF_3SO_3]$ (**8**) as a greyish powder (0.171 g, 0.40 mmol, 38 %).

Mp. 87 °C (dec). **^{1}H NMR** (25 °C, CD_2Cl_2, 300.13 MHz): 0.45 (*s*, $J(^{29}Si-^{1}H)$ = 6.42 Hz, $J(^{13}C-^{1}H)$ = 120.30 Hz, 9H, $Si(CH_3)_3$), 1.45-2.53 (*m*, 8 CH_2), 3.08 (*m*, 1H, PC*H*), 3.49 (*m*, 1H, PC*H*), 3.58 (*m*, 1H, PC*H*), 4.60-4.46 (*m*, 1H, NC*H*), 6.81-6.46 (m, 4H, vinyl-C*H*); **^{13}C{^{1}H} NMR** (25 °C, CD_2Cl_2, 75.47 MHz): 2.8 (s, $Si(CH_3)_3$), 19.1 (*d*, $J(^{31}P-^{13}C)$ = 5.07 Hz, 1 CH_2) 22.0 (*d*, $J(^{31}P-^{13}C)$ = 15.52 Hz, CH_2), 23.9 (*d*, $J(^{31}P-^{13}C)$ = 42.28 Hz, P*C*3), 24.0 (*d*, $J(^{31}P-^{13}C)$ = 59.97 Hz, P*C*H), 24.4 (*d*, $J(^{31}P-^{13}C)$ = 14.86 Hz, PCH_2), 28.2 (*d*, $J(^{31}P-^{13}C)$ = 9.1 Hz, PCH_2) 37.9 (*d*, $J(^{31}P-^{13}C)$ = 54.0 Hz, P*C*H), 40.0 (*d*, $J(^{31}P-^{13}C)$ = 48.2 Hz, P*C*H), 56.4 (*d*, $J(^{31}P-^{13}C)$ = 6.01 Hz, N*C*H), 130.6 (*d*, $J(^{31}P-^{13}C)$ = 10.85 Hz, C_{vinyl}), 133.0 (*d*, $J(^{31}P-^{13}C)$ = 12.13 Hz, C_{vinyl}), 134.3 (*d*, $J(^{31}P-^{13}C)$ = 12.97 Hz, C_{vinyl}), 139.2 (*d*, $J(^{31}P-^{13}C)$ = 13.65 Hz, C_{vinyl}); **^{19}F{^{1}H} NMR** (25 °C, CD_2Cl_2, 282.40 MHz): −78.6; **^{29}Si NMR** (25 °C, CD_2Cl_2, 59.63 MHz): 19.2 (*m*). **^{31}P NMR** (25 °C, CD_2Cl_2, 75.46 MHz): 82.1 (*s*). **IR** (ATR, 25 °C, 16 scans, cm^{-1}): 3068 (w), 3016 (w), 2954 (w), 2918 (w), 2881 (w), 1622 (w), 1467 (w), 1451 (w), 1423 (w), 1391 (w), 1360 (w), 1330 (w), 1259 (s), 1222 (m), 1143 (s), 1111 (m), 1084 (m), 1073 (m), 1028 (m), 990 (m), 968 (m), 951 (m), 914 (m), 842 (s), 813 (m), 773 (m), 752 (m), 714 (m), 694 (m), 680 (m), 664 (m), 633 (s), 610 (m), 594 (m), 570 (m).

Crystals suitable for X-ray crystallographic analysis were obtained from a saturated toluene solution of **8** at 25°C.

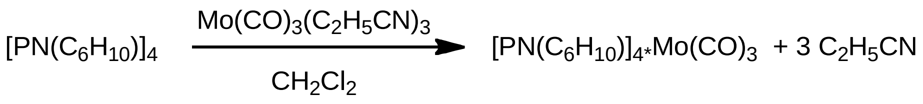
3.4. Synthesis of $[PN(dmb)]_4$ $Mo(CO)_3$



$$[PN(C_6H_{10})]_4 \xrightarrow[\text{toluene}\\ 95°\text{C, 2h}]{Mo(CO)_6} [PN(C_6H_{10})]_4{*}Mo(CO)_3 + 3\ CO$$

Procedure 1:

Procedure 1: **5** (0.150 g, 0.30 mmol) and $Mo(CO)_6$ (0.132 g, 0.5 mmol) are combined in 20 ml toluene and the yellow mixture is refluxed for 2 h at 95°C. Afterwards the solvent is evaporated and residual $Mo(CO)_6$ is removed by sublimation (10^{-3} mbar) at 50°C over a period of 6 h. The residual brownish solids are extracted with toluene (5 ml) and from the filtrate colorless needles of $[PN(dmb)]_4$ $Mo(CO)_3$ (0.045 g, 0.05 mmol, 18%) were grown.



$$[PN(C_6H_{10})]_4 \xrightarrow[CH_2Cl_2]{Mo(CO)_3(C_2H_5CN)_3} [PN(C_6H_{10})]_4{*}Mo(CO)_3 + 3\ C_2H_5CN$$

Procedure 2:

5 (0.080 g, 0.16 mmol) and $Mo(CO)_3(C_2H_5CN)_3$ (0.055 g, 0.16 mmol) are combined in 6 ml CH_2Cl_2 at −50°C. The clear brownish solution was allowed to slowly warm to ambient temperatures over a period of 5 h. Afterwards the solvent was removed *in vacuo* and residues were dried at 60°C for 2 h. The brownish residual solids were re-dissolved in 1 ml CH_2Cl_2 and crystals of $[PN(dmb)]_4$ $Mo(CO)_3$ (0.065 g, 0.09 mmol; 54 %) were grown by vapour diffusion of *n*-hexane into this CH_2Cl_2 solution.

Mp. 207 °C (dec). **Anal**. calc. % (found) $[PN(dmb)]_4$ $Mo(CO)_3$ $0.65(CH_2Cl_2)$: C 44.65 (44.63); H 5.60 (5.58); N 7.53 (7.69). **^{1}H NMR** (25 °C, CD_2Cl_2, 250.13 MHz): 1.60 (*s*, 12H, C*H*$_3$), 1.80 (*s*, 12H, C*H*$_3$), 2.2-3.8 ((12H, C*H*$_2$); **^{13}C{^{1}H} NMR** (25 °C, CD_2Cl_2, 62.90 MHz): 18.2 (*s*, CH_3) 21.4 (s, *C*H$_3$) 33.3 (*m*, P*C*H$_2$), 50.4 (*m*, N*C*H$_2$), 122.6 (*s*, C_{vinyl}) 126.0 (*s*, C_{vinyl}). **^{31}P NMR** (25 °C, CD_2Cl_2, 101.27 MHz): 79.8 (*s*). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2981 (w), 2912 (m), 2856 (m), 1930 (s), 1828 (s), 1435 (m), 1384 (m), 1267 (m), 1251 (m), 1215 (m), 1160 (m), 1097 (m), 1049 (m), 957 (m), 869 (m), 843 (m), 808 (m), 780 (s), 728 (s), 695 (m), 653 (s), 603 (m), 574 (s). **RAMAN**: 2907 (3), 2876 (2), 1928 (7), 1854 (8), 1847 (8), 1837 (9), 1679 (8), 1453 (8), 1398 (8), 1380 (8), 1397 (6), 1245 (7), 784 (5), 745 (5), 721 (5), 705 (5), 696 (3), 676 (5), 668 (5), 656 (6), 606 (4), 571 (4), 505 (5), 482 (5), 452 (8), 445 (10), 382 (2), 288 (1), 264 (1), 239 (3), 230 (4), 211 (2). **MS** (ESI-TOF, m/z): $\{[PN(C_6H_{10})_4Mo(CO)_2+H\}^+$ 657.12.

Crystals suitable for X-ray crystallographic analysis were obtained from a saturated toulene solution of $[PN(dmb)]_4$ $Mo(CO)_3$ at −24°C or by *n*-hexane diffusion into a saturated CH_2Cl_2 solution of $[PN(dmb)]_4$ $Mo(CO)_3$.

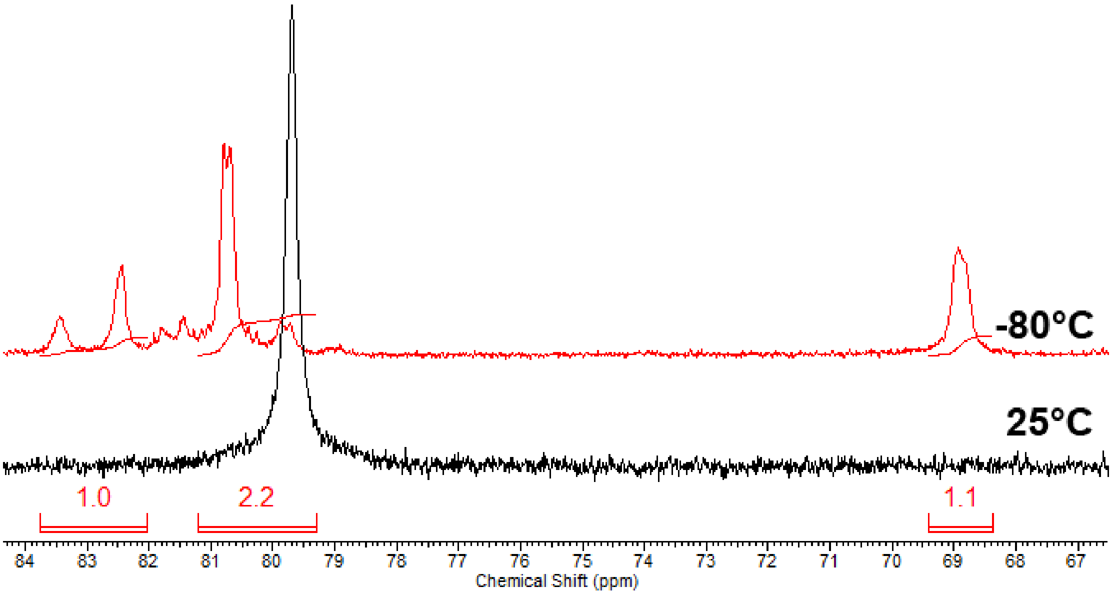


Figure S3. ^{31}P NMR spectra of **5·Mo** at −80 °C (red) and 25°C (black) with a signal ratio of 1:2:1 at −80 °.

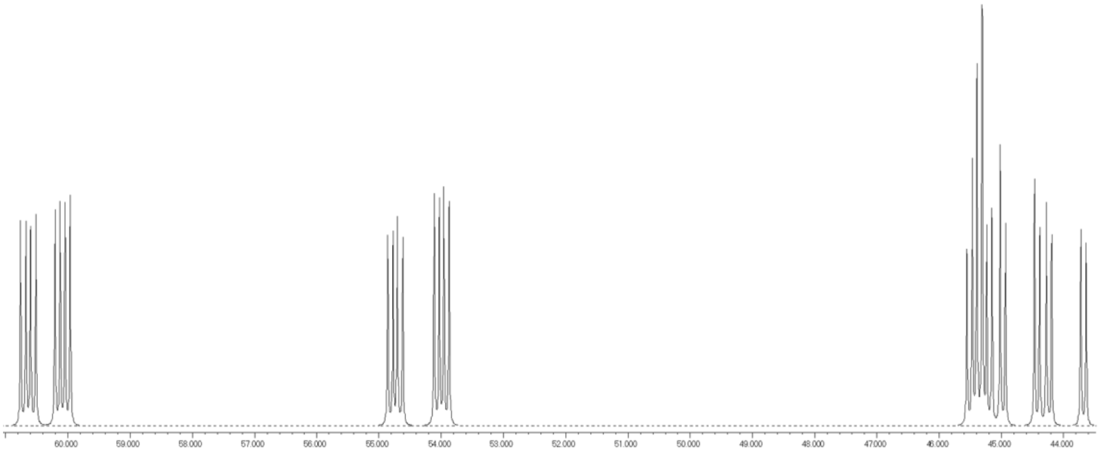


Figure S4. Simulated ^{31}P NMR of the gas phase structure of **5·Mo** with the GIAO method on the B3LYP/6-31g(d,p) level of density functional theory, displaying an ABCD spectrum, visualized using gNMR.[15]

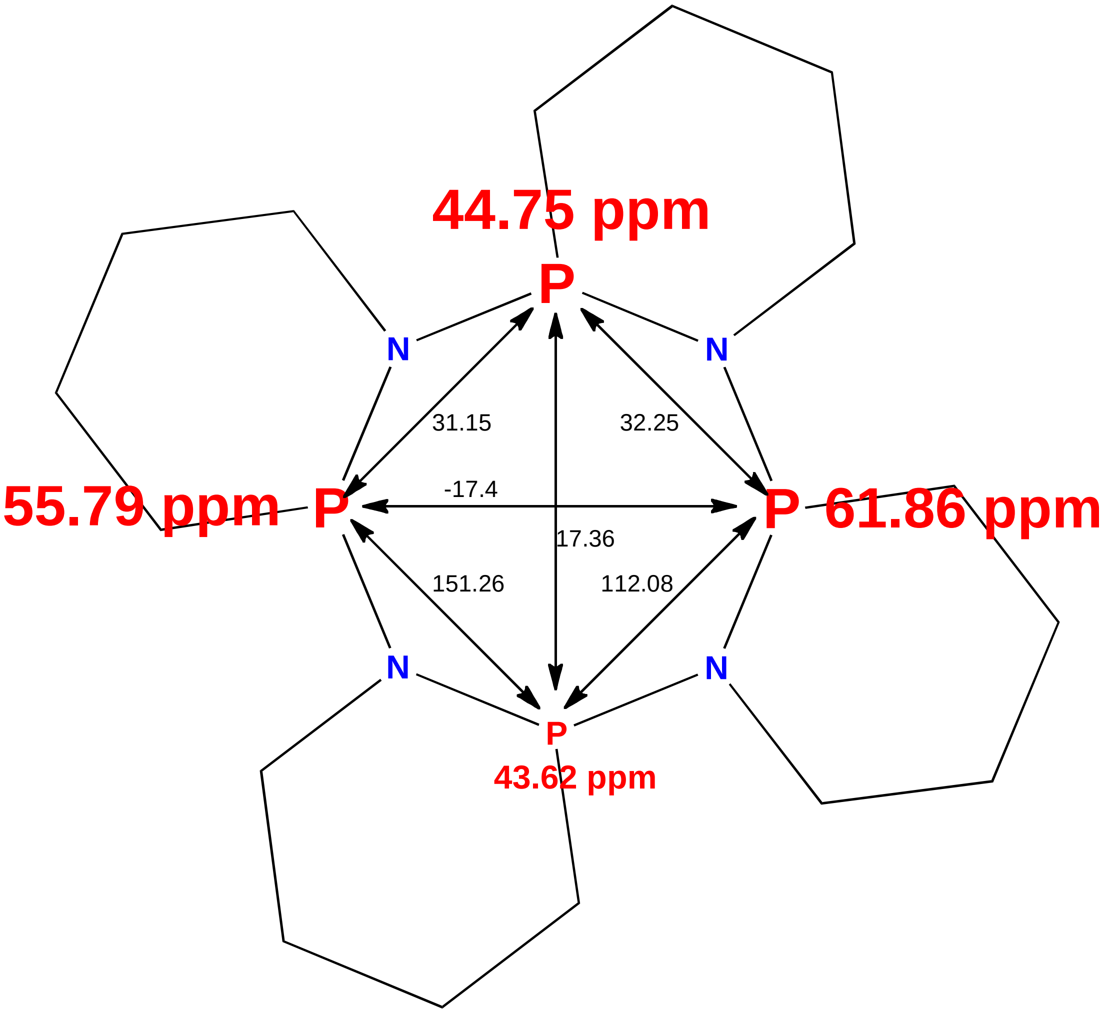


Figure S5. Simulated ^{31}P NMR shifts (red, bigger Ps corresponding to coordinated P atoms) and coupling constants in Hz (values on double arrows) of the gas phase structure of **5·Mo** calculated with the GIAO method on the B3LYP/6-31g(d,p) level of density functional theory.

3.5. Synthesis of [PN(dmb)]$_4$ W$_2$(CO)$_7$

$$[PN(C_6H_{10})]_4 \xrightarrow[CH_2Cl_2]{W(CO)_3(C_2H_5CN)_3} [PN(C_6H_{10})]_{4*}W_2(CO)_7 \ + \ ...$$

5 (0.080 g, 0.16 mmol) and $W(CO)_3(C_2H_5CN)_3$ (0.055 g, 0.16 mmol) are combined in 6 ml CH_2Cl_2 at −50°C. The clear reddish solution was allowed to slowly warm to ambient temperatures over a period of 2 h and was further stirred for 21 days. Afterwards the solvent is removed *in vacuo* and the residues dried at 60°C for 2 h. The residual solids were redisolved in 1 ml CH_2Cl_2 and orange crystals of [PN(dmb)]$_4$ W$_2$(CO)$_7$ besides other unidentified products could be selected by crystal picking.

3.5.1. Structure Discussion of [PN(dmb)]$_4$ W$_2$(CO)$_7$

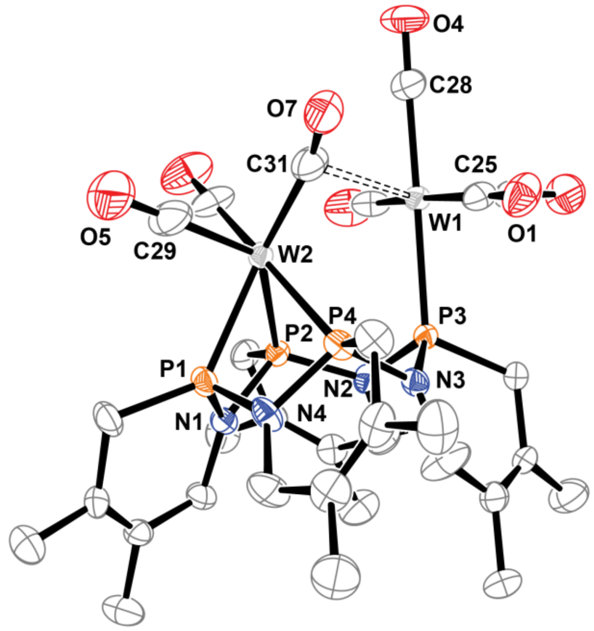
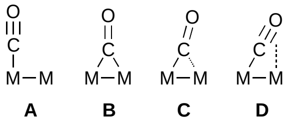
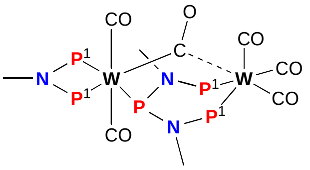


Figure S6. ORTEP drawing of **5·W$_2$**. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): P1-N1 1.674(4), P1-N4 1.671(5), P2-N2 1.687(4), P2-N1 1.698(4), P3-N2 1.727(4), P3-N3 1.703(4), P4-N3 1.693(4), P4-N4 1.694(4), C25-O1 1.141(7), C28-O4 1.155(7), C29-O5 1.59(6), C31-O7 1.178(7), W1-C25 2.021(6), W1-C28 2.021(6), W2-C29 1.981(6), W2-C30 1.940(6), W2-C31 1.999(6), C31-W1 2.786, P1-W2 2.432(1), P2-W2 2.482(1), P3-W1 2.457(1), P4-W2 2.534(1); Σ(<P1) 321.5, Σ(<P2) 316.3, Σ(<P3) 307.9, Σ(<P4) 315.4, Σ(<N) 360.0, W2-C31-O7 163.3(6).

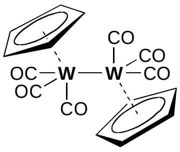


Scheme S1. Different types of bridging carbonyl ligands: (**A**) terminal, (**B**) symmetrically bridging, (**C**) bent semi-bridiging, (**D**) linear semi-bridging.

5·W₂ crystallizes solvent-free in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell. One of the two tungsten centers (W2) is coordinated by three of the four phosphorus atoms of **5** and shows a distorted octahedral coordination environment similar to that of the molybdenum atom in **5·Mo.** W1 possesses only five ligands and thus can formally be considered a 16-electron species. The C31-O7 carbonyl group on W2 is located in a semi-bridging position between the two tungsten centers and seems to partly compensate the electron deficit on W1.[7] The semi-bridging character is nicely illustrated by the W2-C31-O7 angle of 163.3(6)° as all of the remaining carbonyl groups are essentially linear. Additionally, a considerable elongation of the W2−C31 and C31−O7 bonds (W2−C31 1.999(6), C31−O7 1.178(7) Å) is observed together with a close contact to W1 (W1−C31 2.786 Å). These structural parameters in **5·W₂** are similar to those found in **X** (cf. W-C-O 157(1)°; W−C 2.67(1) Å; Scheme S2)[8] and comparable to other metal complexes with carbonyl groups characterized as semi-bridging (Scheme 9).[7] Furthermore, some degree of metal-metal interaction can be assumed as the W1−W2 distance (W1−W2 3.0984(3) Å) is in the range of complexes which necessarily poses a tungsten−tungsten single bond (cf. $[(\eta^5\text{-}(C_5H_5)_2W_2(CO)_6]$[9] (**Y**): W-W 3.222(1); $[W_2(CO)_8(MeCCMe\text{-}CHCHCMe_2)]$[10] : W-W 3.049(1) Å; Scheme S2). Within the ligand the P−N distances are rather short compared to uncoordinated **5** and the three phosphorus atoms coordinated to W2 are forced into a tetrahedral coordination mode, whereas P3 retains its trigonal environment. In contrast to **5·Mo** all PNC_4 moieties point downwards to form a CH-cage below the P_4N_4 crown.



X



Y

Scheme S2. Structure of ditungsten complex **X** (left) with a bridging carbonyl ligand and ditungsten complex **Y** (right) that possesses a W−W bond.

3.6. Synthesis of Tricarbonyltris(propionitrile)molybdenum(0).

A 100 ml is charged with freshly sublimed $Mo(CO)_6$ (2.363 g; 8.95 mmol) and dissolved in C_2H_5CN (25 ml). The colorless mixture is refluxed for 24 h and in the course of the reaction the mixture becomes deep brown. The reaction mixture was concentrated to ca. 10 ml and Et_2O (15 ml) is added to induce crystallization. Storage of the mixture in the freezer at −24°C for 24 h yields $Mo(CO)_3(C_2H_5CN)_3$ as yellow crystalline solid (2.050 g, 5.98 mmol, 67 %).

Crystals suitable for X-ray analysis of $\mathbf{Mo(CO)_3(C_2H_5CN)_3}$ (Figure S6) were obtained from the above reaction mixture at room temperature.

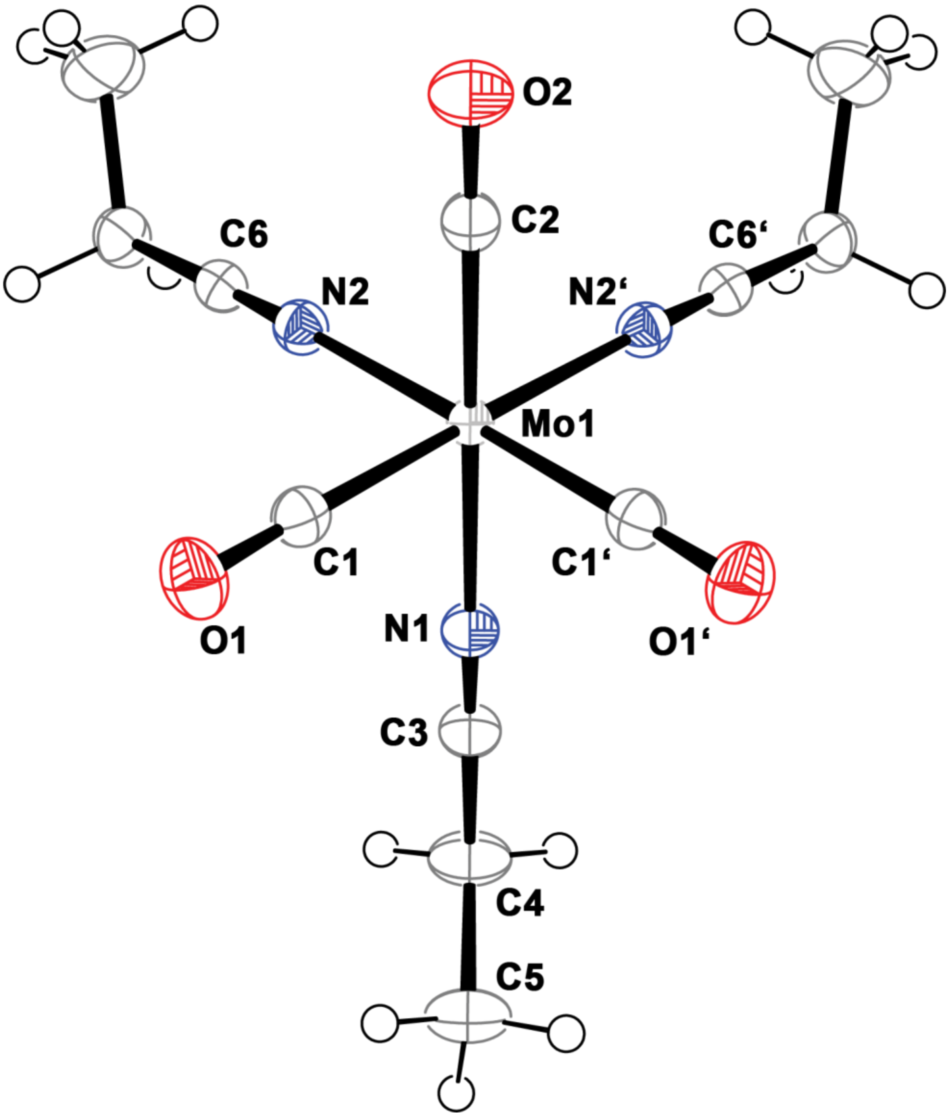


Figure S7. ORTEP drawing of **Mo(CO)$_3$(C$_2$H$_5$CN)$_3$**. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°) are presented in Table S12.

4. Computational Details

Our goal was to study the bonding and enthalpy of formation for tetraphosphazane **5**. Utilizing the experimental structural data and the postulated structure for intermediate **6**, all calculations were carried out with the Gaussian 09 package of molecular orbital programs.[11] The wave functions for the crystal structures were optimized with a 6-31G(d,p) basis set (C, H, N, O, F, Si, P, S, Cl) on the B3LYP level of density functional theory and the optimized structures were checked to be a minimum on the energy hypersurface. A natural bond orbital analysis (NBO)[12] was performed on the B3LYP level of density functional theory. For **5·Mo** the ^{31}P NMR chemical shifts and P−P coupling constants were calculated using the GIAO package implemented in Gaussian 09.[13] The calculated absolute shifts (σ_{iso}) were referenced to the extrapolated absolute chemical shift of 85% H_3PO_4 in the gas phase ($\sigma_{ref} = 328.35$), using the formula $\delta_{calc} = \sigma_{ref} - \sigma_{iso}$.[14] The calculated spectrum was visualized using gNMR.[15]

It should be emphasized that the computation was carried out for a single, isolated (gas-phase) molecule.

4.1. Optimized Structure of 6.

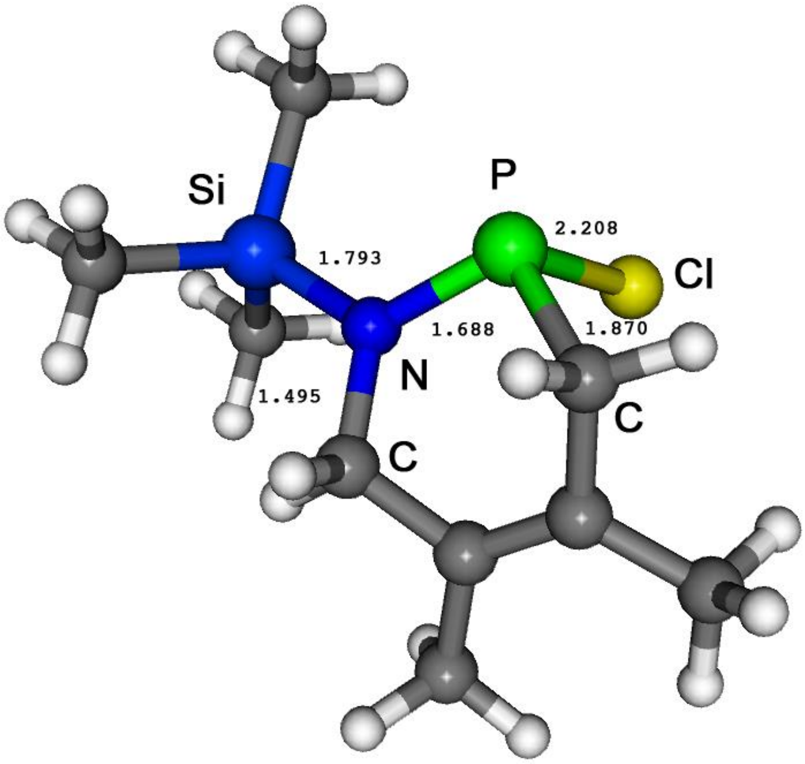


Figure S8. Ball and Stick drawing of the optimized structure of **6.** Selected bond lengths (Å) are presented in the drawing.

Table S14. Gas phase B3LYP/6-31G(d,p) determined xyz coordinates (in Å) for intermediate **6**. Energies given in Hartrees. Calculated ^{31}P NMR shift given in ppm.

H(B3LYP) = -1500,023812
δ(^{31}P) = 121.58 ppm

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	C	-2,38917	0,78732	1,82886
2	Si	-2,27775	0,22942	0,02863
3	C	-3,16101	1,46838	-1,09153
4	N	-0,55444	0,17279	-0,45935
5	P	0,20557	-1,29991	-0,79098
6	Cl	0,96561	-2,07960	1,12869
7	C	-3,04042	-1,48089	-0,15981
8	C	0,18860	1,47141	-0,44648
9	C	1,63294	1,40493	0,00931
10	C	2,42288	0,42541	-0,46413
11	C	3,85799	0,17872	-0,08115

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
12	C	2,04213	2,48789	0,97290
13	C	1,82165	-0,58858	-1,41053
14	H	4,26905	0,94727	0,57501
15	H	3,10610	2,46880	1,21140
16	H	3,94420	-0,78551	0,43475
17	H	1,48619	2,39648	1,91527
18	H	4,49400	0,12249	-0,97381
19	H	1,81233	3,48215	0,56722
20	H	-1,84614	0,09306	2,47804
21	H	-1,97301	1,78779	1,98715
22	H	-3,43391	0,81285	2,15947
23	H	2,50308	-1,42172	-1,60188
24	H	-0,35291	2,17187	0,19832
25	H	1,57117	-0,14328	-2,38526
26	H	0,14088	1,89347	-1,46276
27	H	-2,55883	-2,21971	0,48777
28	H	-2,71836	2,46856	-1,03541
29	H	-4,09877	-1,43146	0,12288
30	H	-4,21471	1,56179	-0,80503
31	H	-2,98584	-1,84894	-1,18843
32	H	-3,12747	1,14700	-2,13794

4.2. Optimized Structure of 5.

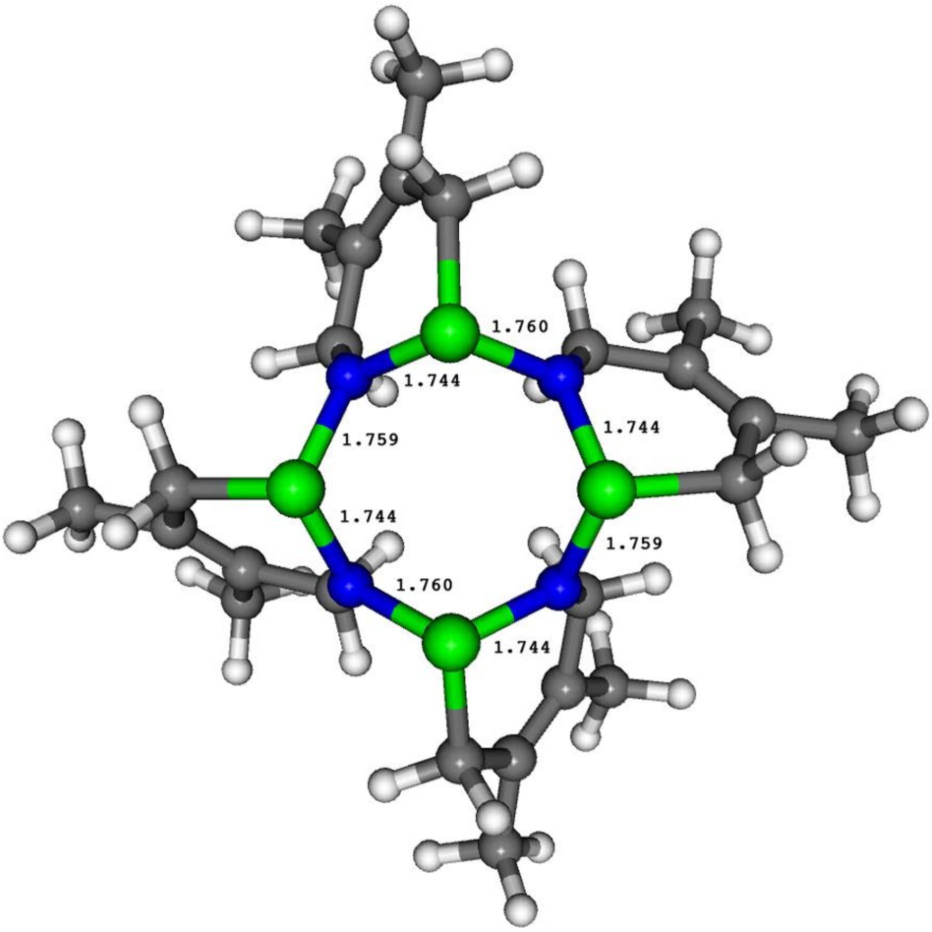


Figure S9. Ball and Stick drawing of the optimized structure of **5**. Selected bond lengths (Å) are presented in the drawing.

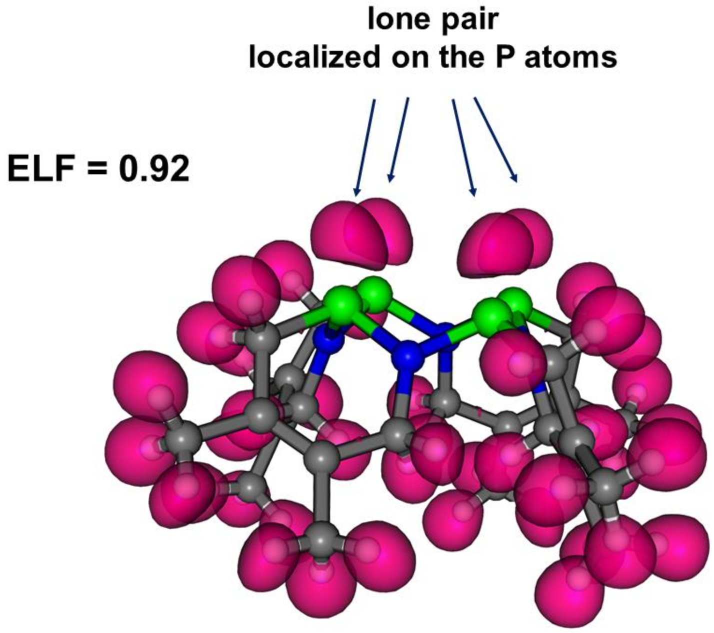


Figure S10. Visualization of the ELF of **5** at isovalue 0.92.

Table S15. Gas phase B3LYP/6-31G(d,p) determined xyz coordinates (in Å) for **5**. Energies given in Hartrees.

H(B3LYP) = -2522,459967
δ(^{31}P) = 30.70 ppm

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	C	1,47405	3,83499	2,28072
2	C	0,85774	3,43060	0,95990
3	C	-0,02547	4,17271	0,27044
4	C	-0,49217	5,55036	0,68471
5	C	1,36309	2,06691	0,52488
6	N	1,12185	1,67001	-0,86824
7	P	-0,38352	2,00397	-1,68238
8	C	-0,64047	3,73404	-1,04360
9	P	2,00364	0,38356	-1,68287
10	C	3,73404	0,64011	-1,04474
11	C	4,17298	0,02507	0,26907
12	C	5,55139	0,49063	0,68219
13	N	1,66899	-1,12102	-0,86766
14	C	2,06637	-1,36180	0,52545
15	C	3,43059	-0,85712	0,95945
16	C	3,83525	-1,47290	2,28042
17	P	0,38354	-2,00396	-1,68237
18	C	0,64047	-3,73403	-1,04358
19	C	0,02547	-4,17270	0,27044
20	C	0,49217	-5,55036	0,68469
21	N	-1,12184	-1,67000	-0,86824
22	C	-0,36310	-2,06691	0,52487
23	C	-0,85776	-3,43060	0,95989
24	C	-0,47409	-3,83501	2,28070
25	P	-2,00363	-0,38355	-1,68287
26	C	-3,73403	-6,40110	-1,04474
27	C	-4,17298	-0,02507	0,26906
28	C	-5,55139	-0,49066	0,68216
29	N	-1,66899	1,12103	-0,86765
30	C	-2,06637	1,36180	0,52545
31	C	-3,43059	0,85711	0,95945
32	C	-3,83526	1,47289	2,28042
33	H	0,96138	4,66494	2,76701
34	H	2,52797	4,11738	2,15452
35	H	1,46291	2,98939	2,98041
36	H	-0,00463	5,93402	1,58143
37	H	-2,98978	1,46161	2,98025

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
38	H	-0,96145	-4,66496	2,76700
39	H	4,66523	-0,95995	2,76641
40	H	-4,66524	0,95994	2,76641
41	H	2,98977	-1,46162	2,98024
42	H	-1,46297	-2,98941	2,98039
43	H	-2,52802	-4,11737	2,15445
44	H	-4,11778	2,52681	2,15456
45	H	-1,57646	5,55869	0,85925
46	H	-0,30671	6,26931	-0,12398
47	H	5,93531	0,00300	1,57877
48	H	4,11777	-2,52682	2,15456
49	H	5,56084	1,57496	0,85648
50	H	0,00462	-5,93404	1,58140
51	H	-5,93533	-0,00304	1,57874
52	H	0,95292	1,31906	1,22502
53	H	-1,31914	0,95067	1,22575
54	H	2,44537	2,05351	0,70245
55	H	1,31913	-0,95066	1,22574
56	H	-0,95294	-1,31906	1,22502
57	H	-2,05228	2,44393	0,70378
58	H	-5,56083	-1,57499	0,85643
59	H	1,57646	-5,55868	0,85927
60	H	-2,44538	-2,05350	0,70242
61	H	6,26955	0,30433	-0,12699
62	H	2,05228	-2,44393	0,70377
63	H	0,30673	-6,26929	-0,12401
64	H	-6,26954	-0,30436	-0,12703
65	H	-1,72525	3,90933	-1,02719
66	H	3,90960	1,72486	-1,02825
67	H	-0,26581	4,38689	-1,84563
68	H	-3,90958	-1,72486	-1,02826
69	H	4,38664	0,26551	-1,84698
70	H	1,72525	-3,90933	-1,02715
71	H	-4,38663	-0,26551	-1,84698
72	H	0,26583	-4,38689	-1,84560

4.3. Optimized Structure of Me_3SiCl.

Table S16. Gas phase B3LYP/6-31G(d,p) determined xyz coordinates (in Å) for Me_3SiCl. Energies given in Hartrees.

H(B3LYP) = -869,414341

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	Si	0,00000	0,00000	-0,34027
2	Cl	0,00000	0,00000	1,77071
3	C	-1,55486	-0,89770	-0,89838
4	C	0,00000	1,79540	-0,89838
5	C	1,55486	-0,89770	-0,89838
6	H	0,00000	1,85574	-1,99307
7	H	-0,88499	2,32402	-0,53138
8	H	0,88499	2,32402	-0,53138
9	H	1,60712	-0,92787	-1,99307
10	H	2,45515	-0,39559	-0,53138
11	H	1,57017	-1,92843	-0,53138
12	H	-1,60712	-0,92787	-1,99307
13	H	-1,57017	-1,92843	-0,53138
14	H	-2,45515	-0,39559	-0,53138

6. Cif-File for 5b.

Crystals of **5b** were of rather poor quality. The positions of the atoms could be refined freely, however the quality of the data did not allow anisotropic refinement. Nevertheless, the connectivity in **5b** is proven. In the following a full Cif-file for **5b** is included.

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 (methyl groups) or with <i>U</i>~iso~(H) = 1.2 times <i>U</i>~eq~(C)
 (methylene  groups, aryl CH, methine groups). Torsion angles of all methyl
 groups were allowed to refine.

 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
```

```
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
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H10B H 0.2791 0.9896 0.7409 0.074 Uiso 1 1 calc R . .
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H11A H 0.2138 1.1986 0.8378 0.120 Uiso 1 1 calc R . .
H11B H 0.1358 1.1716 0.9384 0.120 Uiso 1 1 calc R . .
H11C H -0.0530 1.1967 0.8647 0.120 Uiso 1 1 calc R . .
C12 C 0.401(4) 1.1222(11) 0.7178(17) 0.067(8) Uiso 1 1 d . . .
H12A H 0.4324 1.1606 0.7563 0.100 Uiso 1 1 calc R . .
H12B H 0.3565 1.1356 0.6540 0.100 Uiso 1 1 calc R . .
H12C H 0.5393 1.0952 0.7147 0.100 Uiso 1 1 calc R . .
C13 C -0.102(4) 1.0239(11) 0.5293(16) 0.058(7) Uiso 1 1 d . . .
H13A H -0.2344 1.0324 0.4871 0.070 Uiso 1 1 calc R . .
H13B H -0.0640 1.0652 0.5612 0.070 Uiso 1 1 calc R . .
C14 C 0.102(4) 1.0057(10) 0.4679(16) 0.055(7) Uiso 1 1 d . . .
C15 C 0.226(4) 0.9557(11) 0.4728(15) 0.050(6) Uiso 1 1 d . . .
C16 C 0.187(3) 0.9028(10) 0.5503(14) 0.040(5) Uiso 1 1 d . . .
H16A H 0.2315 0.8600 0.5245 0.048 Uiso 1 1 calc R . .
H16B H 0.2890 0.9121 0.6047 0.048 Uiso 1 1 calc R . .
C17 C 0.136(6) 1.0565(13) 0.387(2) 0.087(9) Uiso 1 1 d . . .
H17A H 0.2625 1.0425 0.3458 0.130 Uiso 1 1 calc R . .
H17B H 0.1731 1.0989 0.4138 0.130 Uiso 1 1 calc R . .
H17C H -0.0055 1.0599 0.3492 0.130 Uiso 1 1 calc R . .
C18 C 0.417(4) 0.9358(10) 0.4084(16) 0.058(7) Uiso 1 1 d . . .
H18A H 0.4250 0.9659 0.3551 0.087 Uiso 1 1 calc R . .
H18B H 0.3884 0.8919 0.3850 0.087 Uiso 1 1 calc R . .
H18C H 0.5633 0.9367 0.4431 0.087 Uiso 1 1 calc R . .
C19 C -0.103(4) 0.7875(10) 0.4885(16) 0.054(7) Uiso 1 1 d . . .
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H19B H -0.0681 0.8210 0.4408 0.064 Uiso 1 1 calc R . .
C20 C 0.087(4) 0.7435(10) 0.4883(17) 0.056(7) Uiso 1 1 d . . .
C21 C 0.222(4) 0.7278(11) 0.5597(16) 0.049(6) Uiso 1 1 d . . .
C22 C 0.179(4) 0.7590(11) 0.6541(17) 0.061(7) Uiso 1 1 d . . .
H22A H 0.2205 0.7275 0.7039 0.073 Uiso 1 1 calc R . .
H22B H 0.2838 0.7964 0.6605 0.073 Uiso 1 1 calc R . .
C23 C 0.130(5) 0.7137(12) 0.3884(18) 0.077(8) Uiso 1 1 d . . .
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H23B H 0.1805 0.7479 0.3452 0.115 Uiso 1 1 calc R . .
H23C H -0.0120 0.6942 0.3646 0.115 Uiso 1 1 calc R . .
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H24B H 0.3463 0.6371 0.5772 0.098 Uiso 1 1 calc R . .
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C27 C 0.216(4) 0.7182(11) 0.9024(16) 0.054(6) Uiso 1 1 d . . .
C28 C 0.169(4) 0.7850(10) 0.8926(17) 0.056(7) Uiso 1 1 d . . .
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H28B H 0.2075 0.8062 0.9532 0.068 Uiso 1 1 calc R . .
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H29B H 0.2072 0.5836 0.8022 0.108 Uiso 1 1 calc R . .
H29C H 0.0125 0.5741 0.8803 0.108 Uiso 1 1 calc R . .
C30 C 0.424(4) 0.7063(11) 0.9639(17) 0.066(7) Uiso 1 1 d . . .
H30A H 0.4705 0.6608 0.9589 0.100 Uiso 1 1 calc R . .
H30B H 0.3869 0.7164 1.0296 0.100 Uiso 1 1 calc R . .
H30C H 0.5511 0.7341 0.9431 0.100 Uiso 1 1 calc R . .

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# MOLECULAR GEOMETRY

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 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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C19 C20 C21 C24 176(2) . . . . ?
C23 C20 C21 C24 -5(4) . . . . ?
C19 C20 C21 C22 0(4) . . . . ?
C23 C20 C21 C22 178(2) . . . . ?
P5 N4 C22 C21 133.6(18) . . . . ?
P4 N4 C22 C21 -50(2) . . . . ?
C20 C21 C22 N4 25(3) . . . . ?
C24 C21 C22 N4 -151.7(19) . . . . ?
N4 P5 C25 C26 92(2) . . . . ?
N5 P5 C25 C26 -19(2) . . . . ?
P5 C25 C26 C27 3(3) . . . . ?
P5 C25 C26 C29 -175.7(17) . . . . ?
C25 C26 C27 C28 -2(4) . . . . ?
C29 C26 C27 C28 176(2) . . . . ?
C25 C26 C27 C30 -180(2) . . . . ?
C29 C26 C27 C30 -1(4) . . . . ?
C26 C27 C28 N5 24(4) . . . . ?
C30 C27 C28 N5 -157.9(19) . . . . ?
P1 N5 C28 C27 138.2(19) . . . . ?
P5 N5 C28 C27 -47(3) . . . . ?

_diffrn_measured_fraction_theta_max    0.996
_diffrn_reflns_theta_full              22.48
_diffrn_measured_fraction_theta_full   0.996
_refine_diff_density_max    0.904
_refine_diff_density_min   -1.514
_refine_diff_density_rms    0.166
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