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Supporting Information

Activation of Small Molecules by Phosphorus Biradicaloids

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Supporting Information

Content

1. Experimental

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

Tetrahydrofuran (thf), benzene, toluene, diethylether were dried over Na/benzophenone, *n*-hexane was dried over Na/benzophenone/tetraglyme. Acetonitrile and acetone were dried over calcium hydride. All solvents were freshly distilled prior to use. $[P(\mu\text{-NTer})]_2$, $[ClP(\mu\text{-NHyp})]_2$, $[ClP(\mu\text{-NDmp})]_2$ and $[ClP(\mu\text{-NDipp})]_2$ were prepared according to literature procedures.[1,2] $Cp_2Ti(btmsa)$, $(Me_3Si)NSN(SiMe_3)$, $Ag(C_6F_5)\cdot CH_3CN$, and PhNCNPh were prepared according to literature procedures.[3,4,5,9] Magnesium (99%, Merck) was stored under Argon atmosphere and used as received. $KMnO_4$ (98%, Merck), Sulphur (99%, Apolda), Selenium (99%, Merck), Tellurium (99%, Alfa Aesar), and PhCCPh (99%, ABCR) were used as received. CS_2 (AlfaAesar) was desulfurized over Mercury and dried over P_4O_{10} and distilled prior to use. Acetylene was consecutively dried over columns filled with KOH and P_4O_{10} and was bubbled to toluene at –60 °C until saturation was achieved. The solution thus obtained was stored at –80 °C until usage.

NMR: ^{29}Si INEPT, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C DEPT, ^{125}Te and ^{77}Se and ^1H NMR spectra were obtained on a Bruker Avance 250, 300 or 500 spectrometer and were referenced internally to the deuterated solvents (^{13}C, CD_2Cl_2: $\delta_{reference} = 54$ ppm, C_6D_6: $\delta_{reference} = 128$ ppm) or to protic impurities (^1H, $CDHCl_2$: $\delta_{reference} = 5.32$ ppm, C_6D_5H: $\delta_{reference} = 7.16$ ppm) or externally (^{125}Te: $Te(OH)_6$, ^{77}Se: $SeMe_2$, ^{31}P: 85 % $H_3PO_{4(aq)}$, ^{19}F: $CFCl_3$, ^{29}Si: $Si(CH_3)_4$). CD_2Cl_2 was dried over P_4O_{10}, C_6D_6 was dried over Na/benzophenone and freshly distilled prior to use.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064nm), or Horiba Scientific LabRam HR 800 were used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikronalysator TruSpec-932 from Leco were used.

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).

MS: Finnigan MAT 95-XP von Thermo Electron.

UV-VIS: Perkin Elmer Lambda 2 UV/VIS Spectrometer.

2. Structure Elucidation

X-ray Structure Determination: X-ray quality crystals all compounds were selected in Kel-F-oil (Riedel deHaen) or Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer using graphitemonochromated Mo Kα radiation (λ = 0.71073). The structures were solved by direct methods (SHELXS-97)[6] and refined by full-matrix least squares procedures (SHELXL-97).[7] Semi-empirical absorption corrections were applied (SADABS).[8] All non hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

The P–(CS_2)–P unit in [P(μ-NTer)]$_2$$CS_2$ was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.9269(1)/0.0731(1)). The P–((CH_3)$_2$CO)–P unit in [P(μ-NTer)]$_2$((CH_3)$_2$CO) was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.620(3)/0.380(3)). The P–((CH_3)$_2$CO)–P unit in [P(μ-NHyp)]$_2$((CH_3)$_2$CO) was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.6822(1)/0.3178(1)). The P–(CH_3CN)–P unit in [P(μ-NHyp)]$_2$(CH_3CN) was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.770(5)/0.230(5)). One Et_2O solvent molecule in [P(μ-NTer)]$_2$(S($NSiMe_3$)$_2$) was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.729(5)/0.271(5)). All (C_6F_5)P units in [(C_6F_5)P(μ-NTer)]$_2$ was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.790(1)/0.210(1), 0.616(1)/ 0.384(1)). The cocrystallised molecule of *n*-hexane was found to be disordered and split into two parts. The occupation of each part was refined freely (0.661(2)/0.339(2)). A Mes*NP moiety of Mes*$_3N_3P_2$ was found to be disordered and split into two parts. The occupation of both parts was refined freely (0.894(6)/0.106(6)). The phenyl group in [P(μ-NTer)]$_2$(PhCCPh) was found to be disordered and split into two parts. The occupation of both parts was refined freely (0.517(8)/0.483(8)). Both symmetry independent molecules of [P(μ-NTer)]$_2$(PhNCNPh) in the asymmetric unit were found to possess disordered P–(PhNCNPh)–P units. Each was split into two parts whose occupation was allowed to refine freely (0.876(1)/0.124(1) and 0.951(1)/0.049(1), respectively). Cocrystallised molecules of the solvent, toluene, were found to be heavily disordered and removed from the model using the PLATON program and its SQUEEZE feature.

Table S1. Crystallographic details of **β-P$_4$(NDmp)$_4$**, **Cp$_2$Ti[P(NDipp)$_2$]$_2$** and **[P(μ-NTer)]$_2$O$_2$**.

	4 **β-P$_4$(NDmp)$_4$**	**6** **Cp$_2$Ti[P(NDipp)$_2$]$_2$**	**Mes*$_3$N$_3$P$_2$**
Chem. formula	$C_{32}H_{36}N_4P_4$	$C_{34}H_{44}N_2PTi$	C54 H87 N3 P2
Form. wght. [g mol^{-1}]	600.53	559.58	840.21
Colour	yellow	yellow	red
Cryst. system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	P-1	$Pbcn$
a [Å]	15.3713(6)	10.4438(6)	28.416(1)
b [Å]	9.9893(4)	16.5835(9)	9.5983(5)
c [Å]	20.3793(9)	19.7588(1)	38.295(2)
α [°]	90	68.597(3)	90
β [°]	103.457(2)	89.014(3)	90
γ [°]	90	79.629(3)	90
V [Å^3]	3043.3(2)	3129.7(3)	10444.7(8)
Z	4	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.311	1.188	1.069
μ [mm^{-1}]	0.28	0.35	0.119
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	36100	55489	64730
Independent reflections	7671	12374	11406
Reflections with $I > 2\sigma(I)$	4311	7626	6457
R$_{int.}$	0.078	0.067	0.09
F(000)	1264	1196	3696
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.052	0.047	0.055
wR_2 (all data)	0.127	0.108	0.139
GooF	0.958	1.01	1.013
Parameters	369	701	651
CCDC #			

Table S1. Crystallographic details of **β-$P_4(NDmp)_4$**, **$Cp_2Ti[P(NDipp)_2]_2$** and **$[P(\mu\text{-}NTer)]_2O_2$**.

	8O$_2$ **$[P(\mu\text{-}NTer)]_2O_2$**	**8O$_2$ · 0.5 C_6H_6** **$[P(\mu\text{-}NTer)]_2O_2$**	**8S$_2$** **$[P(\mu\text{-}NTer)]_2S_2$**
Chem. formula	$C_{48}H_{50}N_2P_2O_2$	$C_{48}H_{50}N_2P_2O_2$ · 0.25 (C_6H_6)	$C_{48}H_{50}N_2P_2S_2$
Form. wght. [g mol^{-1}]	748.84	1536.73	780.96
Colour	yellow	yellow	yellow
Cryst. system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a [Å]	10.7419(3)	12.8161(8)	12.6318(5)
b [Å]	15.3547(5)	15.3259(9)	21.0205(8)
c [Å]	24.7274(7)	21.484(1)	16.0688(7)
α [°]	90	88.717(4)	90
β [°]	95.865(2)	89.674(4)	106.723(2)
γ [°]	90	89.736(4)	90
V [Å^3]	4057.2(2)	4218.6(4)	4086.2(3)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.226	1.210	1.269
μ [mm^{-1}]	0.15	0.145	0.25
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	65703	84563	53511
Independent reflections	14034	19304	9856
Reflections with $I > 2\sigma(I)$	9583	9248	7215
R$_{int.}$	0.060	0.100	0.067
F(000)	1592	1634	1656
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.047	0.059	0.048
wR_2 (all data)	0.130	0.148	0.133
GooF	1.015	0.994	1.024
Parameters	499	1026	500
CCDC #			

Table S2. Crystallographic details of **[P(μ-NTer)]$_2$S$_2$**, **[P(μ-NTer)]$_2$Se$_2$** and **[P(μ-NTer)]$_2$Te$_2$**.

	8Se$_2$	**8Te$_2$**	**9**
	[P(μ-NTer)]$_2$Se$_2$	**[P(μ-NTer)]$_2$Te$_2$**	**[P(μ-NTer)]$_2$ (H$_2$CCH$_2$)**
Chem. formula	$C_{48}H_{50}N_2P_2Se_2$	$C_{48}H_{50}N_2P_2Te_2 \cdot (C_6H_{14})$	$C_{50}H_{54}N_2P_2$
Form. wght. [g mol^{-1}]	874.76	1058.21	744.89
Colour	orange	dark green	colourless
Cryst. system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	12.7117(5)	12.5213(8)	12.599(1)
b [Å]	20.9924(9)	23.4301(1)	21.062(2)
c [Å]	16.1587(6)	16.8909(9)	15.989(2)
α [°]	90	90	90
β [°]	106.168(2)	90.927(3)	107.039(4)
γ [°]	90	90	90
V [Å^3]	4141.4(3)	4954.7(5)	4056.5(6)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.403	1.419	1.220
μ [mm^{-1}]	1.90	1.28	0.145
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	193	173
Measured reflections	54560	43998	33263
Independent reflections	12061	9204	9323
Reflections with $I > 2\sigma(I)$	8982	6131	4915
R$_{int.}$	0.050	0.074	0.088
$F(000)$	1800	2144	1592
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.040	0.057	0.056
wR_2 (all data)	0.105	0.149	0.149
GooF	1.052	1.035	1.005
Parameters	499	554	503
CCDC #			

Table S3. Crystallographic details of **[P(μ-NTer)]$_2$CS$_2$**, **[P(μ-NTer)]$_2$((CH$_3$)$_2$CO)** and **[P(μ-NHyp)]$_2$((CH$_3$)$_2$CO)**.

	10	**11**	**11Hyp**
	[P(μ-NTer)]$_2$CS$_2$	**[P(μ-NTer)]$_2$ ((CH$_3$)$_2$CO)**	**[P(μ-NHyp)]$_2$ ((CH$_3$)$_2$CO)**
Chem. formula	$C_{49}H_{50}P_2N_2S_2$	$C_{51}H_{56}N_2P_2O$	$C_{21}H_{60}N_2OP_2Si_8$
Form. wght. [g mol^{-1}]	792.97	774.92	643.37
Colour	green	colourless	yellow
Cryst. system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/c$
a [Å]	12.5814(6)	22.8742(9)	16.5810(8)
b [Å]	21.2606(1)	15.3061(7)	18.3811(1)
c [Å]	16.2114(8)	24.7109(1)	13.4374(6)
α [°]	90	90	90
β [°]	106.038(2)	90	105.686(2)
γ [°]	90	90	90
V [Å^3]	4167.6(3)	8651.7(6)	3942.9(3)
Z	4	8	4
$\rho_{calc.}$ [g cm^{-3}]	1.264	1.190	1.084
μ [mm^{-1}]	0.24	0.14	0.37
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	44823	61137	66010
Independent reflections	9470	10887	12555
Reflections with $I > 2\sigma(I)$	5576	6899	8660
R$_{int.}$	0.068	0.058	0.058
$F(000)$	1680	3312	1400
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.061	0.051	0.043
wR_2 (all data)	0.150	0.139	0.109
GooF	1.024	1.046	1.058
Parameters	525	570	403
CCDC #			

Table S4. Crystallographic details of **$[P(\mu\text{-NTer})]_2(CH_3CN)$**, **$[P(\mu\text{-NTer})]_2(S(NSiMe_3)_2)$** and **$[(C_6F_5)P(\mu\text{-NTer})]_2$.**

	12	**13**	**14**
	$[P(\mu\text{-NTer})]_2$ $(S(NSiMe_3)_2)$	**$[P(\mu\text{-NTer})]_2$ (PhNCNPh)**	**$[P(\mu\text{-NTer})]_2$ (CH_3CN)**
Chem. formula	$C_{54}H_{69}N_4P_2SSi_2$ $\cdot$ 2 $(C_4H_{10}O)$	$C_{61}H_{60}N_4P_2$ $\cdot$ 1.125 (C_7H_8)	$C_{50}H_{53}N_3P_2$
Form. wght. [g mol^{-1}]	1072.55	1014.72	757.89
Colour	colourless	colourless	yellow
Cryst. system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a [Å]	14.9697(4)	11.7212(4)	12.6279(4)
b [Å]	11.9960(3)	20.7236(8)	21.1223(6)
c [Å]	34.4792(9)	23.880(1)	16.1140(6)
α [°]	90	104.108(2)	90
β [°]	95.5380(10)	95.184(2)	106.055(2)
γ [°]	90	95.184(2)	90
V [Å^3]	6162.8(3)	5560.9(4)	4130.5(2)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.156	1.212	1.219
μ [mm^{-1}]	0.19	0.125	0.14
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
Measured reflections	90953	163748	45174
Independent reflections	17951	35287	8564
Reflections with $I > 2\sigma(I)$	13139	21229	5084
$R_{int.}$	0.059	0.055	0.074
F(000)	2316	2161	1616
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.050	0.061	0.059
wR_2 (all data)	0.135	0.149	0.156
GooF	1.036	1.024	1.032
Parameters	708	1317	547
CCDC #			

Table S5. Crystallographic details of **[P(μ-NTer)]$_2$(PhCCPh)** and **[P(μ-NTer)]$_2$(PhNCNPh).**

	15H	**15Ph**
	[P(μ-NTer)]$_2$ (HCCH)	**[P(μ-NTer)]$_2$ (PhCCPh)**
Chem. formula	$C_{50}H_{52}N_2P_2$	$C_{60}H_{60}N_2P_2$
Form. wght. [g mol^{-1}]	742.88	895.06
Colour	colourless	yellow
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a [Å]	12.5531(5)	17.968(2)
b [Å]	21.0733(8)	11.3732 (1)
c [Å]	15.9788(6)	23.893 (2)
α [°]	90	90
β [°]	106.707(2)	98.566 (4)
γ [°]	90	90
V [Å^3]	4048.5(3)	4828.2 (8)
Z	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.219	1.231
μ [mm^{-1}]	0.145	0.133
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	173	173
Measured reflections	58209	43213
Independent reflections	11815	8719
Reflections with $I > 2\sigma(I)$	7460	7185
$R_{int.}$	0.065	0.040
$F(000)$	1584	1904
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.052	0.044
wR_2 (all data)	0.140	0.128
GooF	1.026	1.042
Parameters	507	320
CCDC #		

Scheme S1. Numbering scheme of ***β*-P$_4$(NDmp)$_4$ (4)**.

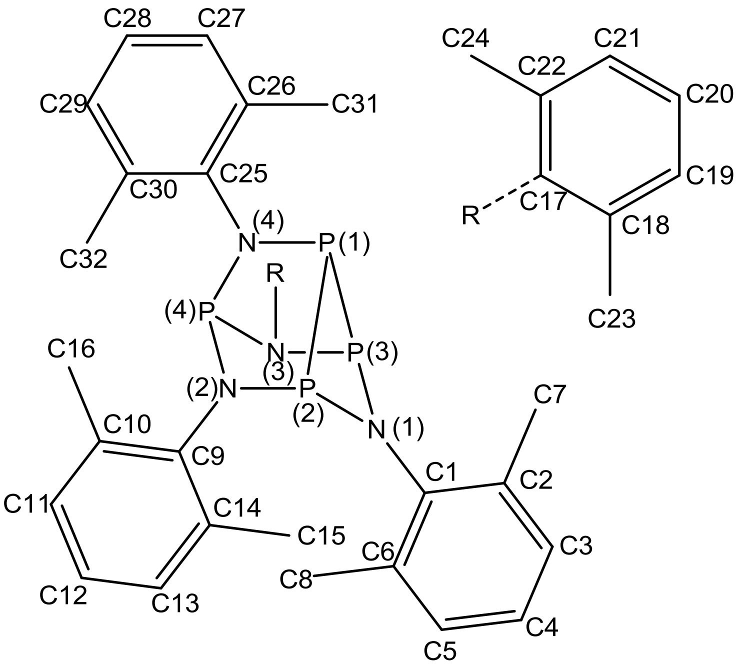


Table S6. Selected bond lengths (Å) and angles (°) of ***β*-P$_4$(NDmp)$_4$**.

P1—N4	1.708(2)	**N3—C17**	1.450(3)
P1—P2	2.2558(9)	**N4—C25**	1.456(3)
P1—P3	2.2858(10)	**N1—P3—P1**	82.19(8)
P2—N1	1.719(2)	**N4—P1—P2**	96.97(7)
P2—N2	1.721(2)	**N4—P1—P3**	96.54(8)
P3—N3	1.7227(19)	**P2—P1—P3**	75.72(3)
P3—N1	1.730(2)	**N1—P2—N2**	105.64(10)
P4—N3	1.726(2)	**N1—P2—P1**	83.34(7)
P4—N4	1.731(2)	**N2—P2—P1**	93.18(7)
P4—N2	1.7315(18)	**N3—P3—N1**	105.85(9)
N1—C1	1.441(3)	**N3—P3—P1**	92.68(7)
N2—C9	1.460(3)	**N3—P4—N4**	96.64(10)

N3—P4—N2	99.24(9)	**P2—P1—P3—N3**	84.64(7)
N4—P4—N2	96.27(9)	**N4—P1—P3—N1**	−116.55(10)
C1—N1—P2	123.26(16)	**P2—P1—P3—N1**	−21.00(7)
C1—N1—P3	128.30(16)	**N2—P2—N1—P3**	62.50(13)
P2—N1—P3	107.86(11)	**P1—P2—N1—P3**	−28.95(9)
C9—N2—P2	120.02(15)	**N3—P3—N1—P2**	−61.97(13)
C9—N2—P4	117.56(15)	**P1—P3—N1—P2**	28.61(9)
P2—N2—P4	118.71(10)	**N1—P2—N2—P4**	−64.28(14)
C17—N3—P3	120.63(15)	**P1—P2—N2—P4**	19.69(12)
C17—N3—P4	119.97(15)	**N3—P4—N2—P2**	55.57(14)
P3—N3—P4	119.02(11)	**N4—P4—N2—P2**	−42.23(14)
C25—N4—P1	123.65(15)	**N1—P3—N3—P4**	63.01(14)
C25—N4—P4	124.08(16)	**P1—P3—N3—P4**	−19.63(11)
P1—N4—P4	111.83(11)	**N4—P4—N3—P3**	42.49(13)
N4—P1—P3—N3	−10.92(9)	**N2—P4—N3—P3**	−55.00(13)
N4—P1—P2—N1	116.10(10)	**P2—P1—N4—P4**	−38.09(11)
P3—P1—P2—N1	21.09(7)	**P3—P1—N4—P4**	38.26(11)
N4—P1—P2—N2	10.71(10)	**N3—P4—N4—P1**	−50.29(12)
P3—P1—P2—N2	−84.30(7)	**N2—P4—N4—P1**	49.81(13)

Scheme S2. Numbering scheme of **$Cp_2Ti[P(NDipp)_2]_2$ (6)**.

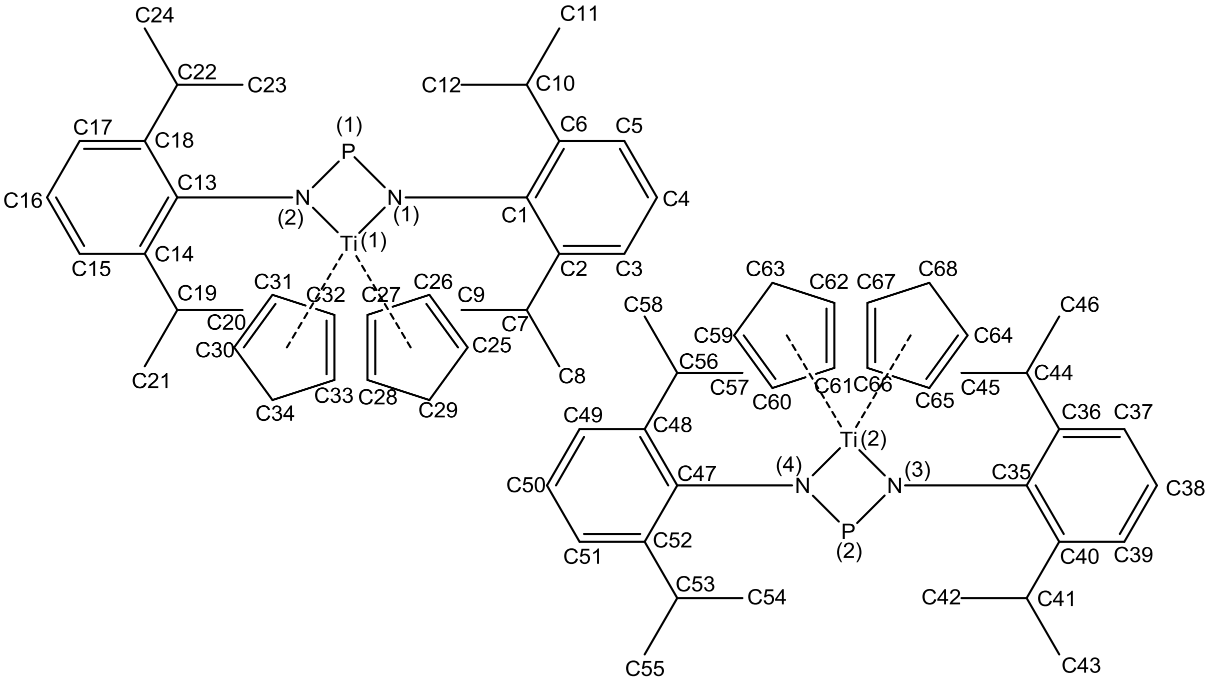


Table S7. Selected bond lengths (Å) and angles (°) of **$Cp_2Ti[P(NDipp)_2]_2$**.

P1—N1	1.6008(18)	**N4—C47**	1.440(3)
P1—N2	1.6040(19)	**N1—P1—N2**	99.79(9)
P1—Ti1	2.9555(7)	**N2—Ti1—N1**	65.01(6)
Ti1—N2	2.2652(18)	**C1—N1—P1**	119.99(14)
Ti1—N1	2.2959(18)	**C1—N1—Ti1**	141.85(14)
N1—C1	1.432(3)	**P1—N1—Ti1**	97.04(8)
N2—C13	1.429(3)	**C13—N2—P1**	122.51(15)
P2—N4	1.5988(19)	**C13—N2—Ti1**	137.78(15)
P2—N3	1.6058(19)	**P1—N2—Ti1**	98.16(9)
P2—Ti2	2.9612(8)	**N4—P2—N3**	99.74(10)
Ti2—N3	2.2758(18)	**N3—Ti2—N4**	64.83(6)
Ti2—N4	2.2946(18)	**C35—N3—P2**	119.65(15)

N3—C35	1.437(3)	**C35—N3—Ti2**	140.51(14)
P2—N3—Ti2	97.95(9)	**C29—Ti1—N2—C13**	83.5(2)
C47—N4—P2	119.35(15)	**N1—Ti1—N2—P1**	−0.07(7)
C47—N4—Ti2	142.44(14)	**N4—P2—N3—C35**	−165.39(17)
P2—N4—Ti2	97.42(9)	**N4—P2—N3—Ti2**	2.08(10)
N2—P1—N1—C1	−170.57(16)	**N4—Ti2—N3—C35**	161.2(3)
N2—P1—N1—Ti1	−0.09(9)	**N4—Ti2—N3—P2**	−1.58(7)
N2—Ti1—N1—C1	166.7(2)	**N3—P2—N4—C47**	−174.13(16)
N2—Ti1—N1—P1	0.07(7)	**Ti2—P2—N4—C47**	−172.1(2)
N1—P1—N2—C13	−168.01(17)	**N3—P2—N4—Ti2**	−2.06(10)
Ti1—P1—N2—C13	−168.1(2)	**N3—Ti2—N4—C47**	170.2(3)
C25—Ti1—N2—C13	77.4(2)	**N3—Ti2—N4—P2**	1.59(7)

Scheme S3. Numbering scheme of **Mes*$_3$N$_3$P$_2$**.

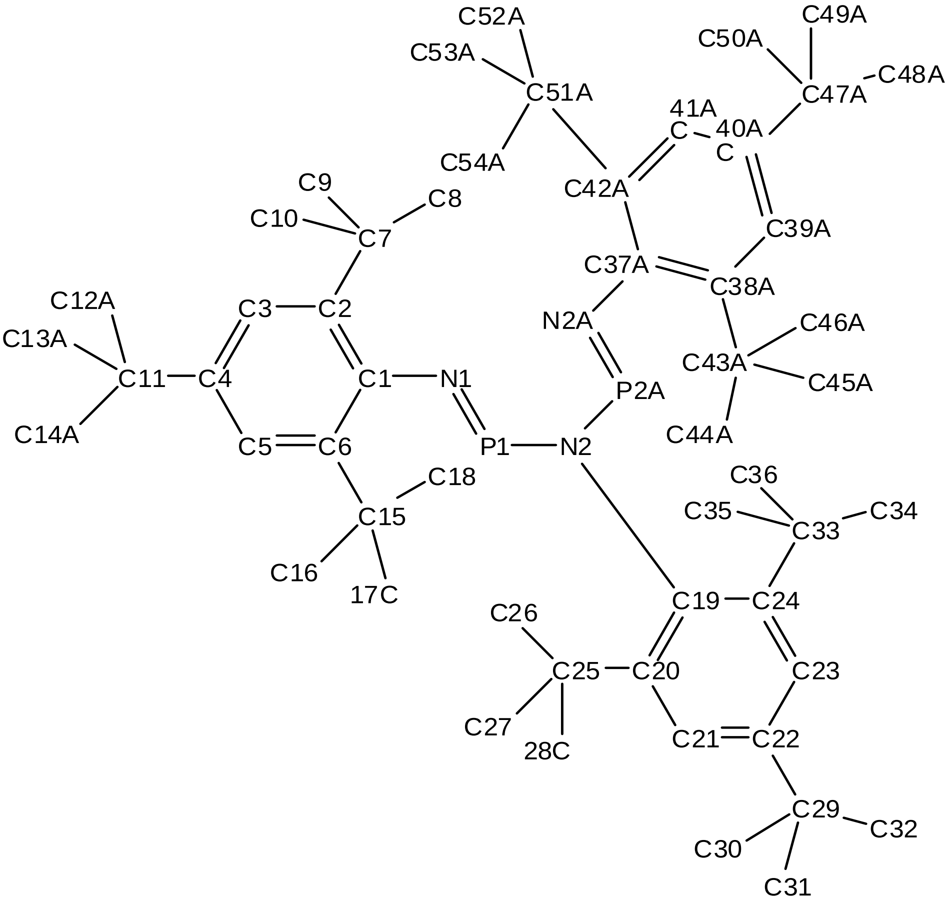


Table S8. Selected bond lengths (Å) and angles (°) of **Cp$_2$Ti[P(NDipp)$_2$]$_2$**.

P1–N1	1.535(2)	**P2A–N3A**	1.534(3)
P1–N2	1.706 (2)	**N3A–C37A**	1.418(3)
N1–C1	1.415(3)	**P2B–N3B**	1.53(1)
N2–C19	1.465(3)	**N3B–C37B**	1.424(9)
N2–P2A	1.746(2)	**N1–P1–N2**	106.1(1)
N2–P2B	1.76(2)	**C1–N1–P1**	140.8(2)
C19–N2–P1	114.1(2)	**C19–N2–P2A**	128.3(2)
P1–N2–P2A	117.4(1)	**C19–N2–P2B**	119.2(5)

P1–N2–P2B	123.6(5)	**P2A–N2–P2B**	14.0(5)
N3A–P2A–N2	108.4(2)	**C37A–N3A–P2A**	137.5(3)
N3B–P2B–N2	112(1)	**C37B–N3B–P2B**	135(2)
N2–P1–N1–C1	178.9(2)	**N1–P1–N2–C19**	–179.5(2)
N1–P1–N2–P2A	6.0(2)	**N1–P1–N2–P2B**	20.7(6)
C19–N2–P2A–N3A	9.4(3)	**P1–N2–P2A–N3A**	–177.1(3)
N2–P2A–N3A–C37A	–174.1(6)	**P2A–N3A–C37A–C38A**	162.4(6)

Scheme S4. Numbering scheme of **$[\mathrm{P}(\mu\text{-NTer})]_2\mathrm{O}_2$ (8O_2)**.

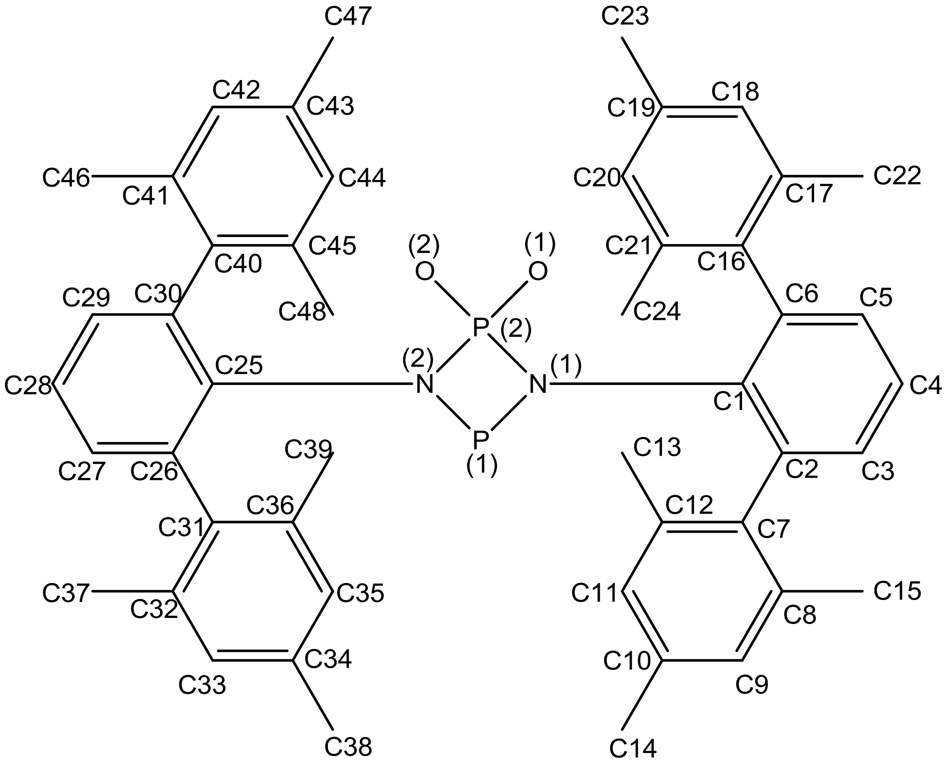
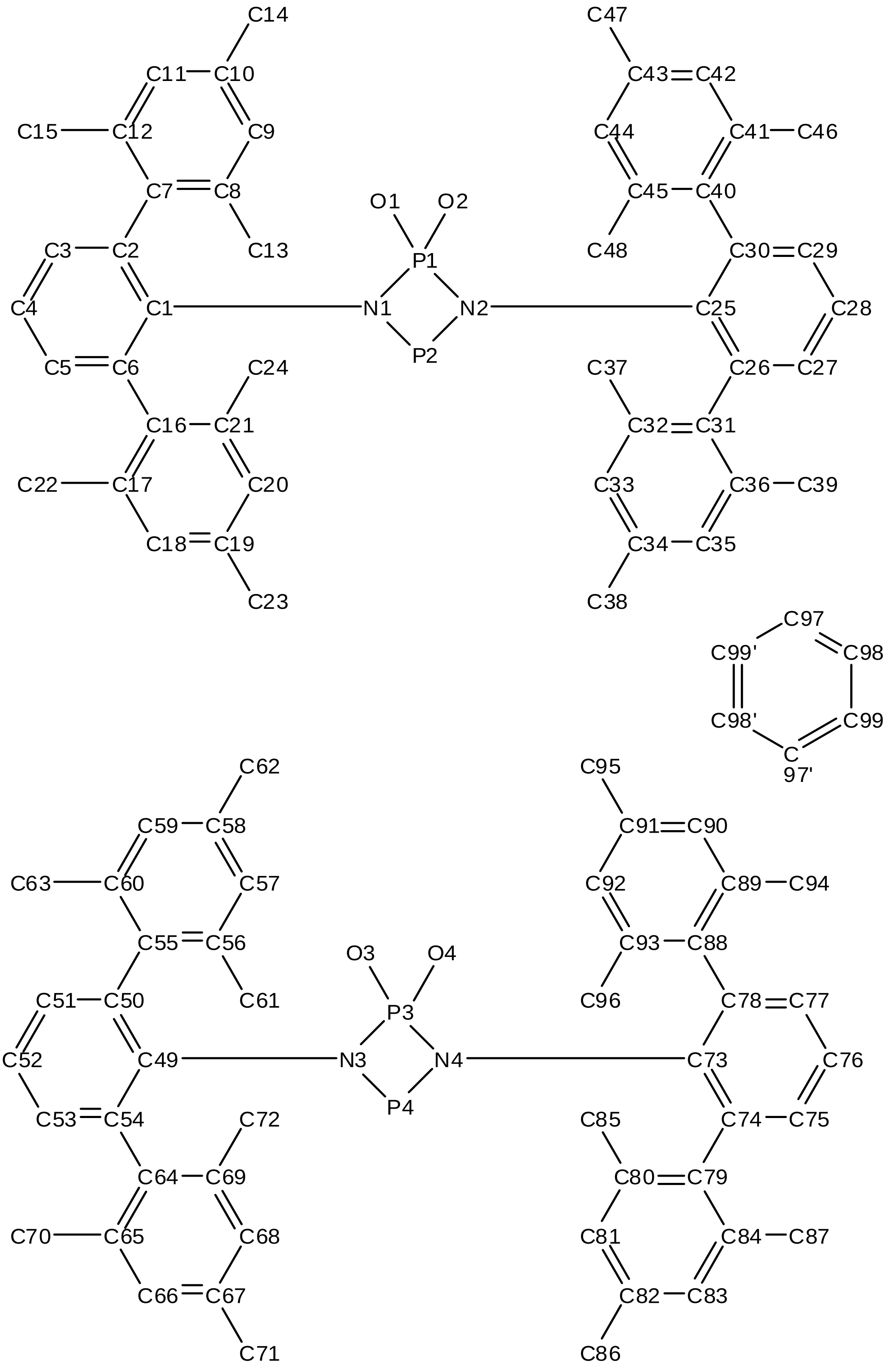


Table S9. Selected bond lengths (Å) and angles (°) of **$[\mathrm{P}(\mu\text{-NTer})]_2\mathrm{O}_2$**.

P1—N2	1.6432(11)	**C25—N2—P2**	129.17(9)
P1—N1	1.6450(11)	**O1—P2—P1**	116.90(5)
P2—O1	1.4606(12)	**O2—P2—P1**	116.76(5)
P1—P2	2.5811(5)	**N2—P1—N1**	87.49(5)
P2—N1	1.7986(11)	**N2—P2—N1**	78.42(5)
P2—N2	1.7980(12)	**O1—P2—N2**	114.17(6)
P2—O2	1.4587(12)	**O2—P2—N2**	106.36(6)
N1—C1	1.4315(14)	**O1—P2—N1**	106.84(6)
N2—C25	1.4314(15)	**O2—P2—N1**	114.72(6)
C1—N1—P1	127.02(9)	**O2—P2—O1**	126.34(7)
C1—N1—P2	132.19(9)	**P1—N1—P2**	97.00(5)
C25—N2—P1	127.34(9)	**P1—N2—P2**	97.09(5)

N2—P1—P2—O2	−83.14(8)	**O2—P2—N1—P1**	−102.71(7)
N1—P1—P2—O2	97.06(8)	**O1—P2—N1—P1**	112.13(7)
N2—P1—P2—O1	95.98(8)	**N2—P2—N1—P1**	0.13(6)
N1—P1—P2—O1	−83.82(8)	**N1—P1—N2—C25**	153.68(12)
N1—P1—P2—N2	−179.80(9)	**P2—P1—N2—C25**	153.55(14)
N2—P1—P2—N1	179.80(9)	**N1—P1—N2—P2**	0.14(6)
N2—P1—N1—C1	159.91(12)	**O2—P2—N2—C25**	−40.32(13)
P2—P1—N1—C1	160.04(14)	**O1—P2—N2—C25**	103.63(12)
N2—P1—N1—P2	−0.14(6)	**N1—P2—N2—C25**	−152.95(12)
O2—P2—N1—C1	98.87(13)	**P1—P2—N2—C25**	−152.82(15)
O1—P2—N1—C1	−46.29(14)	**O2—P2—N2—P1**	112.50(6)
N2—P2—N1—C1	−158.29(13)	**O1—P2—N2—P1**	−103.55(7)
P1—P2—N1—C1	−158.42(16)	**N1—P2—N2—P1**	−0.13(6)

Scheme S5. Numbering scheme of **[P(μ-NTer)]$_2$O$_2$ (8O$_2$ · 0.25 C$_6$H$_6$)**.



Symmetry code: (‘) 1-x, -y, 1-z

Table S10. Selected bond lengths (Å) and angles (°) of **[P(μ-NTer)]$_2$O$_2$ · 0.25 C$_6$H$_6$**.

P1–O1	1.4609(19)	**P3–O3**	1.459(2)
P1–O2	1.4615(18)	**P3–O4**	1.4587(19)
P1–N1	1.786(2)	**P3–N4**	1.786(2)
P1–N2	1.792(2)	**P3–N3**	1.792(2)
P1–P2	2.5853(10)	**P3–P4**	2.5844(10)
P2–N2	1.645(2)	**P4–N4**	1.643(2)
P2–N1	1.653(2)	**P4–N3**	1.644(2)
N1–C1	1.439(3)	**N3–C49**	1.429(3)
N2–C25	1.436(3)	**N4–C73**	1.432(3)
O1–P1–O2	125.72(11)	**O3–P3–O4**	125.66(12)
O1–P1–N1	107.06(10)	**O3–P3–N4**	106.97(11)
O2–P1–N1	114.61(11)	**O4–P3–N4**	115.10(12)
O1–P1–N2	114.57(11)	**O3–P3–N3**	114.58(11)
O2–P1–N2	106.74(10)	**O4–P3–N3**	106.62(11)
N1–P1–N2	78.45(10)	**N4–P3–N3**	78.15(10)
O1–P1–P2	117.30(8)	**O3–P3–P4**	117.53(8)
O2–P1–P2	116.98(8)	**O4–P3–P4**	116.81(9)
N2–P2–N1	86.64(10)	**N4–P4–N3**	86.68(11)
O1–P1–P2–N2	96.13(14)	**O3–P3–P4–N4**	–83.10(15)
O2–P1–P2–N2	–83.47(14)	**O4–P3–P4–N4**	97.55(15)
N1–P1–P2–N2	179.87(16)	**N3–P3–P4–N4**	–178.98(16)

Scheme S6. Numbering scheme of **[P(μ-NTer)]$_2$S$_2$ (8S$_2$)**.

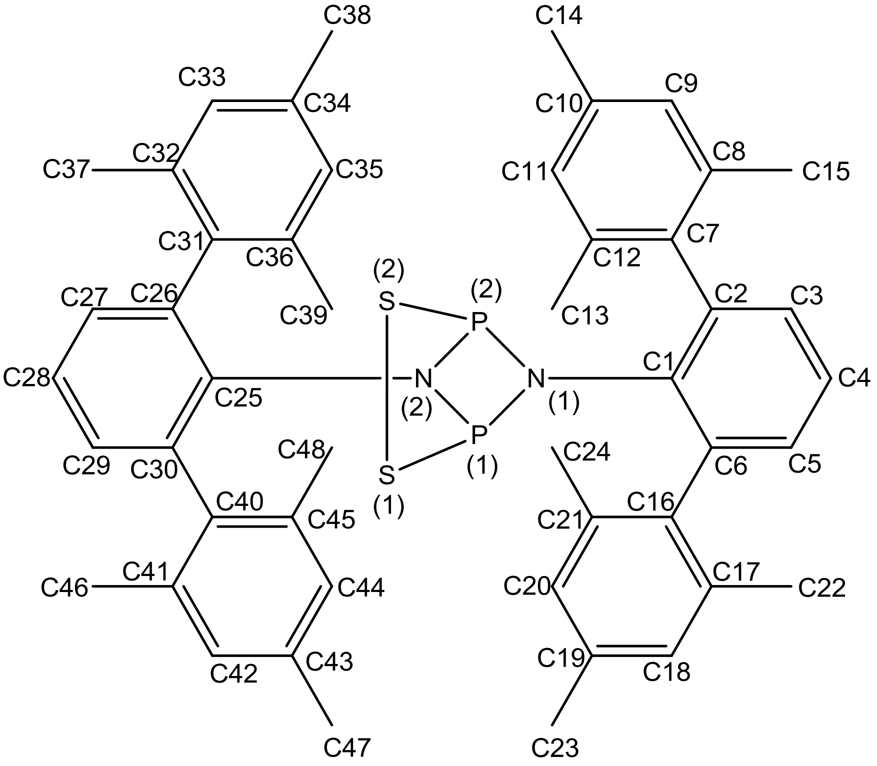


Table S11. Selected bond lengths (Å) and angles (°)of **[P(μ-NTer)]$_2$S$_2$**.

P1—N2	1.7066(17)	**C1—N1—P2**	129.55(13)
P1—N1	1.7689(16)	**C24—N2—P1**	133.96(13)
P1—S1	2.1755(8)	**C24—N2—P2**	129.30(13)
P1—P2	2.5557(7)	**N2—P1—N1**	80.14(7)
P2—N2	1.7288(16)	**N2—P1—S1**	100.19(6)
P2—N1	1.7328(17)	**N1—P1—S1**	93.89(6)
P2—S2	2.1774(9)	**S2—P2—P1**	83.07(3)
S1—S2	2.0752(10)	**N2—P2—N1**	80.55(8)
N1—C1	1.422(2)	**N1—P2—S2**	97.02(6)
N2—C25	1.422(2)	**N2—P2—S2**	95.89(6)
C1—N1—P1	124.36(13)	**S1—P1—P2**	83.99(3)

S2—S1—P1	95.66(3)	**P1—P2—S2—S1**	5.62(3)
S1—S2—P2	96.69(3)	**P1—P2—N1—C1**	−142.0(2)
P2—N1—P1	93.74(8)	**N2—P2—N1—P1**	−22.58(8)
P1—N2—P2	96.13(8)	**S2—P2—N1—P1**	72.25(6)
N2—P2—N1—C1	−164.53(17)	**N2—P1—N1—C1**	167.78(16)
S2—P2—N1—C1	−69.70(16)	**S1—P1—N1—C1**	68.09(15)
N2—P1—P2—N1	−145.21(12)	**P2—P1—N1—C1**	144.85(19)
S1—P1—P2—N1	102.43(8)	**N2—P1—N1—P2**	22.92(8)
N1—P1—P2—N2	145.21(12)	**S1—P1—N1—P2**	−76.76(7)
S1—P1—P2—N2	−112.35(9)	**N1—P1—N2—C25**	165.65(19)
N2—P1—P2—S2	107.00(9)	**S1—P1—N2—C25**	−102.14(18)
N1—P1—P2—S2	−107.78(8)	**P2—P1—N2—C25**	−171.3(2)
S1—P1—P2—S2	−5.35(3)	**N1—P1—N2—P2**	−23.07(8)
N2—P1—S1—S2	−33.60(6)	**S1—P1—N2—P2**	69.15(7)
N1—P1—S1—S2	47.07(6)	**N1—P2—N2—C25**	−164.56(18)
P2—P1—S1—S2	5.60(3)	**S2—P2—N2—C25**	99.28(16)
P1—S1—S2—P2	−6.59(3)	**P1—P2—N2—C25**	171.9(2)
N1—P2—S2—S1	−35.89(6)	**N1—P2—N2—P1**	23.54(8)
N2—P2—S2—S1	45.28(6)	**S2—P2—N2—P1**	−72.62(7)

Scheme S7. Numbering scheme of **[P(μ-NTer)]$_2$Se$_2$ (8Se$_2$)**.

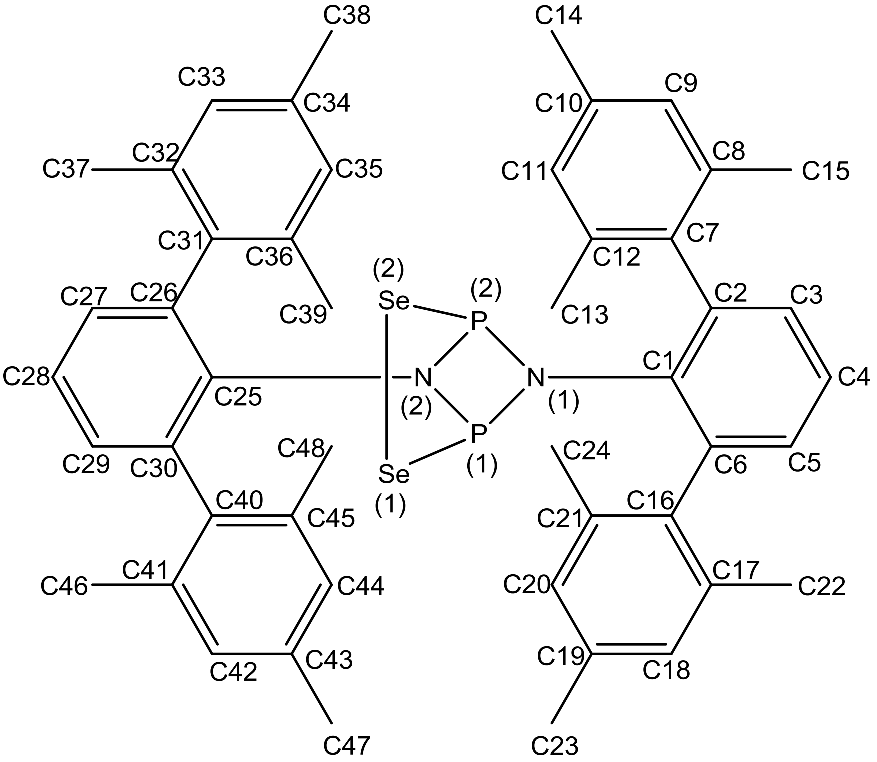


Table S12. Selected bond lengths (Å) and angles (°) of **[P(μ-NTer)]$_2$Se$_2$**.

P1—N2	1.7107(15)	**C25—N2—P1**	134.06(13)
P1—N1	1.7659(16)	**C25—N2—P2**	128.67(12)
P1—Se1	2.3323(5)	**N2—P1—N1**	80.27(7)
P1—P2	2.5758(7)	**N2—P1—Se1**	101.31(6)
P2—N1	1.7290(15)	**N1—P1—Se1**	94.40(5)
P2—N2	1.7272(16)	**Se2—P2—P1**	86.26(2)
P2—Se2	2.3327(6)	**N2—P2—N1**	80.86(7)
Se1—Se2	2.3314(4)	**N1—P2—Se2**	98.19(5)
N1—C1	1.418(2)	**N2—P2—Se2**	96.11(6)
N2—C25	1.419(2)	**Se1—P1—P2**	87.35(2)
C1—N1—P2	129.85(13)	**Se2—Se1—P1**	92.202(15)
C1—N1—P1	125.32(12)	**Se1—Se2—P2**	93.381(15)

P2—N1—P1	94.95(7)	**P1—P2—N1—C1**	−145.90(19)
P1—N2—P2	97.04(8)	**N2—P2—N1—P1**	−19.42(7)
N2—P2—N1—C1	−165.32(17)	**Se2—P2—N1—P1**	75.50(6)
Se2—P2—N1—C1	−70.40(16)	**N2—P1—N1—C1**	167.82(16)
N2—P1—P2—N1	−150.13(11)	**Se1—P1—N1—C1**	67.08(14)
Se1—P1—P2—N1	99.57(8)	**P2—P1—N1—C1**	148.17(18)
N1—P1—P2—N2	150.13(11)	**N2—P1—N1—P2**	19.65(7)
Se1—P1—P2—N2	−110.29(8)	**Se1—P1—N1—P2**	−81.09(6)
N2—P1—P2—Se2	103.67(8)	**N1—P1—N2—C25**	165.58(18)
N1—P1—P2—Se2	−106.19(8)	**Se1—P1—N2—C25**	−101.84(17)
Se1—P1—P2—Se2	−6.621(17)	**P2—P1—N2—C25**	−174.7(2)
N2—P1—Se1—Se2	−32.92(6)	**N1—P1—N2—P2**	−19.75(7)
N1—P1—Se1—Se2	48.02(5)	**Se1—P1—N2—P2**	72.84(7)
P2—P1—Se1—Se2	6.615(17)	**N1—P2—N2—C25**	−164.75(16)
P1—Se1—Se2—P2	−7.313(19)	**Se2—P2—N2—C25**	97.90(15)
N1—P2—Se2—Se1	−34.88(5)	**P1—P2—N2—C25**	175.1(2)
N2—P2—Se2—Se1	46.73(5)	**N1—P2—N2—P1**	20.15(8)
P1—P2—Se2—Se1	6.628(17)	**Se2—P2—N2—P1**	−77.20(6)

Scheme S8. Numbering scheme of **[P(μ-NTer)]$_2$Te$_2$**·(C_6H_{14}) **(8Te$_2$)**.

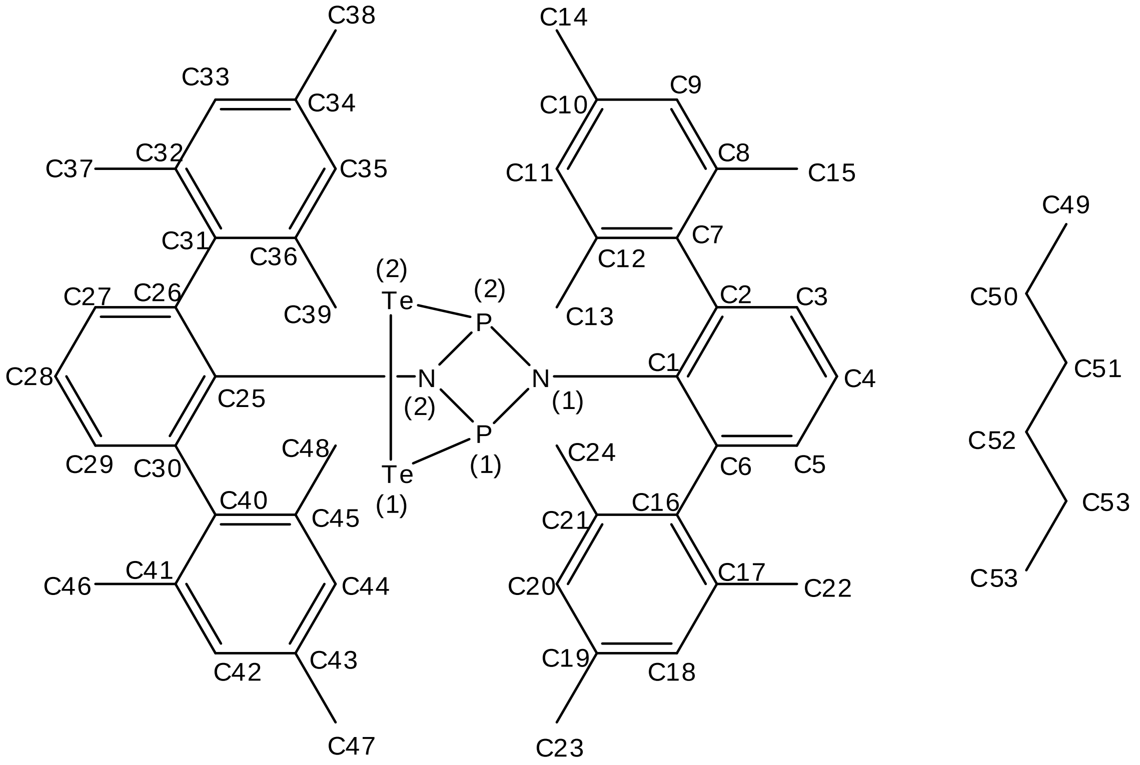


Table S13. Selected bond lengths (Å) and angles (°) of **[P(μ-NTer)]$_2$Te$_2$**·(C_6H_{14}).

P1—N1	1.704(5)	**C25—N2—P2**	133.1(4)
P1—N2	1.746(5)	**C25—N2—P1**	128.6(4)
Te1—P1	2.6003(19)	**N1—P1—N2**	80.8(2)
P1—P2	2.600(2)	**N2—P1—Te1**	94.40(17)
P2—N2	1.720(6)	**N1—P1—Te1**	101.89(18)
P2—N1	1.752(5)	**P1—P2—Te2**	90.29(7)
Te2—P2	2.6137(18)	**N2—P2—N1**	80.2(2)
Te1—Te2	2.6853(9)	**N1—P2—Te2**	93.79(17)
N1—C1	1.412(8)	**N2—P2—Te2**	102.32(18)
N2—C25	1.415(8)	**P2—P1—Te1**	90.36(7)

C1—N1—P1	132.6(4)	**P1—Te1—Te2**	88.71(4)
C1—N1—P2	127.7(4)	**P2—Te2—Te1**	88.21(4)
P1—N1—P2	97.6(3)	**Te1—P1—N1—C1**	86.8(5)
P2—N2—P1	97.2(3)	**N2—P1—N1—P2**	15.6(2)
P1—Te1—Te2—P2	11.67(5)	**Te1—P1—N1—P2**	−77.0(2)
Te2—Te1—P1—N1	28.88(17)	**N2—P2—N1—C1**	179.2(5)
Te2—Te1—P1—N2	−52.61(19)	**P1—P2—N1—C1**	−164.9(6)
Te2—Te1—P1—P2	−11.73(5)	**Te2—P2—N1—C1**	−78.9(5)
N1—P1—P2—N2	156.2(4)	**N2—P2—N1—P1**	−15.9(2)
Te1—P1—P2—N2	−96.3(3)	**Te2—P2—N1—P1**	86.0(2)
N2—P1—P2—N1	−156.2(4)	**N1—P2—N2—C25**	−175.8(6)
Te1—P1—P2—N1	107.6(3)	**P1—P2—N2—C25**	168.7(7)
N1—P1—P2—Te2	−95.5 (3)	**Te2—P2—N2—C25**	92.4(5)
N2—P1—P2—Te2	108.3(3)	**N1—P2—N2—P1**	15.5(2)
Te1—P1—P2—Te2	12.05(6)	**Te2—P2—N2—P1**	−76.3(2)
Te1—Te2—P2—N2	28.66(17)	**N1—P1—N2—C25**	174.6(5)
Te1—Te2—P2—N1	−52.08(18)	**P2—P1—N2—C25**	−169.5(6)
Te1—Te2—P2—P1	−11.67(5)	**Te1—P1—N2—C25**	−84.0(5)
N2—P1—N1—C1	179.4(6)	**N1—P1—N2—P2**	−15.9(2)
P2—P1—N1—C1	163.8(7)	**Te1—P1—N2—P2**	85.5(2)

Scheme S9. Numbering scheme of **[P(*μ*-NTer)]$_2$(H$_2$CCH$_2$) (9)**.

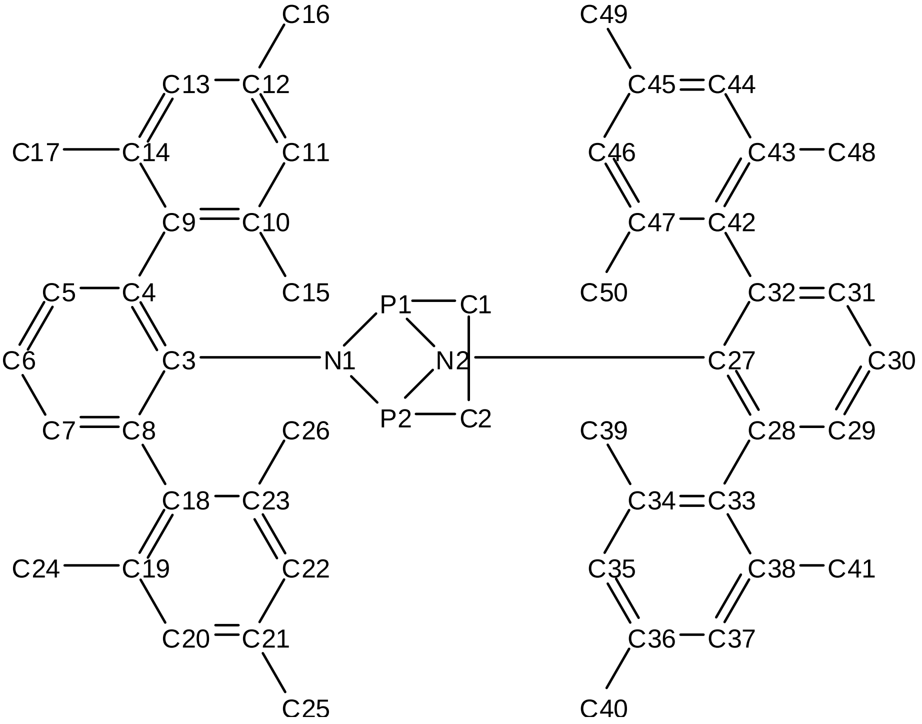


Table S14. Selected bond lengths (Å) and angles (°) of **[P(*μ*-NTer)]$_2$(H$_2$CCH$_2$)**.

P1—N2	1.715(2)	**N2—P1—N1**	79.99(9)
P1—N1	1.787(2)	**N2—P1—C1**	95.29(12)
P1—C1	1.870(3)	**N1—P1—C1**	89.82(11)
P1—P2	2.5316(10)	**C1—P1—P2**	74.25(10)
P2—N2	1.741(2)	**N2—P2—N1**	80.09(9)
P2—N1	1.758(2)	**N2—P2—C2**	91.38(11)
P2—C2	1.863(3)	**C2—P2—P1**	73.98(9)
C1—C2	1.520(4)	**P2—N1—P1**	91.13(9)
P2—N2—P1	93.29(7)	**P1—N2—P2**	94.18(10)
C1—P1—P2—C2	-5.52(14)	**C2—C1—P1**	105.00(18)
P1—C1—C2—P2	-9.2(2)	**C1—C2—P2**	105.93(18)

Scheme S10. Numbering scheme of **[P(*μ*-NTer)]$_2$CS$_2$ (10)**.

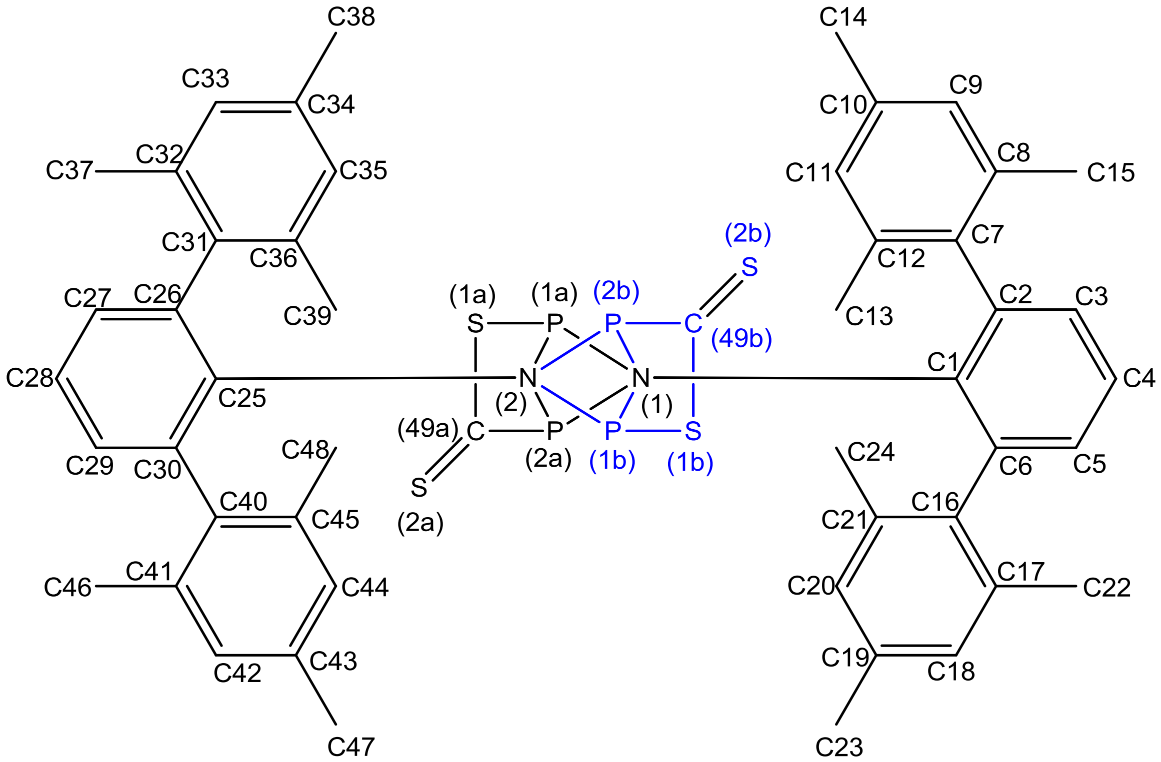


Table S15. Selected bond lengths (Å) and angles (°) of **[P(*μ*-NTer)]$_2$CS$_2$**.

N1—C1	1.426(3)	**P1A—P2A**	2.5441(12)
N1—P2B	1.452(15)	**P2A—C49A**	1.915(4)
N1—P1A	1.737(3)	**S1A—C49A**	1.721(4)
N1—P1B	1.760(12)	**S2A—C49A**	1.610(3)
N1—P2A	1.777(2)	**P1B—S1B**	2.251(9)
N2—C25	1.418(3)	**P1B—P2B**	2.551(9)
N2—P2A	1.721(2)	**P2B—C49B**	1.920(10)
N2—P1A	1.721(2)	**S1B—C49B**	1.706(10)
N2—P2B	1.752(16)	**S2B—C49B**	1.606(9)
N2—P1B	1.919(13)	**C1—N1—P2B**	127.4(7)
P1A—S1A	2.2450(16)	**C1—N1—P1A**	131.3(2)

C1—N1—P1B	121.5(5)	**N1—P2B—C49B**	88.3(11)
P2B—N1—P1B	104.7(7)	**N2—P2B—C49B**	93.7(13)
C1—N1—P2A	125.39(19)	**C49B—P2B—P1B**	78.9(5)
P1A—N1—P2A	92.77(11)	**C49B—S1B—P1B**	92.4(6)
C25—N2—P2A	134.19(19)	**S2B—C49B—S1B**	128.5(10)
C25—N2—P1A	126.9(2)	**S2B—C49B—P2B**	120.2(9)
P2A—N2—P1A	95.33(11)	**S1B—C49B—P2B**	111.2(7)
C25—N2—P2B	137.8(5)	**C25—N2—P1A—N1**	−172.5(3)
C25—N2—P1B	134.0(4)	**P2A—N2—P1A—N1**	26.54(12)
P2B—N2—P1B	87.9(5)	**C25—N2—P1A—S1A**	92.7(2)
N2—P1A—N1	80.48(12)	**P2A—N2—P1A—S1A**	−68.28(10)
N2—P1A—S1A	92.82(10)	**C25—N2—P1A—P2A**	161.0(3)
N1—P1A—S1A	95.21(9)	**C1—N1—P1A—N2**	−170.1 (3)
S1A—P1A—P2A	77.73(5)	**P2A—N1—P1A—N2**	−25.55(12)
N2—P2A—N1	79.36(11)	**C1—N1—P1A—S1A**	−78.1(3)
N2—P2A—C49A	96.69(14)	**P2A—N1—P1A—S1A**	66.44(10)
N1—P2A—C49A	91.71(13)	**C1—N1—P1A—P2A**	−144.5(3)
C49A—P2A—P1A	78.35(11)	**C25—N2—P2A—N1**	175.3(3)
C49A—S1A—P1A	91.27(12)	**P1A—N2—P2A—N1**	−25.99(12)
S2A—C49A—S1A	127.6(2)	**C25—N2—P2A—C49A**	−94.2(3)
S2A—C49A—P2A	120.4(2)	**P1A—N2—P2A—C49A**	64.49(14)
S1A—C49A—P2A	111.86(18)	**C25—N2—P2A—P1A**	−158.7(4)
N1—P1B—N2	74.6(4)	**C1—N1—P2A—N2**	173.3(3)
N1—P1B—S1B	81.8(4)	**P1A—N1—P2A—N2**	25.65(12)
N2—P1B—S1B	93.7(5)	**C1—N1—P2A—C49A**	76.8(3)
S1B—P1B—P2B	76.9(4)	**P1A—N1—P2A—C49A**	−70.84(14)
N1—P2B—N2	87.9(7)	**C1—N1—P2A—P1A**	147.7(3)

N1—P1A—P2A—N2	−140.83(18)	**C1—N1—P2B—N2**	−170.5(3)
S1A—P1A—P2A—N2	108.28(13)	**P1B—N1—P2B—N2**	−18.7(6)
S1A—P1A—P2A—N1	−110.90(12)	**C1—N1—P2B—C49B**	−76.7(14)
N2—P1A—P2A—C49A	−113.76(16)	**P1B—N1—P2B—C49B**	75.2(13)
N1—P1A—P2A—C49A	105.41(15)	**C1—N1—P2B—P1B**	−151.9(7)
S1A—P1A—P2A—C49A	−5.48(10)	**C25—N2—P2B—N1**	−170.3(3)
N2—P1A—S1A—C49A	45.79(14)	**P1B—N2—P2B—N1**	16.5(6)
N1—P1A—S1A—C49A	−34.90(14)	**C25—N2—P2B—C49B**	101.5(11)
P2A—P1A—S1A—C49A	5.98(11)	**P1B—N2—P2B—C49B**	−71.6(11)
P1A—S1A—C49A—S2A	167.9(2)	**C25—N2—P2B—P1B**	173.2(7)
P1A—S1A—C49A—P2A	−8.38(15)	**S1B—P1B—P2B—N1**	95.0(7)
N2—P2A—C49A—S2A	152.57(19)	**N1—P1B—P2B—N2**	154.8(9)
N1—P2A—C49A—S2A	−127.94(19)	**S1B—P1B—P2B—N2**	−110.1(6)
P1A—P2A—C49A—S2A	−169.1(2)	**N1—P1B—P2B—C49B**	−100.0(17)
N2—P2A—C49A—S1A	−30.82(17)	**N2—P1B—P2B—C49B**	105.2(17)
N1—P2A—C49A—S1A	48.66(17)	**S1B—P1B—P2B—C49B**	−5.0(16)
P1A—P2A—C49A—S1A	7.54(13)	**N1—P1B—S1B—C49B**	39.2(17)
C1—N1—P1B—N2	171.6(2)	**N2—P1B—S1B—C49B**	−34.7(17)
P2B—N1—P1B—N2	17.6(6)	**P2B—P1B—S1B—C49B**	5.5(17)
C1—N1—P1B—S1B	75.4(5)	**P1B—S1B—C49B—S2B**	176(4)
P2B—N1—P1B—S1B	−78.6(6)	**P1B—S1B—C49B—P2B**	−8(2)
C1—N1—P1B—P2B	153.9(7)	**N1—P2B—C49B—S2B**	142(3)
C25—N2—P1B—N1	172.3(3)	**N2—P2B—C49B—S2B**	−130(3)
P2B—N2—P1B—N1	−14.0(5)	**P1B—P2B—C49B—S2B**	−177(3)
C25—N2—P1B—S1B	−107.3(5)	**N1—P2B—C49B—S1B**	−34(2)
P2B—N2—P1B—S1B	66.4(6)	**N2—P2B—C49B—S1B**	54(3)
C25—N2—P1B—P2B	−173.6(6)	**P1B—P2B—C49B—S1B**	7(2)

Scheme S11. Numbering scheme of **[P(μ-NTer)]$_2$((CH$_3$)$_2$CO) (11)**.

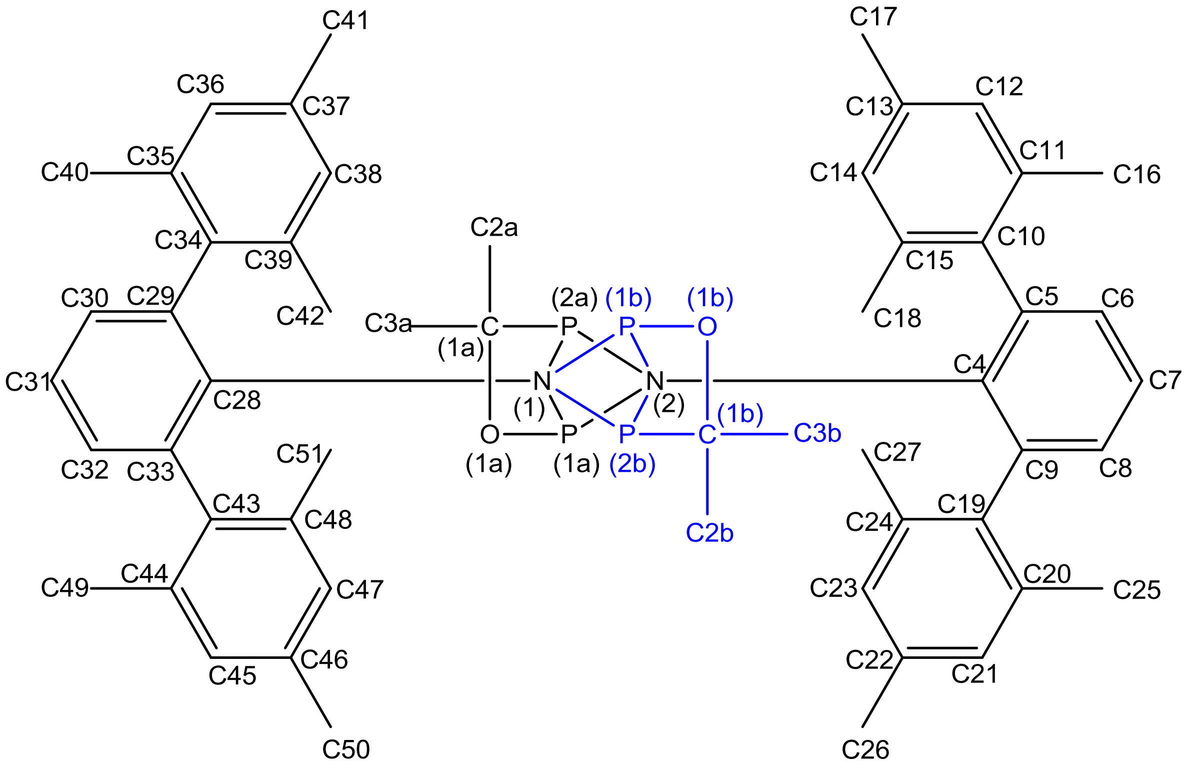


Table S16. Selected bond lengths (Å) and angles (°) of **[P(μ-NTer)]$_2$((CH$_3$)$_2$CO)**.

P1A—O1A	1.661(3)	**P1B—O1B**	1.670(4)
P1A—N1	1.778(2)	**P1B—N1**	1.794(2)
P1A—N2	1.790(2)	**P1B—N2**	1.797(2)
P1A—P2A	2.5138(18)	**P1B—P2B**	2.519(3)
P2A—N2	1.7331(18)	**P2B—N1**	1.708(3)
P2A—N1	1.7561(17)	**P2B—N2**	1.709(3)
P2A—C1A	1.918(10)	**P2B—C1B**	1.919(14)
O1A—C1A	1.466(16)	**O1B—C1B**	1.47(2)
C1A—C2A	1.507(15)	**C1B—C2B**	1.51(2)
C1A—C3A	1.526(15)	**C1B—C3B**	1.53(2)
N1—C4	1.419(2)	**O1B—C1B—C2B**	107.1(17)
N2—C28	1.415(2)	**O1B—C1B—C3B**	109.3(17)

O1A—P1A—N1	96.77(13)	**C2B—C1B—C3B**	111.8(8)
O1A—P1A—N2	97.14(12)	**O1B—C1B—P2B**	103.4(5)
N1—P1A—N2	77.44(10)	**C2B—C1B—P2B**	113.1(16)
O1A—P1A—P2A	76.29(10)	**C3B—C1B—P2B**	111.7(16)
N2—P2A—N1	79.51(8)	**C4—N1—P2B**	131.84(15)
N2—P2A—C1A	92.4(5)	**C4—N1—P2A**	129.10(13)
N1—P2A—C1A	92.6(5)	**C4—N1—P1A**	129.80(13)
C1A—P2A—P1A	69.7(4)	**P2A—N1—P1A**	90.69(8)
C1A—O1A—P1A	111.0(3)	**C4—N1—P1B**	127.02 (13)
O1A—C1A—C2A	106.6(11)	**P2B—N1—P1B**	91.95(12)
O1A—C1A—C3A	109.7(11)	**C28—N2—P2B**	132.80(15)
C2A—C1A—C3A	112.6(5)	**C28—N2—P2A**	134.01(13)
O1A—C1A—P2A	103.1(3)	**C28—N2—P1A**	128.35(13)
C2A—C1A—P2A	112.6(10)	**P2A—N2—P1A**	91.05(9)
C3A—C1A—P2A	111.7(10)	**C28—N2—P1B**	130.57(12)
O1B—P1B—N1	95.30(17)	**P2B—N2—P1B**	91.81(13)
O1B—P1B—N2	95.02(17)	**O1A—P1A—P2A—N2**	116.24(13)
N1—P1B—N2	76.84(9)	**O1A—P1A—P2A—N1**	−115.07(14)
O1B—P1B—P2B	76.36(17)	**N2—P1A—P2A—N1**	128.69(14)
N1—P2B—N2	81.55(15)	**O1A—P1A—P2A—C1A**	0.9(6)
N1—P2B—C1B	92.2(7)	**N1—P1A—P2A—C1A**	116.0(6)
N2—P2B—C1B	90.5(7)	**N2—P1A—P2A—C1A**	−115.3(6)
C1B—P2B—P1B	69.7(6)	**N1—P1A—O1A—C1A**	−40.8(8)
C1B—O1B—P1B	110.5(5)	**N2—P1A—O1A—C1A**	37.4(8)
N2—P2A—C1A—O1A	−41.1(9)	**N2—P1A—N1—C4**	−179.63(18)
N1—P2A—C1A—O1A	38.5(9)	**P2A—P1A—N1—C4**	−146.2(2)
O1B—P1B—P2B—N1	113.81(18)	**O1A—P1A—N1—P2A**	62.39(12)

O1B—P1B—P2B—N2	−113.32(18)	**N2—P1B—N1—C4**	−179.81(17)
N1—P1B—P2B—N2	132.88(19)	**P2B—P1B—N1—C4**	149.5(2)
O1B—P1B—P2B—C1B	−1.2(9)	**O1B—P1B—N1—P2B**	−63.24(19)
N1—P1B—P2B—C1B	−115.0(9)	**N1—P2B—N2—C28**	−171.82(19)
N2—P1B—P2B—C1B	112.1(9)	**P1B—P2B—N2—C28**	156.4(2)
N1—P1B—O1B—C1B	40.1(12)	**C1B—P2B—N2—P1B**	−60.3(8)
N2—P1B—O1B—C1B	−37.2(12)	**N1—P2A—N2—C28**	174.16(18)
N1—P2B—C1B—O1B	−38.9(14)	**P1A—P2A—N2—C28**	−151.7(2)
N2—P2B—C1B—O1B	42.7(14)	**C1A—P2A—N2—P1A**	58.0(5)
N2—P2B—N1—C4	−178.94(19)	**N1—P1A—N2—C28**	−171.82(17)
P1B—P2B—N1—C4	−147.0(2)	**P2A—P1A—N2—C28**	154.2(2)
C1B—P2B—N1—P1B	58.3(8)	**O1A—P1A—N2—P2A**	−61.43(13)
N2—P2A—N1—C4	−179.03(17)	**N1—P1B—N2—C28**	172.13(18)
P1A—P2A—N1—C4	146.6(2)	**P2B—P1B—N2—C28**	−157.2(2)
C1A—P2A—N1—P1A	−57.5(5)	**O1B—P1B—N2—P2B**	63.62(18)

Scheme S12. Numbering scheme of **[P(*μ*-NTer)]$_2$(S(NSiMe$_3$)$_2$) (12)**.

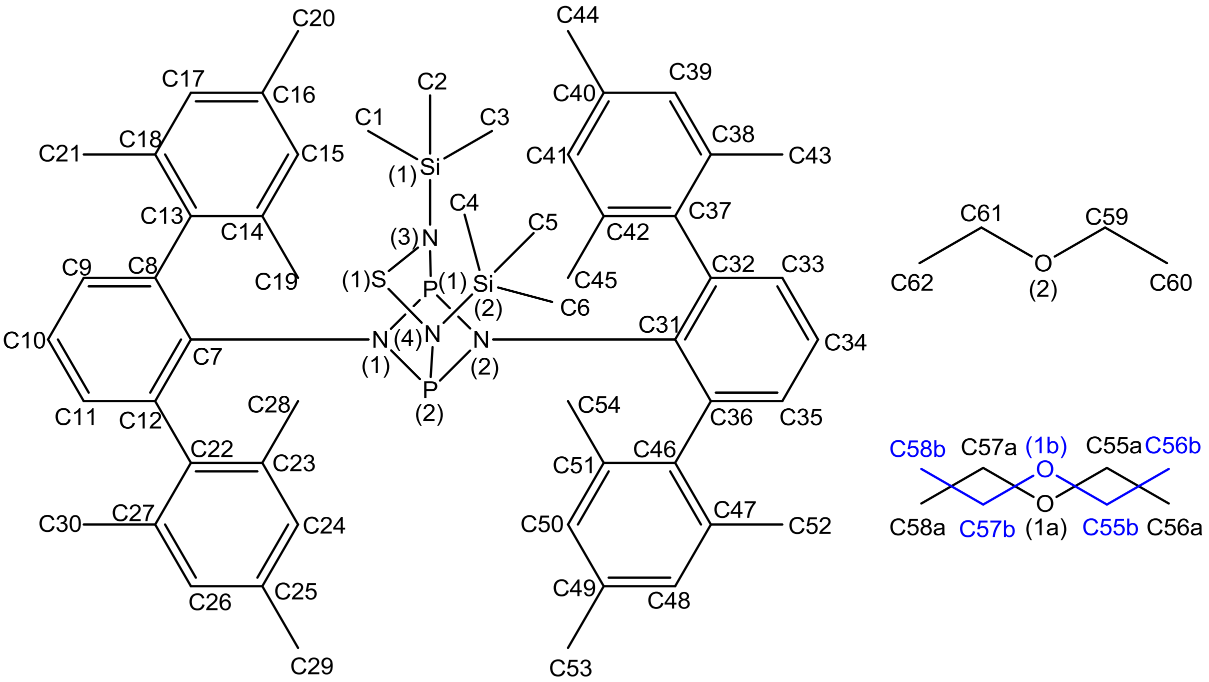


Table S17. Selected bond lengths (Å) and angles (°) of **[P(*μ*-NTer)]$_2$(S(NSiMe$_3$)$_2$)**.

P1—N3	1.7271(14)	**C7—N1—P1**	127.71(10)
P1—N2	1.7514(13)	**C7—N1—P2**	122.04(11)
P1—N1	1.7607(13)	**N3—P1—N2**	99.15(6)
P1—P2	2.6172(6)	**N3—P1—N1**	99.19(6)
P2—N4	1.7146(14)	**N2—P1—N1**	81.74(6)
P2—N1	1.7627(14)	**N3—P1—P2**	90.47(5)
P2—N2	1.7738(13)	**N4—P2—N1**	103.36(7)
S1—N3	1.7040(14)	**N4—P2—N2**	97.61(6)
S1—N4	1.7250(14)	**N1—P2—N2**	81.05(6)
Si1—N3	1.7650(14)	**N4—P2—P1**	92.30(5)
Si2—N4	1.7658(14)	**N3—S1—N4**	104.06(7)
N1—C7	1.4283(19)	**P1—N1—P2**	95.94(6)

N2—C31	1.4188(19)	**C31—N2—P1**	132.18(11)
C31—N2—P2	129.27(11)	**P2—P1—N2—C31**	−162.16(17)
P1—N2—P2	95.87(6)	**N4—S1—N3—P1**	−49.31(10)
S1—N3—P1	116.22(8)	**N4—S1—N3—Si1**	125.48(8)
S1—N3—Si1	115.09(8)	**N2—P1—N3—S1**	−11.00(9)
P1—N3—Si1	128.44(8)	**N1—P1—N3—S1**	72.03(9)
P2—N4—S1	116.58(8)	**P2—P1—N3—S1**	30.69(8)
P2—N4—Si2	132.31(8)	**N2—P1—N3—Si1**	175.03(10)
S1—N4—Si2	110.89(7)	**N1—P1—N3—Si1**	−101.94(10)
N3—P1—P2—N4	−4.25(7)	**P2—P1—N3—Si1**	−143.28(9)
N1—P1—P2—N2	153.63(9)	**N1—P2—N4—S1**	−63.61(10)
N2—P1—P2—N4	98.86(8)	**N2—P2—N4—S1**	18.95(10)
N1—P1—P2—N4	−107.51(8)	**P1—P2—N4—S1**	−22.62(8)
N3—P1—P2—N1	103.26(8)	**N1—P2—N4—Si2**	122.32(11)
N3—P1—P2—N2	−103.11(8)	**N2—P2—N4—Si2**	−155.12(11)
P2—P1—N1—C7	−138.99(16)	**P1—P2—N4—Si2**	163.30(11)
N2—P1—N1—P2	17.62(6)	**N3—S1—N4—P2**	44.38(10)
P1—P2—N1—C7	142.24(15)	**N3—S1—N4—Si2**	−140.31(8)

Scheme S13. Numbering scheme of **[P(*μ*-NTer)]$_2$(PhNCNPh) (13)**.

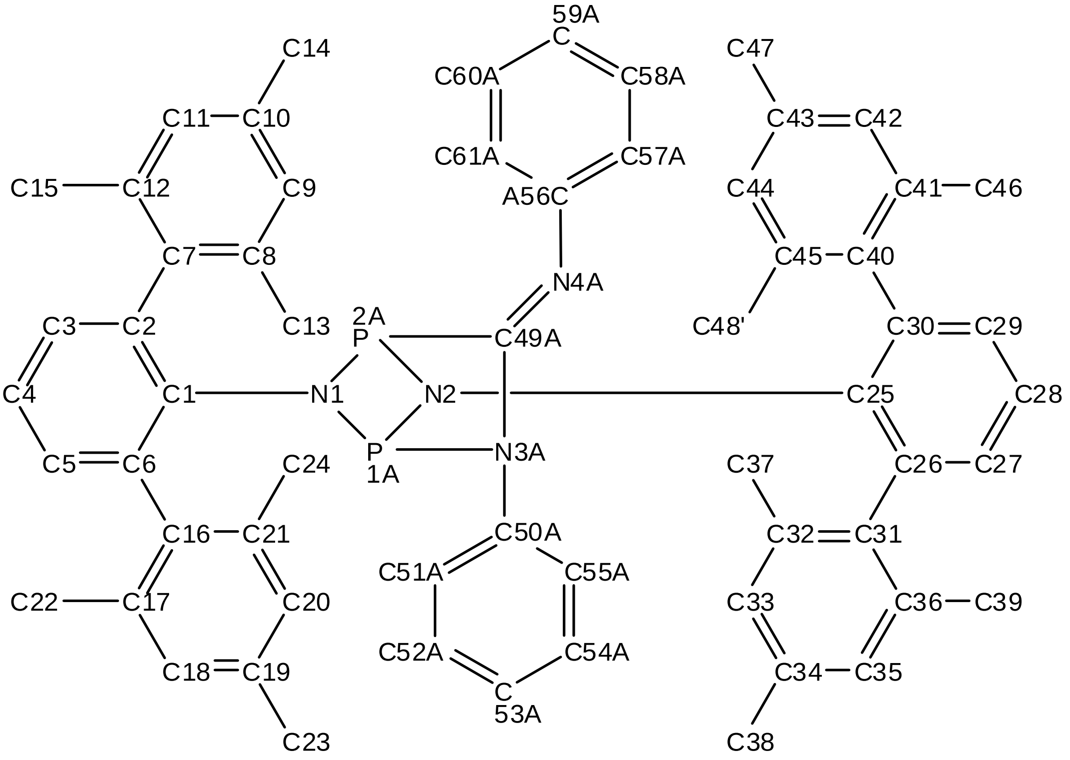


Table S18. Selected bond lengths (Å) and angles (°) of **[P(*μ*-NTer)]$_2$(PhNCNPh)**.

P1A—N2	1.747(1)	**P1A—N1**	1.770(1)
P1A—C49A	1.938(2)	**P1A—P2A**	2.525(1)
P2A—N2	1.721(2)	**P2A—N3A**	1.769(2)
P2A—N1	1.773(2)	**N3A—C49A**	1.401(2)
N3A—C50A	1.429(2)	**N4A—C49A**	1.271(2)
N4A—C56A	1.402(2)	**N2—P1A—N1**	79.37(6)
N2—P1A—C49A	88.79(7)	**N1—P1A—C49A**	91.22(7)
N2—P1A—P2A	42.88(6)	**N1—P1A—P2A**	44.59(5)
C49A—P1A—P2A	69.87(6)	**N2—P2A—N3A**	95.74(8)
N2—P2A—N1	79.99(7)	**N3A—P2A—N1**	91.76(8)
N2—P2A—P1A	43.69(5)	**N3A—P2A—P1A**	74.58(6)
N1—P2A—P1A	44.50(4)	**P2A—N3A—C49A—N4A**	-169.36(15)

Scheme S14. Numbering scheme of **[P(μ-NTer)]$_2$(CH$_3$CN) (14)**.

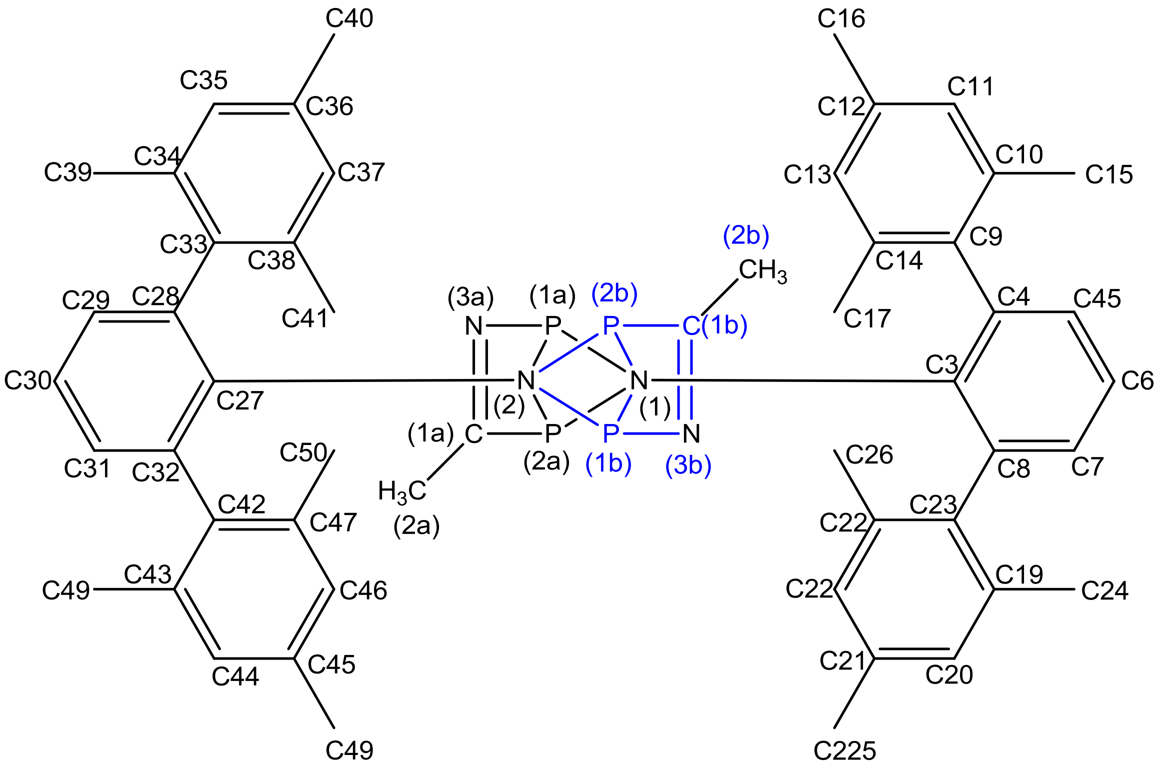


Table S19. Selected bond lengths (Å) and angles (°) of **[P(μ-NTer)]$_2$(CH$_3$CN)**.

P1A—N2	1.729 (4)	**P2B—N1**	1.544 (11)
P1A—N1	1.806 (3)	**P2B—N2**	1.734 (12)
P1A—N3A	1.810 (5)	**P2B—C1B**	1.912 (10)
P1A—P2A	2.508 (2)	**N3B—C1B**	1.375 (11)
P2A—N2	1.711 (3)	**C1B—C2B**	1.321 (10)
P2A—N1	1.795 (3)	**N1—C3**	1.420 (3)
P2A—C1A	1.918 (5)	**N2—C27**	1.414 (3)
C1A—C2A	1.341 (6)	**N3A—P1A—P2A**	74.83 (16)
P1B—N1	1.742 (9)	**N2—P1A—N1**	78.17 (14)
P1B—N2	1.795 (10)	**N2—P1A—N3A**	95.7 (2)
P1B—N3B	1.812 (9)	**N1—P1A—N3A**	96.05 (17)
P1B—P2B	2.504 (8)	**P2B—N1—P1B**	99.1 (5)

N2—P2A—N1	78.92(13)	**C3—N1—P1A**	129.8(2)
N2—P2A—C1A	93.0(2)	**P2A—N1—P1A**	88.29(15)
N1—P2A—C1A	90.63(18)	**C27—N2—P2A**	134.06(18)
N2—P2A—P1A	43.47(12)	**C27—N2—P1A**	128.02(19)
N1—P2A—P1A	46.02(12)	**P2A—N2—P1A**	93.62(13)
C1A—P2A—P1A	69.33(17)	**C27—N2—P2B**	137.7(4)
C1A—N3A—P1A	107.1(4)	**C27—N2—P1B**	131.8(3)
C2A—C1A—N3A	128.3(5)	**P2B—N2—P1B**	90.4(4)
C2A—C1A—P2A	122.7(4)	**N1—P1A—P2A—N2**	−129.0(2)
N3A—C1A—P2A	108.6(3)	**N3A—P1A—P2A—N2**	116.3(2)
N1—P1B—N2	78.1(4)	**N2—P1A—P2A—N1**	129.0(2)
N1—P1B—N3B	83.7(5)	**N3A—P1A—P2A—N1**	−114.68(19)
N2—P1B—N3B	94.2(5)	**N2—P1A—P2A—C1A**	−118.6(2)
N3B—P1B—P2B	75.9(4)	**N1—P1A—P2A—C1A**	112.4(2)
N1—P2B—N2	85.5(5)	**N3A—P1A—P2A—C1A**	−2.32(19)
N1—P2B—C1B	83.0(6)	**N2—P1A—N3A—C1A**	41.0(3)
N2—P2B—C1B	86.5(7)	**N1—P1A—N3A—C1A**	−37.6(3)
N1—P2B—P1B	43.4(3)	**P2A—P1A—N3A—C1A**	3.2(3)
N2—P2B—P1B	45.8(3)	**P1A—N3A—C1A—C2A**	168.5(4)
C1B—P2B—P1B	68.6(4)	**P1A—N3A—C1A—P2A**	−4.3(3)
C1B—N3B—P1B	104.6 (7)	**N2—P2A—C1A—C2A**	152.7(4)
C2B—C1B—N3B	130.3(12)	**N1—P2A—C1A—C2A**	−128.4(4)
C2B—C1B—P2B	119.6(11)	**P1A—P2A—C1A—C2A**	−170.1(4)
N3B—C1B—P2B	110.0(7)	**N2—P2A—C1A—N3A**	−34.1(3)
C3—N1—P2B	127.3(5)	**N1—P2A—C1A—N3A**	44.9(3)
C3—N1—P1B	123.6(4)	**N2—P2A—N1—C3**	171.1(2)
C3—N1—P2A	122.99(18)	**P1A—P2A—C1A—N3A**	3.2(3)

N2—P1B—P2B—N1	−150.3(7)	**C1A—P2A—N1—C3**	78.2(3)
N3B—P1B—P2B—N1	98.1(6)	**P1A—P2A—N1—C3**	138.1(3)
N1—P1B—P2B—N2	150.3(7)	**N2—P2A—N1—P1A**	33.00(15)
N3B—P1B—P2B—N2	−111.7(6)	**C1A—P2A—N1—P1A**	−59.92(19)
N1—P1B—P2B—C1B	−102.9(8)	**N2—P1A—N1—C3**	−165.9(2)
N2—P1B—P2B—C1B	106.8(9)	**N3A—P1A—N1—C3**	−71.3(3)
N3B—P1B—P2B—C1B	−4.8(8)	**P2A—P1A—N1—C3**	−133.2(3)
N1—P1B—N3B—C1B	43.8(11)	**N2—P1A—N1—P2A**	−32.71(14)
N2—P1B—N3B—C1B	−33.7(11)	**N3A—P1A—N1—P2A**	61.88(18)
P2B—P1B—N3B—C1B	6.5(10)	**N1—P2A—N2—C26**	168.3(3)
P1B—N3B—C1B—C2B	168.8(18)	**C1A—P2A—N2—C26**	−101.6(3)
P1B—N3B—C1B—P2B	−8.8(14)	**P1A—P2A—N2—C26**	−156.9(4)
N1—P2B—C1B—C2B	146.2(16)	**N1—P2A—N2—P1A**	−34.73(18)
N2—P2B—C1B—C2B	−127.9(16)	**C1A—P2A—N2—P1A**	55.3(2)
P1B—P2B—C1B—C2B	−171.3(17)	**N1—P1A—N2—C27**	−166.3(2)
N1—P2B—C1B—N3B	−35.9(13)	**N3A—P1A—N2—C27**	98.6(3)
N2—P2B—C1B—N3B	50.0(13)	**P2A—P1A—N2—C27**	159.1(3)
P1B—P2B—C1B—N3B	6.6(11)	**N1—P1A—N2—P2A**	34.61(15)
N2—P2B—N1—C3	−166.5(2)	**N3A—P1A—N2—P2A**	−60.41(19)
C1B—P2B—N1—C3	−79.5(7)	**N1—P2B—N2—C27**	−164.3(3)
P1B—P2B—N1—C3	−145.6(5)	**C1B—P2B—N2—C27**	112.5(6)
N2—P2B—N1—P1B	−20.9(5)	**P1B—P2B—N2—C27**	175.7(6)
C1B—P2B—N1—P1B	66.1(6)	**N1—P2B—N2—P1B**	20.0(5)
N2—P1B—N1—C3	167.9(2)	**C1B—P2B—N2—P1B**	−63.3(6)
N3B—P1B—N1—C3	72.2(5)	**N1—P1B—N2—C26**	165.9(3)
P2B—P1B—N1—C3	147.3(6)	**N3B—P1B—N2—C26**	−111.5(5)
N2—P1B—N1—P2B	20.5(5)	**P2B—P1B—N2—C26**	−176.2(6)

Scheme S15. Numbering scheme of **[P(μ-NTer)]$_2$(PhCCPh) (15Ph)**.

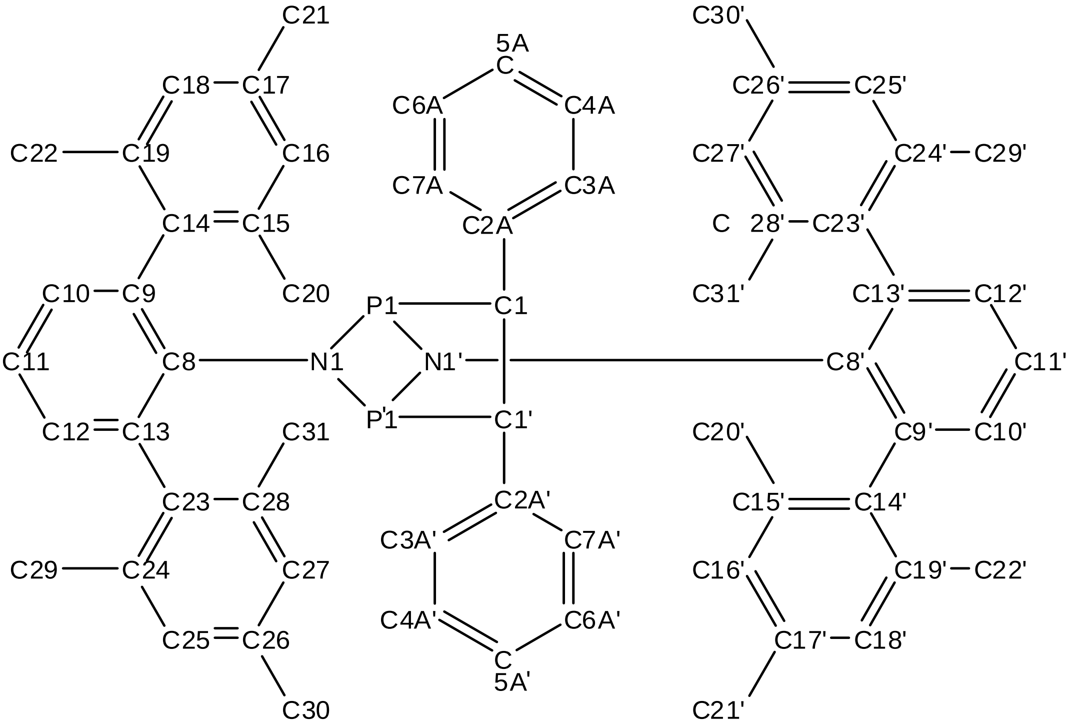


Table S20. Selected bond lengths (Å) and angles (°) of **[P(μ-NTer)]$_2$(PhCCPh)**.

P1—N1	1.7474(8)	**N1—P1—N1'**	79.53(4)
P1—N1'	1.7635(8)	**N1—P1—C1**	92.39(4)
P1—C1	1.915(1)	**N1'—P1—C1**	92.44(4)
P1—P1'	2.5204(5)	**P1—N1—P1'**	91.76(4)
C1—C1	1.349(2)	**C1'—C1—C2**	132.33(7)
C1—C2	1.473(2)	**C1'—C1—P1**	107.80(3)
C2—C1—C1'—C2'	133.48(5)	**N1—P1—P1'—N1'**	7.5(2)

symmetry code: (') 1–x, y, 0.5–z.

Scheme S16. Numbering scheme of **[P(*μ*-NTer)]$_2$(HCCH) (15H)**.

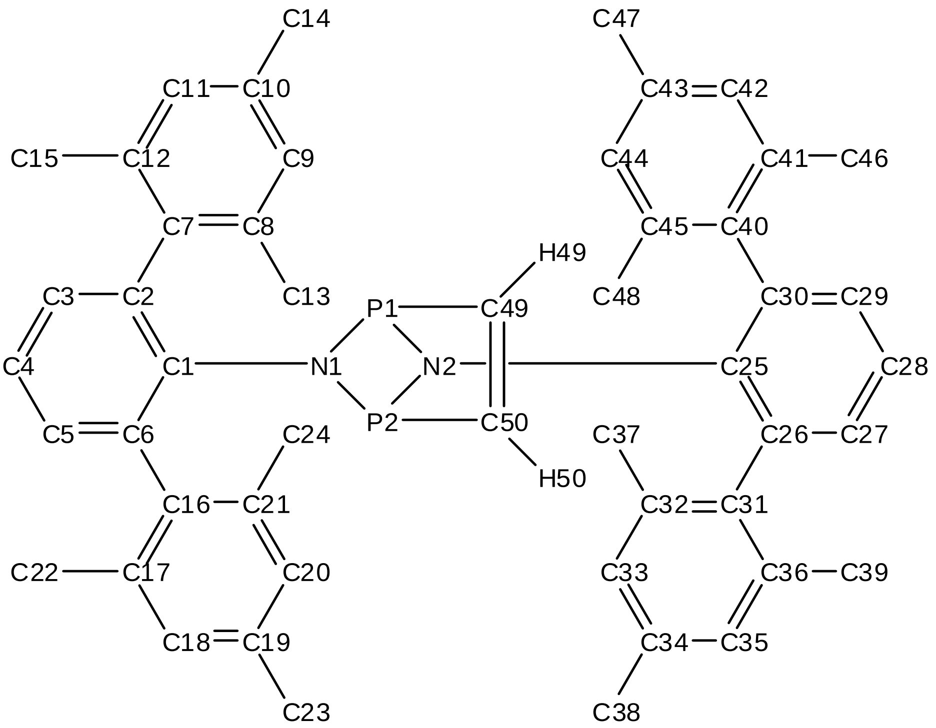
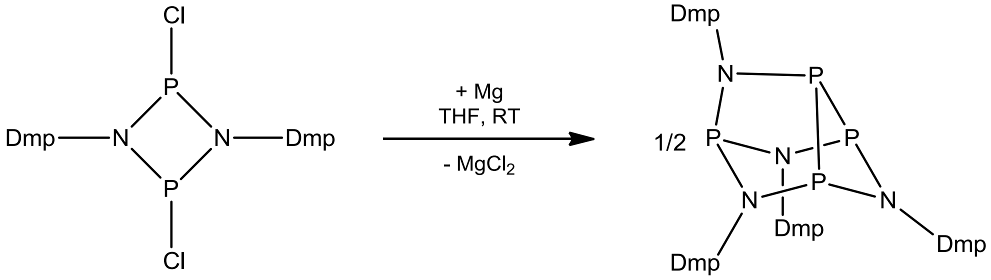


Table S21. Selected bond lengths (Å) and angles (°) of **[P(*μ*-NTer)]$_2$(HCCH)**.

P1—N2	1.7455(14)	**N2—P1—N1**	79.14(7)
P1—N1	1.7631(15)	**N2—P1—C49**	92.14(8)
P1—C49	1.883(2)	**N1—P1—C49**	91.42(9)
P1—P2	2.5235(6)	**C49—P1—P2**	71.37(7)
P2—N2	1.7251(15)	**N2—P2—N1**	79.20(7)
P2—N1	1.7806(14)	**N2—P2—C50**	92.84(9)
P2—C50	1.891(2)	**N1—P2—C50**	90.69(8)
C49—C50	1.317(3)	**C50—P2—P1**	71.33(7)
P2—N2—P1	93.29(7)	**C50—C49—P1**	108.92(16)
C49—C50—P2	108.37(16)	**N1—P1—P2—N2**	133.18(10)
C49—P1—P2—C50	0.69(9)		

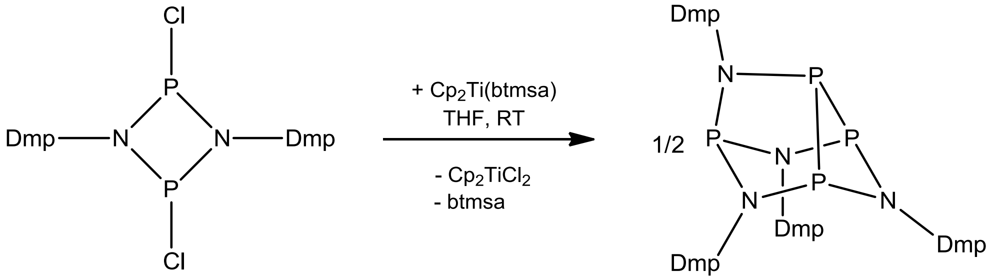
3. Syntheses of compounds

3.1. Synthesis of 2,4,7,8-tetrakis(2,6-dimethylphenyl)-2,4,7,8-tetraaza-1,3,5,6-tetraphosphatricyclo[3.2.1.0^{3,6}]octane (4).



[ClP(μ-NDmp)]$_2$ (0.186 g, 0.5 mmol) and an excess of magnesium (0.086 g, 2.0 mmol) were combined and dissolved in 10 ml of THF. The initial colourless solution was stirred one day at ambient temperature resulting in a yellow solution. The solvent was removed *in vacuo* and the yellow residue was extracted with benzene (10 ml) and filtered (F4). The solvent was removed and the resulting yellow residue was dried *in vacuo* yielding 0.138 g (0.23 mmol, 92%) of β-P$_4$(NDmp)$_4$ as a yellow microcrystalline solid.

Procedure 2

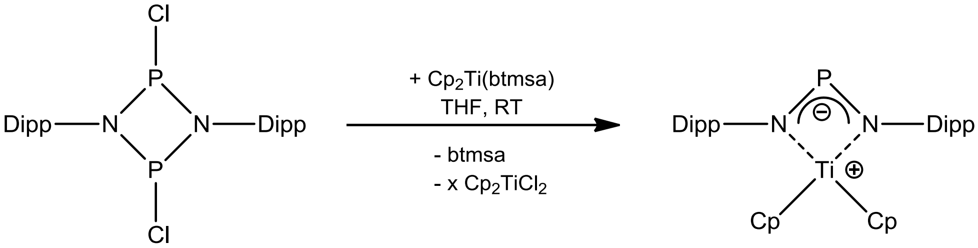


[ClP(μ-NDmp)]$_2$ (0.186 g, 0.5 mmol) and titanocene bis(trimethylsilyl)acetylene Cp$_2$Ti(btmsa) (0.175 g, 0.5 mmol) were combined and dissolved in 10 ml of THF. The initially yellow/brown solution was stirred one day at ambient temperature resulting in a red suspension. The solvent was removed *in vacuo,* and the red residue was extracted with *n*-hexane (10 ml) and washed several times by repeated backdistillations of the solvent and filtered (F4). The solvent was removed and the resulting yellow residue was dried *in vacuo* yielding 0.132 g (0.22 mmol, 88%) of β-$P_4(NDmp)_4$ as a yellow microcrystalline solid.

Mp.: 189 °C (dec.). **Anal. calc. % (found)**: C, 64.00 (63.58); H, 6.04 (6.34); N, 9.33 (8.99). **$^{31}P\{^{1}H\}$ NMR** (25 °C, C_6D_6, 121.5 MHz): δ = 185.2 (d, 2P, $^{1}J(^{31}P\text{-}^{31}P)$ = 137 Hz, *P*P*P*), 106.6 (d, $^{2}J(^{31}P\text{-}^{31}P)$ = 15 Hz, *P*N_3), 31.5 (dt, $^{1}J(^{31}P\text{-}^{31}P)$ = 137 Hz, $^{2}J(^{31}P\text{-}^{31}P)$ = 15 Hz, P*P*P). **^{1}H NMR** (25 °C, C_6D_6, 300.13 MHz): δ = 2.32 (s, 6H, *o*-CH_3), 6.84 (m, 3H, C*H*). **IR** (ATR, 25 °C, 16 scans, cm^{-1}): 3062 (w), 3015 (w), 2951 (w), 2915 (w), 2855 (w), 2730 (w), 1590 (w), 1463 (s), 1456 (m), 1445 (m), 1435 (m), 1423 (w), 1417 (m), 1373 (w), 1257 (m), 1200 (m), 1180 (m), 1098 (m), 1068 (w), 1024 (w), 985 (w), 927 (m), 838 (s), 818 (s), 762 (vs), 731 (w), 703 (m), 667 (w), 570 (m). **Raman** (460 mW, 25 °C, 150 scans, cm^{-1}): 3067 (3), 3040 (3), 2953 (3), 2920 (7), 2866 (2), 2737 (1), 1593 (10), 1470 (2), 1445 (2), 1381 (2), 1259 (7), 1169 (2), 1107 (3), 991 (1), 897 (1), 752 (1), 735 (1), 685 (1), 590 (1), 565 (3), 530 (1), 507 (1), 463 (1), 446 (1), 428 (1), 401 (1), 349 (1), 230 (1), 79 (1). **MS** (CI pos., *iso*-butane); m/z (%): 122 (89) $[DmpNH_3]^+$, 150 (20) $[(Dmp)NP]^+$, 271 (100) $[(Dmp)N(H)PN(H)(Dmp)]^+$, 420 (71) $[(DmpNHP)_2NDmp]^+$, 601 (44) $[M + H]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated Et_2O solution of β-$P_4(NDmp)_4$ to –40 °C.

3.2. Synthesis of titanocene-1,3-bis(2,6-isopropylphenyl)-1,3-diaza-2-phosphaallyl (6).



$[ClP(\mu\text{-}NDipp)]_2$ (0.355 g, 0.73 mmol) and titanocene bis(trimethylsilyl)acetylene $Cp_2Ti(btmsa)$ (0.259 g, 0.74 mmol) were combined and dissolved in 10 ml of THF. The initially yellow/brown solution was stirred one day at ambient temperature resulting in a red suspension. The solvent was removed *in vacuo,* and the red residue was extracted with *n*-hexane (10 ml) and washed several times by repeated backdistillations of the solvent and filtered (F4). The solvent is removed and the resulting yellow residue was dried *in vacuo* yielding a mixture of several products. A separation was not successful.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling the filtered saturated reaction mixture in Et_2O to –40 °C.

3.3. Attempted Synthesis of $Mes^*_2N_2P_2$

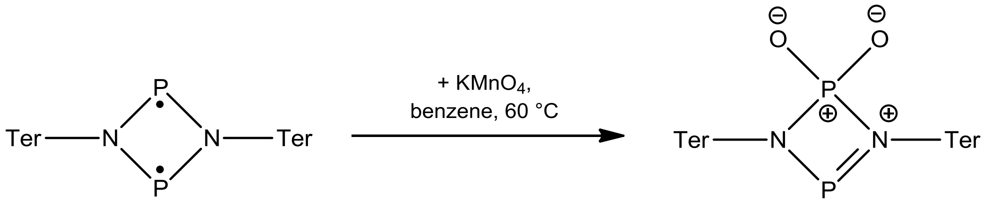
$$\mathrm{Mes^*NPCl} + \mathrm{Mg} \xrightarrow[\mathrm{r.t.}]{\mathrm{thf}} \mathrm{(Mes^*NH)_2PCl} + \mathrm{(Mes^*NP)_2NMes^*} + \text{"}\mathrm{MgP_x}\text{"}$$

To a stirred solution of Mes*NPCl (230 mg, 0.706 mmol) and diphenylacetylene (182 mg, 1.02 mmol) in 5 ml of tetrahydrofurane, magnesium turnings (51 mg, 2.09 mmol) are added. The initially red suspension is stirred at room temperature for 6 hours and darkens within 30 minutes. After completion of the reaction, volatiles are removed in vacuo. The residue is then extracted with 3+2 ml of n-hexane, resulting in a dark red filtrate (G4). The solution is then concentrated until crystallisation commences and left undisturbed overnight, which leads to the deposition of colourless, yellowish-orange and dark red needle-shaped crystals. The compounds were identified by single-crystal diffraction experiments.

^{31}P NMR (298 K, C_6D_6, 121.5 MHz): 306 (s, br), 271 (s). **IR** (ATR, cm^{-1}): 3064 (w), 2956 (s), 2905 (m), 2868 (m), 1599 (m), 1494 (w), 1477 (w), 1463 (w), 1443 (w), 1417 (w), 1391 (w), 1360 (m), 1267 (w), 1243 (m), 1215 (m), 1180 (w), 1157 (w), 1126 (w), 1106 (w), 1070 (w), 1026 (w), 997 (w), 983 (w), 917 (w), 877 (m), 840 (m), 777 (vw), 755 (s), 733 (m), 689 (s), 667 (w), 645 (w), 573 (w), 536 (w). **Raman** (784 nm, D0, 60s, 4 Acc., cm^{-1}): 3059 (1), 2962 (4), 2907 (5), 2872 (2), 2706 (1), 2217 (7), 1597 (27), 1592 (sh, 17), 1524 (3), 1479 (4), 1464 (6), 1445 (9), 1402 (32), 1394 (sh, 16), 1382 (11), 1363 (9), 1350 (8), 1290 (100), 1246 (6), 1244 (18), 1152 (7), 1138 (13), 1124 (3), 1035 (1), 1021 (2), 994 (10), 921 (3), 907 (3), 866 (2), 837 (2), 822 (8), 778 (3), 764 (2), 760 (2), 751 (1), 701 (1), 636 (2), 621 (1), 570 (5), 561 (5), 535 (2), 482 (3), 444 (1), 377 (1), 256 (4).

red = tolane

3.4. 1,1-Dioxido-2,4-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-*cyclo*-1,3-diphospha-2,4-diazane ($8O_2$).



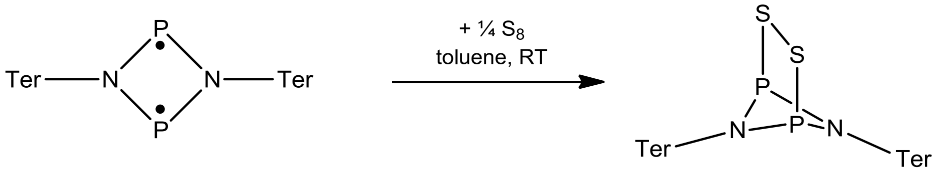
$[P(\mu\text{-NTer})]_2$ (0.110 g, 0.15 mmol) and crystalline potassium permanganate (0.047 g, 0.3 mmol) were combined and dissolved in 10 ml of benzene. The initially orange solution was stored without stirring one day at 60 °C resulting in a yellow solution. Excess of potassium permanganate was removed by filtration, the solvent was removed *in vacuo* and the resulting yellow residue was washed once with a small amount of Et_2O. The residue was dried *in vacuo* yielding 0.106 g (0.14 mmol, 93%) of $[P(\mu\text{-NTer})]_2O_2$ as a yellow microcrystalline solid.

$[P(\mu\text{-NTer})]_2O_2$ can be obtained by reaction of $[P(\mu\text{-NTer})]_2$ with dry oxygen. Solvent-free $[P(\mu\text{-NTer})]_2$ was stirred in an atmosphere of pure oxygen for 48 hours. The solid turned yellow in the process, yielding quantitative amounts of $[P(\mu\text{-NTer})]_2O_2$.

Mp.: 286 °C (dec.). **Anal. calc. % (found)**: C, 76.98 (76.55); H, 6.73 (7.06); N, 3.74 (3.69). **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 121.5 MHz): $\delta = 272.1$ (d, $^2J(^{31}P\text{-}^{31}P) = 13$ Hz, N–*P*–N), $\delta = 17.6$ (d, $^2J(^{31}P\text{-}^{31}P) = 13$ Hz, N–PO_2–N). **^1H NMR** (25 °C, C_6D_6, 300.13 MHz): $\delta = 2.01$ (s, 12H, *o*-CH_3), 2.18 (s, 6H, *p*-CH_3), 6.79 (m, 1H, *p*-C*H*), 6.82 (s, 4H, *m*-Mes), 6.84 (m, 2H, *m*-C*H*). **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 75.5 MHz): $\delta = 21.0$ (s, *o*-CH_3), 21.4 (s, *p*-CH_3), 126.9 (s, *C*H), 128.5 (s, *C*H), 129.8 (s), 130.8 (s, *C*H), 136.1 (t, $J(^{13}C\text{-}^{31}P) = 3.8$ Hz), 136.8 (s), 138.6 (s), 138.8 (t, $J(^{13}C\text{-}^{31}P) = 3.3$ Hz). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2998 (w), 2971 (w), 3944 (m), 2853 (w), 2730 (w), 1610 (m), 1574 (w), 1567 (w), 1557 (w), 1504 (w), 1494 (w), 1486 (w), 1470 (w), 1461 (w), 1454 (m), 1441 (m), 1434 (m), 1412 (s), 1377 (m), 1343 (m), 1295 (w), 1267 (m), 1220 (vs), 1187 (w), 1164 (w), 1124 (w), 1085 (m), 1030 (w), 1008 (w), 985 (m), 954 (m), 939 (m), 910 (m), 888 (m), 844 (s), 800 (s), 776 (m), 750 (m), 740 (m), 716 (s), 697 (w), 676 (m), 601 (m), 559 (m), 551 (w), 534 (w). **Raman** (25 mW, 4 scans, 6 s accumulation time, 25 °C, cm^{-1}): 3048 (2), 3012 (1), 2914 (3), 2856 (1), 2728 (1), 1612 (3), 1578 (3), 1483 (2), 1428 (3), 1381 (2), 1304 (8), 1291 (9), 1186 (2), 1159 (1), 1127 (1), 1086 (4), 1012 (2), 1004 (2), 945 (1), 875 (5), 801 (1), 754 (2), 739 (2), 737 (2), 698 (1), 654 (1), 592 (3), 577 (10), 567 (5), 557 (3), 523 (4), 509 (2), 431 (3), 420 (1), 394 (2), 381 (1), 355 (1), 341 (1), 324 (1), 299 (2), 264 (3), 242 (3), 232 (4), 212 (3). **MS** (CI pos., *iso*-butane); m/z (%): 330 (100) [Ter–NH$_3$]$^+$, 386 (27) [Ter–NH + *iso*-butane]$^+$, 716 (23) [M – 2O]$^+$, 721 (18), 749 (33) [M + H]$^+$, 767 (44) [M + H$_3$O$^+$].

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated *n*-hexane solution of [P(μ-NTer)]$_2$O$_2$ to 5 °C.

3.5. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-2,3-dithia-5,6-diaza-1,4-diphosphabicyclo[2.1.1]hexane (8S$_2$).

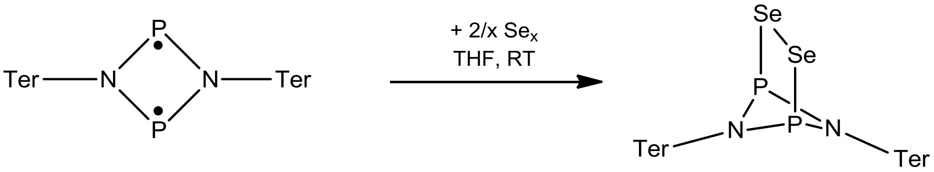


[P(μ-NTer)]$_2$ (0.150 g, 0.21 mmol) was dissolved in 5 ml of toluene which results in an orange solution. A solution of sulphur (0.07 g, 0.22 mmol) in 5 ml of toluene was added dropwise at ambient temperature resulting in a yellow solution. The solution was stirred for 15 min. The solvent was removed *in vacuo* and the yellow residue was extracted with *n*-hexane and filtered (F4). Removal of solvent *in vacuo* yields 0.138 g (0.18 mmol, 86%) of [P(μ-NTer)]$_2$S$_2$ as a yellow microcrystalline solid.

Mp.: 282 °C (dec.). **Anal. calc. % (found)**: C, 73.82 (73.77); H, 6.45 (6.36); N, 3.59 (3.75). **^{31}P{^{1}H} NMR** (25 °C, C$_6$D$_6$, 121.5 MHz): δ = 223.7 (s). **^{1}H NMR** (25 °C, C$_6$D$_6$, 300.13 MHz): δ = 2.11 (s, 12H, *o*-C*H*$_3$), 2.32 (s, 6H, *p*-C*H*$_3$), 6.59 (m, 2H, *m*-C*H*), 6.68 (m, 1H, *p*-C*H*), 6.78 (s, 4H, *m*-Mes). **^{13}C{^{1}H} NMR** (25 °C, C$_6$D$_6$, 75.5 MHz): δ = 21.3 (br, *o*-*C*H$_3$), 21.5 (br, *p*-*C*H$_3$), 122.4 (s, *C*H), 128.9 (s, *C*H), 130.8 (s, *C*H), 131.2 (t, J(^{13}C-^{31}P) = 2.7 Hz), 135.5 (t, J(^{13}C-^{31}P) = 3.3 Hz), 135.8 (s), 137.8 (s), 138.7 (t, J(^{13}C-^{31}P) = 3.7 Hz). **IR** (ATR, 25 °C, 64 scans, cm^{-1}): 3044 (w), 2998 (w), 2970 (w), 2944 (m), 2911 (m), 2850 (w), 2727 (w), 1609 (m), 1574 (w), 1567 (w), 1485 (w), 1470 (w), 1455 (m), 1441 (w), 1434 (m), 1403 (s), 1372 (m), 1284 (w), 1271 (w), 1249 (w), 1241 (w), 1219 (s), 1163 (w), 1080 (s), 1028 (m), 1004 (m), 967 (w), 945 (w), 900 (w), 862 (m), 848 (s), 842 (vs), 818 (m), 795 (s), 770 (w), 757 (s), 743 (m), 732 (m), 693 (s), 647 (w), 521 (w), 574 (w), 558 (w), 545 (m), 533 (w). **Raman** (400 mW, 25 °C, 400 scans, cm^{-1}): 3048 (3), 3013 (3), 2976 (2), 2947 (3), 2918 (9), 2858 (2), 2731 (1), 1614 (6), 1582 (5), 1483 (2), 1424 (3), 1381 (4), 1306 (10), 1289 (5), 1248 (1), 1190 (1), 1165 (1), 1092 (2), 1007 (2), 947 (1), 739 (1), 594 (3), 581 (9), 565 (4), 525 (2), 492 (4), 475 (1), 426 (2), 384 (2), 367 (2), 349 (3), 272 (4), 151 (5), 97 (9), 79 (4). **MS** (CI pos., *iso*-butane); m/z (%): 330 (100) $[Ter–NH_3]^+$, 386 (33) $[Ter–NH + iso\text{-butane}]^+$, 687 (55) $[Ter–N(H)PN(H)–Ter]^+$, 781 (100) $[M + H]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated toluene solution of $[P(\mu\text{-NTer})]_2S_2$ to –40 °C.

3.6. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-2,3-diselena-5,6-diaza-1,4-diphosphabicyclo[2.1.1]hexane (8Se₂).

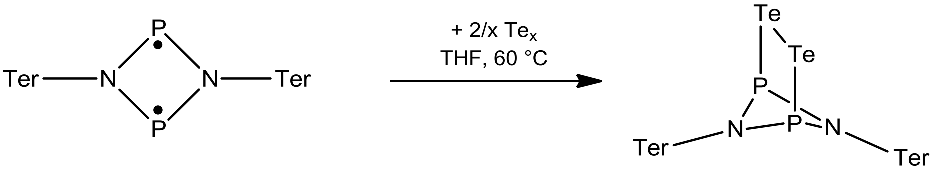


$[P(\mu\text{-NTer})]_2$ (0.115 g, 0.16 mmol) and black selenium (0.06 g, 0.78 mmol) were combined and dissolved in 8 ml of THF and stirred over 2 h resulting in a brown/grey suspension. The suspension was filtered and the solvent was removed *in vacuo*. The orange residue was extracted with benzene and filtered (F4). Removal of solvent *in vacuo* yields 0.129 g (0.15 mmol, 93%) of $[P(\mu\text{-NTer})]_2Se_2$ as an orange microcrystalline solid.

Mp.: 295 °C (dec.). **Anal. calc. % (found)**: C, 65.90 (65.52); H, 5.76 (5.89); N, 3.20 (3.33). **$^{31}P\{^1H\}$ NMR** (25 °C, C_6D_6, 121.5 MHz): $\delta = 218.1$ (s). **$^{77}Se\{^1H\}$ NMR** (25 °C, C_6D_6, 57.3 MHz): $\delta = 346.4$ (m). **^1H NMR** (25 °C, C_6D_6, 300.13 MHz): $\delta = 2.13$ (s, 12H, *o*-CH_3), 2.32 (s, 6H, *p*-CH_3), 6.56 (m, 2H, *m*-C*H*), 6.66 (m, 1H, *p*-C*H*), 6.77 (s, 4H, *m*-Mes). **$^{13}C\{^1H\}$ NMR** (25 °C, C_6D_6, 75.5 MHz): $\delta = 21.5$ (br, *o*-CH_3), 21.6 (br, *p*-CH_3), 122.3 (s, *C*H), 128.9 (s, *C*H), 130.8 (t, $J(^{13}C\text{-}^{31}P) = 2.6$ Hz), 131.2 (s, *C*H), 135.5 (t, $J(^{13}C\text{-}^{31}P) = 3.4$ Hz), 135.7 (s), 137.8 (d, $J(^{13}C\text{-}^{31}P) = 0.4$ Hz), 138.7 (t, $J(^{13}C\text{-}^{31}P) = 3.7$ Hz). **IR** (ATR, 25 °C, 16 scans, cm^{-1}): 3043 (w), 2997 (w), 2945 (m), 2911 (m), 2850 (w), 2726 (w), 1609 (m), 1580 (w), 1574 (w), 1567 (w), 1454 (m), 1434 (m), 1403 (s), 1372 (m), 1281 (w), 1271 (w), 1240 (w), 1218 (s), 1163 (w), 1080 (s), 1028 (m), 965 (w), 945 (w), 901 (s), 850

(s), 842 (vs), 822 (m), 795 (s), 752 (s), 732 (m), 693 (s), 646 (w), 591 (w), 574 (w), 557 (w), 545 (m), 532 (w). **Raman** (460 mW, 25 °C, 150 scans, cm^{-1}): 3046 (2), 3009 (3), 2980 (2), 2947 (2), 2916 (7), 2856 (2), 2731 (1), 1613 (5), 1584 (4), 1484 (1), 1422 (3), 1381 (3), 1306 (7), 1287 (4), 1248 (1), 1192 (1), 1165 (1), 1092 (1), 1007 (1), 947 (1), 737 (1), 592 (2), 581 (7), 563 (4), 544 (3), 527 (1), 490 (1), 473 (1), 426 (1), 309 (2), 297 (3), 276 (2), 261 (2), 237 (10), 153 (2), 91 (4), 77 (2). **MS** (CI pos., *iso*-butane); m/z (%): 330 (100) $[Ter–NH_3]^+$, 386 (33) $[Ter–NH + iso\text{-butane}]^+$, 687 (55) $[Ter–N(H)PN(H)–Ter]^+$, 876 (100) $[M + H]^+$.
Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated Et_2O solution of $[P(\mu\text{-NTer})]_2Se_2$ to 5 °C.

3.7. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-2,3-ditellura-5,6-diaza-1,4-diphosphabicyclo[2.1.1]hexane (8Te₂)

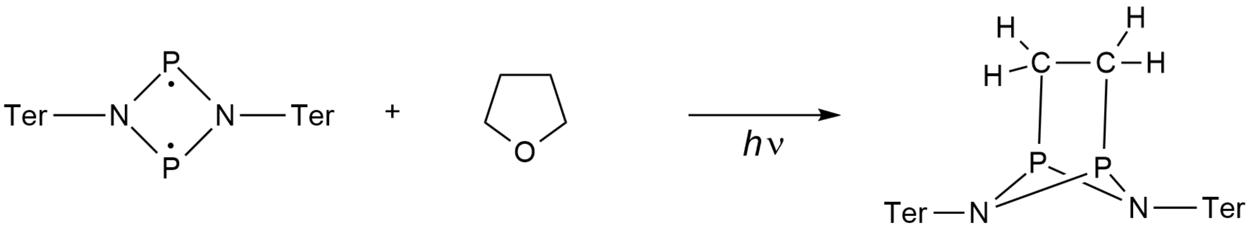


$[P(\mu\text{-NTer})]_2$ (0.100 g, 0.14 mmol) and tellurium (0.06 g, 0.47 mmol) were combined and dissolved in 10 ml of THF. The suspension was stored without stirring 14 days at 60 °C resulting in a dark green suspension. The suspension was filtered and the solvent was removed *in vacuo*. The dark green residue was extracted with benzene (10 mL) and filtered (F4). Removal of solvent *in vacuo* yields 0.123 g (0.13 mmol, 91%) of $[P(\mu\text{-NTer})]_2Te_2$ as dark green microcrystalline solid.

Mp.: 304 °C (dec.). **Anal. calc. % (found)**: (+ 1 molecule *n*-hexane) C, 61.29 (60.97); H, 6.10 (6.64); N, 2.65 (2.82). **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 121.5 MHz): $\delta = 2016$. (s). **^{125}Te{^{1}H} NMR** (25 °C, C_6D_6, 78.9 MHz): $\delta = 287.5$ (s). **^{1}H NMR** (25 °C, C_6D_6, 300.13 MHz): $\delta = 2.17$ (s, 12H, *o*-CH_3), 2.34 (s, 6H, *p*-CH_3), 6.50 (m, 2H, *m*-C*H*), 6.63 (m, 1H, *p*-C*H*), 6.77 (s, 4H, *m*-Mes). **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 75.5 MHz): $\delta = 21.2$ (s, *o*-CH_3), 22.2 (s, *p*-CH_3), 122.3 (s, *C*H), 128.9 (s, *C*H), 130.5 (t, $J(^{13}C\text{-}^{31}P) = 2.1$ Hz), 131.4 (s, *C*H), 135.3 (t, $J(^{13}C\text{-}^{31}P) = 3.3$ Hz), 135.9 (s), 138.1 (s), 139.1 (t, $J(^{13}C\text{-}^{31}P) = 3.6$ Hz). **IR** (ATR, 25 °C, 64 scans, cm^{-1}): 2953 (m), 2913 (m), 2869 (w), 2850 (m), 2727 (w), 1610 (m), 1579 (w), 1575 (w), 1567 (w), 1484 (w), 1481 (w), 1454 (m), 1434 (w), 1407 (s), 1374 (s), 1336 (w), 1281 (w), 1223 (vs), 1163 (w), 1085 (m), 1029 (m), 1005 (m), 986 (w), 961 (w), 945 (w), 903 (s), 849 (s), 841 (s), 794 (s), 759 (w), 749 (s), 695 (m), 666 (w), 647 (w), 585 (w), 573 (m), 557 (w), 549 (w), 535 (w). **MS** (CI pos., *iso*-butane); m/z (%): 330 (31) [Ter–NH$_3$]$^+$, 386 (10) [Ter–NH + *iso*-butane]$^+$, 687 (27) [Ter–N(H)PN(H)–Ter]$^+$, 716 (100) [M – 2Te]$^+$, 972 (21) [M]$^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated *n*-hexane solution of [P(μ-NTer)]$_2$Te$_2$ to –40 °C.

3.8. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-5,6-triaza-1,4-diphosphabicyclo[2.1.1]hexane (9).

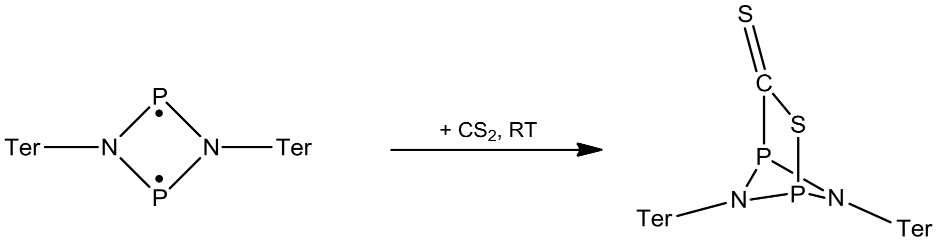


A stirred solution of [P(μ-NTer)]$_2$ (230 mg, 0.32 mmol) in 420 ml tetrahydrofurane is irradiated in an irradiation device equipped with a medium pressure mercury immersion lamp for three hours. The solution is kept at 0 °C with the aid of an appropriately sized ice bath. The initially orange solution turns yellow after 15 minutes of irradiation. The reaction can be monitored by ^{31}P NMR and is quantitative by this respect. After completion of the reaction, the solution is transferred into a Schlenk-flask via cannula. The solvent is removed *in vacuo*, resulting in a pale yellow solid. The solid is dissolved in 5 ml benzene, filtered (G4) and slowly concentrated to incipient crystallisation. The solution is left undisturbed over night, which results in the deposition of colourless crystals. The supernatant is removed via syringe and the crystals are dried in vacuo, yielding 148 mg (0.20 mmol, 62%) of [P(μ-NTer)]$_2$(C$_2$H$_4$).

Mp: 262 °C (dec.). **EA** found (calc.): C 79.32 (80.62), H 7.64 (7.31), N 3.82 (3.76). **^{1}H NMR** (298 K, C$_6$D$_6$, 250.1 MHz): 0.68 (m, P-C*H*$_2$, 4H), 1.77 (s, *o*-C*H*$_3$, 24H), 2.30 (s, *p*-C*H*$_3$, 12H), 6.51 (d, *m*-C*H*, 4H) 6.65 (m, *p*-C*H*, 2H), 6.71 (s, m-C*H*, 8H). **^{13}C NMR** (298 K, C$_6$D$_6$, 62.9

MHz): 20.84 (t, J(P-C) = 2.0 Hz, *o*-*C*H3), 21.47 (s, *p*-*C*H3), 29.81 (s, C*H*2), 120.00 (s), 128.47 (s), 128.71 (s), 130.53 (s), 131.15 (s), 134.01 (s), 137.40 (s), 138.07 (t, J(C-P) = 3.0 Hz, *p*-*C*H). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 223.2. **IR** (ATR, cm^{-1}): 2944 (w), 2914 (w), 2853 (vw), 1610 (w), 1574 (vw), 1455 (vw), 1403 (w), 1372 (w), 1305 (w), 1229 (s), 1148 (w), 1125 (w), 1098 (vw), 1082 (w), 1020 (w), 982 (m), 892 (m), 845 (m), 806 (w), 793 (w), 769 (vw), 757 (w), 739 (w), 688 (w), 665 (vw), 640 (w), 607 (w), 587 (vw), 575 (vw), 553 (vw), 545 (w). **Raman** (784 nm, D0, 30s, 4 Acc., cm^{-1}): 3042 (7), 3014 (10), 2920 (22), 2857 (5), 2731 (3), 1615 (36), 1583 (26), 1484 (14), 1407 (18), 1382 (30), 1378 (22), 1306 (70), 1272 (16), 1190 (11), 1167 (9), 1162 (8), 1099 (9), 1090 (16), 1008 (22), 958 (6), 947 (9), 738 (14), 706 (6), 609 (72), 592 (23), 580 (100), 565 (55), 556 (25), 548 (31), 526 (36), 514 (15), 491 (13), 466 (10), 425 (17), 359 (7), 318 (10), 277 (31), 273 (33), 243 (30), 216 (8). **MS** (CI, pos., *iso*-butane) *m/z* (%): 315 (33) TerH$^+$, 330 (100) $TerNH_3^+$, 386 (53) $[(TerNP)C_2H_4]^+$, 705 (11), 716 (28) $[(TerNP)_2]^+$, 745 (81) $[(TerNP)_2C_2H_4+H]^+$, 801 (25) $[(TerNP)_2C_2H_4+C_4H_9]^+$.

3.9. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-2-thia-5,6-diaza-1,4-diphosphabicyclo[2.1.1]hexane-3-thione (10).

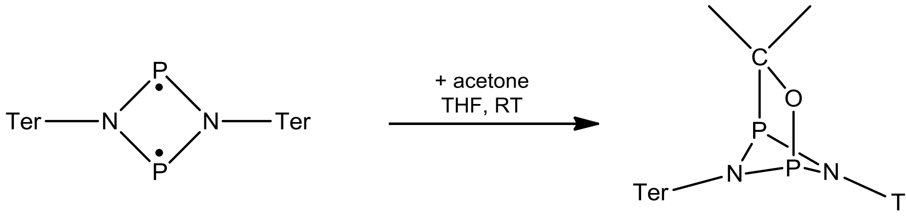


To solid $[P(\mu\text{-}NTer)]_2$ (0.110 g, 0.15 mmol) CS_2 (1 ml, 1.26 g, 16.55 mmol) was added resulting in a colour change from orange to green. Filtration (F4) and removal of excess CS_2 yields 0.121 g (0.15 mmol, 99%) of $[P(\mu\text{-}NTer)]_2CS_2$ as green microcrystalline solid. For further purification the crude product was recrystallized from a 10:1 CS_2:toluene solution at –40 °C yielding 0.115 g (0.14 mmol, 95%) of $[P(\mu\text{-}NTer)]_2CS_2$ as green crystals.

Mp.: 247 °C (dec.). **Anal. calc. % (found)**: C, 74.21 (73.94); H, 6.36 (6.57); N, 3.53 (3.55). **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 121.5 MHz): $\delta = 275.2$ (d, $^2J(^{31}P\text{-}^{31}P)$, = 23 Hz, N–*P*–C), $\delta = 195.1$ (d, $^2J(^{31}P\text{-}^{31}P)$ = 23 Hz, N–*P*–S). **^{1}H NMR** (25 °C, C_6D_6, 300.13 MHz): $\delta = 1.99$ (s, 6H, *o*-C*H3*), 2.04 (s, 6H, *o*-C*H3*), 2.28 (s, 6H, *p*-C*H3*), 6.67 (m, 3H, C*H*), 6.76 (s, 4H, *m*-Mes). **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 75.47 MHz): $\delta = 21.2$ (s, *o*-*C*H3), 21.5 (s, *p*-*C*H3), 122.7 (s, *C*H), 128.4 (s, *C*H), 129.3 (s, *C*H), 130.8 (s, *C*H), 131.1 (s), 135.4 (s), 136.1 (s), 138.1 (s), 138.2 (s), 138.8 (s). **IR** (ATR, 25 °C, 16 scans, cm^{-1}): 3042 (w), 2996 (w), 2971 (w), 2944 (m), 2912 (m), 2851 (m), 2729 (w), 1609 (m), 1579 (w), 1574 (w), 1567 (w), 1485 (w), 1454 (m), 1441 (m), 1434 (m), 1404 (s), 1373 (m), 1285 (w), 1270 (w), 1249 (m), 1240 (m), 1221 (s), 1163 (w), 1094 (s), 1081 (s), 1029 (m), 1005 (m), 946 (w), 900 (s), 850 (s), 843 (vs), 795 (s), 775 (m), 759 (s), 740 (s), 690 (m), 647 (w), 589 (w), 573 (w), 559 (m), 543 (w). **Raman** (460 mW, 25 °C, 150 scans, cm^{-1}): 3046 (4), 3013 (5), 2987 (3), 2916 (9), 2858 (3), 2733 (1), 1614 (7), 1582 (6), 1483 (2), 1425 (3), 1383 (4), 1306 (10), 1290 (4), 1250 (1), 1192 (1), 1163 (1), 1099 (4), 947 (1), 907 (1), 741 (1), 954 (3), 581 (9), 565 (5), 527 (2), 513 (1), 490 (2), 473 (2), 459 (1), 426 (2), 382 (2), 369 (1), 342 (1), 295 (3), 272 (3), 234 (2), 154 (3), 95 (8), 79 (6). **MS** (CI pos., *iso*-butane); m/z (%): 330 (100) $[\text{Ter–NH}_3]^+$, 386 (33) $[\text{Ter–NH} + \textit{iso}\text{-butane}]^+$, 687 (55) $[\text{Ter–N(H)PN(H)–Ter}]^+$, 716 (49) $[\text{M} - \text{CS}_2]^+$, 767 (40), 795 (5) $[\text{M} + 2\text{H}]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a 10:1 CS_2:toluene solution of $[\text{P}(\mu\text{-NTer})]_2\text{CS}_2$ to –40 °C.

3.10. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-3,3-dimethyl-2-oxa-5,6-diaza-1,4-diphosphabicyclo[2.1.1]hexane (11).



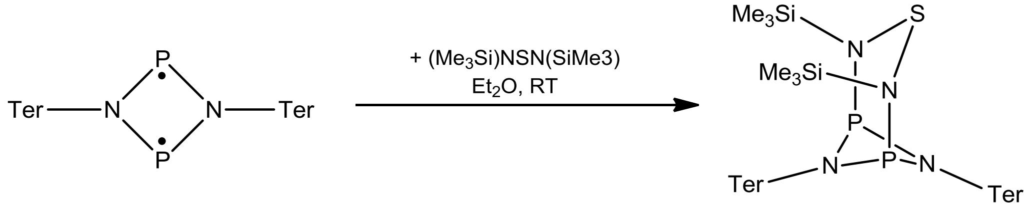
An excess of dry Acetone (1 mL) was added drop wise to a solution of $[\text{P}(\mu\text{-NTer})]_2$ (0.115 g, 0.16 mmol) in 5 mL of THF at ambient temperature. The initial orange solution was stirred 3 h at ambient temperature resulting in a colourless solution. The solvent and excess of acetone were removed and the resulting colourless residue was dried *in vacuo* yielding 0.115 g (0.14 mmol, 97%) of $[\text{P}(\mu\text{-NTer})]_2((\text{CH}_3)_2\text{CO})$ as a colourless microcrystalline solid.

Mp.: 220 °C (dec.). **Anal. calc. % (found)**: C, 79.04 (78.84); H, 7.28 (7.30); N, 3.61 (3.51). **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 121.5 MHz): $\delta = 216.2$ (d, $^{2}J(^{31}\text{P-}^{31}\text{P})$, = 13 Hz, N–*P*–C), $\delta = 185.9$ (d, $^{2}J(^{31}\text{P-}^{31}\text{P}) = 13$ Hz, N–*P*–O). **^{1}H NMR** (25 °C, C_6D_6, 300.13 MHz): $\delta = 1.11$ (d,

$^{3}J(^{1}\text{H}-^{31}\text{P}) = 9.5$ Hz, 6 H, PC(CH_3)$_2$). $\delta = 2.07$ (s, 12 H, *o*-CH_3), 2.20 (s, 12H, *o*-CH_3), 2.37 (s, 12H, *p*-CH_3), 6.67 (m, 6 H, C*H*), 6.78 (s, 8 H, *m*-Mes). **^{13}C{^{1}H} NMR** (25 °C, C_6D_6, 75.47 MHz): $\delta = 21.2$ (s, *o*-*C*H$_3$), 21.5 (s, *p*-*C*H$_3$), $\delta = 26.6$ (d, $^{2}J(^{13}\text{C}-^{31}\text{P}) = 14.3$ Hz, PC(*C*H$_3$)$_2$), $\delta = 84.5$ (dd, $^{1}\text{J}(^{13}\text{C}-^{31}\text{P}) = 34.6$ Hz, $^{2}J(^{13}\text{C}-^{31}\text{P}) = 5.5$ Hz (P*C*(CH$_3$)$_2$), 120.2 (s, *C*H), 128.8 (s), 129.2 (s, *C*H), 129.8 (s), 131.8 (s, *C*H), 136.7 (s), 137.0 (s), 138.0 (s), 140.4 (s). **IR** (ATR, 25 °C, 32 scans, cm^{-1}): 2997 (w), 2973 (w), 2945 (w), 2913 (m), 2852 (w), 2728 (w), 1611 (m), 1580 (w), 1574 (w), 1568 (w), 1485 (w), 1455 (m), 1434 (m), 1428 (w). 1405 (s), 1373 (m), 1336 (w), 1287 (w), 1266 (w), 1236 (m), 1223 (s), 1186 (w), 1143 (m), 1079 (m), 1029 (m), 1005 (m), 973 (w), 942 (m), 910 (m), 887 (s), 840 (vs), 810 (m), 793 (s), 776 (w), 754 (s), 717 (w), 695 (w), 686 (m), 666 (w), 647 (w), 617 (w), 595 (w), 588 (w), 574 (w), 560 (w), 550 (m), 534 (w).

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated toluene solution of [P(μ-NTer)]$_2$((CH$_3$)$_2$CO) to –40 °C.

3.11. Synthesis of 6,7-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-2,4-bis(trimethylsilyl)-3-thia-2,4,6,7-tetraaza-1,5-diphosphabicyclo[3.1.1]heptane (12).



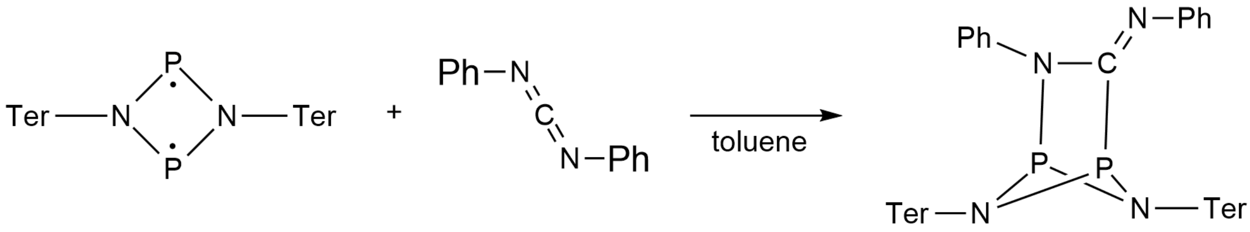
N,*N'*-bis(trimethylsilyl)sulphurdimide (0.035g, 0.17 mmol) was added drop wise to a solution of [P(μ-NTer)]$_2$ (0.110 g, 0.15 mmol) in 18 mL of Et$_2$O ambient temperature. The initial orange solution was stirred 5 min at ambient temperature resulting in a yellow solution. The solvent and excess of sulphurdiimide were removed *in vacuo* and the resulting colourless residue was dried *in vacuo* yielding 0.137 g (0.14 mmol, 97%) of [P(μ-NTer)]$_2$(S(NSiMe$_3$)) as a yellow microcrystalline solid.

Mp.: 214 °C (dec.). **Anal. calc. % (found)**: C, 70.22 (69.93); H, 7.42 (7.83); N, 6.07 (6.11). **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 121.5 MHz): $\delta = 214.7$ (s). **^{29}Si NMR** (25 °C, C_6D_6, 59.6 MHz):

1.5 (m, PN(*Si(*CH_3)$_3$). **IR** (ATR, 25 °C, 16 Scans, cm^{-1}): 2993 (w), 2967 (w), 2950 (m), 2914 (m), 2853 (w), 2727 (w), 1609 (m), 1575 (w), 1568 (w), 1494 (m), 1453 (w), 1445 (w), 1434 (w), 1399 (s), 1373 (m), 1291 (w), 1268 (w), 1244 (s), 1231 (s), 1221 (s), 1188 (m), 1165 (w), 1118 (w), 1102 (w), 1091 (m), 1032 (w), 1004 (w), 909 (s), 895 (m), 878 (s), 834 (vs), 791 (s), 753 (s), 740 (m), 688 (s), 647 (w), 635 (w), 592 (m), 577 (w), 552 (w), 538 (w). **MS** (CI pos., *iso*-butane); *m/z* (%): 207 (6) [$Me_3Si–NSN–SiMe_3$ + H]$^+$, 330 (82) [Ter–NH_3]$^+$, 386 (24) [Ter–NH + *iso*-butane]$^+$, 447 (100) [Ter–N(H)PN(H)–$SiMe_3$]$^+$, 477 (59) [(Ter–N)P($NSiMe_3$)S]$^+$, 519 (41), 551 (16), 687 (5) [Ter–N(H)PN(H)–Ter]$^+$, 716 (12) [M – Me_3Si–NSN–$SiMe_3$]$^+$, 923 (21) [M]$^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated *n*-hexane solution of [P(μ-NTer)]$_2$(S($NSiMe_3$)) to –40 °C.

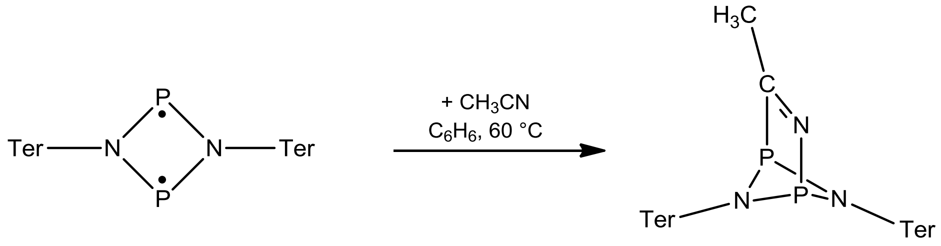
3.12. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-3-(phenylimino)-2,5,6-triaza-1,4-diphosphabicyclo[2.1.1]hexane (13).



To a stirred solution of [P(μ-NTer)]$_2$ (168 mg, 0.19 mmol) in 4 ml toluene, a solution of freshly prepared diphenylcarbodiimide (41 mg, 0.21 mmol) in 1 ml toluene is added dropwise at room temperature. The initially orange solution changes its colour to yellow in the process. The reaction can be monitored by ^{31}P NMR spectroscopy. After completion of the addition, the mixture is stirred overnight, filtered (G4), and then concentrated until crystallisation commences. The solution is then left undisturbed overnight, which leads to the deposition of colourless crystals. The supernatant is removed via syringe and the solid is dried *in vacuo.*, yielding 62 mg (0.06 mmol, 26%) of [P(μ-NTer)]$_2$(PhNCNPh) · 1.125 C_7H_8.

Mp: 191 °C (dec.). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 2.08 (s, 6 H, CH_3), 2.13 (s, 6 H, CH_3), 2.15 (s, 6 H, CH_3), 2.21 (s, 6 H, CH_3), 2.27 (s, 6 H, CH_3), 2.35 (s, 6 H, CH_3), 6.67 (s, 8 H, *p*-CH_{Mes}), 6.72-6.76 (m, 6 H, *m/p*-CH_{Ter}), 6.95-7.02 (s, 4 H, CH_{Ph}), 7.07-7.18 (s, 6 H, CH_{Ph}). **^{13}C NMR** (298 K, C_6D_6, 62.9 MHz): 21.07 (s, CH_3), 21.20 (s, CH_3), 21.23 (s, CH_3), 21.31 (s, CH_3), 21.33 (s, CH_3), 21.54 (s, CH_3), 121.60 (s, CH), 123.76 (s, CH), 125.48 (s, CH), 128.85 (s, CH), 128.91 (s, CH), 128.94 (s, CH), 129.03 (s, CH), 129.40 (s, CH), 130.71 (s, CH), 130.85 (s, CH), 130.93 (s, CH), 131.44 (s), 132.37 (s), 136.31 (s), 136.64 (s), 137.56 (s), 137.71 (s), 138.57 (dd, *J*(C-P) = 1.7 Hz, *J*(C-P) = 4.4 Hz), 138.11 (dd, *J*(C-P) = 2.2 Hz, *J*(C-P) = 4.9 Hz) 141.07 (s), 141.27 (s), 149.66 (d, *J*(C-P) = 3.3 Hz), 153.26 (dd, *J*(C-P) = 14.3 Hz, *J*(C-P) = 1.9 Hz), 187.84 (dd, ^1J(C-P) = 59 Hz, ^2J(C-P) = 3.9 Hz, P-N-*C*-P). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 207.0 (d, $^2J_{PP}$ = 7 Hz), 226.6 (d, $^2J_{PP}$ = 7 Hz). **Raman** (633 nm, D1, 50s, 5 Acc., cm^{-1}): 3038 (14), 3010 (23), 2965 (14), 2940 (19), 2912 (47), 2850 (15), 2726 (4), 1639 (62), 1594 (80), 1561 (100), 1534 (38), 1511 (36), 1479 (15), 1463 (13), 1433 (27), 1429 (26), 1408 (23), 1335 (40), 1303 (19), 1276 (27), 1261 (27), 1249 (49), 1228 (16), 1200 (7), 1182 (8), 1159 (17), 1135 (11), 1096 (7), 1022 (8), 999 (57), 951 (2), 890 (3), 750 (5), 739 (6), 706 (17), 611 (5), 563 (8), 530 (9), 513 (6), 450 (3), 402 (6).

3.13. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-3-methyl-2,5,6-triaza-1,4-diphosphabicyclo[2.1.1]hex-2-ene (14).

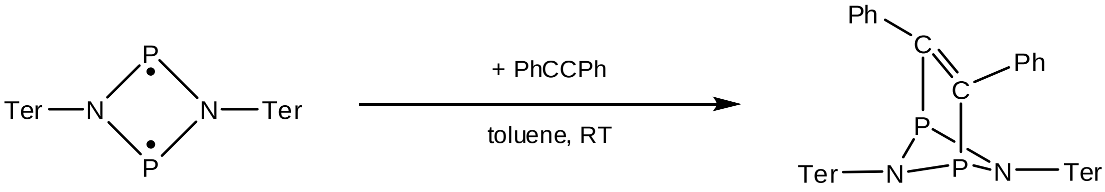


An excess of dry acetonitrile (3 mL) was added to a solution of [P(μ-NTer)]$_2$ (0.110 g, 0.15 mmol) in 3 mL of benzene at ambient temperature. The orange solution was stored without stirring 30 days at 60 °C resulting in a yellowish solution with orange crystals grown within. The solvent excess of acetonitrile were removed and the resulting orange crystals were dried *in vacuo* yielding 0.10 g (0.14 mmol, 94%) of [P(μ-NTer)]$_2$(CH_3CN) as an orange crystalline solid.

Mp.: 260 °C (dec.). **Anal. calc. % (found)**: C, 79.23 (79.46); H, 7.05 (7.14); N, 5.54 (5.35). **^{31}P{^{1}H} NMR** (25 °C, C_6D_6, 121.5 MHz): δ = 206.8 (d, ^2J(^{31}P-^{31}P) = 12 Hz, N–*P*–CN), δ = 187.1 (d, ^2J(^{31}P-^{31}P) = 12 Hz, N–*P*–NC). **^{1}H NMR** (25 °C, C_6D_6, 300.13 MHz): δ = 2.04 (s, 12H, *o*-C*H*$_3$), 2.06 (s, 12H, *o*-C*H*$_3$), δ = 2.10 (s, 3H, NCC*H*$_3$), 2.32 (s, 12H, *p*-C*H*$_3$), 6.74 (m, 6H, C*H*), 6.79 (s, 8H, *m*-Mes). **IR** (ATR, 25 °C, 16 scans, cm^{-1}): 2996 (w), 2972 (w), 2944 (w), 2914 (m), 2853 (w), 2728 (w), 1610 (m), 1580 (w), 1574 (w), 1568 (w), 1485 (w), 1448 (m), 1434 (m), 1403 (s), 1375 (m), 1259 (m), 1232 (s), 1188 (m), 1123 (w), 1086 (m), 1070 (w), 1032 (w), 1005 (w), 984 (m), 946 (w), 931 (w), 894 (m), 844 (vs), 803 (w), 793 (m), 783 (w), 749 (s), 731 (m), 691 (m), 666 (w), 647 (w), 628 (w), 605 (w), 596 (w), 573 (w), 561 (w), 550 (w), 536 (m), 528 (m).

Crystals suitable for X-ray crystallographic analysis were obtained directly from the benzene/acetonitrile reaction solution.

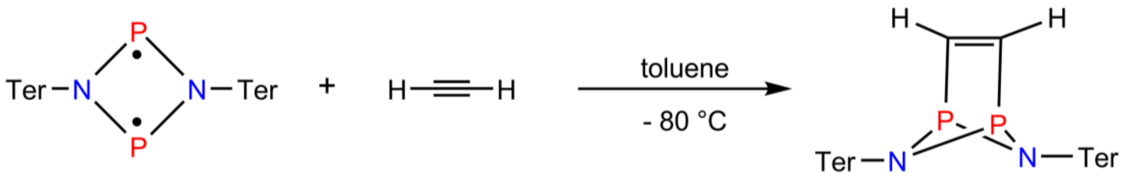
3.14. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-2,3-diphenyl-5,6-triaza-1,4-diphosphabicyclo[2.1.1]hex-2-ene (15Ph).



To a stirred solution of [P(μ-NTer)]$_2$ (137 mg, 0.19 mmol) in 2.5 ml toluene, a solution of diphenylacetylene (34 mg, 0.19 mmol) in 1.5 ml toluene is added dropwise at room temperature. The initially orange solution immediately changes its colour to yellow. The reaction can be monitored by ^{31}P NMR spectroscopy and is quantitative by this respect. After completion of the addition, the mixture is concentrated until crystallisation commences. The solution is then left undisturbed overnight, which leads to the deposition of yellow crystals. The supernatant is removed via syringe and the solid is dried *in vacuo*, yielding 108 mg (0.12 mmol, 65%) of [P(μ-NTer)]$_2$(C$_2$Ph$_2$).

Mp: 256 °C (dec.). **EA** found (calc.): C 81.91 (82.19), H 6.80 (6.76), N 3.33 (3.13). **^{1}H NMR** (298 K, CD$_2$Cl$_2$, 250.1 MHz): 1.81 (s, 24 H, *o*-C*H*$_3$), 2.32 (s, 12 H, *p*-C*H*$_3$), 6.55 (d, 4 H, *m*-C*H*$_{\text{Mes}}$), 6.59 (s br, 8 H, *m*-*C*H$_{\text{Mes}}$), 6.70 (m, 2 H, *p*-C*H*$_{\text{Mes}}$), 6.99 (m, 4 H, C*H*$_{\text{Ph}}$), 7.07-7.24 (m, 6 H, C*H*$_{\text{Ph}}$). **^{13}C NMR** (298 K, CD$_2$Cl$_2$, 62.9 MHz): 21.38 (s, *o*-*C*H$_3$), 21.55 (s, *p*-*C*H$_3$), 119.95 (s, *p*-*C*H$_{\text{Mes}}$), 127.61 (s, *C*H), 128.02 (s, *C*H), 128.27 (s, *C*H), 128.33 (s, *C*H), 128.40 (s), 128.58 (s, *m*-*C*H$_{\text{Mes}}$), 128.75 (s), 129.39 (t, J(^{13}C-^{31}P) = 2.2 Hz), 129.51 (s), 131.94 (s), 136.40 (d, J(^{13}C-^{31}P) = 2.7 Hz), 136.74 (d, J(^{13}C-^{31}P) = 2.3 Hz), 137.00 (t, J(^{13}C-^{31}P) = 2.3 Hz), 137.16 (s), 137.46 (t, J(^{13}C-^{31}P) = 1.8 Hz), 137.76 (t, J(^{13}C-^{31}P) = 2.9 Hz), 171.09 (dd, ^1J(^{13}C-^{31}P) = 50 Hz, ^2J(^{13}C-^{31}P) = 8.5 Hz, P-*C*=*C*-P). **^{31}P NMR** (298 K, CD$_2$Cl$_2$, 121.5 MHz): 246.2. **IR** (ATR, 25 °C, cm^{-1}): 3051 (vw), 3014 (vw), 2991 (vw), 2964 (w), 2941 (w), 2914 (w), 2874 (vw), 2852 (w), 1610 (w), 1581 (vw), 1574 (vw), 1495 (vw), 1483 (w), 1456 (w), 1441 (w), 1435 (w), 1404 (m), 1375 (m), 1286 (vw), 1267 (vw), 1225 (m), 1159 (cw), 1090 (w), 1028 (w), 1011 (vw), 984 (vw), 955 (vw), 939 (vw), 891 (w), 845 (m), 835 (m), 801 (w), 795 (m), 781 (w), 752 (m), 735 (w), 717 (vw), 689 (m), 667 (vw), 650 (vw), 638 (vw), 613 (vw), 598 (vw), 588 (vw), 561 (w), 552 (vw), 536 (w). **Raman** (784 nm, D0, 30s, 4 Acc., cm^{-1}): 3061 (10), 3024 (5), 2920 (15), 2856 (5), 1614 (35), 1597 (100), 1587 (47), 1578 (34), 1559 (76), 1485 (21), 1442 (24), 1419 (20), 1384 (26), 1378 (25), 1308 (49), 1289 (28), 1264 (33), 1193 (10), 1187 (13), 1162 (24), 1157 (30), 1145 (38), 1105 (12), 1032 (16), 1003 (88), 989 (7), 946 (10), 848 (5), 774 (5), 747 (12), 707 (6), 622 (17), 617 (17), 581 (67), 565 (48), 554 (19), 545 (16), 526 (20), 516 (10), 486 (8), 474 (10), 426 (9), 297 (4), 286 (9), 274 (17), 264 (23), 243 (27). **MS** (CI, pos., *iso*-butane) *m*/*z* (%): 235 (18) [PhCCPh+C$_4$H$_9$]$^+$, 315 (59) [TerH+H]$^+$, 330 (47) TerNH$_3^+$, 386 (57) [TerNH$_2$+C$_4$H$_9$]$^+$, 568 (80) [TerNP$_2$(PhCCPh)+H]$^+$, 687 (14) [Ter$_2$N$_2$PH]$^+$, 716 (100) [(TerNP)$_2$]$^+$, 895 (78) [M+H]$^+$, 951 (28) [M+C$_4$H$_9$]$^+$.

3.15. Synthesis of 5,6-bis[2,6-bis(2,4,6-trimethylphenyl)phenyl]-5,6-triaza-1,4-diphosphabicyclo[2.1.1]hex-2-ene (15H).



To a solution of [P(μ-NTer)]$_2$ (192 mg, 0.27 mmol) in toluene (4 ml), a solution of acetylene in toluene (5 ml) is quickly added at –80 °C. The initially orange solution discolours immediately, is stirred for further 15 minutes at –80 °C and then warmed to ambient temperature. A colourless solid precipitates. The reaction is quantitative by respect of ^{31}P NMR spectroscopy. To the suspension, 30 ml of toluene are added, which is then warmed to approx. 50 °C. Afterwards, the suspension is filtered and the filtrate cooled to 4°C, which results in the formation of colourless crystals in good yield (174 mg, 0.23 mmol, 87%).

Mp: 243 °C (dec.). **EA** found (calc.): C 80.08 (80.84), H 7.11 (7.06), N 3.97 (3.77). **^{1}H NMR** (298 K, CD$_2$Cl$_2$, 250.1 MHz): 1.79 (s, 24 H, *o*-C*H*$_3$), 2.41 (s, 12 H, *p*-C*H*$_3$), 6.61 (d, $^1J_{HH}$ = 7.4

Hz, 4 H, *m*-C*H*), 6.71 (m, 2 H, *p*-C*H*), 6.79 (s, 8 H, *m*-CH_{Mes}), 7.69 (m, AA'XX', $J_{AA'}$ = 7.9 Hz, $J_{AX'}$ = 50.0 Hz, J_{AX} = 9.7 Hz, $J_{XX'}$ = -10.9 Hz). **^{13}C{^{1}H} NMR** (298 K, CD_2Cl_2, 62.9 MHz): 20.81 (s, *o*-*C*H_3), 21.52 (s, *p*-*C*H_3), 120.12 (s, *C*H), 125.66 (s, *C*H), 128.46 (s, *C*H), 129.39 (s, *C*H), 129.99 (s, *C*H), 130.78 (t, J_{CP} = 2.5 Hz, *C*H), 136.32 (t, J_{CP} = 2.7 Hz), 137.50 (s), 138.32 (t, J_{CP} = 3.3 Hz), 168.05 (dd, $^{1}J_{CP}$ = 59.4 Hz, $^{2}J_{CP}$ = 6.6 Hz, P*CC*P). **^{31}P NMR** (298 K, CD_2Cl_2, 121.5 MHz): 212.3 (m, AA'XX', $J_{AA'}$ = 7.9 Hz, $J_{AX'}$ = 50.0 Hz, J_{AX} = 9.7 Hz, $J_{XX'}$ = -10.9 Hz). **IR** (ATR, cm^{-1}): 3057 (vw), 3028 (w), 2999 (w), 2968 (w), 2945 (w), 2914 (m), 2852 (w), 2727 (vw), 1610 (w), 1579 (w), 1483 (w), 1454 8w), 1429 (w), 1406 (s), 1371 (m), 1292 (w), 1269 (vw), 1254 (w), 1228 (s), 1200 (w), 1080 (m), 1030 (w), 1005 (w), 959 (vw), 947 (vw), 914 (vw), 887 (s), 858 (w), 845 (s), 835 (s), 810 (w), 795 (m), 768 (w), 756 (s), 729 (m), 689 (s), 654 (s), 640 (s), 617 (w), 602 (vw), 584 (vw), 575 (w), 561 (vw), 546 (w), 538 (w). **Raman** (784 nm, cm^{-1}): 3038 (18), 3009 (16), 2949 (13), 2913 (41), 2854 (9), 2728 (4), 1610 (57), 1580 (48), 1479 (14), 1434 (20), 1411 (23), 1379 (36), 1302 (89), 1282 (45), 1246 (12), 1230 (11), 1185 (12), 1163 (10), 1095 (10), 1081 (33), 1028 (5), 1003 (35), 984 (8), 943 (13), 922 (2), 907 (2), 865 (4), 808 (3), 784 (5), 754 (6), 734 (24), 713 (4), 701 (4), 683 (3), 662 (5), 628 (4), 572 (100), 558 (63), 547 (31), 520 (45), 511 (50), 496 (15), 477 (8), 456 (34), 418 (46), 375 (11), 332 (100), 304 (26), 270 (35), 260 (39), 236 (59). **MS** (CI, pos., *iso*-butane) *m*/*z* (%): 330 (50) $[TerNH_3]^+$, 360 (18), 386 (11) $[TerNH_2+C_4H_9]^+$, 416 (14), 743 (100) $[M+H]^+$, 799 (16) $[M+C_4H_9]^+$.

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