SUPPLEMENTARY INFORMATION

Concerted addition of aldehydes to the singlet biradical $[P(\mu\text{-NTer})]_2$

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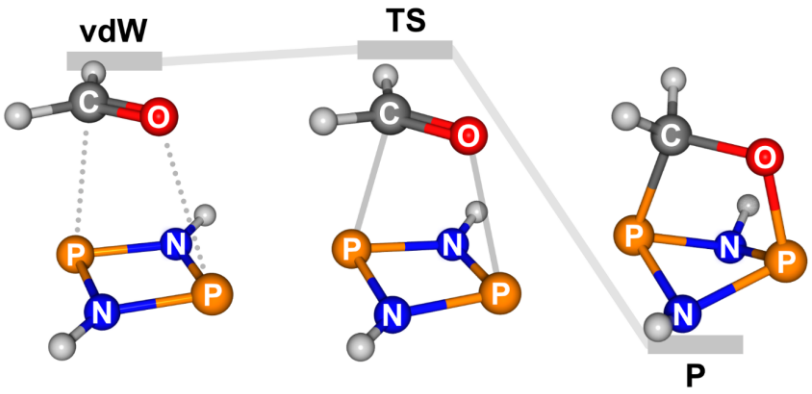

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1 Experimental

General Information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk or Drybox techniques. All glassware was heated three times *in vacuo* using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, which were purged three times with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
benzene, toluene	local trade	dried over Na/benzophenone freshly distilled prior to use
THF	local trade	dried over Na/benzophenone freshly distilled prior to use
PhCHO	local trade	dried over molecular sieve freshly distilled prior to use
EtCHO	local trade	dried over molecular sieve freshly distilled prior to use
$C_6H_4NO_2CHO$	old stock	sublimed
C_6H_4ClCHO	old stock	sublimed
C_6D_6	euriso-top	dried over Na freshly distilled prior to use
C_7D_8	euriso-top	dried over Na freshly distilled prior to use
$[P(\mu\text{-NTer})]_2$ (**1**)	synthesized[1]	used as synthesized
KO*t*Bu	old stock	sublimed

NMR spectra were recorded on Bruker spectrometers AVANCE 250, AVANCE 300 or AVANCE 500 and were referenced internally to the deuterated solvent (C_6D_6 $\delta_{ref.}$ = 128.06 ppm, $\delta_{ref.,2}$ = 67.21 ppm, toluene-d_8 $\delta_{ref.,1}$ = 20.40 ppm, $\delta_{ref.,2}$ = 125.49 ppm), to protic impurities in the deuterated solvent (^{1}H: C_6HD_5 $\delta_{ref.}$ = 7.16 ppm, $\delta_{ref,2}$ = 3.58 ppm, toluene-d_7 $\delta_{ref,1}$ = 2.09 ppm, $\delta_{ref,2}$ = 6.98 ppm)[2] or externally (^{31}P: 85% H_3PO_4 $\delta_{ref.}$ = 0 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable).

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: very weak (vw, 0–10%), weak (w, 10–30%), medium (m, 30–60%), strong (s, 60–90%), very strong (vs, 90–100%).

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by a red laser (633 nm, 17 mW, air-cooled HeNe laser). All measurements were carried out at ambient temperature unless stated otherwise.

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyser.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 20 °C/min. Clearing points are reported.

Mass spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples.

2 Structure elucidation

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K during measurement. The data were collected on a Bruker D8 Quest diffractometer or a Bruker Kappa Apex II diffractometer using Mo K_α radiation (λ = 0.71073 Å). The structures were solved by iterative methods (SHELXT)[3] and refined by full matrix least squares procedures (SHELXL).[4] Semi-empirical absorption corrections were applied (SADABS).[5] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Table S2: Crystallographic details of **2** · 0.5 C_6H_6, **3** · 0.5 C_7H_8, **4**.

Compound	**2** · 0.5 C_6H_6	**3** · 0.5 C_7H_8	**4**
Chem. Formula	$C_{55}H_{56}N_2OP_2 \cdot 0.5\ C_6H_6$	$C_{55}H_{55}N_3O_3P_2 \cdot 0.5(C_7H_8)$	$C_{55}H_{55}ClN_2OP_2$
Formula weight [g/mol]	862.01	914.02	857.40
Colour	colourless	yellow	colourless
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	11.8530(5)	12.0792(9)	12.060(3)
b [Å]	24.4713(9)	16.788(1)	24.498(6)
c [Å]	16.8584(6)	27.116(2)	16.669(4)
α [°]	90	73.506(2)	90
β [°]	108.606(2)	78.572(2)	110.821(5)
γ [°]	90	70.114(2)	90
V [Å^3]	4634.3(3)	4926.5(6)	4603(2)
Z	4	4	4
$\rho_{calcd.}$ [g/cm^3]	1.235	1.232	1.237
μ [mm^{-1}]	0.138	0.137	0.194
T [K]	123(2)	123(2)	123(2)
Measured reflections	106140	163409	91246
Independent reflections	14743	17319	13415
Reflections with $I > 2\sigma(I)$	10397	13871	9680
R_{int}	0.0895	0.0705	0.0734
$F(000)$	1836	1940	1816
$R_1(R[F^2>2\sigma(F^2)])$	0.0489	0.0714	0.0487
w$R_2(F^2)$	0.1299	0.1788	0.1269
GooF	1.014	1.115	1.016
No. of Parameters	599	1160	562
CCDC #	2125924	2125926	2125927

Table S3: Crystallographic details of **5**, **6**.

Compound	**5**	**6**
Chem. Formula	$C_{51}H_{56}N_2OP_2$	$C_{59}H_{65}KN_2O_2P_2$
Formula weight [g/mol]	774.91	935.17
Colour	colourless	colourless
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	11.909(5)	16.750(2)
b [Å]	21.941(9)	17.111(2)
c [Å]	16.937(7)	17.953(2)
α [°]	90	90
β [°]	108.673(9)	94.172(2)
γ [°]	90	90
V [Å^3]	4193(3)	5131.7(9)
Z	4	4
$\rho_{calcd.}$ [g/cm^3]	1.228	1.210
μ [mm^{-1}]	0.144	0.210
T [K]	123(2)	123(2)
Measured reflections	97316	106650
Independent reflections	13359	18574
Reflections with $I > 2\sigma(I)$	10208	13393
R_{int}	0.0581	0.0699
$F(000)$	1656	1992
$R_1(R[F^2>2\sigma(F^2)])$	0.0464	0.0498
w$R_2(F^2)$	0.1272	0.1290
GooF	1.047	1.032
No. of Parameters	518	610
CCDC #	2125925	2125928

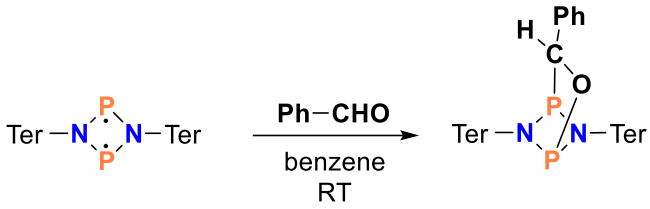
Table S4: Selected bond lengths [Å], angles and dihedral angles [°] in the solid state.

	2	**3**	**4**	**5**	**6**
P–N	1.734(2)–1.776(1)	1.727(4)–1.774(4)	1.739(2)–1.776(2)	1.736(1)–1.770(1)	1.650(1)–1.826(1)
P–C	1.911(2)	1.927(4)	1.916(1)	1.900(2)	1.885(1)
P–O	1.672(1)	1.680(2)	1.673(2)	1.656(1)	1.676(1), 1.670(1)[a]
C–O	1.450(2)	1.455(5)	1.455(2)	1.451(2)	1.439(2), 1.465(2)[b]
N–P–N	78.81(6), 79.90(6)	79.1(1), 80.1(2)	78.87(6), 79.74(6)	78.79(5), 79.52(5)	102.30(6)
P–N–P	90.88(6), 92.40(6)	90.8(1), 92.7(2)	90.85(6), 92.33(6)	91.57(5), 91.32(5)	115.84(6)
N–P–P–N	132.72(1)	133.5(2)	132.47(9)	131.73(8)	100.04(8)

[a] P–O(*t*Bu), [b] O–C(Me_3)

3 Syntheses of compounds

3.1 [P(μ-NTer)]$_2$·PhCHO (2)



PhCHO (30 mg, 0.28 mmol) is added to a solution of [P(μ-NTer)]$_2$ (200 mg, 0.28 mmol) in benzene (10 mL) at RT with a microliter syringe, resulting in an immediate colour change from orange to light yellow. The reaction mixture is stirred for further three hours. After the reaction time, all volatile components are removed *in vacuo* (1×10^{-3} mbar) at 50 °C (water bath). The residue is dissolved in fresh benzene and insoluble solids are removed by filtration over celite. The clear solution is concentrated *in vacuo* (1×10^{-3} mbar) to incipient crystallization and stored overnight. After removal of the supernatant colourless crystals remain. **Yield:** 193 mg (0.234 mmol, 84 %).

Mp. 138-143 °C. **CHN** calcd. (found) in %: C 80.27 (79.70), H 6.86 (6.56), N 3.40 (3.22). **^{31}P{^{1}H} NMR** (toluene-*d8*, 121.5 MHz) δ = 178.5 (d, $^{2}J(^{31}P, ^{31}P)$ = 15 Hz, 1 P, *P*-CH), 214.9 (d, $^{2}J(^{31}P, ^{31}P)$ = 15 Hz, 1 P, *P*-O). **^{1}H NMR** (toluene-*d8*, 300.1 MHz): δ = 1.61 (s, 6 H, *o/p*-C*H*$_3$), 2.04 (s, 6 H, *o/p*-C*H*$_3$), 2.09 (s, 6 H, *o/p*-C*H*$_3$), 2.11 (s, 6 H, *o/p*-C*H*$_3$), 2.35 (s, 6 H, o/*p*-C*H*$_3$), 2.38 (s, 6 H, o/*p*-C*H*$_3$), 4.86 (d, ^{2}J (^{1}H-^{31}P) = 11.3 Hz, 1 H, OC*H*), 6.56-7.06 (14 H (*Ter*), 5 H (*Ph*CHO)). **^{13}C{^{1}H} NMR** (toluene-*d8*, 75.5 MHz) δ =20.9 (s, o/*p*-CH$_3$) 21.3 (s, o/*p*-CH$_3$), 21.4 (s, o/*p*-CH$_3$), 21.6 (s, o/*p*-CH$_3$), 120.8 (s, *C*H (arom.)), 121.2 (s, *C*H (arom.)), 126.7 (s, *C*H (arom.)), 127.4 (s, *C*H (arom.)), 128.1 (s, *C*H (arom.)), 129.0 (s, *C*H (arom.)), 129.1 (s, *C*H (arom.)), 130.2 (s, *C*H (arom.)), 130.9 (s, *C*H (arom.)), 131.3 (s, *C*H (arom.)), 136.8 (s, *C*H (arom.)), 137.2 (s, *C*H (arom.)). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2912(m), 2853 (w), 1610 (w), 1581 (w), 1482 (w), 1402 (s), 1375 (m), 1290(w), 1224

(vs), 1148 (m), 1082 (m), 1031 (w), 934 (m), 897 (s), 843 (vs), 791(m), 769 (m), 754 (s), 732 (m), 705 (vs), 690 (s), 658 (m), 567 (m), 478 (m), 462 (m), 439 (s). **Raman** (633 nm, 15 s, 20 scans, cm^{-1}): $\tilde{\nu}$ =3130 (1), 3083 (1), 3070 (2), 3046 (2), 3008 (2), 2967 (1), 2947 (2), 2918 (5), 2855 (1), 2729 (1), 1703 (1), 1612 (4), 1604 (4), 1581 (2), 1498 (1), 1482 (1), 1438 (2), 1421 (1), 1405 (1), 1383 (2), 1377 (2), 1344 (1), 1303 (8), 1283 (2), 126 (4), 1249 (1), 1238 (1), 1227 (1), 1209 (3), 1188 (1), 1172 (1), 1165 (1), 1159 (1), 1149 (2), 1099 (1), 1090 (1), 1032 (1), 102 (10), 1004 (6), 993 (3), 945 (1), 845 (1), 743 (1), 735 (1), 727 (1), 705 (1), 693 (1), 657 (2), 620 (2), 616 (2), 592 (2), 580 (7), 568 (3), 559 (2), 551 (1), 546 (2), 536 (1), 523 (2), 511 (1), 504 (1), 474 (1), 461 (1), 422 (1), 379 (1), 352 (1), 338 (1), 326 (1), 285 (1), 266 (2), 233 (2), 219 (1), 188 (1), 155 (2). **MS** (CI, pos., isobutane) *m/z*: 823 $[MH]^+$, 716 $[(TerNP)_2]^+$, 418 $[TerNCHPhH]^+$, 330 $[TerNH_3]^+$, 107 $[PhCHOH]^+$.

Single crystals suitable for X-ray diffraction can be grown from saturated benzene solution at ambient temperature.

Figure S1: NMR, IR and Raman spectra of $[P(\mu\text{-NTer})]_2 \cdot PhCHO$ (solvent signals indicated by asterisks).

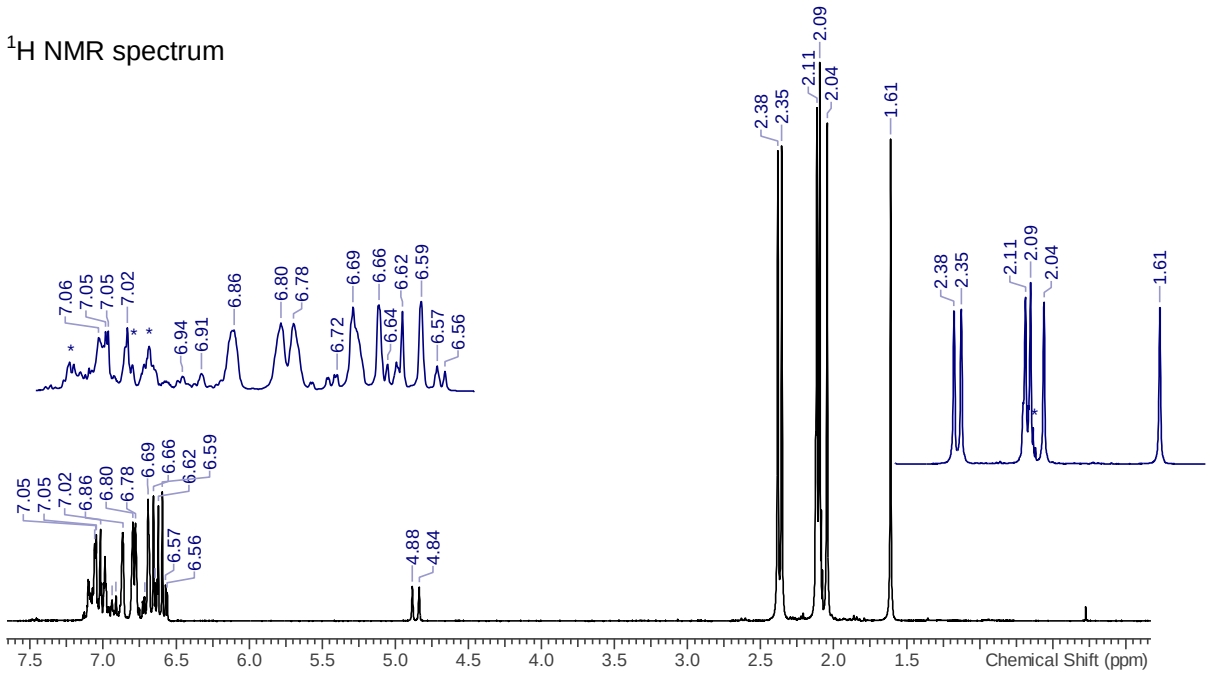
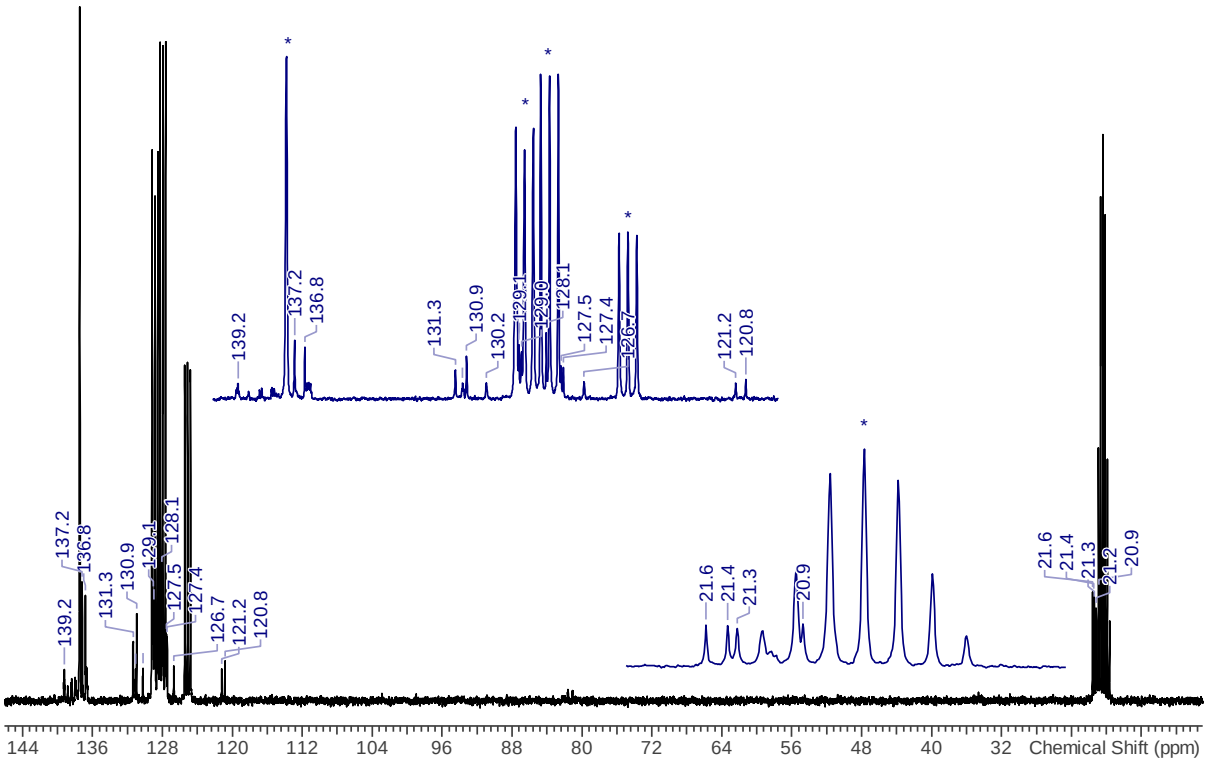


Figure S1 continued.

^{13}C NMR spectrum



^{31}P NMR spectrum

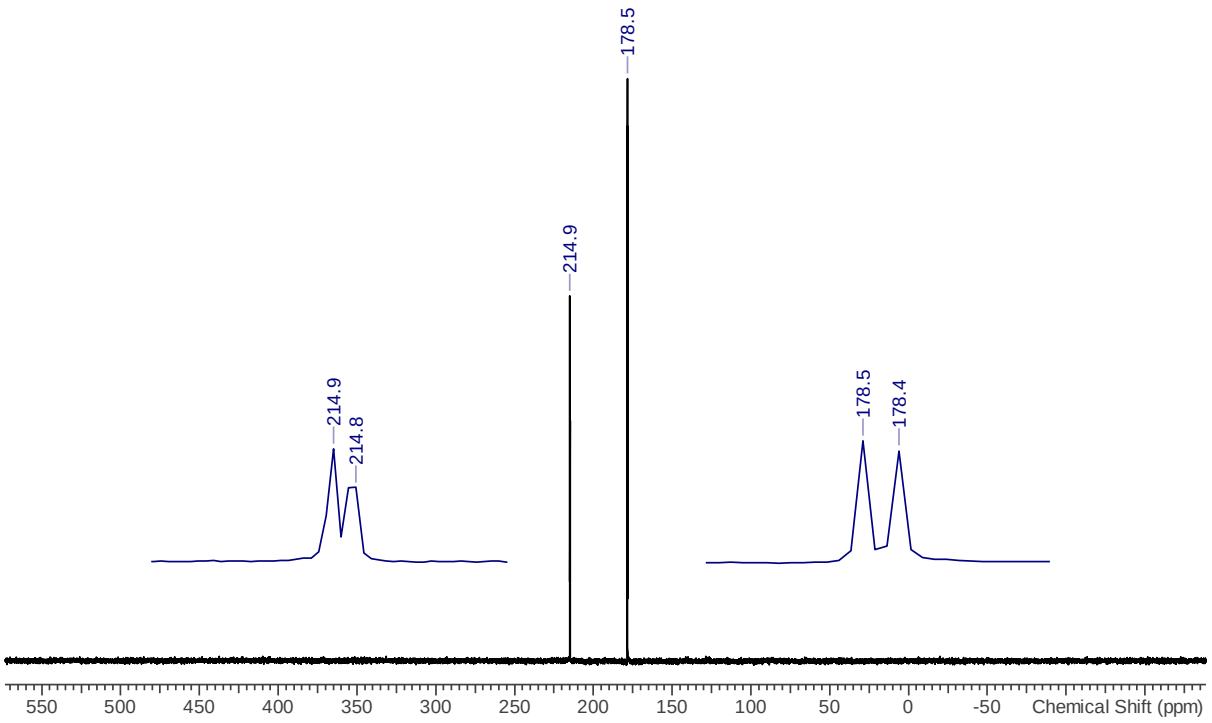
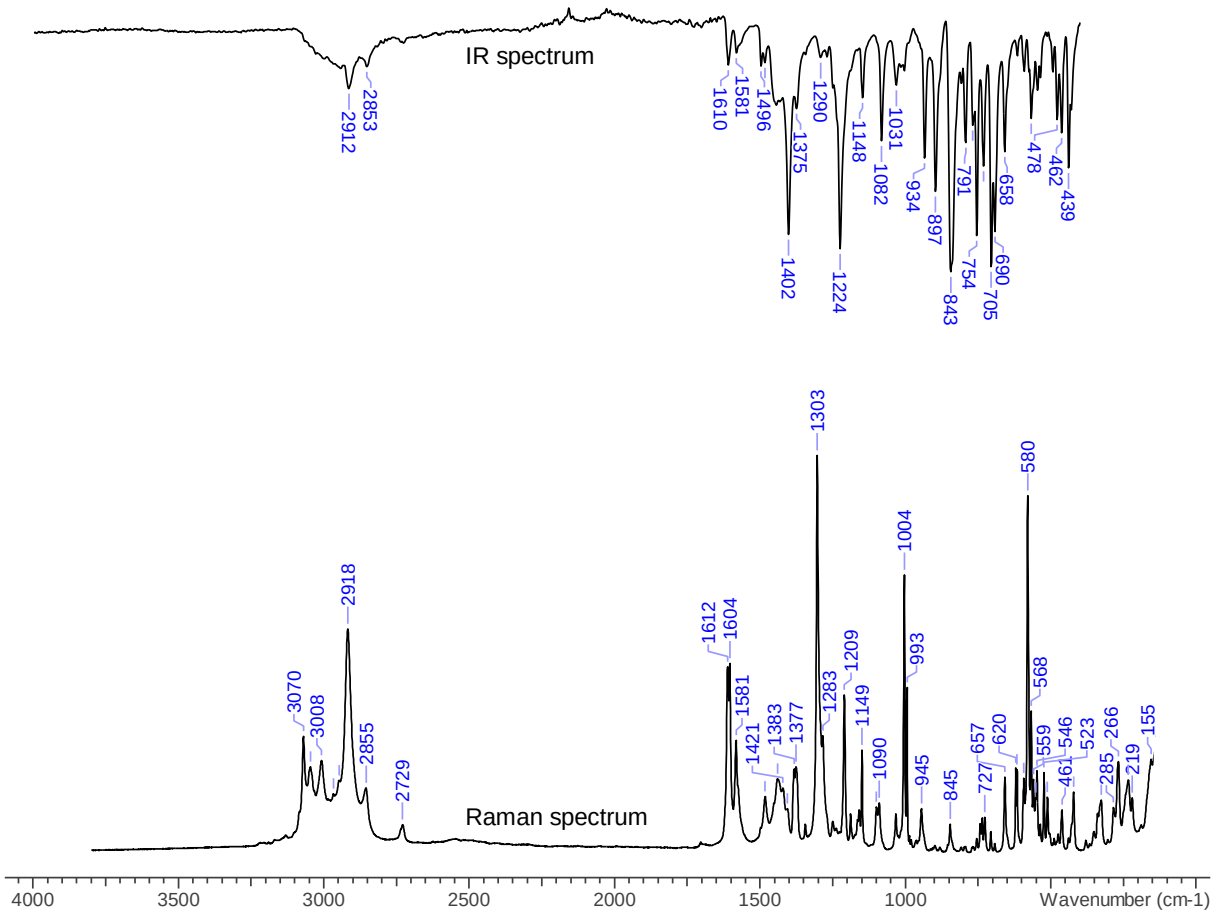
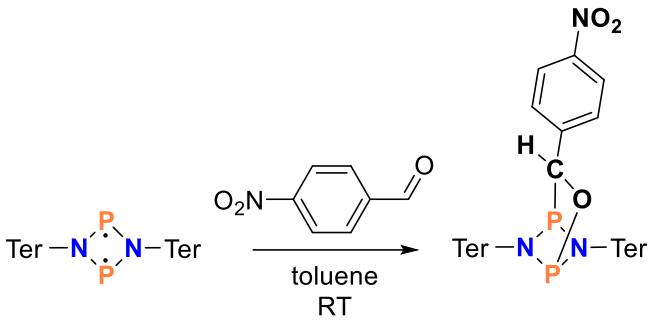


Figure S1 continued.



3.2 [P(μ-NTer)]$_2$ · $C_6H_4NO_2CHO$ (3)



p-Nitrobenzaldehyde (42.1 mg, 0.28 mmol) and [P(μ-NTer)]$_2$ (200 mg, 0.28 mmol) are dissolved in toluene (10 mL) at RT, resulting in a brown solution that is stirred for three hours. After the reaction time, all volatile components are removed *in vacuo* (1×10^{-3} mbar) at 50 °C (water bath). The residue is dissolved in fresh toluene and insoluble solids are removed by filtration over celite. The clear solution is concentrated *in vacuo* (1×10^{-3} mbar) to incipient crystallization and stored overnight. Brown crystals can be obtained. **Yield:** 140 mg (0.16 mmol, 57 %).

Mp. 150-155 °C **CHN** calcd. (found) in %: C 76.11 (75.83), H 6.39 (6.56), N 4.84 (4.72). **^{31}P{^{1}H} NMR** (toluene-*d8*, 121.5 MHz): δ = 180.1 (d, $^2J(^{31}P, ^{31}P)$ = 17 Hz, 1 P, *P*-CH), 216.6 (d, $^2J(^{31}P, ^{31}P)$ = 17 Hz, 1 P, *P*-O). **^{1}H NMR** (toluene-*d8*, 300.1 MHz): δ = 1.44 (s, 6 H, *o/p*-CH_3), 2.00 (s, 6 H, *o/p*-CH_3), 2.03 (s, 6 H, *o/p*-CH_3), 2.06 (s, 6 H, *o/p*-CH_3), 2.34 (s, 6 H, o/*p*-CH_3), 2.35 (s, 6 H, o/*p*-CH_3), 4.76 (d, $^2J(^1H, ^{31}P)$ =10.7 Hz, 1H, OC*H*PhNO$_2$), 6.47-7.03 (14H, Ter, 2H, *Ph*NO$_2$), 7.90 (s, 1H, *Ph*NO$_2$), 7.93 (s, 1H, *Ph*NO$_2$). **^{13}C{^{1}H} NMR** (toluene-*d8*, 75.5 MHz): δ = 20.9 (s, *o/p*-CH_3), 21.2 (s, o/*p*-CH_3), 21.4 (s, *o/p*-CH_3), 21.5 (s, *o/p*-CH_3), 21.8 (s, *o/p*-CH_3), 21.9 (s, *o/p*-CH_3), 81.5 (dd, $^1J(^{13}C, ^{31}P)$ =41.8 Hz, $^2J(^{13}C, ^{31}P)$ =3.9 Hz, POCHP), 121.7(s, *C*H (arom.)), 122.2 (s, *C*H (arom.)), 127.6 (s, *C*H (arom.)), 127.7 (s, *C*H (arom.)), 129.3 (s, *C*H (arom.)), 129.4 (s, *C*H (arom.)), 129.5 (s, *C*H (arom.)), 129.7 (s, *C*H (arom.)), 131.0 (s, *C*H(arom.)), 131.5 (s, *C*H (arom.)), 136.8 (s, *C* (arom.)), 137.1 (s, *C* (arom.)), 137.5 (s, *C* (arom.)), 137.5 (s, *C* (arom.)), 138.0 (s, *C* (arom.)), 138.3 (s, *C* (arom.)), 139.0 (s, *C* (arom.)), 139.5 (s, *C* (arom.)), 146.5 (s, *C* (arom.)), 147.3 (s, *C* (arom.)). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2906 (m), 2844 (w), 1601 (w), 1510 (m), 1434 (m),

1397 (s), 1371 (m), 1338 (s), 1264 (m), 1216 (vs), 1079 (m), 1027 (m), 1007 (m), 1138 (m), 982 (m), 933 (s), 92 (m), 892 (s), 847 (vs), 838 (vs), 791 (s), 752 (s), 709 (s), 688 (s), 653 (s), 557 (m), 534 (m), 477 (s), 462 (m), 436 (s), 429 (s). **Raman** (633 nm, 15 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3044 (1), 3003 (1), 2918 (1), 2855 (1), 2731 (1), 2675 (1), 2484 (1), 2449 (1), 1593 (10), 1491 (1), 1417 (1), 1375 (1), 1342 (10), 1337 (10), 1302 (2), 1283 (1), 1221 (1), 1206 (5), 1185 (1), 1177 (1), 1158 (1), 1140 (3), 1106 (7), 1014 (1), 935 (1), 836 (1), 827 (2), 804 (1), 723 (1), 709 (1), 654 (2), 623 (1), 593 (1), 578 (1), 567 (1), 554 (1), 542 (1), 534 (1), 475 (1), 461 (2), 418 (1), 336 (1), 317 (1), 292 (1), 229 (1). **MS** (CI, pos., isobutane) *m/z*: 659, 463 $[TerNCHPhNO_2H]^+$, 386 $[TerNH_2C_4H_9]^+$, 372, 368, 330 $[TerNH_3]^+$, 326, 152 $[PhNO_2CHOH]^+$.

Single crystals suitable for X-ray diffraction can be grown from saturated toluene solution at ambient temperature.

Figure S2: NMR, IR and Raman spectra of $[P(\mu\text{-NTer})]_2 \cdot C_6H_4NO_2CHO$ (solvent signals indicated by asterisks).

^{1}H NMR spectrum

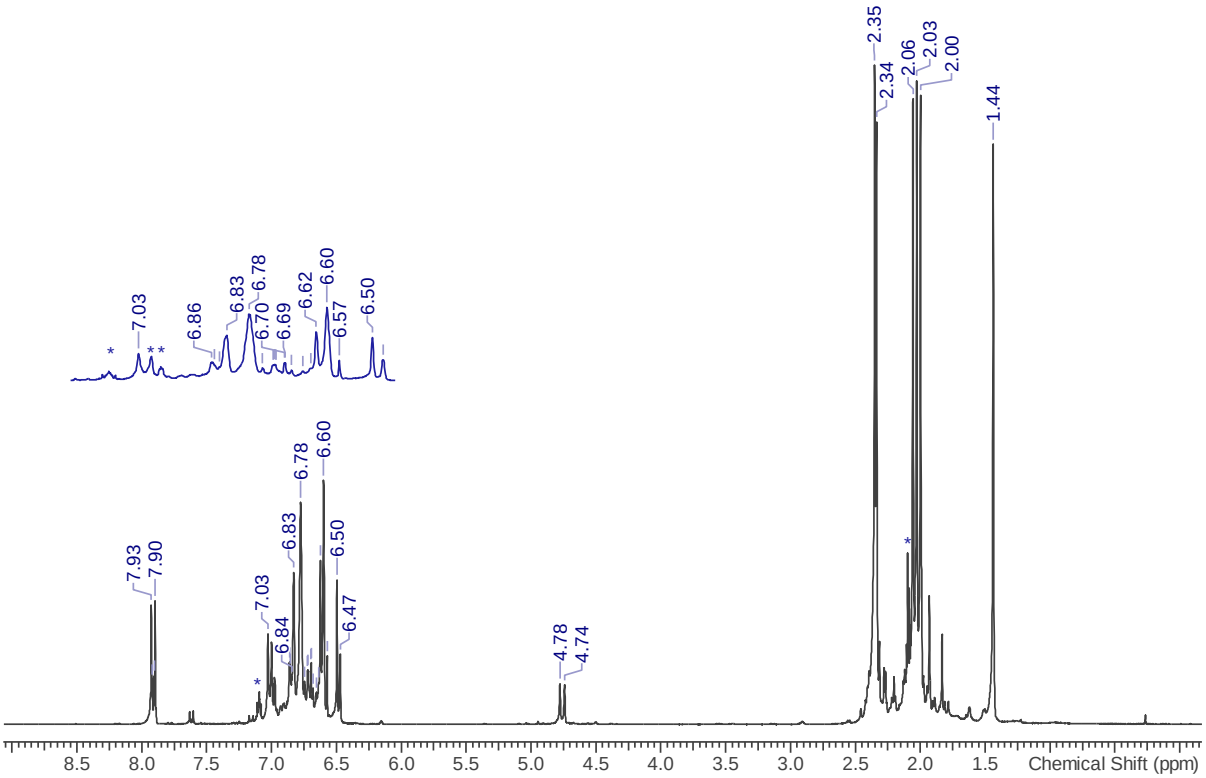
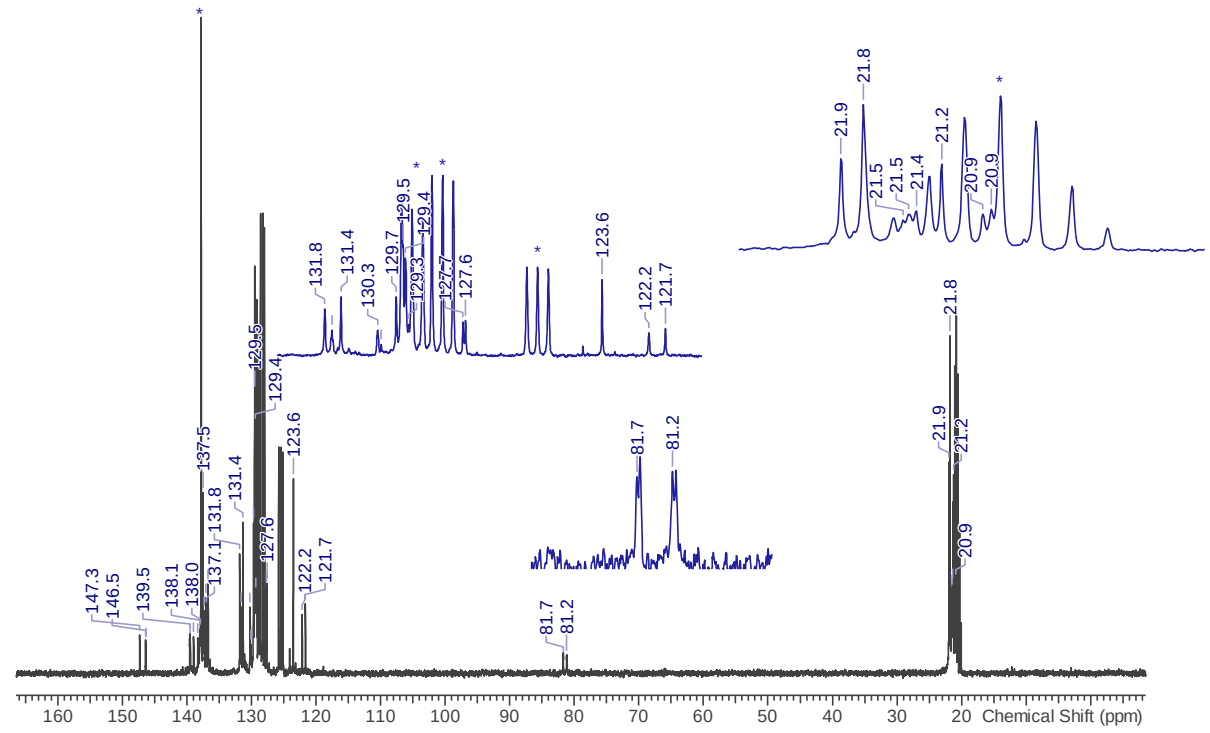


Figure S2 continued.

^{13}C NMR spectrum



^{31}P {^{1}H} NMR spectrum

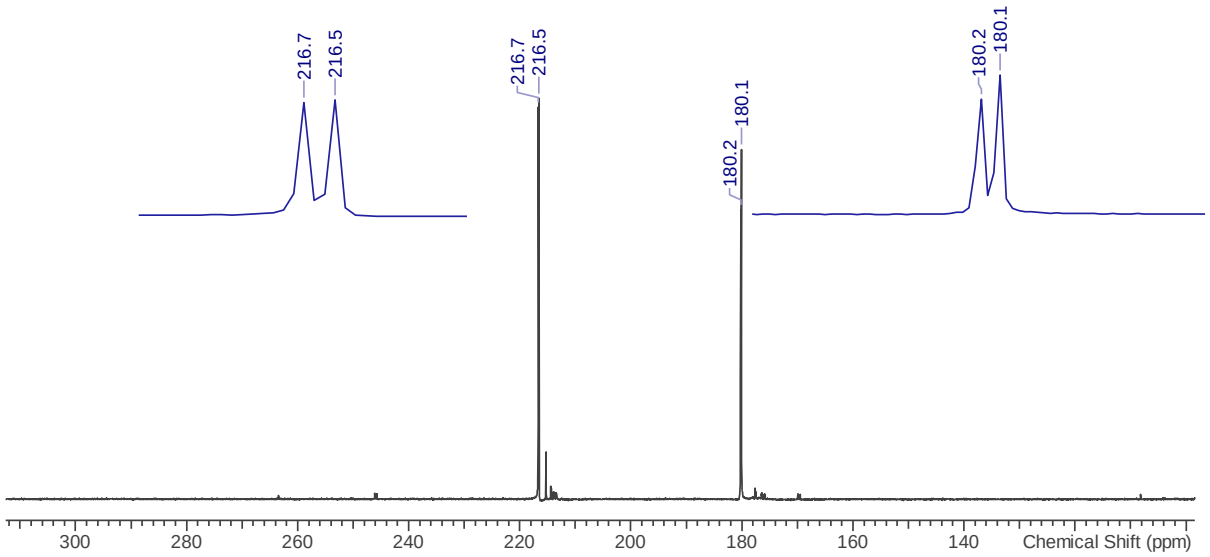
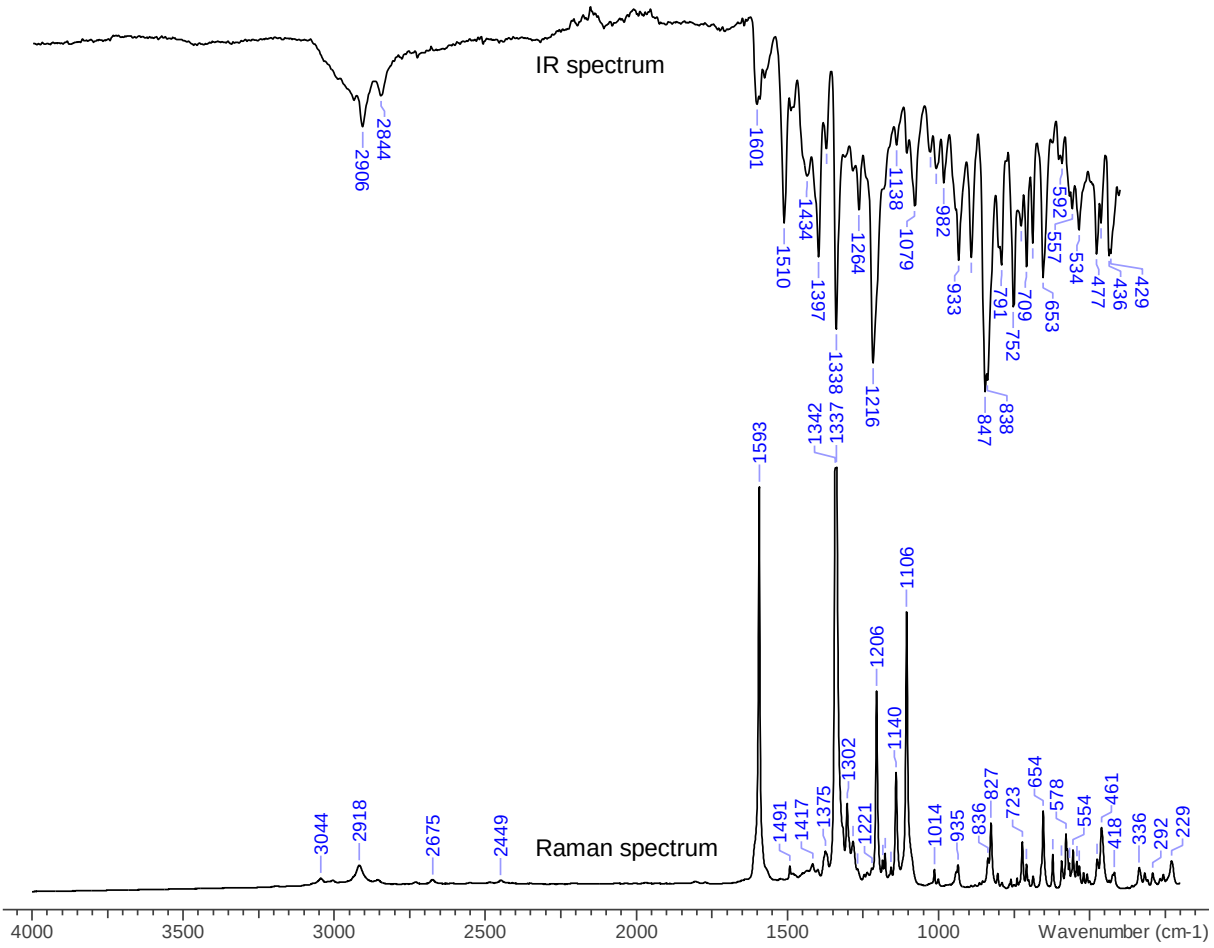
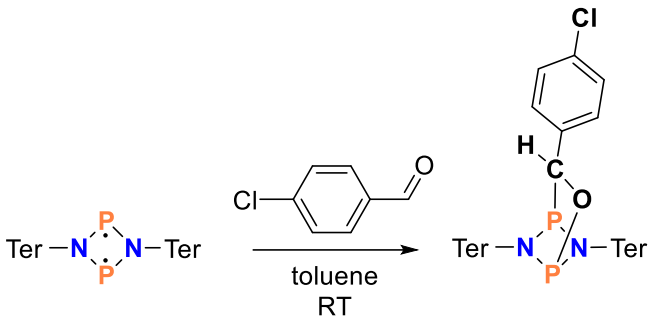


Figure S2 continued.



3.3 [P(μ-NTer)]$_2$ · C_6H_4ClCHO (4)



p-Chlorobenzaldehyde (39 mg, 0.28 mmol) and [P(μ-NTer)]$_2$ (200 mg, 0.28 mmol) are dissolved in toluene (10 mL) at RT, resulting in a light green solution that is stirred for three hours. After the reaction time, all volatile components are removed *in vacuo* (1×10^{-3} mbar) at 50 °C (water bath). The residue is dissolved in fresh toluene and insoluble solids are removed by filtration over celite. The clear solution is concentrated *in vacuo* (1×10^{-3} mbar) to incipient crystallization and stored overnight. After removal of the supernatant colourless crystals are obtained. **Yield:** 199 mg (0.23 mmol, 83 %).

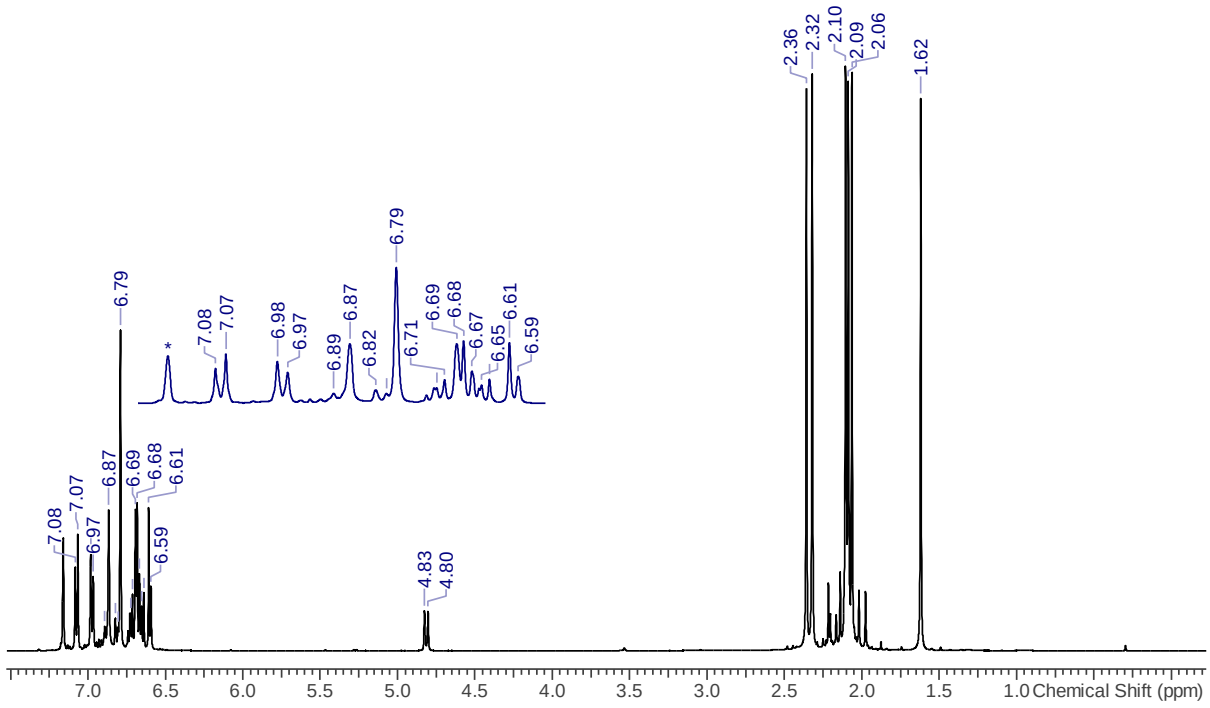
Mp. 157-162 °C **CHN** calcd. (found) in %: C 77.04 (76.57), H 6.47 (6.00), N 3.27 (3.07). **^{31}P{^{1}H} NMR** (C_6D_6, 202.5 MHz): δ = 178.3 (s (br), 1 P, *P*-CH), 215.4 (s (br), 1 P, *P*-O). **^{31}P{^{1}H} NMR** (toluene-*d8*, 121.5 MHz): δ = 178.4 (d, $^2J(^{31}P, ^{31}P)$ = 16 Hz, 1 P, *P*-CH), 215.5 (d, $^2J(^{31}P, ^{31}P)$ = 16 Hz, 1 P, *P*-O). **^{1}H NMR** (C_6D_6, 500.2 MHz): δ = 1.62 (s, 6 H, *o/p*-CH_3), 2.06 (s, 6 H, *o/p*-CH_3), 2.09 (s, 6 H, *o/p*-CH_3), 2.10 (s, 6 H, *o/p*-CH_3), 2.32 (s, 6 H, o/*p*-CH_3), 2.36 (s, 6 H, o/*p*-CH_3) 4.82 (d, $^2J(^1H, ^{31}P)$ =11.1 Hz, 1H, OC*H*PhCl), 6.59-7.08 (14H, Ter, 4H, *Ph*Cl). **^{1}H NMR** (toluene-*d8*, 300.1 MHz): δ = 1.57 (s, 6 H, *o/p*-CH_3), 2.02 (s, 6 H, *o/p*-CH_3), 2.05 (s, 6 H, *o/p*-CH_3), 2.08 (s, 6 H, *o/p*-CH_3), 2.34 (s, 6 H, o/*p*-CH_3), 2.36 (s, 6 H, o/*p*-CH_3) 4.74 (d, $^2J(^1H, ^{31}P)$ =11.3 Hz, 1H, OC*H*PhCl), 6.53-7.06 (14H, Ter, 4H, *Ph*Cl). **^{13}C{^{1}H} NMR** (C_6D_6, 125.8 MHz): δ = 20.7 (s, *p/o*-CH_3), 21.0 (s, *p/o*-CH_3), 21.0 (s, *p/o*-CH_3), 21.2 (s, *p/o*-CH_3) 21.5 (s, *p/o*-CH_3), 21.7 (s, *p/o*-CH_3), 21.8 (s, *p/o*-CH_3), 21.9 (s, *p/o*-CH_3), 81.1 (dd, $^1J(^{13}C, ^{31}P)$ =41.4 Hz, $^2J(^{13}C, ^{31}P)$ =3.7 Hz, POCHP), 121.5 (s, *C*H (arom.)), 121.8 (s, *C*H (arom.)), 128.7 (s, *C*H (arom.)), 129.4 (s, *C*H (arom.)), 129.5 (s, *C*H (arom.)), 129.5 (s, *C*H (arom.)), 131.3 (s, *C*H (arom.)), 131.7 (s, *C*H (arom.)), 133.0 (s, *C*

(arom.)), 136.8 (s, *C* (arom.)), 137.0 (s, *C* (arom.)), 137.1 (s (br.), *C* (arom.)), 137.4 (s, *C* (arom.)), 137.5 (s, *C* (arom.)), 137.7 (s, *C* (arom.)), 138.2 (s, *C* (arom.)), 138.9 (s, *C* (arom.)), 139.4, (s, *C* (arom.)), 139.6 (s, *C* (arom.)). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2936 (w), 2908 (w), 2846 (w), 2723 (vw), 1699 (vw), 1605 (w), 1570 (w), 1484 (m), 1397 (s), 1373 (m), 1286 (w), 1264 (w), 1221 (s), 1149 (m), 1079 (s), 1029 (m), 1013 (m), 982 (w), 943 (w), 923 (s), 892 (s), 836 (vs), 791 (m), 752 (s), 732 (s), 701 (w), 688 (m), 670 (s), 660 (s), 625 (w), 592 (m), 567 (m), 542 (m), 493 (m), 481 (s), 436 (s), 423 (m). **Raman** (633 nm, 15 s, 20 scans, cm^{-1}): $\tilde{\nu}$ =3060 (2), 3046 (2), 3021 (2), 3016 (2), 3010 (2), 2952 (2), 2920 (3), 2859 (2), 2733 (2), 1613 (3), 1595 (3), 1581 (3), 1483 (1), 1440 (1), 1421 (2), 1384 (2), 1304 (4), 1290 (3), 1272 (1), 1205 (3), 1187 (1), 1153 (1),1088 (3), 1005 (1), 945 1), 735 (1), 703 (1), 663 (1), 627 (1), 594 (3), 581 (4), 576 (3), 522 (1), 510 (1), 486 (1), 463 (1), 422 (1), 378 (1), 351 (1), 339 (1), 321 (1), 270 (2), 242 (2). **MS** (CI, pos., isobutane) *m/z*: 893 $[M]^+$, 716 $[(TerNP)_2]^+$, 452 $[TerNCHPhClH]^+$, 358 $[TerNP]^+$, 141 $[PhClCHOH]^+$.

Single crystals suitable for X-ray diffraction can be grown from saturated toluene solution at ambient temperature.

Figure S3: NMR, IR and Raman spectra of [P(μ-NTer)]$_2$·C_6H_4ClCHO (solvent signals indicated by asterisks).

^{1}H NMR spectrum



^{13}C NMR spectrum

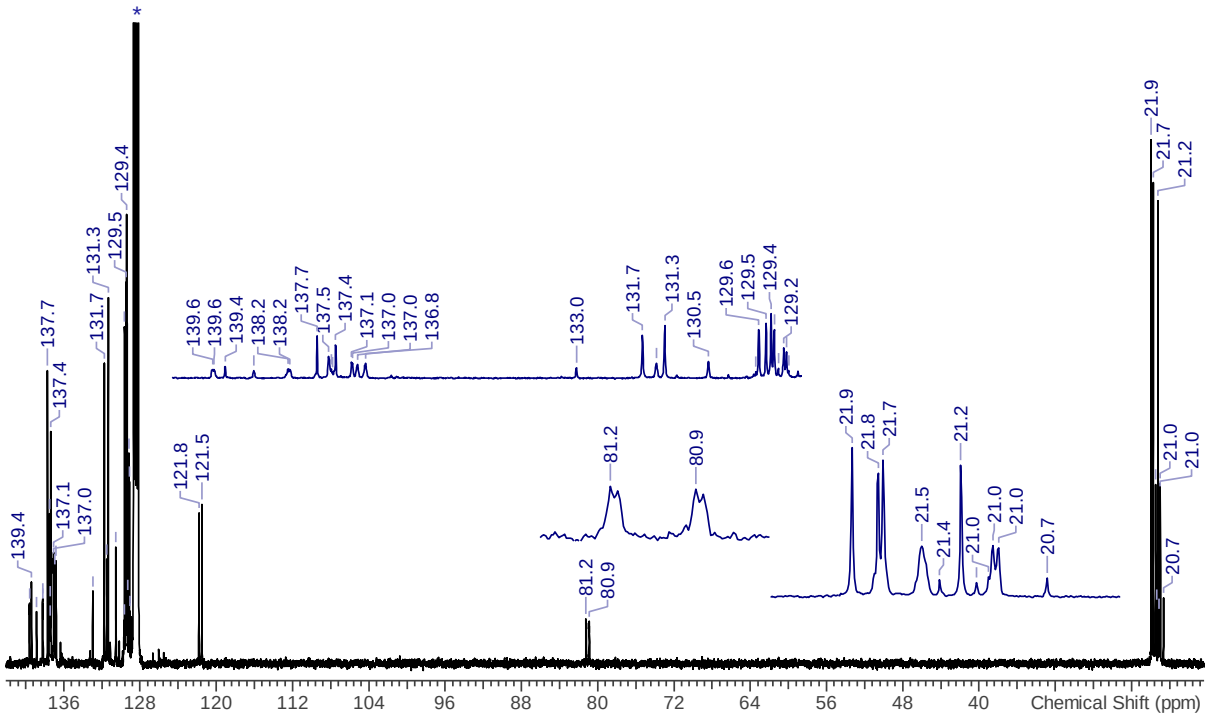


Figure S3 continued.

^{31}P NMR spectrum

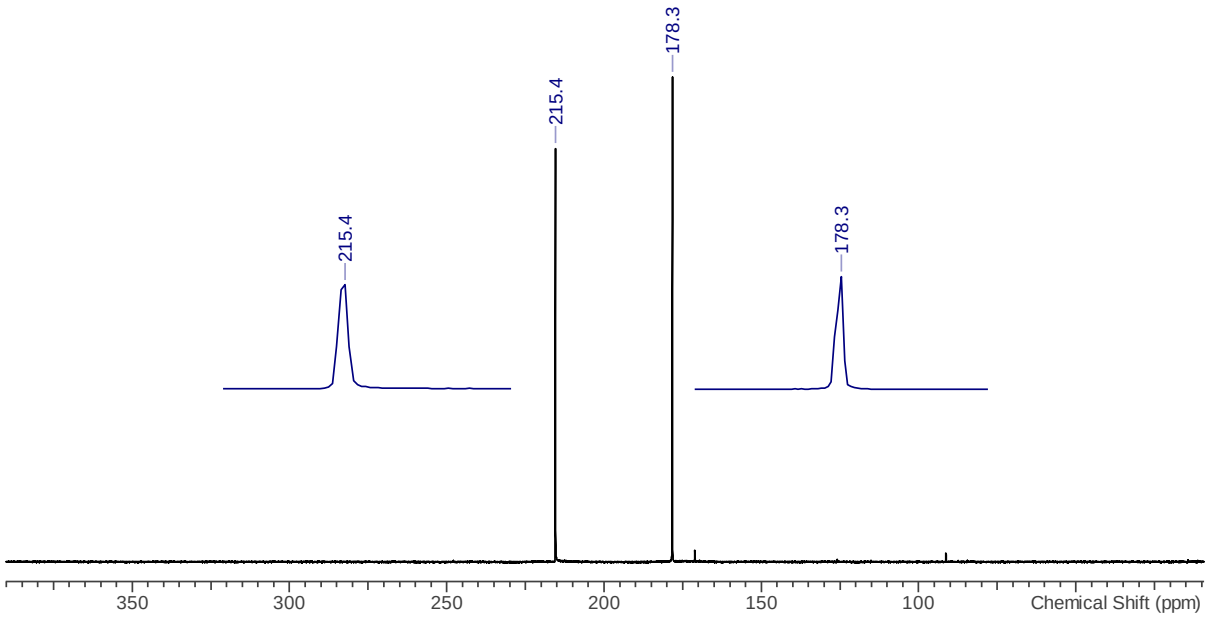
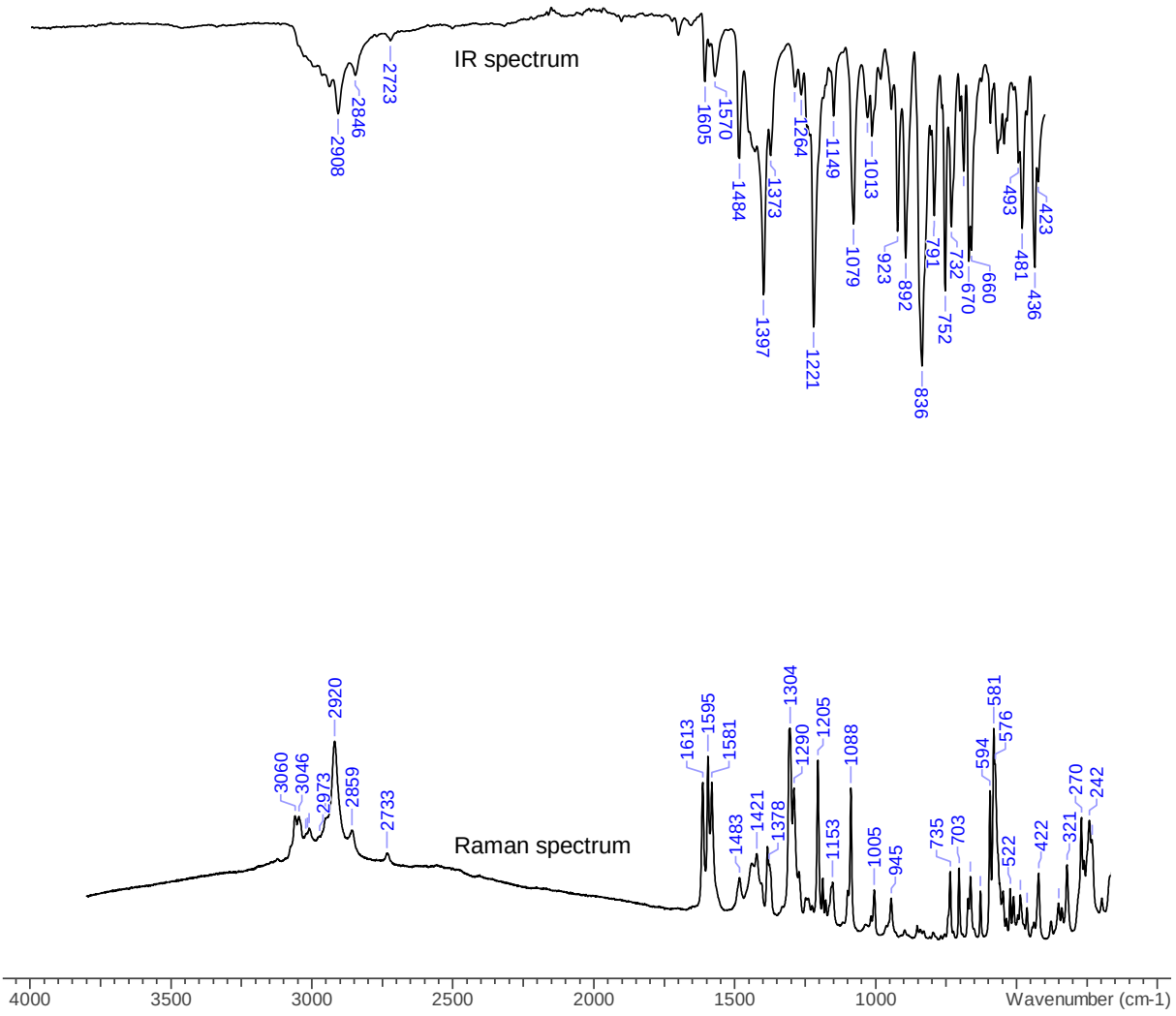
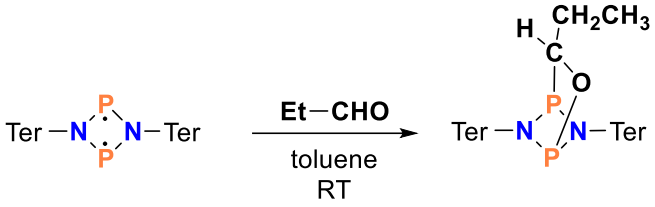


Figure S3 continued.



3.4 [P(μ-NTer)]$_2$ · EtCHO (5)



EtCHO (16 mg, 0.28 mmol) is added to a solution of [P(μ-NTer)]$_2$ (200 mg, 0.28 mmol) in toluene (10 mL) at RT with a microliter syringe, resulting in an immediate colour change from orange to light yellow. The reaction mixture is stirred for further three hours. After the reaction time, all volatile components are removed *in vacuo* (1×10^{-3} mbar) at 50 °C (water bath). The residue is dissolved in fresh toluene and insoluble solids are removed by filtration over celite. The clear solution is concentrated *in vacuo* (1×10^{-3} mbar) to incipient crystallization and stored overnight. After removal of the supernatant colourless crystals remain. **Yield:** 172 mg (0.22 mmol, 79 %).

Mp. 140-145°C **CHN** calcd. (found) in %: C 78.92 (78.52), H 7.15 (6.74), N 3.68 (3.27). **^{31}P{^{1}H} NMR** (C_6D_6, 121.5 MHz): δ = 176.6 (d, ^2J(^{31}P, ^{31}P) = 13 Hz, 1 P, *P*-CH), 212.1 (d, ^2J(^{31}P, ^{31}P) = 13 Hz, 1 P, *P*-O). **^{31}P{^{1}H} NMR** (toluene-*d8*, 121.5 MHz): δ = 176.4 (d, ^2J(^{31}P, ^{31}P) = 14 Hz, 1 P, *P*-CH), 211.9 (d, ^2J(^{31}P, ^{31}P) = 14 Hz, 1 P, *P*-O). **^{1}H NMR** (C_6D_6, 300.1 MHz): δ = 0.74 (t, ^3J(^{1}H,^{1}H) =7.4 Hz, 3H, OCH$_2$C*H*$_3$), 1.10 (m, 1H, OC*H*$_2$CH$_3$), 1.40 (m, 1H, OC*H*$_2$CH$_3$), 1.89 (s, 6 H, *o/p*-C*H*$_3$), 1.98 (s, 6 H, *o/p*-C*H*$_3$), 2.16 (s, 6 H, *o/p*-C*H*$_3$), 2.30 (s, 6 H, *o/p*-C*H*$_3$), 2.31 (s, 6 H, o/*p*-C*H*$_3$), 2.35 (s, 6 H, o/*p*-C*H*$_3$) 3.47 (m, 1H, OC*H*CH$_2$), 6.67-6.94 (14 H (*Ter*)). **^{1}H NMR** (toluene-*d8*, 300.1 MHz): δ = 0.71 (t, ^3J(^{1}H,^{1}H) =7.4 Hz, 3H, OCH$_2$C*H*$_3$), 1.10 (m, 1H, OC*H*$_2$CH$_3$), 1.40 (m, 1H, OC*H*$_2$CH$_3$), 1.84 (s, 6 H, *o/p*-C*H*$_3$), 1.92 (s, 6 H, *o/p*-C*H*$_3$), 2.11 (s, 6 H, *o/p*-C*H*$_3$), 2.24 (s, 6 H, *o/p*-C*H*$_3$), 2.30 (s, 6 H, o/*p*-C*H*$_3$), 2.35 (s, 6 H, o/*p*-C*H*$_3$) 3.40 (m, 1H, OC*H*CH$_2$), 6.61-6.89 (14 H (*Ter*)). **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz): δ = 21.5 (s, *p/o*-CH$_3$), 21.8 (s, *p/o*-CH$_3$), 21.9 (s, *p/o*-CH$_3$), 120.9 (s, *C* (arom.)), 121.4 (s, *C* (arom.)), 129.1 (s, *C* (arom.)), 129.3 (s, *C* (arom.)), 129.6 (s, *C* (arom.)), 131.3 (s, *C* (arom.)), 137.4 (s, *C* (arom.)). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ =2914 (m), 2855 (w), 1610 (w), 1581 (w), 1496 (w), 1482 (w), 1402 (s), 1375 (m), 1268 (w), 1224 (vs), 1148 (m), 1082

(m), 1031 (m), 985 (w), 934 (s), 897 (s), 843 (vs), 806 (m), 794 (m), 769 (m), 754 (s), 732 (s), 705 (vs), 690 (s), 658 (m), 592 (m), 567 (m), 478 (m), 462 (m), 439 (s), 429 (m). **Raman** (633 nm, 15 s, 20 scans, cm^{-1}): $\tilde{\nu}$ =3072 (1), 3041 (1), 2988 (1), 2916 (3), 2856 (1), 2730 (1), 1613 (4), 1582 (3), 1482 (1), 1421 (2), 1379 (2), 1374 (1), 1337 (1), 1305 (8), 1284 (2), 1270 (1), 1257 (1), 1246 (1), 1240 (1), 1188 (1), 1160 (1), 1102 (1), 1092 (2), 1006 (1), 959 (1), 956 (1), 945 (1), 738 (2), 728 (1), 710 (1), 703 (1), 641 (1), 591 (4), 580 (6), 569 (4), 551 (1), 544 (1), 523 (1), 511 (1), 501 (1), 486 (2), 465 (2), 422 (3), 356 (1), 338 (1), 319 (1), 271 (3), 255 (1), 237 (2), 233 (2), 155 (3), 119 (4). **MS** (CI, pos., isobutane) *m/z*: 831 $[MC_4H_9]^+$, 775 $[MH]^+$, 716 $[(TerNP)_2]^+$, 330 $[TerNH_3]^+$.

Single crystals suitable for X-ray diffraction can be grown from saturated toluene solution at ambient temperature.

Figure S4: NMR, IR and Raman spectra of [P(μ-NTer)]$_2$·EtCHO (solvent signals indicated by asterisks).

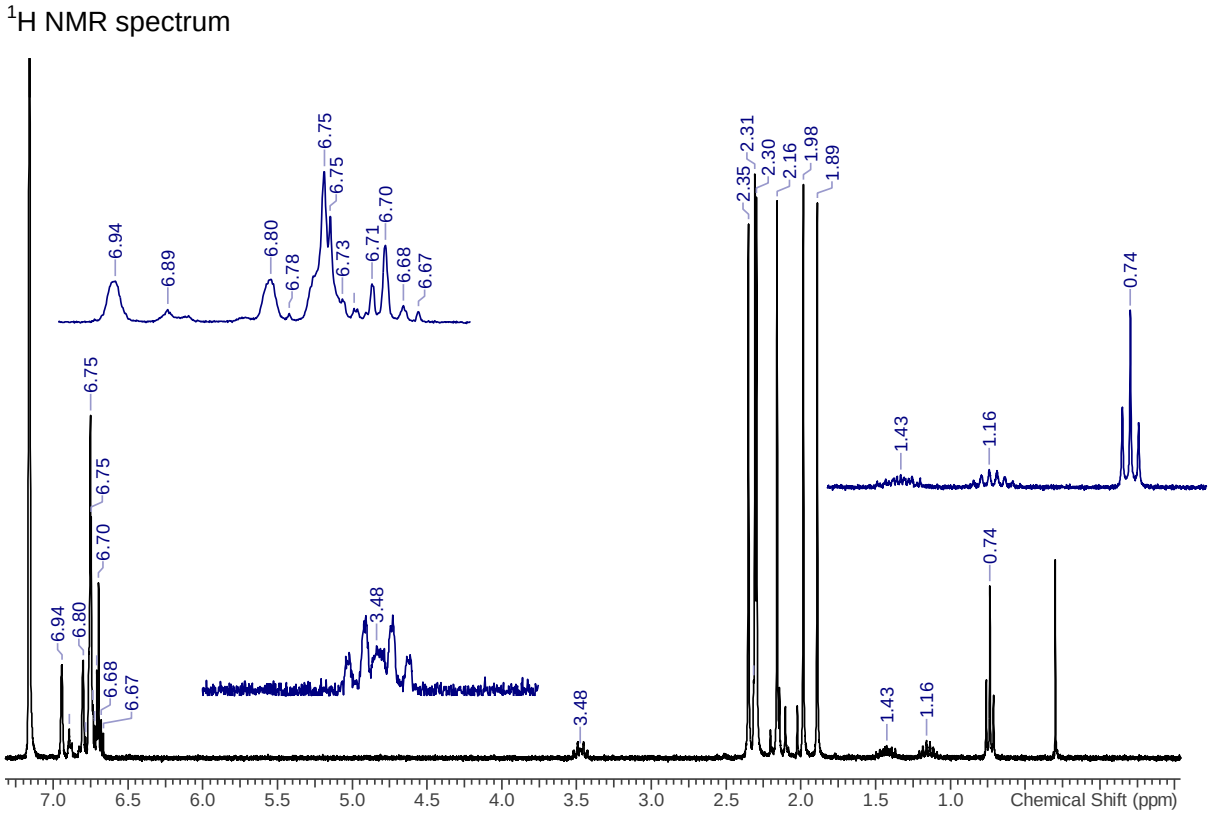
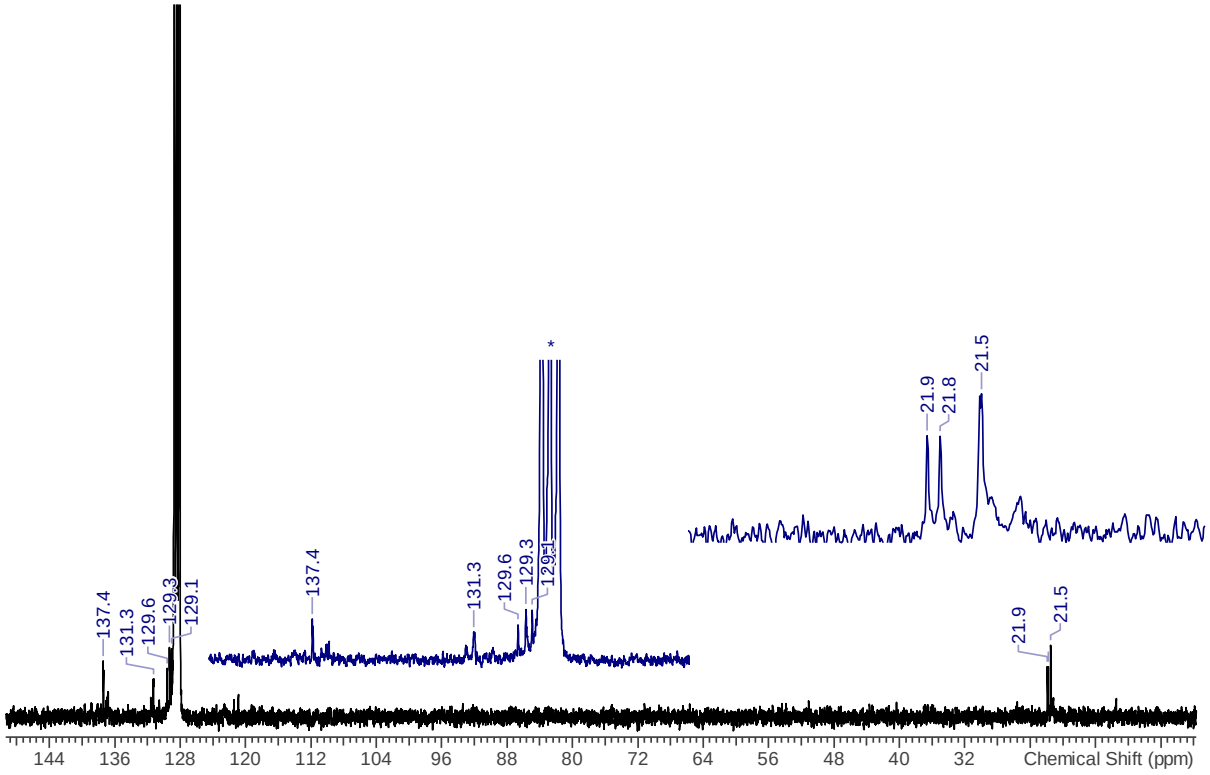


Figure S4 continued.

^{13}C NMR spectrum



^{31}P NMR spectrum

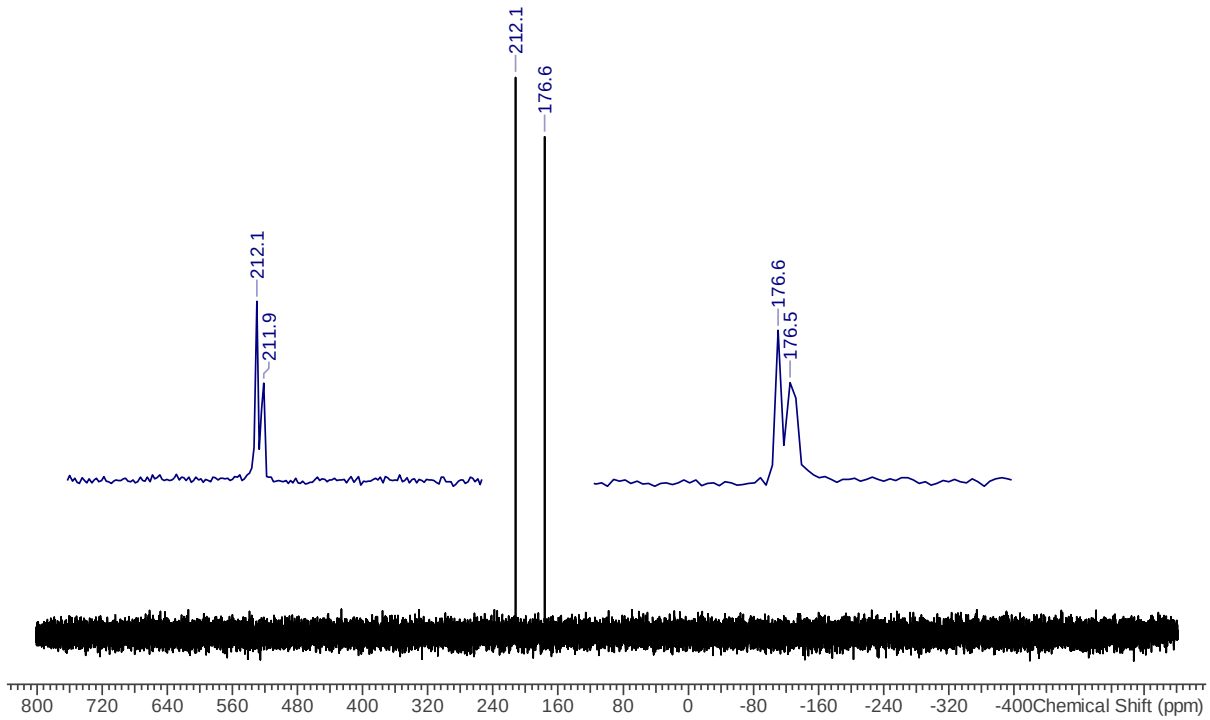
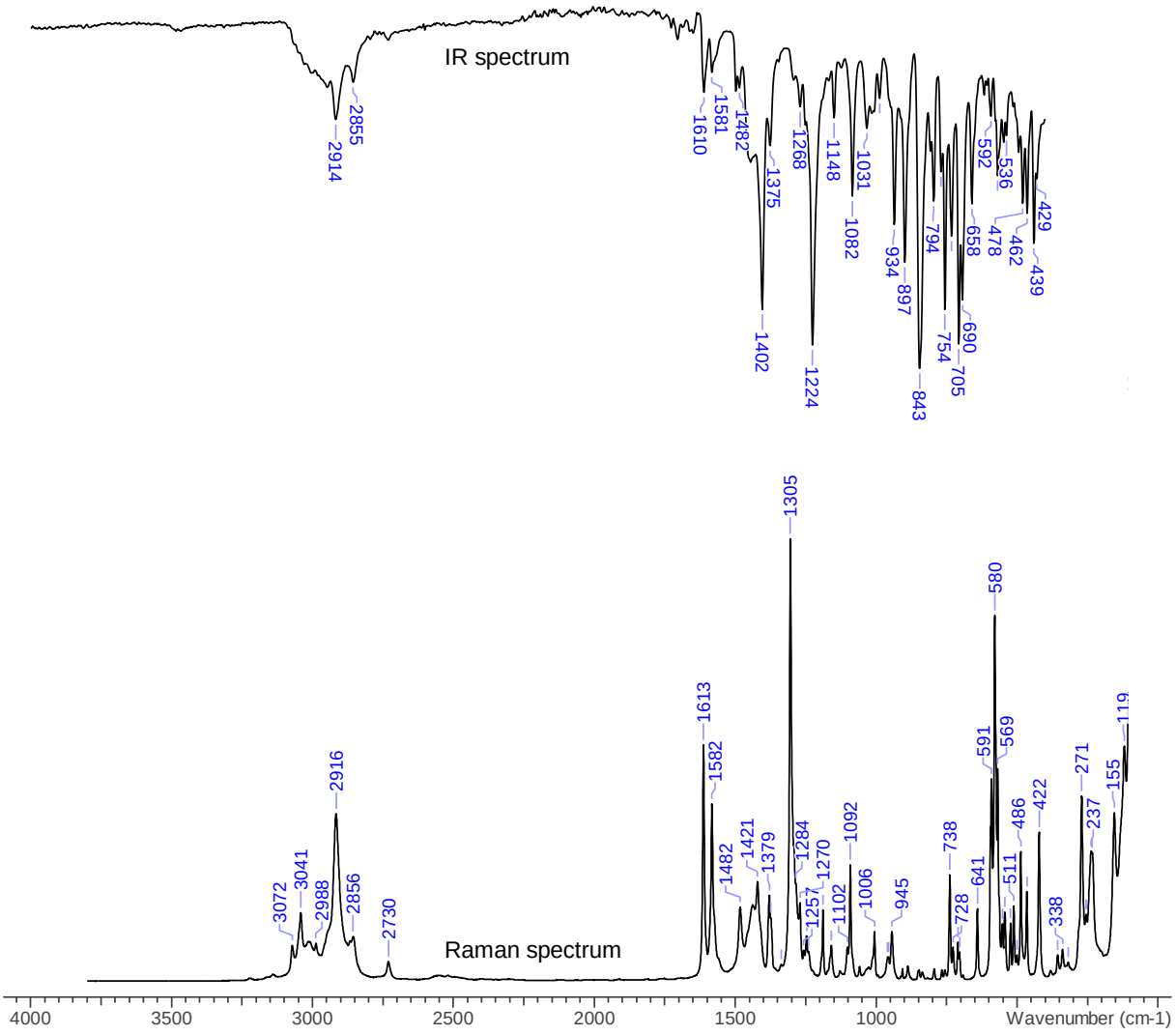
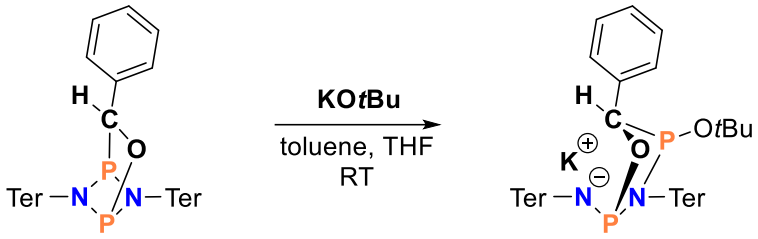


Figure S4 continued.



3.5 [TerNP]$_2$ · PhCHO · KOtBu (6)



KO*t*Bu (27 mg, 0.24 mmol) is added to a solution of [P(μ-NTer)]$_2$ · PhCHO (200 mg, 0.24 mmol) in toluene (10 mL) at RT. For solubility a few drops of THF are added. The reaction mixture is stirred overnight, its colour starting to change from orange to light orange after about 30 minutes. After the reaction, all volatile components are removed *in vacuo* (1×10^{-3} mbar) at 50 °C (water bath). The residue is dissolved in fresh toluene and insoluble solids are removed by filtration over celite. The clear solution is concentrated *in vacuo* (1×10^{-3} mbar) to incipient crystallization and stored until crystallization. After removal of the supernatant brownish crystals remain. **Yield:** 176 mg (0.188 mmol, 78 %).

Mp. 137-145°C **CHN** calcd. (found) in %: C 75.85 (75.39), H 6.91 (7.11), N 3.00 (2.74). **^{31}P{^{1}H} NMR** (toluene-*d8,* 202.5 MHz): δ = 148.6 (s, 1 P, *P*-CH), 183.9 (s,1 P, *P*-O). **^{1}H NMR** (toluene-*d8*, 500.2 MHz): δ = 0.84 (d, ^4J (^{1}H, ^{31}P) = 0.6 Hz, 9 H, OC(C*H*$_3$)$_3$), 1.77 (s, 3 H, *o/p*-C*H*$_3$), 2.04-2.35 (24 H, *o/p*-C*H*$_3$), 2.38 (s, 6 H, *o/p*-C*H*$_3$), 2.45 (s, 3 H, o/*p*-C*H*$_3$), 6.15 (d, ^2J (^{1}H, ^{31}P) = 4.3 Hz, 1H, OC*H*Ph), 6.37 (s, 1H, H (arom.)), 6.51-7.14 (17 H (arom.)). **^{13}C{^{1}H} NMR** (toluene-*d8*, 125.8 MHz): δ = 21.2 (s, *p/o*-CH$_3$), 21.3 (s, *p/o*-CH$_3$), 21.5 (s, *p/o*-CH$_3$), 22.0 (s, *p/o*-CH$_3$), 30.9 (s), 31.0 (s), 75.3 (d, *J* = 12.4 Hz), 113.7(s), 125.6 (s), 126.8 (s), 127.7 (s), 128.1 (s, *C*H), 128.2 (s), 129.8 (*J* = 9.6 Hz), 131.1 (s), 136.5 (s), 136.9 (s), 138.6 (s), 139.5 (s), 140.2 (s), 142.1 (s). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2968 (m), 2914 (m), 2855 (w), 1610 (w), 1579 (w), 1443 (s), 1404 (s), 1377 (m), 1224 (s), 1181 (m), 1146 (m), 1082 (m), 1031 (m), 1014 (m), 932 (s), 897 (s), 845 (vs), 794 (s), 754 (s), 730 (s), 703 (vs), 693 (vs), 658 (m), 567 (m), 478 (s), 462 (s), 439 (s). **Raman** (633 nm, 15 s, 20 scans, cm^{-1}): $\tilde{\nu}$ =3068 (3), 3046 (3), 3006 (3), 2916 4), 2854 (3), 2730 (3), 1611 (5), 1603 (5), 1580 (4), 1481 (3), 1436 (3), 1419 (3), 1376 (3), 1302 (7), 1283 (4), 1208 (4), 1186 (3),

1157 (3), 1146 (3), 1089 (3), 1029 (3), 1002 (6), 943 (3), 843 (2), 786 (2), 734 (2), 725 (2), 703 (2), 657 (3), 619 (3), 614 (3), 589 (3), 578 (7), 566 (4), 521 (3), 509 (2), 460 (2), 419 (2), 324 (2), 282 (2), 267 (3), 235 (3), 218 (3), 152 (3). **MS** (CI, pos., isobutane) *m/z*: 823 $[(TerNP)_2PhCHOH]^+$, 716 $[(TerNP)_2]^+$, 687, 540, 506, 484, 432 $[TerNPOtBuH]^+$, 418 $[TerNCHPhH]^+$, 330 $[TerNH_3]^+$, 107 $[PhCHOH]^+$.

Single crystals suitable for X-ray diffraction can be grown from saturated toluene solution at ambient temperature.

Figure S5: NMR, IR and Raman spectra of $[TerNP]_2 \cdot PhCHO \cdot KOtBu$ (solvent signals indicated by asterisks).

^{1}H NMR spectrum

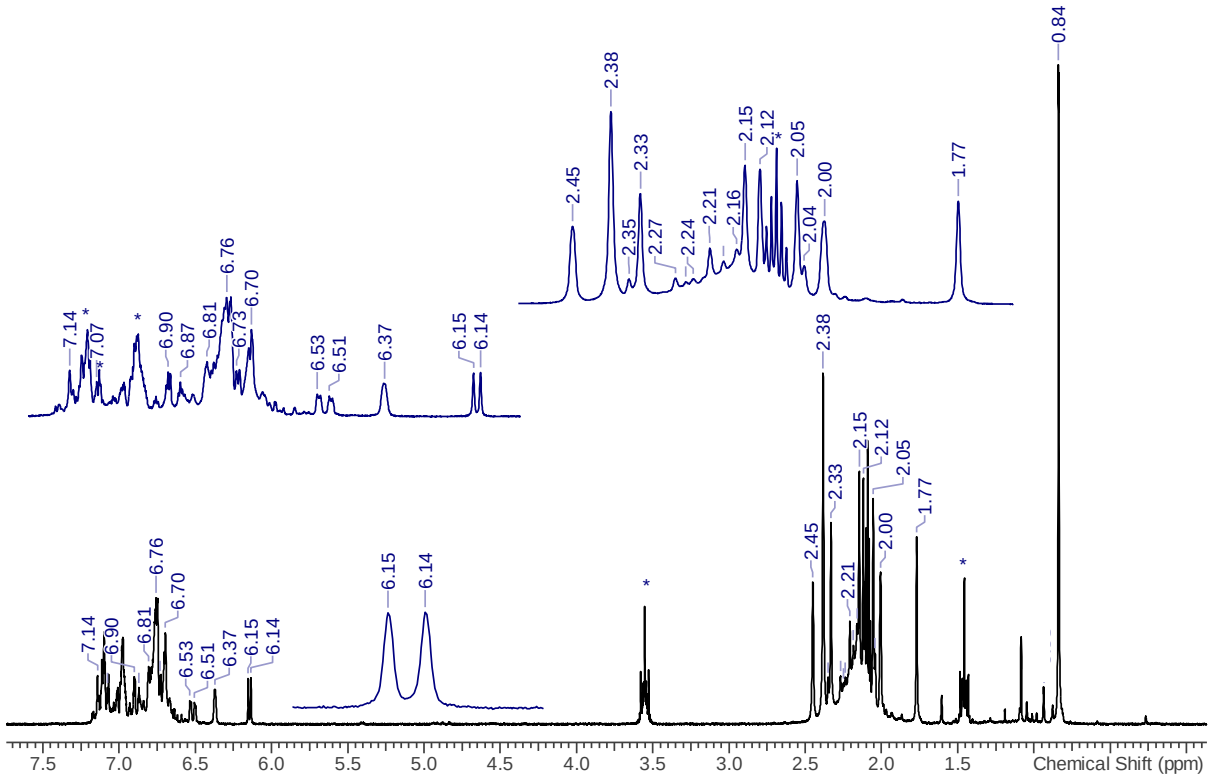
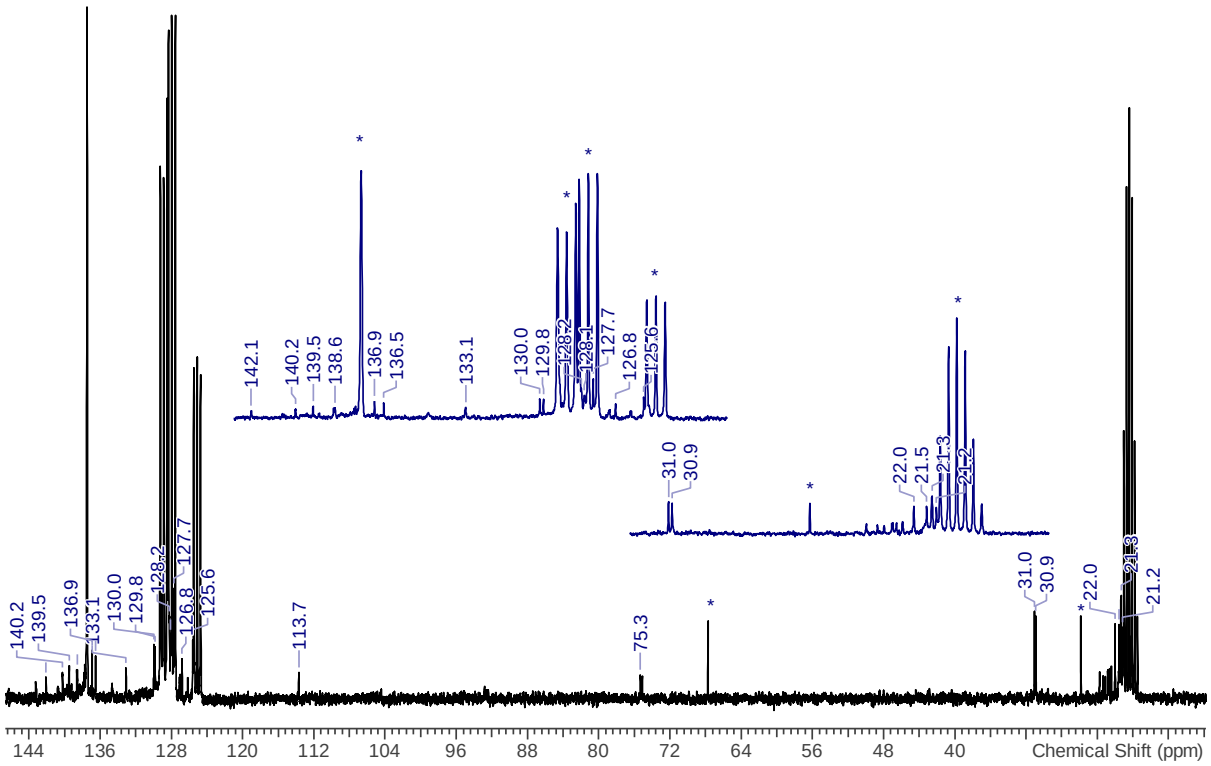


Figure S5 continued.

^{13}C NMR spectrum



^{31}P NMR spectrum

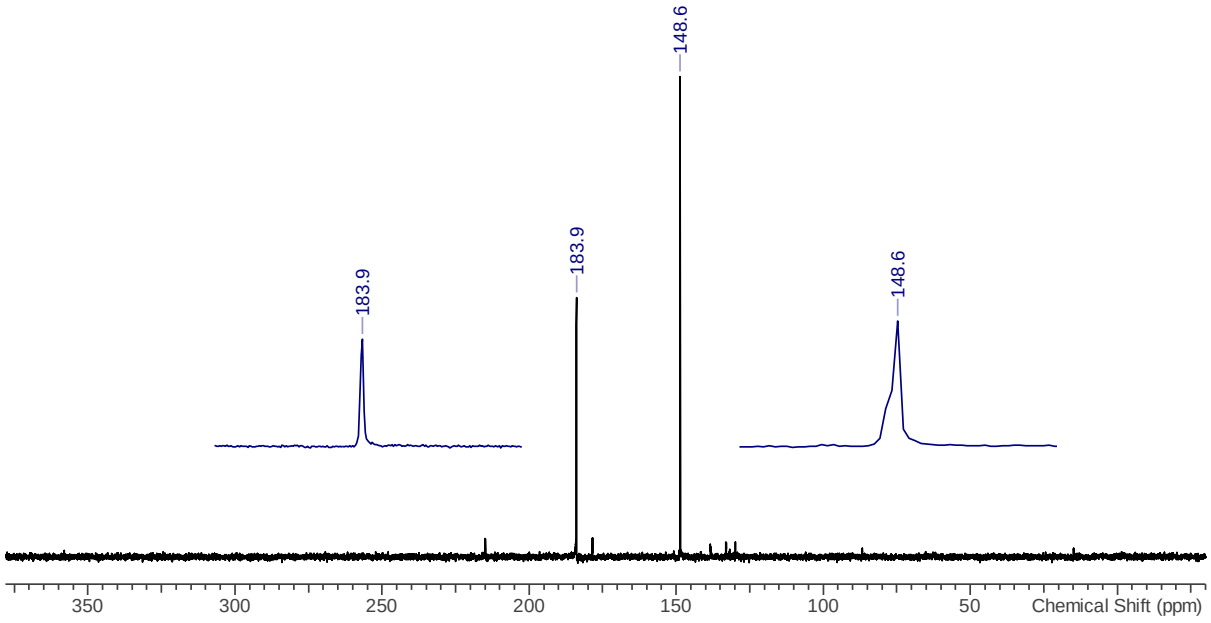
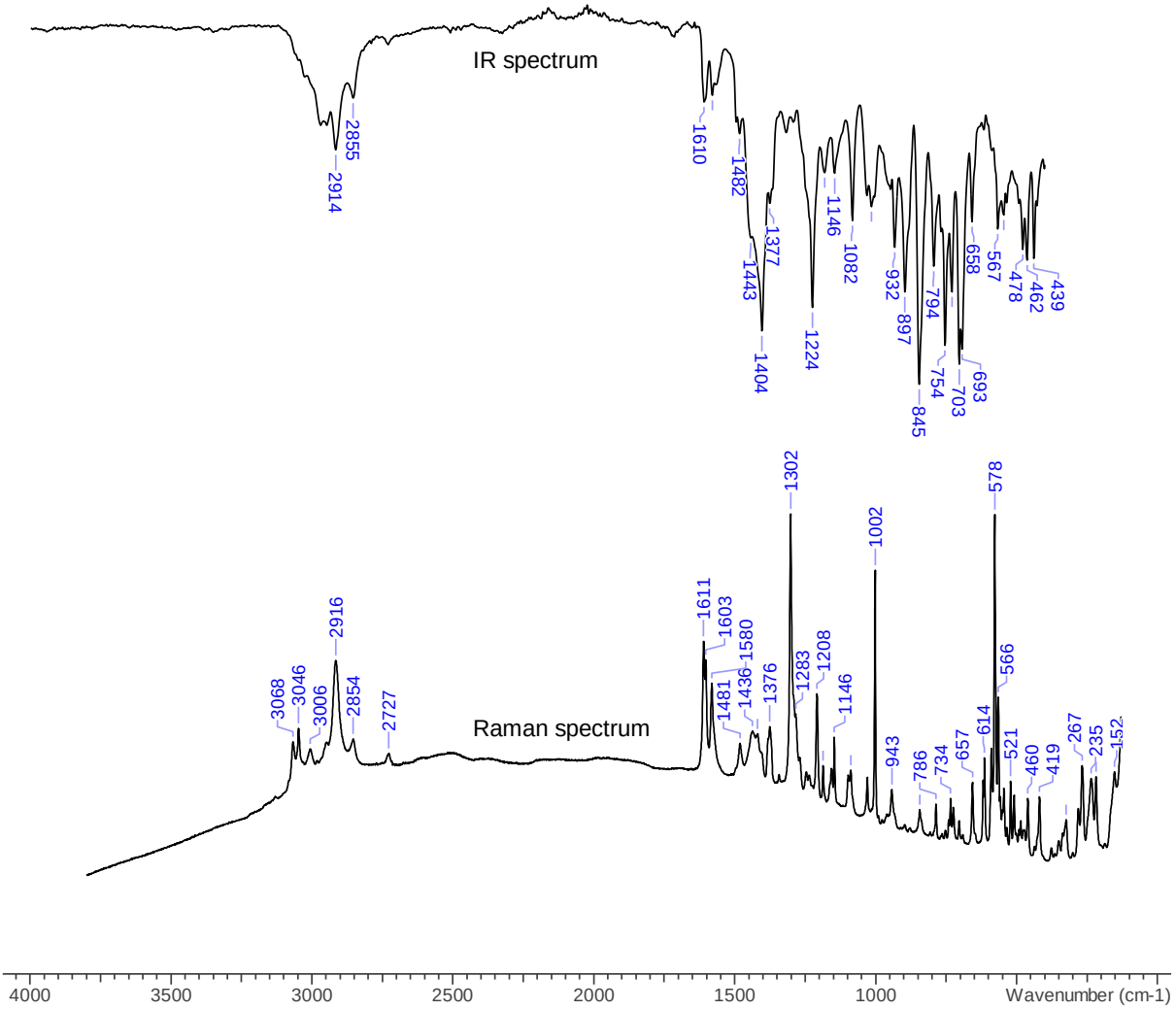


Figure S5 continued.



4 Additional spectroscopic details

4.1 NMR data of compounds 2-5

In the following section, a summary of experimental NMR data of the compounds **2**-**5** can be found.

Table S5: ^{1}H and ^{31}P NMR data of **2**-**5** (solvent toluene-*d8*).

	2	**3**	**4**	**5**
^{1}H NMR shift (C*H*O) [ppm]	4.86	4.76	4.74	3.40
coupling constant (C*H*O) $^{2}J(^{1}H, ^{31}P)$ [Hz]	11.3	10.7	11.3	m
^{31}P NMR shift (*P*–CH) [ppm]	178.5	180.1	178.4	176.4
^{31}P NMR shift (*P*–O) [ppm]	214.9	216.6	215.5	211.9

5 Computational details

5.1 General remarks

Computations were carried out using Gaussian09,[6] ORCA 5.0.3,[7–9] as well as NBO 6.0.[10–13]

DFT structure optimizations using analytic gradients employed the pure exchange-correlation functional PBE[14,15] or the hybrid exchange-correlation functional B3LYP[16–21] (using VWN5[16] for the local correlation term) in conjunction with Grimme's dispersion correction D3(BJ)[22,23] and the def2-TZVP basis set[24] (notation PBE-D3/def2-TZVP or B3LYP-D3/def2-TZVP). The resolution-of-identity (RI) approximation was applied, using Weigend's accurate Coulomb-fitting basis set (W06 or def2/J).[25] Numerical integration of the exchange-correlation energy was done on Gaussian's "ultrafine" grid or ORCA's default XC grid ("DefGrid2"). The exact exchange term of the hybrid functional B3LYP was approximated by the Chain Of Spheres approximation (COSX),[26] using the default COSX grid ("DefGrid2") for numerical integration. All structures were fully optimized and confirmed as minima or transition states by analytic frequency analyses.

Accurate electronic energies for the optimized structures were computed using single-point DLPNO-CCSD(T)[27–30] calculations employing the def2-TZVP basis set and def2-TZVP/C correlation fitting basis[31] (notation: DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-TZVP or DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3/def2-TZVP). For all model systems, the "TightPNO" thresholds were applied in the DLPNO approximation (default "NormalPNO" settings otherwise). Thermodynamic quantities at this level of theory were calculated using the DLPNO-CCSD(T) single point energy and the thermal corrections at the PBE-D3/def2-TZVP or B3LYP-D3/def2-TZVP level of theory, respectively. The T_1 diagnostic was evaluated in each case to ensure reliable results (empirically, CCSD(T) results are considered reliable if $T_1 < 0.02$).[32,33]

Ab-initio structure optimizations were performed using ORCA at the CCSD(T)[34–39]/def2-TZVP level of theory using numerical gradients. All structures were fully optimized and confirmed as minima or transition states by numerical frequency analyses. The T_1 diagnostic was evaluated in each case to assess the multireference character of the wavefunction and verify that the single-reference coupled-cluster approach is viable. Improved electronic energies were computed at the DLPNO-CCSD(T)/def2-QZVPP[24] level of theory (using the appropriate def2-QZVPP/C correlation fitting basis[31] and "TightPNO" thresholds as well as the RIJCOSX approximation for the Coulomb and exchange integrals; notation: DLPNO-CCSD(T)/def2-QZVPP// CCSD(T)/def2-TZVP).

Reaction paths were investigated using a combination of relaxed potential energy surface scans, the nudged elastic band (NEB) method,[40–45] as well as transition state searches using the eigenvector-following method.[46–49]

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase.

5.2 Summary of calculated data

Table S6. Summary of calculated data (structures optimized at PBE-D3/def2-TZVP, single point energies at DLPNO-CCSD(T)/def2-TZVP). All energies given in atomic units.

		PBE-D3					DLPNO-CCSD(T)	
Compd.	**PG**	N_{imag}	E_{tot}	**ZPE**	ΔH[a]	ΔG[b]	$E_{CCSD(T)}$	T_1
PhCHO	C_S	0	−345.2874	0.1064	0.1138	0.0757	−344.9510	0.013
$C_6H_4NO_2CHO$	C_S	0	−549.7013	0.1085	0.1186	0.0732	−549.1853	0.015
C_6H_4ClCHO	C_S	0	−804.7246	0.0972	0.1058	0.0642	−804.0788	0.012
EtCHO	C_1	0	−192.9814	0.0817	0.0878	0.0540	−192.8117	0.013
$[P(\mu\text{-NTer})]_2$ (**1**)	D_2	0	−2649.5088	0.8217	0.8776	0.7310	−2646.8693	0.010
2	C_1	0	−2994.8492	0.9329	0.9946	0.8365	−2991.8779	0.010
3	C_1	0	−3199.2697	0.9353	0.9996	0.8354	−3196.1170	0.011
4	C_1	0	−3454.2873	0.9238	0.9867	0.8254	−3451.0073	0.010
5	C_1	0	−2842.5482	0.9088	0.9687	0.8149	−2839.7414	0.010
6	C_1	0	−3827.5205	1.0528	1.1249	0.9594		
H_2	$D_{\infty h}$	0	−1.1661	0.0098	0.0131	−0.0017	-1.1683	0.006
HC≡CH	$D_{\infty h}$	0	-77.2526	0.0259	0.0298	0.0069	-77.1837	0.013
$H_2C=CH_2$	D_{2h}	0	-78.5029	0.0496	0.0536	0.0287	-78.4290	0.011
$H_2C=O$	C_{2v}	0	-114.4206	0.0256	0.0294	0.0046	-114.3314	0.016
$[P(\mu\text{-NH})]_2$ (**1H**)	D_{2h}	0	−793.0526	0.0322	0.0378	0.0057	−792.3371	0.012
1H···H_2 vdW	C_{2v}	0	−794.2236	0.0454	0.0528	0.0167	−793.5069	0.012
1H···H_2 TS	C_{2v}	1	−794.2132	0.0460	0.0513	0.0192	−793.4867	0.016
1H · H_2	C_{2v}	0	−794.2368	0.0490	0.0547	0.0218	−793.5255	0.014
1H···HC≡CH vdW	C_S	0	−870.3124	0.0591	0.0688	0.0259	−869.5237	0.012
1H···HC≡CH TS	C_{2v}	1	−870.3123	0.0589	0.0678	0.0269	−869.5209	0.012
1H · HC≡CH	C_{2v}	0	−870.3728	0.0640	0.0706	0.0355	−869.5832	0.015
1H···$H_2C=CH_2$ vdW			—[c]					
1H···$H_2C=CH_2$ TS			—[c]					
1H · $H_2C=CH_2$	C_{2v}	0	−871.6142	0.0868	0.0938	0.0578	−870.8232	0.014
1H···$H_2C=O$ vdW			—[c]					
1H···$H_2C=O$ TS			—[c]					
1H · $H_2C=O$	C_S	0	−907.5414	0.0641	0.0706	0.0348	−906.7369	0.015

[a] Thermal correction to enthalpy (298 K); [b] thermal correction to Gibbs energy (298 K, 1 atm); [c] no stationary point found.

Table S7. Summary of calculated data (structures optimized at B3LYP-D3/def2-TZVP, single point energies at DLPNO-CCSD(T)/def2-TZVP). All energies given in atomic units.

		B3LYP-D3					DLPNO-CCSD(T)	
Compd.	**PG**	N_{imag}	E_{tot}	**ZPE**	ΔH[a]	ΔG[b]	$E_{CCSD(T)}$	T_1
PhCHO	Cs	0	−345.52597	0.1095	0.1168	0.0790	−344.9510	0.013
[P(μ-NTer)]$_2$ (**1**)	D2	0	−2651.1473	0.8454	0.8997	0.7689	−2646.8688	0.010
1···OC(H)Ph vdW	C1	0	−2996.6875	0.9585	1.0196	0.8751	−2991.8263	0.011
2	C1	0	−2996.7298	0.9609	1.0205	0.8796	−2991.8770	0.010
H_2	$D_{\infty h}$	0	−1.1732	0.0101	0.0134	−0.0014	−1.1683	0.006
HC≡CH	$D_{\infty h}$	0	−77.3157	0.0268	0.0306	0.0078	−77.1835	0.013
$H_2C=CH_2$	D_{2h}	0	−78.5697	0.0509	0.0549	0.0301	−78.4289	0.011
$H_2C=O$	C_{2v}	0	−114.4969	0.0265	0.0303	0.0055	−114.3315	0.015
[P(μ-NH)]$_2$ (**1H**)	D_{2h}	0	−793.3473	0.0333	0.0386	0.0071	−792.3372	0.012
1H···H_2 vdW	C_{2v}	0	−794.5242	0.0469	0.0540	0.0188	−793.5071	0.012
1H···H_2 TS	C_{2v}	1	−794.5068	0.0469	0.0521	0.0202	−793.4869	0.016
1H · H_2	C_{2v}	0	−794.5426	0.0504	0.0561	0.0231	−793.5261	0.013
1H···HC≡CH vdW	C_S	0	−870.6693	0.0611	0.0706	0.0280	−869.5244	0.012
1H···HC≡CH TS	C_{2v}	1	−870.6660	0.0615	0.0694	0.0311	−869.5183	0.013
1H · HC≡CH	C_{2v}	0	−870.7238	0.0660	0.0724	0.0376	−869.5833	0.014
1H···$H_2C=CH_2$ vdW	C_{2v}	0	−871.9250	0.0860	0.0954	0.0536	−870.7702	0.011
1H···$H_2C=CH_2$ TS	C_{2v}	1	−871.9242	0.0864	0.0944	0.0559	−870.7679	0.012
1H · $H_2C=CH_2$	C_{2v}	0	−871.9697	0.0893	0.0961	0.0605	−870.8235	0.013
1H···$H_2C=O$ vdW			—[c]					
1H···$H_2C=O$ TS			—[c]					
1H · $H_2C=O$	C_S	0	−907.9089	0.0661	0.0725	0.0370	−906.7375	0.015

[a] Thermal correction to enthalpy (298 K); [b] thermal correction to Gibbs energy (298 K, 1 atm); [c] no stationary point found.

Table S8. Summary of calculated data (structures optimized at CCSD(T)/def2-TZVP, single point energies at DLPNO-CCSD(T)/def2-QZVPP). All energies given in atomic units (E_h).

		CCSD(T)					DLPNO-CCSD(T)	
Compd.	**PG**	N_{imag}	E_{tot}	**ZPE**	ΔH[a]	ΔG[b]		
H_2	$D_{\infty h}$	0	−1.1683	0.0101	0.0134	−0.0014	−1.1740	0.006
HC≡CH	$D_{\infty h}$	0	−77.1843	0.0262	0.0301	0.0072	−77.2089	0.014
$H_2C{=}CH_2$	D_{2h}	0	−78.4294	0.0507	0.0547	0.0298	−78.4618	0.011
$H_2C{=}O$	C_{2v}	0	−114.3322	0.0266	0.0304	0.0056	−114.3690	0.015
$[P(\mu\text{-}NH)]_2$ (**1H**)	D_{2h}	0	−792.3391	0.0332	0.0386	0.0069	−792.4225	0.012
1H···H_2 vdW	C_{2v}	0	−793.5095	0.0461	0.0538	0.0171	−793.5996	0.012
1H···H_2 TS	C_{2v}	1	−793.4888	0.0474	0.0525	0.0206	−793.5819	0.016
1H · H_2	C_{2v}	0	−793.5273	0.0509	0.0566	0.0238	−793.6211	0.014
1H···HC≡CH vdW	C_S	0	−869.5277	0.0603	0.0700	0.0267	−869.6357	0.012
1H···HC≡CH TS	C_{2v}	1	−869.5214	0.0612	0.0691	0.0308	−869.6294	0.013
1H · HC≡CH	C_{2v}	0	−869.5862	0.0660	0.0723	0.0376	−869.6965	0.014
1H···$H_2C{=}CH_2$ vdW	C_{2v}	—[c]	−870.7735		—[c]		−870.8893	0.011
1H···$H_2C{=}CH_2$ TS	C_{2v}	—[c]	−870.7709		—[c]		−870.8871	0.012
1H · $H_2C{=}CH_2$	C_{2v}	—[c]	−870.8257		—[c]		−870.9448	0.013
1H···$H_2C{=}O$ vdW	C_S	0	−906.6785	0.0621	0.0712	0.0294	−906.7987	0.016
1H···$H_2C{=}O$ TS	C_S	1	−906.6780	0.0626	0.0703	0.0315	−906.7986	0.018
1H · $H_2C{=}O$	C_S	0	−906.7400	0.0664	0.0727	0.0373	−906.8638	0.014

[a] Thermal correction to enthalpy (298 K); [b] thermal correction to Gibbs energy (298 K, 1 atm); [c] no frequency calculation performed due to system size.

Table S9. Computed reaction energies in kJ/mol (ΔH, $\Delta G°$ at 298.15 K, c° = 1 mol/L).

Reaction		DLPNO-CCSD(T)//PBE-D3[a]			DLPNO-CCSD(T)//B3LYP[b]			CCSD(T)[c]			DLPNO-CCSD(T)//CCSD(T)[d]		
		ΔU_0	ΔH	$\Delta G°$	ΔU_0	ΔH	$\Delta G°$	ΔU_0	ΔH	$\Delta G°$	ΔU_0	ΔH	$\Delta G°$
1 + Ph-CHO → **2**		−138.3	−142.7	−80.7	−134.7	−139.7	−75.1						
1 + O_2N-C_6H_4-CHO → **3**		−150.4	−154.9	−89.8									
1 + Cl-C_6H_4-CHO → **4**		−142.4	−146.7	−84.1									
1 + Et-CHO → **5**		−144.4	−149.9	−88.0									
1H + H_2 → **1H** · H_2	vdW	4.5	0.9	21.5	5.0	1.1	22.3	1.7	−0.6	16.9	−0.9	−3.2	14.3
	TS	59.3	49.8	81.0	58.2	49.1	79.0	59.4	50.2	80.4	48.9	39.7	70.0
	Prod.	−34.9	−43.1	−14.1	−35.8	−43.2	−16.2	−32.4	−40.3	−12.4	−44.7	−52.6	−24.7
1H + HC≡CH → **1H** · HC≡CH	vdW	−5.0	−4.3	19.6	−7.2	−6.3	16.5	−9.0	−7.6	13.9	−9.2	−7.8	13.7
	TS	1.8	0.3	29.4	9.8	6.8	40.8	9.9	6.6	41.2	9.6	6.3	41.0
	Prod.	−148.4	−155.8	−111.5	−149.0	−156.0	−112.8	−147.8	−155.3	−111.2	−153.8	−161.3	−117.3
1H + H_2C=CH_2 → **1H** · H_2C=CH_2	vdW		—[e]		−6.2	−5.9	24.5	−7.6[f]	−7.5[f]	23.4[f]	−7.9[f]	−7.8[f]	23.1[f]
	TS		—[e]		1.0	−2.5	36.5	0.3[f]	−3.3[f]	36.1[f]	−1.3[f]	−4.9[f]	34.6[f]
	Prod.	−136.7	−143.5	−96.2	−137.1	−143.6	−97.2	−136.1[f]	−142.7[f]	−95.9[f]	−145.0[f]	−151.7[f]	−104.9[f]
1H + H_2C=O → **1H** · H_2C=O	vdW		—[e]			—[e]		−12.9	−13.2	17.5	−13.1	−13.5	17.3
	TS		—[e]			—[e]		−10.3	−14.1	24.3	−11.5	−15.3	23.1
	Prod.	−163.4	−170.8	−123.2	−164.1	−171.3	−124.6	−163.0	−170.5	−123.1	−172.6	−180.1	−132.8

[a] DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-TZVP; [b] DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3/def2-TZVP; [c] CCSD(T)/def2-TZVP; [d] DLPNO-CCSD(T)/def2-QZVPP//CCSD(T)/def2-TZVP; [e] no stationary point found; [f] estimated using the thermal correction terms at the B3LYP-D3/def2-TZVP level of theory. Evaluation of the thermal corrections of the other model systems implies that the average error with respect to the thermal corrections computed at the CCSD(T)/def2-TZVP level of theory is below 0.5 mE_h (~1 kJ/mol).

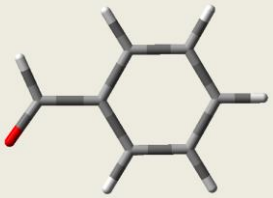
As can be inferred from Table S9, both PBE-D3 and B3LYP-D3 perform equally well in predicting the structures of the reaction products of the model reactions. Thus, the reaction energies including DLPNO-CCSD(T) electronic energies are close to those of the canonical CCSD(T) calculations. However, B3LYP-D3 performs considerably better in predicting the structures of the van-der-Waals (vdW) complexes as well as transition states (TS). Yet, both DFT methods fail to identify the TS of the addition of $H_2C{=}O$, which according to coupled-cluster calculations lies only ~2 kJ/mol higher in energy than the vdW complex (ΔU_0). The reaction barrier ($\Delta G^{\ddagger}$ = 23 kJ/mol) is therefore of entropic nature.

In the fourth column of Table S9, we included electronic energies calculated at the DLPNO-CCSD(T)/def2-QZVPP level of theory (quadruple-zeta basis) to investigate the basis set truncation error. In most cases, the energies are quite similar to the results at the triple-zeta level, with some notable exceptions: All addition products as well as the TS of the H_2 addition are stabilized by ~10 kJ/mol when using the QZ basis. The energies of the other transition states as well as the vdW complexes, however, remain nearly unaffected by the change in the number of basis functions, indicating that these values are well converged and, in particular, are not compromised by basis set superposition errors (BSSE).

5.3 Optimized structures (.xyz-files)

5.3.1 PhCHO

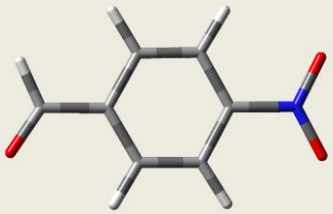
```
14
PhCHO @ PBE-D3/def2-TZVP - Cs
C           0.57235       -2.15794       -0.00000
C           1.61832       -1.23165       -0.00000
C           1.33077        0.13251       -0.00000
C          -0.00000        0.57315        0.00000
C          -1.04707       -0.36255        0.00000
C          -0.75944       -1.72301        0.00000
H           0.79403       -3.22660       -0.00000
H           2.65369       -1.57538       -0.00000
H           2.13739        0.87049       -0.00000
H          -2.07413        0.00639        0.00000
H          -1.56980       -2.45368        0.00000
C          -0.28309        2.02482        0.00000
O          -1.39583        2.52201        0.00000
H           0.63438        2.67065        0.00000
```



```
14
PhCHO @ B3LYP-D3/def2-TZVP - Cs
C           0.59275       -2.18334        0.00000
C           1.63383       -1.26193        0.00000
C           1.34852        0.09703       -0.00000
C           0.02492        0.53653       -0.00000
C          -1.01764       -0.39428       -0.00000
C          -0.73246       -1.74907       -0.00000
H           0.81176       -3.24365        0.00000
H           2.66083       -1.60319        0.00000
H           2.15124        0.82571       -0.00000
H          -2.03686       -0.03083       -0.00000
H          -1.53738       -2.47272       -0.00000
C          -0.25917        1.98561        0.00000
O          -1.36405        2.47473        0.00000
H           0.64462        2.63065        0.00000
```

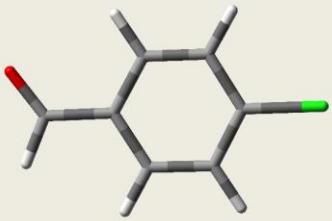
5.3.2 $C_6H_4NO_2CHO$

```
16
O2N-C6H4-CHO @ PBE-D3/def2-TZVP - Cs
C          -0.00000         1.04455         0.00000
C           1.27456         0.48221         0.00000
C           1.38064        -0.90596        -0.00000
C           0.22899        -1.70532        -0.00000
C          -1.04312        -1.11029        -0.00000
C          -1.16437         0.27319         0.00000
H           2.14700         1.13335         0.00000
H           2.36473        -1.38074        -0.00000
H          -1.92226        -1.75639        -0.00000
H          -2.13287         0.77068         0.00000
C           0.36808        -3.18336        -0.00000
O          -0.56573        -3.96354        -0.00000
H           1.42759        -3.54832        -0.00000
N          -0.12465         2.52590         0.00000
O          -1.26169         2.99786         0.00000
O           0.91739         3.18193         0.00000
```



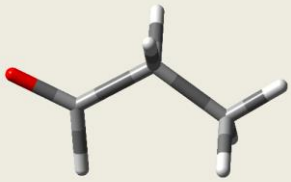
5.3.3 C_6H_4ClCHO

```
14
Cl-C6H4-CHO @ PBE-D3/def2-TZVP - Cs
C          -1.20207         0.57727         0.00000
C          -1.21492        -0.82007         0.00000
C          -0.00059        -1.50073         0.00000
C           1.21326        -0.79985        -0.00000
C           1.20281         0.60455        -0.00000
C           0.00000         1.29768        -0.00000
H          -2.16442        -1.35433         0.00000
H           0.01094        -2.59369         0.00000
H           2.15744         1.13333        -0.00000
H          -0.02439         2.38713        -0.00000
C           2.48828        -1.54588        -0.00000
O           3.59566        -1.03623        -0.00000
H           2.36821        -2.66094        -0.00000
Cl         -2.70786         1.44120         0.00000
```

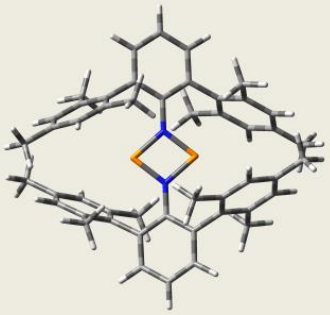


5.3.4 EtCHO

```
10
EtCHO @ PBE-D3/def2-TZVP - C1
C           1.68796         0.28603        -0.17895
C           0.47437        -0.59422         0.14616
H           2.60890        -0.31139        -0.19749
H           1.57474         0.76665        -1.16072
H           1.81819         1.07897         0.57254
H           0.30226        -1.36344        -0.61937
H           0.64424        -1.10565         1.11153
C          -0.77999         0.22698         0.30244
O          -1.81918         0.04378        -0.29557
H          -0.68888         1.07184         1.04023
```



5.3.5 [P(μ-NTer)]$_2$ (1)



```
102
[P(μ-NTer)]2 @ PBE-D3/def2-TZVP - D2
N          -0.00000        0.00000       -1.11373
N          -0.00000        0.00000        1.11373
P           1.34195       -0.00000        0.00000
P          -1.34195        0.00000        0.00000
C           0.00000       -0.00000        2.51579
C           1.15163        0.41324        3.22973
C          -1.15163       -0.41324        3.22973
C           1.13077        0.40397        4.62874
C          -1.13077       -0.40397        4.62874
C           0.00000       -0.00000        5.33560
H           2.02606        0.73377        5.15966
H          -2.02606       -0.73377        5.15966
H           0.00000       -0.00000        6.42632
C           0.00000       -0.00000       -2.51579
C           1.15163       -0.41324       -3.22973
C          -1.15163        0.41324       -3.22973
C           1.13077       -0.40397       -4.62874
C          -1.13077        0.40397       -4.62874
C           0.00000       -0.00000       -5.33560
H           2.02606       -0.73377       -5.15966
H          -2.02606        0.73377       -5.15966
H           0.00000       -0.00000       -6.42632
C          -2.38047        0.88753       -2.53313
C          -3.49608        0.03544       -2.39727
C          -2.43121        2.20977       -2.03338
C          -4.64223        0.52090       -1.75802
C          -3.59631        2.65199       -1.40490
C          -4.71164        1.82010       -1.25104
H          -5.50022       -0.14530       -1.63830
H          -3.62928        3.67224       -1.01242
C           2.38047       -0.88753       -2.53313
C           3.49608       -0.03544       -2.39727
C           2.43121       -2.20977       -2.03338
C           4.64223       -0.52090       -1.75802
C           3.59631       -2.65199       -1.40490
C           4.71164       -1.82010       -1.25104
H           5.50022        0.14530       -1.63830
H           3.62928       -3.67224       -1.01242
C          -2.38047       -0.88753        2.53313
C          -3.49608       -0.03544        2.39727
C          -2.43121       -2.20977        2.03338
C          -4.64223       -0.52090        1.75802
C          -3.59631       -2.65199        1.40490
C          -4.71164       -1.82010        1.25104
H          -5.50022        0.14530        1.63830
H          -3.62928       -3.67224        1.01242
C           2.38047        0.88753        2.53313
C           2.43121        2.20977        2.03338
C           3.49608        0.03544        2.39727
C           3.59631        2.65199        1.40490
C           4.64223        0.52090        1.75802
C           4.71164        1.82010        1.25104
H           3.62928        3.67224        1.01242
H           5.50022       -0.14530        1.63830
C          -3.44308        1.39457        2.86433
H          -4.42258        1.87762        2.75186
H          -3.13262        1.47615        3.91534
H          -2.71204        1.96531        2.26893
```

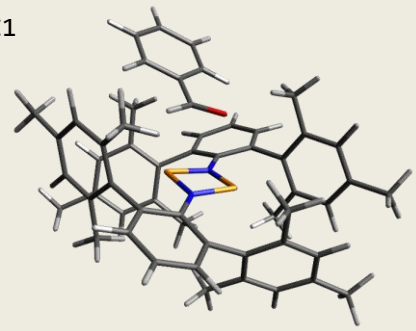
```
C          -1.23308       -3.11288        2.13905
H          -0.84812       -3.15778        3.16829
H          -1.47900       -4.13121        1.81134
H          -0.40954       -2.74129        1.50731
C          -5.94791       -2.31721        0.55159
H          -5.71638       -2.65276       -0.47111
H          -6.38857       -3.17686        1.07962
H          -6.71366       -1.53261        0.48677
C           3.44308       -1.39457        2.86433
H           4.42258       -1.87762        2.75186
H           3.13262       -1.47615        3.91534
H           2.71204       -1.96531        2.26893
C           1.23308        3.11288        2.13905
H           0.40954        2.74129        1.50731
H           0.84812        3.15778        3.16829
H           1.47900        4.13121        1.81134
C           5.94791        2.31721        0.55159
H           5.71638        2.65276       -0.47111
H           6.38857        3.17686        1.07962
H           6.71366        1.53261        0.48677
C           5.94791       -2.31721       -0.55159
H           5.71638       -2.65276        0.47111
H           6.38857       -3.17686       -1.07962
H           6.71366       -1.53261       -0.48677
C          -5.94791        2.31721       -0.55159
H          -5.71638        2.65276        0.47111
H          -6.38857        3.17686       -1.07962
H          -6.71366        1.53261       -0.48677
C          -1.23308        3.11288       -2.13905
H          -0.84812        3.15778       -3.16829
H          -1.47900        4.13121       -1.81134
H          -0.40954        2.74129       -1.50731
C           1.23308       -3.11288       -2.13905
H           0.84812       -3.15778       -3.16829
H           1.47900       -4.13121       -1.81134
H           0.40954       -2.74129       -1.50731
C           3.44308        1.39457       -2.86433
H           4.42258        1.87762       -2.75186
H           3.13262        1.47615       -3.91534
H           2.71204        1.96531       -2.26893
C          -3.44308       -1.39457       -2.86433
H          -4.42258       -1.87762       -2.75186
H          -3.13262       -1.47615       -3.91534
H          -2.71204       -1.96531       -2.26893
```

```
102
[P(μ-NTer)]2 @ B3LYP-D3/def2-TZVP - D2
N          -0.00000        0.00000       -1.11290
N          -0.00000        0.00000        1.11290
P           1.32466        0.00000       -0.00000
P          -1.32467        0.00000        0.00000
C          -0.00000        0.00000        2.51855
C           1.14131        0.42159        3.23091
C          -1.14131       -0.42159        3.23091
C           1.12017        0.41413        4.62316
C          -1.12017       -0.41413        4.62316
C          -0.00000        0.00000        5.32734
H           2.00486        0.74869        5.15045
H          -2.00486       -0.74869        5.15045
H          -0.00000        0.00000        6.40949
C          -0.00000        0.00000       -2.51855
C           1.14131       -0.42159       -3.23091
```

```
C          -1.14131        0.42159       -3.23091
C           1.12017       -0.41413       -4.62316
C          -1.12017        0.41413       -4.62316
C          -0.00000       -0.00000       -5.32734
H           2.00486       -0.74869       -5.15045
H          -2.00487        0.74869       -5.15045
H          -0.00000       -0.00000       -6.40949
C          -2.37292        0.89765       -2.54151
C          -3.47232        0.04124       -2.38772
C          -2.42770        2.21256       -2.04626
C          -4.60835        0.51312       -1.73377
C          -3.58036        2.64430       -1.40286
C          -4.67944        1.80551       -1.22992
H          -5.44920       -0.15580       -1.59648
H          -3.61625        3.65519       -1.01160
C           2.37292       -0.89765       -2.54151
C           3.47231       -0.04124       -2.38772
C           2.42770       -2.21255       -2.04625
C           4.60835       -0.51311       -1.73377
C           3.58037       -2.64429       -1.40286
C           4.67944       -1.80550       -1.22992
H           5.44919        0.15581       -1.59648
H           3.61625       -3.65518       -1.01159
C          -2.37292       -0.89765        2.54151
C          -3.47232       -0.04124        2.38772
C          -2.42770       -2.21256        2.04626
C          -4.60835       -0.51312        1.73377
C          -3.58036       -2.64430        1.40286
C          -4.67944       -1.80551        1.22992
H          -5.44920        0.15580        1.59648
H          -3.61625       -3.65519        1.01160
C           2.37292        0.89765        2.54151
C           2.42770        2.21256        2.04626
C           3.47231        0.04124        2.38772
C           3.58037        2.64429        1.40286
C           4.60835        0.51311        1.73377
C           4.67944        1.80550        1.22992
H           3.61625        3.65518        1.01159
H           5.44919       -0.15581        1.59648
C          -3.41287        1.39009        2.84865
H          -4.38253        1.87371        2.73252
H          -3.11048        1.47275        3.89307
H          -2.68347        1.95042        2.25736
C          -1.23521       -3.12196        2.15958
H          -0.86947       -3.17995        3.18624
H          -1.48093       -4.12808        1.82093
H          -0.40868       -2.75063        1.54753
C          -5.90505       -2.29156        0.50589
H          -5.65682       -2.62384       -0.50501
H          -6.35928       -3.14138        1.02158
H          -6.65700       -1.50616        0.42827
C           3.41287       -1.39009        2.84866
H           4.38252       -1.87371        2.73253
H           3.11047       -1.47275        3.89308
H           2.68346       -1.95043        2.25737
C           1.23522        3.12196        2.15957
H           0.40868        2.75063        1.54753
H           0.86948        3.17995        3.18624
H           1.48094        4.12807        1.82092
C           5.90506        2.29154        0.50588
H           5.65683        2.62382       -0.50501
H           6.35928        3.14137        1.02158
H           6.65700        1.50614        0.42827
```

```
C           5.90506        -2.29154        -0.50588
H           5.65682        -2.62382         0.50501
H           6.35928        -3.14137        -1.02158
H           6.65700        -1.50614        -0.42827
C          -5.90506         2.29155        -0.50589
H          -5.65682         2.62383         0.50501
H          -6.35928         3.14138        -1.02158
H          -6.65700         1.50615        -0.42827
C          -1.23521         3.12197        -2.15958
H          -0.86947         3.17995        -3.18624
H          -1.48093         4.12808        -1.82092
H          -0.40868         2.75063        -1.54753
C           1.23522        -3.12196        -2.15957
H           0.86947        -3.17995        -3.18624
H           1.48093        -4.12807        -1.82092
H           0.40868        -2.75063        -1.54753
C           3.41287         1.39009        -2.84866
H           4.38252         1.87371        -2.73253
H           3.11048         1.47275        -3.89308
H           2.68346         1.95043        -2.25737
C          -3.41287        -1.39009        -2.84866
H          -4.38253        -1.87371        -2.73253
H          -3.11048        -1.47275        -3.89308
H          -2.68347        -1.95042        -2.25737
```

5.3.6 [P(μ-NTer)]$_2$···PhCHO (vdW)



```
116
[P(μ-NTer)]2···PhCHO (vdW) @ B3LYP-D3/def2-TZVP - C1
N           0.20876        -0.84645         0.26708
P          -1.09511         0.29209         0.09295
P           1.50181         0.14178        -0.23033
C           0.14994        -2.21999         0.55490
N           0.26106         1.32659        -0.24842
C          -0.86296        -0.41404        -2.61703
O           0.36642        -0.49671        -2.66453
C          -0.99076        -2.74304         1.20853
C           1.22212        -3.07960         0.22760
C           0.33672         2.71905        -0.44625
C          -1.78696        -1.56970        -2.70863
H          -1.35724         0.55494        -2.73857
C          -1.10321        -4.12195         1.36603
C          -2.04314        -1.87769         1.82432
C           1.05923        -4.45205         0.40752
C           2.58313        -2.60138        -0.17173
C           1.57534         3.38143        -0.31249
C          -0.81271         3.48382        -0.74079
C          -3.11736        -1.33503        -3.06667
C          -1.35010        -2.88927        -2.57280
H          -1.98469        -4.51223         1.85768
C          -0.10524        -4.98384         0.93910
C          -1.72346        -1.09221         2.95228
C          -3.36034        -1.88226         1.34136
H           1.88475        -5.10179         0.14540
C           3.06164        -2.71811        -1.48964
C           3.45565        -2.15645         0.84181
C           1.65400         4.75140        -0.55018
C           2.81707         2.71015         0.16487
C          -0.68950         4.85358        -0.96289
C          -2.18317         2.90430        -0.80025
H          -3.46490        -0.31449        -3.15621
```

```
C          -3.98283       -2.39134       -3.31189
C          -2.21602       -3.94540       -2.81159
H          -0.33336       -3.07825       -2.27574
H          -0.21192       -6.05316        1.06641
C          -2.70879       -0.31089        3.54045
C          -0.33154       -1.05559        3.51661
C          -4.31369       -1.06774        1.95149
C          -3.77372       -2.73405        0.17654
C           4.37334       -2.34678       -1.76987
C           2.20128       -3.21488       -2.61498
C           4.76241       -1.80891        0.51651
C           3.01118       -2.04234        2.27446
H           2.61749        5.23303       -0.44081
C           0.53514        5.49515       -0.88731
C           2.97298        2.46406        1.54023
C           3.85225        2.40221       -0.72830
H          -1.58694        5.41490       -1.19089
C          -2.76419        2.61136       -2.04527
C          -2.92731        2.73834        0.37979
H          -5.00877       -2.19353       -3.59676
C          -3.53320       -3.70243       -3.19173
H          -1.86396       -4.96269       -2.69600
H          -2.44962        0.29407        4.40253
C          -4.01057       -0.27313        3.04679
H           0.32426       -0.45242        2.88481
H           0.10897       -2.05069        3.57713
H          -0.33284       -0.61442        4.51299
H          -5.31998       -1.05391        1.54811
H          -4.06039       -3.73780        0.50360
H          -2.97049       -2.85159       -0.54238
H          -4.63115       -2.29852       -0.33416
H           4.73042       -2.43909       -2.78946
C           5.24031       -1.88865       -0.78557
H           1.51471       -2.42677       -2.92813
H           1.61288       -4.08517       -2.32377
H           2.81613       -3.49289       -3.47103
H           5.42429       -1.47904        1.30721
H           3.87301       -1.94411        2.93406
H           2.42812       -2.90690        2.59194
H           2.38647       -1.15809        2.41632
H           0.61280        6.55981       -1.06405
C           4.17324        1.93471        1.99853
C           1.85340        2.74295        2.50512
C           5.04235        1.88269       -0.22559
C           3.67229        2.58614       -2.21137
C          -4.04202        2.06485       -2.08049
C          -2.03465        2.91111       -3.32878
C          -4.20426        2.18996        0.29858
C          -2.36146        3.11804        1.72152
H          -4.20607       -4.52853       -3.38341
C          -5.05432        0.59184        3.69797
C           6.65152       -1.49901       -1.12756
H           4.29182        1.74340        3.05942
C           5.22750        1.65453        1.13329
H           1.00152        2.08462        2.31675
H           1.48782        3.76706        2.41153
H           2.17930        2.58480        3.53268
H           5.84252        1.64811       -0.91756
H           4.52971        2.19047       -2.75502
H           3.55460        3.63835       -2.47875
H           2.77901        2.06490       -2.56352
H          -4.48470        1.82589       -3.04136
C          -4.76462        1.81545       -0.91631
```

```
H          -2.48445         2.37819        -4.16657
H          -0.98014         2.64090        -3.27231
H          -2.07226         3.98041        -3.55416
H          -4.76643         2.03637         1.21053
H          -1.85945         4.08543         1.68849
H          -1.63020         2.37702         2.05392
H          -3.15080         3.15957         2.47128
H          -5.97581         0.60789         3.11536
H          -4.70418         1.62060         3.80979
H          -5.29950         0.22659         4.69872
H           7.04487        -2.11233        -1.93959
H           7.31443        -1.60521        -0.26818
H           6.69905        -0.45710        -1.45544
C           6.54262         1.15729         1.66637
C          -6.09969         1.12702        -0.97215
H           7.17358         1.99412         1.97983
H           7.09356         0.59655         0.91234
H           6.40198         0.51542         2.53768
H          -5.96417         0.04227        -1.02320
H          -6.67028         1.42613        -1.85313
H          -6.69735         1.34254        -0.08582
```

5.3.7 [P(μ-NTer)]$_2$·PhCHO (2)

```
116
[P(μ-NTer)]2·PhCHO @ PBE-D3/def2-TZVP - C1
N           0.22027        -0.88769         0.43586
P          -1.14391         0.20561         0.06442
P           1.28394        -0.01097        -0.66052
C           0.18098        -2.25583         0.73969
N           0.23450         1.29966        -0.09827
C          -1.01691        -0.22537        -1.82696
O           0.40193        -0.36714        -2.06309
C          -0.92241        -2.77924         1.47144
C           1.25165        -3.12353         0.38867
C           0.32811         2.65858        -0.42090
C          -1.83149        -1.39878        -2.27110
H          -1.36375         0.68005        -2.34216
C          -0.99110        -4.15518         1.71390
C          -1.98593        -1.90130         2.04049
C           1.13712        -4.49208         0.66461
C           2.55154        -2.63122        -0.16115
C           1.60162         3.28428        -0.33056
C          -0.79827         3.44566        -0.77818
C          -3.15422        -1.18876        -2.69315
C          -1.33094        -2.70545        -2.26429
H          -1.84948        -4.53697         2.26952
C           0.01519        -5.02284         1.29621
C          -1.66940        -1.01123         3.09671
C          -3.31858        -1.98461         1.57851
H           1.97129        -5.14025         0.38805
C           2.94968        -2.87763        -1.49612
C           3.46165        -2.00713         0.72837
C           1.73347         4.63009        -0.69156
C           2.80837         2.61178         0.23424
C          -0.61743         4.79338        -1.11602
C          -2.19460         2.92359        -0.76189
H          -3.55886        -0.17476        -2.69316
C          -3.94754        -2.25735        -3.10902
C          -2.12001        -3.77392        -2.69177
H          -0.31723        -2.88243        -1.91967
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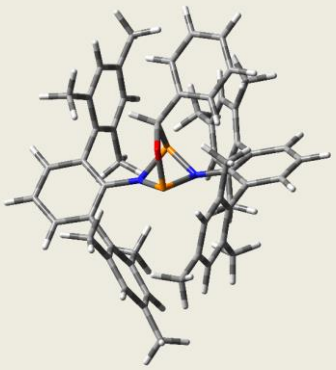

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H         -0.05379       -6.09215        1.49866
C         -2.67295       -0.20028        3.63040
C         -0.27527       -0.91412        3.65151
C         -4.28758       -1.14096        2.13545
C         -3.72896       -2.95242        0.50312
C          4.20597       -2.43493       -1.92518
C          2.06982       -3.58004       -2.49522
C          4.71397       -1.60758        0.26016
C          3.10188       -1.75698        2.16666
H          2.72111        5.08832       -0.60872
C          0.63928        5.39014       -1.09781
C          2.88590        2.38682        1.62779
C          3.92178        2.32894       -0.58483
H         -1.50018        5.37728       -1.38447
C         -2.88261        2.69669       -1.97615
C         -2.87449        2.76487        0.46789
H         -4.97263       -2.07354       -3.43662
C         -3.43180       -3.55610       -3.11795
H         -1.70659       -4.78412       -2.68155
H         -2.41703        0.48391        4.44460
C         -3.98939       -0.24075        3.15835
H          0.37912       -0.34876        2.97025
H          0.18087       -1.90586        3.77684
H         -0.27714       -0.40163        4.62242
H         -5.31013       -1.19252        1.75053
H         -3.97477       -3.93801        0.93047
H         -2.93450       -3.11502       -0.23332
H         -4.62097       -2.59137       -0.02499
H          4.49756       -2.61966       -2.96312
C          5.10032       -1.78983       -1.06975
H          1.47575       -2.85082       -3.06756
H          1.37221       -4.27876       -2.01761
H          2.68094       -4.14170       -3.21503
H          5.40905       -1.13894        0.95857
H          3.99641       -1.50802        2.75203
H          2.60850       -2.62653        2.62264
H          2.40569       -0.90847        2.25419
H          0.75989        6.44110       -1.36266
C          4.07990        1.90638        2.17328
C          1.71600        2.67765        2.52737
C          5.10127        1.86651        0.00675
C          3.83989        2.47097       -2.08122
C         -4.20545        2.24579       -1.93483
C         -2.21938        2.93825       -3.30780
C         -4.20061        2.32125        0.46054
C         -2.19436        3.05451        1.77701
H         -4.04889       -4.39134       -3.45251
C         -5.05357        0.63340        3.76518
C          6.43511       -1.30662       -1.56736
H          4.13409        1.73993        3.25302
C          5.20741        1.65995        1.38415
H          0.87324        2.00573        2.30487
H          1.34631        3.70417        2.38574
H          1.99111        2.54871        3.58221
H          5.96116        1.65030       -0.63251
H          4.78098        2.16029       -2.55388
H          3.62168        3.50243       -2.39249
H          3.03180        1.84141       -2.48751
H         -4.72731        2.05552       -2.87738
C         -4.87641        2.03062       -0.72589
H         -2.71502        2.36437       -4.10263
H         -1.15303        2.67340       -3.29235
H         -2.26829        4.00276       -3.58689
```

```
H          -4.71418        2.18667        1.41457
H          -1.53146        3.92724        1.70741
H          -1.57775        2.19715        2.09426
H          -2.93412        3.23036        2.56894
H          -5.94183        0.69002        3.12093
H          -4.68587        1.65578        3.93806
H          -5.37887        0.24068        4.74184
H           6.89830       -2.03292       -2.25057
H           7.12997       -1.12191       -0.73687
H           6.32547       -0.36210       -2.12435
C           6.49888        1.20081        2.00650
C          -6.26960        1.46425       -0.70298
H           7.01583        2.03493        2.50736
H           7.18598        0.79402        1.25180
H           6.32734        0.42651        2.76929
H          -6.23545        0.36221       -0.68911
H          -6.84451        1.76317       -1.59048
H          -6.82017        1.78534        0.19200
```

```
116
[P(μ-NTer)]2·PhCHO @ B3LYP-D3/def2-TZVP - C1
N           0.24726       -0.87510        0.38792
P          -1.13294        0.20098        0.06581
P           1.23990       -0.00419       -0.76521
C           0.22661       -2.24068        0.70600
N           0.20975        1.29218       -0.19279
C          -1.10396       -0.28280       -1.80143
O           0.30310       -0.40701       -2.09665
C          -0.83174       -2.75542        1.49438
C           1.26991       -3.10864        0.30708
C           0.31108        2.66600       -0.44037
C          -1.91505       -1.48302       -2.17265
H          -1.48281        0.58491       -2.33289
C          -0.89332       -4.12304        1.74342
C          -1.85866       -1.86385        2.10753
C           1.16434       -4.46973        0.58691
C           2.54729       -2.61277       -0.29032
C           1.56780        3.28498       -0.25447
C          -0.79239        3.46218       -0.81293
C          -3.24902       -1.30485       -2.54813
C          -1.40199       -2.77603       -2.13867
H          -1.71612       -4.49927        2.33771
C           0.07936       -4.99211        1.27339
C          -1.47770       -0.95932        3.12017
C          -3.20127       -1.91799        1.70088
H           1.97249       -5.11838        0.27216
C           2.87499       -2.79795       -1.64519
C           3.49063       -2.01455        0.57001
C           1.71523        4.63858       -0.54677
C           2.73117        2.58429        0.36166
C          -0.60200        4.81723       -1.07982
C          -2.18398        2.93438       -0.87497
H          -3.66234       -0.30566       -2.57418
C          -4.04201       -2.39121       -2.89179
C          -2.19023       -3.86365       -2.49263
H          -0.38532       -2.93397       -1.83076
H           0.01557       -6.05272        1.47742
C          -2.42679       -0.09805        3.65500
C          -0.06229       -0.89457        3.62251
C          -4.11715       -1.02319        2.25444
C          -3.68927       -2.91043        0.68264
C           4.09047       -2.31081       -2.12210
```

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C          1.96042       -3.48238       -2.62448
C          4.70277       -1.57334        0.05632
C          3.20773       -1.82207        2.03412
H          2.68599        5.09342       -0.39400
C          0.64514        5.41005       -0.97357
C          2.70912        2.31100        1.74150
C          3.88355        2.30605       -0.38606
H         -1.46419        5.40811       -1.36314
C         -2.78991        2.67896       -2.11768
C         -2.92126        2.76736        0.30839
H         -5.07293       -2.23148       -3.18269
C         -3.51409       -3.67781       -2.87222
H         -1.76746       -4.85984       -2.45977
H         -2.12360        0.59893        4.42886
C         -3.75160       -0.10155        3.22364
H          0.59037       -0.43003        2.88292
H          0.33739       -1.88946        3.82217
H         -0.00647       -0.30782        4.53915
H         -5.14405       -1.04874        1.90700
H         -3.95525       -3.85787        1.16043
H         -2.93813       -3.13268       -0.06823
H         -4.57866       -2.53737        0.17688
H          4.32538       -2.44240       -3.17276
C          5.01209       -1.68437       -1.29414
H          1.30102       -2.75828       -3.10710
H          1.33790       -4.23731       -2.14865
H          2.54389       -3.96825       -3.40726
H          5.42225       -1.12795        0.72937
H          4.13594       -1.68907        2.58901
H          2.66410       -2.66477        2.45922
H          2.60272       -0.92784        2.19460
H          0.77485        6.46329       -1.18477
C          3.84580        1.78572        2.34585
C          1.48777        2.59844        2.57150
C          5.00529        1.79508        0.26192
C          3.91168        2.50861       -1.87697
C         -4.09441        2.19981       -2.14906
C         -2.04345        2.91108       -3.40532
C         -4.22393        2.27791        0.23322
C         -2.32644        3.08907        1.65124
H         -4.12886       -4.52528       -3.14698
C         -4.75578        0.84645        3.81916
C          6.30033       -1.13598       -1.84183
H          3.82472        1.58133        3.41086
C          5.01123        1.53718        1.62671
H          0.65083        1.97014        2.26475
H          1.16575        3.63537        2.45769
H          1.68458        2.41254        3.62693
H          5.89407        1.58277       -0.32049
H          4.87027        2.19572       -2.29030
H          3.74466        3.54966       -2.15703
H          3.12852        1.91962       -2.36133
H         -4.55254        1.98975       -3.10959
C         -4.82012        1.96831       -0.98143
H         -2.54780        2.42236       -4.23892
H         -1.01934        2.53840       -3.35316
H         -1.97240        3.97744       -3.63315
H         -4.77835        2.12578        1.15085
H         -1.64468        3.93646        1.59754
H         -1.76383        2.23627        2.03974
H         -3.11021        3.31585        2.37346
H         -5.68232        0.85557        3.24419
H         -4.36581        1.86557        3.85541
```

```
H          -5.00547         0.56101         4.84474
H           6.67628        -1.74506        -2.66532
H           7.07121        -1.08678        -1.07172
H           6.15434        -0.12243        -2.22634
C           6.23931         1.00845         2.31596
C          -6.19537         1.36274        -1.03881
H           6.65229         1.74841         3.00663
H           7.01934         0.75470         1.59751
H           6.01433         0.11424         2.90247
H          -6.13106         0.27824        -1.17033
H          -6.77318         1.75879        -1.87578
H          -6.75077         1.54922        -0.11926
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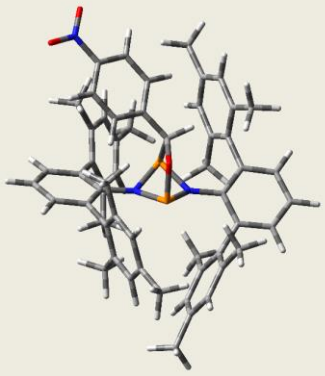
5.3.8 [P(μ-NTer)]$_2$·C$_6$H$_4$NO$_2$CHO (3)



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118
[P(μ-NTer)]2·C6H4NO2CHO @ PBE-D3/def2-TZVP - C1
P           1.40633         0.33477        -0.69167
P          -0.69191        -0.74213         0.25782
O           0.22432         0.61808        -1.88417
N           0.88214        -1.30445        -0.29022
N           0.33741         0.65819         0.67023
C          -1.02415         0.00290        -1.52418
C           1.33087        -2.50719        -0.85201
C          -0.05463         1.89213         1.21399
H          -1.18052        -0.88202        -2.15476
C          -2.20589         0.90387        -1.61757
C           2.73358        -2.71610        -0.94233
C           0.45215        -3.53496        -1.28127
C          -1.13021         1.93594         2.14524
C           0.64271         3.09134         0.90258
C          -3.47276         0.33834        -1.85462
C          -2.10647         2.29328        -1.45954
C           3.21577        -3.88351        -1.54546
C           3.73649        -1.80168        -0.32156
C           0.98348        -4.69362        -1.86334
C          -1.02611        -3.47409        -1.09694
C          -1.55927         3.17431         2.63462
C          -1.78414         0.69350         2.64783
C           0.17639         4.30402         1.42612
C           1.92511         3.10467         0.13504
H          -3.56025        -0.74320        -1.97124
C          -4.60562         1.13675        -1.94481
C          -3.23039         3.10646        -1.55541
H          -1.13669         2.73518        -1.25710
H           4.29713        -4.02472        -1.59895
C           2.35465        -4.86974        -2.02085
C           4.62929        -1.05738        -1.12075
C           3.87948        -1.79493         1.08581
H           0.28840        -5.47295        -2.18208
C          -1.59255        -3.73125         0.17243
C          -1.87054        -3.27590        -2.21424
H          -2.39083         3.18926         3.34118
C          -0.93413         4.36270         2.26455
C          -1.05040        -0.20588         3.46246
C          -3.14000         0.41928         2.35962
H           0.72581         5.21395         1.17629
C           2.02043         3.63071        -1.17483
C           3.10481         2.68190         0.79846
H          -5.59180         0.71455        -2.13169
C          -4.47140         2.51856        -1.79962
```

```
H          -3.16429        4.18670       -1.43558
H           2.74905       -5.77910       -2.47549
C           5.66611       -0.35042       -0.50272
C           4.44937       -0.96399       -2.61212
C           4.91863       -1.05811        1.66012
C           2.95050       -2.58707        1.96485
C          -2.98515       -3.71564        0.31217
C          -0.73073       -4.02063        1.37029
C          -3.25601       -3.27107       -2.02770
C          -1.30113       -3.07437       -3.59503
H          -1.28224        5.31834        2.65754
C          -1.66390       -1.37716        3.90991
C           0.37513        0.07073        3.85248
C          -3.70607       -0.77838        2.81503
C          -4.00270        1.37878        1.58691
C           3.26447        3.64156       -1.81578
C           0.83401        4.16646       -1.93045
C           4.32702        2.74137        0.12822
C           3.06601        2.16082        2.20833
N          -5.66842        3.37013       -1.88945
H           6.35673        0.22237       -1.12697
C           5.83540       -0.34266        0.88323
H           5.28500       -0.42123       -3.07329
H           3.52095       -0.41930       -2.85229
H           4.37024       -1.95007       -3.08932
H           5.02576       -1.06211        2.74866
H           2.90312       -3.64079        1.65191
H           1.92394       -2.19465        1.90942
H           3.27645       -2.54981        3.01237
H          -3.41539       -3.89955        1.29921
C          -3.83415       -3.46677       -0.76723
H           0.18946       -4.55057        1.09277
H          -1.27960       -4.62348        2.10590
H          -0.43754       -3.08461        1.87460
H          -3.90404       -3.10667       -2.89365
H          -0.40319       -2.44014       -3.58177
H          -2.04486       -2.61946       -4.26281
H          -0.99272       -4.03246       -4.04185
H          -1.08836       -2.06426        4.53693
C          -2.98758       -1.69424        3.58290
H           0.67493       -0.55840        4.70074
H           0.52259        1.12469        4.12548
H           1.05917       -0.13917        3.01615
H          -4.74655       -0.99646        2.55809
H          -3.42692        1.95707        0.85646
H          -4.48243        2.10590        2.26172
H          -4.80463        0.84514        1.06074
H           3.32309        4.03589       -2.83428
C           4.42798        3.19085       -1.19072
H           1.14135        4.98656       -2.59361
H           0.05010        4.54357       -1.26235
H           0.39257        3.38200       -2.56466
H           5.22883        2.42522        0.65475
H           2.68930        1.12659        2.23299
H           2.40630        2.76130        2.84958
H           4.07302        2.15137        2.64496
O          -5.51626        4.58976       -1.77109
O          -6.75624        2.81379       -2.07389
C           6.97177        0.40567        1.52685
C          -5.32344       -3.37661       -0.57576
C          -3.62136       -2.96471        4.08095
C           5.74613        3.18873       -1.91497
H           7.71576       -0.28756        1.94982
```

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H           6.61930        1.03943        2.35507
H           7.49111        1.04741        0.80205
H          -5.86824       -3.68569       -1.47843
H          -5.62263       -2.33929       -0.35103
H          -5.65965       -4.00061        0.26358
H          -2.95632       -3.82922        3.93711
H          -4.56958       -3.16867        3.56516
H          -3.83736       -2.90309        5.15935
H           5.82919        2.30573       -2.56924
H           6.59020        3.15946       -1.21251
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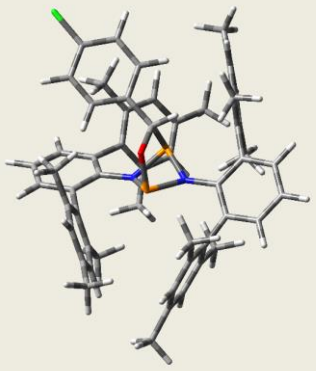
5.3.9 [P(μ-NTer)]$_2$·C$_6$H$_4$ClCHO (4)



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116
[P(μ-NTer)]2C6H4ClCHO @ PBE-D3/def2-TZVP - C1
Cl          5.58156       -4.03305       -2.25645
C           4.26486       -2.90611       -2.06410
C           2.98998       -3.37785       -1.75200
C           4.50033       -1.53833       -2.21333
C           1.94581       -2.46848       -1.58883
H           2.81873       -4.44684       -1.62600
H           5.50179       -1.18236       -2.45538
C           3.44378       -0.64399       -2.05703
C           2.15034       -1.09361       -1.74733
H           0.95763       -2.83409       -1.32854
H           3.62413        0.42624       -2.17578
C           1.05441       -0.09060       -1.58048
P           0.84512        0.62268        0.21781
O          -0.25825       -0.58731       -1.91906
H           1.26432        0.78933       -2.20259
P          -1.36838       -0.24649       -0.68069
N          -0.70088        1.33259       -0.24971
N          -0.28798       -0.69629        0.63642
C          -1.05885        2.58173       -0.77115
C           0.01548       -1.97059        1.13834
C          -0.10610        3.54808       -1.18676
C          -2.44119        2.90724       -0.83456
C          -0.78969       -3.10006        0.82473
C           1.11352       -2.12850        2.03098
C          -0.54930        4.76267       -1.72704
C           1.36482        3.36135       -1.03116
C          -2.83492        4.12682       -1.39689
C          -3.50896        2.05781       -0.23003
C          -0.40837       -4.36067        1.30190
C          -2.09576       -2.99202        0.10554
C           1.45446       -3.41073        2.47419
C           1.88473       -0.96010        2.54546
H           0.20286        5.49150       -2.03577
C          -1.90345        5.05457       -1.85733
C           1.96933        3.53227        0.23519
C           2.17308        3.12621       -2.16748
H          -3.90200        4.35589       -1.42995
C          -4.46399        1.41434       -1.04463
C          -3.64068        2.01362        1.17710
H          -1.04046       -5.21484        1.05032
C           0.72117       -4.53366        2.09808
C          -3.21359       -2.49706        0.82287
C          -2.27942       -3.47659       -1.21099
H           2.30471       -3.51224        3.15087
C           3.24892       -0.79055        2.21820
C           1.25595       -0.02928        3.41033
```

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H          -2.22878        6.00591       -2.27961
C           3.35723        3.39647        0.35119
C           1.14846        3.85392        1.45319
C           3.55543        2.99719       -2.00413
C           1.56946        3.01591       -3.54396
C          -5.54977        0.77191       -0.44130
C          -4.30347        1.36862       -2.54061
C          -4.73293        1.34486        1.73672
C          -2.64027        2.69268        2.07201
H           1.00084       -5.52490        2.45626
C          -4.46249       -2.45327        0.20204
C          -3.08006       -2.00803        2.23832
C          -3.54588       -3.38724       -1.79941
C          -1.16075       -4.06579       -2.02755
C           3.92980        0.33688        2.69448
C           3.99759       -1.78579        1.37531
C           1.98144        1.06917        3.87514
C          -0.17747       -0.19302        3.83377
H           3.81577        3.51358        1.33546
C           4.16575        3.10610       -0.74877
H           0.72095        2.93607        1.88992
H           0.31275        4.52498        1.21472
H           1.77016        4.32069        2.22840
H           4.17445        2.80260       -2.88501
H           0.61264        2.47495       -3.53154
H           2.25539        2.50460       -4.23266
H           1.35425        4.01084       -3.96443
H          -6.28705        0.27514       -1.07723
C          -5.71058        0.73366        0.94553
H          -3.35341        0.88141       -2.81387
H          -4.28403        2.37128       -2.99061
H          -5.12051        0.79920       -3.00295
H          -4.83087        1.31909        2.82585
H          -2.96142        2.65151        3.12090
H          -2.50071        3.74709        1.79060
H          -1.65328        2.21211        1.99412
H          -5.31666       -2.08112        0.76988
C          -4.64879       -2.87015       -1.11797
H          -4.06670       -1.91170        2.70957
H          -2.60510       -1.01528        2.26541
H          -2.45892       -2.67958        2.84707
H          -3.67247       -3.75238       -2.82264
H          -0.39979       -4.55000       -1.40305
H          -0.66236       -3.28360       -2.62107
H          -1.55253       -4.81201       -2.73209
H           4.97617        0.47582        2.40785
C           3.31755        1.28191        3.51723
H           4.42541       -2.58743        1.99873
H           4.83038       -1.30216        0.84866
H           3.35193       -2.26973        0.63502
H           1.48530        1.78208        4.54008
H          -0.41093       -1.23859        4.07758
H          -0.86177        0.10428        3.02443
H          -0.39798        0.43099        4.70975
C           5.64379        2.87959       -0.58498
C          -6.90410        0.06576        1.57433
C          -5.99218       -2.76384       -1.78626
C           4.07525        2.47312        4.03809
H           6.03821        3.41407        0.29002
H           6.20519        3.20396       -1.47225
H           5.85552        1.80760       -0.43672
H          -6.60996       -0.57486        2.41954
H          -7.44690       -0.55347        0.84699
```

```
H          -7.61343        0.81039        1.96919
H          -6.20562       -3.64582       -2.40696
H          -6.02954       -1.88443       -2.44945
H          -6.79958       -2.65644       -1.04918
H           4.33732        2.34259        5.10014
H           3.47686        3.39359        3.96723
H           5.01136        2.62640        3.48377
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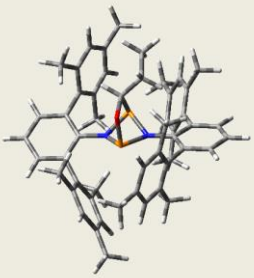
5.3.10 [P(μ-NTer)]$_2$·EtCHO (5)



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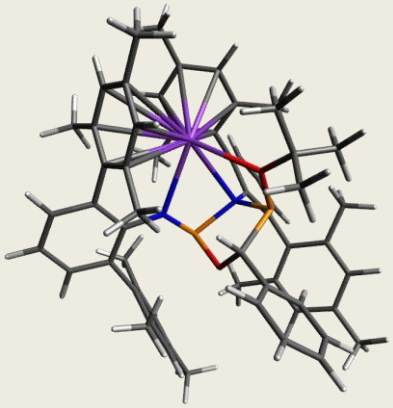
112
[P(μ-NTer)]2·EtCHO @ PBE-D3/def2-TZVP - C1
P          -1.27295       -0.08081       -0.58628
P           1.25382        0.03400       -0.30316
O          -0.67932       -0.05579       -2.16583
N          -0.13484        1.09594        0.05969
N          -0.00775       -1.15567        0.05912
C           0.77113        0.02121       -2.16124
C          -0.19790        2.49268        0.13444
C           0.00249       -2.55444       -0.00530
H           1.15530       -0.91020       -2.60080
C           1.28028        1.22285       -2.94074
C           0.90351        3.22853        0.65571
C          -1.37426        3.19807       -0.23365
C          -1.18725       -3.25971        0.32698
C           1.16793       -3.29757       -0.33030
H           1.02122        2.15121       -2.40576
H           0.74528        1.26356       -3.90374
C           2.78666        1.13774       -3.18778
C           0.83028        4.62540        0.71902
C           2.13001        2.57389        1.19090
C          -1.40241        4.59434       -0.14216
C          -2.62922        2.50572       -0.64624
C          -1.20680       -4.65617        0.24185
C          -2.41181       -2.58649        0.84960
C           1.10178       -4.69555       -0.39165
C           2.49402       -2.65683       -0.55861
H           3.15264        2.03399       -3.70741
H           3.03315        0.26153       -3.80506
H           3.34447        1.03776       -2.24565
H           1.68726        5.16472        1.12702
C          -0.30551        5.32059        0.31428
C           2.06751        1.82871        2.39187
C           3.37288        2.75658        0.54561
H          -2.32234        5.10639       -0.43206
C          -2.99191        2.39444       -2.00649
C          -3.51065        2.04231        0.35854
H          -2.13196       -5.17218        0.50687
C          -0.07791       -5.38431       -0.12705
C          -2.41955       -2.09018        2.17291
C          -3.58807       -2.53408        0.07281
H           2.01384       -5.24140       -0.64173
C           3.04539       -2.59612       -1.85827
C           3.25345       -2.20341        0.54630
H          -0.34538        6.40839        0.37916
C           3.23898        1.26517        2.90379
C           0.76800        1.63509        3.12460
C           4.51771        2.16189        1.08788
C           3.49988        3.58346       -0.70794
C          -4.20083        1.77131       -2.33521
C          -2.09365        2.88977       -3.10619
```

```
C          -4.71753        1.45076       -0.01620
C          -3.14499        2.14966        1.81380
H          -0.11003       -6.47318       -0.17715
C          -3.60332       -1.55922        2.69263
C          -1.18048       -2.13781        3.02444
C          -4.75384       -2.00911        0.63936
C          -3.58817       -2.97793       -1.36581
C           4.30300       -2.01041       -2.03740
C           2.31596       -3.16729       -3.04680
C           4.51677       -1.65232        0.32336
C           2.71186       -2.29147        1.94572
H           3.18303        0.69229        3.83379
C           4.47536        1.41627        2.26759
H           0.94372        1.24493        4.13556
H           0.11767        0.92446        2.59082
H           0.20649        2.57710        3.20303
H           5.47353        2.29129        0.57177
H           3.60049        4.65434       -0.47069
H           2.61838        3.48932       -1.35480
H           4.38991        3.28854       -1.27973
H          -4.47093        1.67379       -3.39058
C          -5.07319        1.28579       -1.35801
H          -1.51065        3.76705       -2.79825
H          -2.67730        3.14873       -3.99995
H          -1.37970        2.10131       -3.38771
H          -5.39524        1.09783        0.76324
H          -2.81219        3.16382        2.07735
H          -2.31589        1.46706        2.06115
H          -3.99646        1.87864        2.45107
H          -3.60262       -1.17792        3.71792
C          -4.78661       -1.52239        1.94808
H          -0.39780       -1.48199        2.61365
H          -0.75578       -3.15210        3.05882
H          -1.39730       -1.81506        4.05105
H          -5.66154       -1.96578        0.03170
H          -4.57539       -2.82260       -1.82076
H          -3.32099       -4.03866       -1.47530
H          -2.85033       -2.40559       -1.95114
H           4.71210       -1.93752       -3.04903
C           5.04868       -1.51902       -0.96207
H           1.22615       -3.06986       -2.95085
H           2.52212       -4.24448       -3.15290
H           2.63754       -2.67880       -3.97706
H           5.09448       -1.29960        1.17968
H           3.51364       -2.15704        2.68320
H           2.21379       -3.25340        2.12949
H           1.96514       -1.50071        2.12502
C           5.72785        0.83000        2.86168
C          -6.35080        0.58922       -1.74066
C          -6.05846       -0.98633        2.54883
C           6.37135       -0.83613       -1.17960
H           6.16501        1.51043        3.61021
H           6.49383        0.65519        2.09320
H           5.52542       -0.12257        3.37235
H          -6.15297       -0.45550       -2.03075
H          -6.83616        1.07669       -2.59825
H          -7.06358        0.57042       -0.90492
H          -5.88758       -0.03308        3.07170
H          -6.47429       -1.68752        3.28977
H          -6.82709       -0.82341        1.78088
```

```
H           6.23993        0.25796       -1.21412
H           6.83501       -1.14275       -2.12705
H           7.07483       -1.05233       -0.36309
```

5.3.11 TerNP]$_2$·PhCHO·KOtBu (6)



```
131
[P(μ-NTer)]2·PhCHO·KOtBu @ PBE-D3/def2-TZVP - C1
K         -12.92317       -6.27583      -12.24264
P         -10.40696       -7.82836      -14.27279
P         -11.89226       -9.73097      -12.43083
O         -10.71508       -6.26194      -13.65813
N         -11.89730       -8.61611      -13.92568
N         -12.19676       -8.67504      -11.18840
C         -14.62570       -7.60237      -14.43425
C         -14.43354       -6.30938      -14.97628
C         -15.08630       -5.21668      -14.39246
C         -15.95115       -5.37181      -13.29966
C         -16.13285       -6.66072      -12.78732
C         -15.48378       -7.78105      -13.33003
C         -13.03026       -6.68694       -9.27364
C         -11.86746       -5.88930       -9.40168
C         -11.99485       -4.52471       -9.69073
C         -13.24741       -3.91059       -9.84141
C         -14.38634       -4.70717       -9.68106
C         -14.30007       -6.07861       -9.39420
C          -9.58268       -8.55560      -12.71206
O         -10.19424       -9.82530      -12.51041
C          -9.93909       -5.10125      -14.09132
C         -12.66976       -9.15135      -15.02156
C         -12.46279       -9.10322       -9.89813
C         -14.02333       -8.75939      -15.15908
C         -13.55111       -6.11146      -16.17797
H         -14.93226       -4.22085      -14.81821
C         -16.67885       -4.18946      -12.71782
H         -16.79922       -6.80637      -11.93426
C         -15.68117       -9.13901      -12.71572
C         -12.91886       -8.13361       -8.93811
C         -10.50912       -6.50793       -9.23192
H         -11.08791       -3.92057       -9.79030
C         -13.35950       -2.43720      -10.13268
H         -15.37476       -4.25185       -9.78805
C         -15.55826       -6.88835       -9.22596
H          -9.85134       -7.86451      -11.89239
C          -8.09117       -8.68566      -12.79385
C          -9.73857       -5.08195      -15.60806
C          -8.59502       -5.11116      -13.36358
C         -10.78079       -3.90084      -13.65294
C         -12.14790      -10.10016      -15.94096
C         -12.28898      -10.43803       -9.39325
C         -14.85122       -9.37704      -16.10685
H         -12.53636       -6.49354      -15.99335
H         -13.93487       -6.66838      -17.04596
H         -13.48285       -5.04924      -16.44759
H         -16.00469       -3.33189      -12.57531
H         -17.48796       -3.85650      -13.38677
H         -17.12984       -4.43525      -11.74753
H         -16.49464       -9.12539      -11.97897
H         -15.90302       -9.90073      -13.47552
H         -14.76074       -9.46465      -12.20308
C         -13.25419       -8.49487       -7.62954
```

```
H        -10.38287       -6.90682       -8.21428
H        -10.39705       -7.36066       -9.91800
H         -9.71071       -5.77961       -9.42769
H        -13.24237       -1.84233       -9.21280
H        -12.58093       -2.10252      -10.83369
H        -14.33984       -2.18657      -10.56133
H        -15.72531       -7.15137       -8.17092
H        -16.43570       -6.32812       -9.57597
H        -15.49534       -7.84120       -9.77067
C         -7.28036       -8.15400      -11.78300
C         -7.48673       -9.34576      -13.87148
H         -9.13499       -5.93515      -15.94347
H        -10.70479       -5.11695      -16.12913
H         -9.22186       -4.15601      -15.89882
H         -8.75209       -5.15889      -12.27645
H         -7.99353       -5.98220      -13.65879
H         -8.02024       -4.20250      -13.59512
H        -10.94666       -3.92316      -12.56494
H        -10.26927       -2.95970      -13.89798
H        -11.75492       -3.90338      -14.16527
C        -13.00560      -10.68287      -16.88807
C        -10.71557      -10.52657      -16.05137
C        -12.64869      -10.75658       -8.07773
C        -11.64939      -11.56197      -10.14842
C        -14.35496      -10.35559      -16.96070
H        -15.89235       -9.05522      -16.17871
H        -13.59071       -7.71150       -6.94530
C        -13.14378       -9.80896       -7.18440
H         -7.74685       -7.64425      -10.93662
C         -5.89056       -8.27449      -11.84675
C         -6.09985       -9.47198      -13.93525
H         -8.11062       -9.76451      -14.66081
H        -12.58241      -11.41945      -17.57385
C        -10.25072      -11.69166      -15.40689
C         -9.88819       -9.86916      -16.99400
H        -12.50305      -11.78913       -7.75032
C        -10.24283      -11.69445      -10.10062
C        -12.42645      -12.59012      -10.72505
H        -15.00502      -10.83875      -17.69156
H        -13.40284      -10.08160       -6.16099
H         -5.27109       -7.85690      -11.05099
C         -5.29680       -8.93468      -12.92454
H         -5.64341       -9.98870      -14.78145
C         -8.95407      -12.14744      -15.67972
C        -11.10321      -12.47044      -14.44713
C         -8.60045      -10.35964      -17.23197
C        -10.38321       -8.67590      -17.76419
C         -9.64229      -12.82916      -10.65167
C         -9.40142      -10.62965       -9.45493
C        -11.78768      -13.72017      -11.24565
C        -13.91794      -12.45051      -10.83923
H         -4.21089       -9.03147      -12.97641
H         -8.59871      -13.04395      -15.16354
C         -8.11214      -11.50020      -16.58531
H        -10.82792      -12.23994      -13.40885
H        -12.16965      -12.23964      -14.55304
H        -10.96120      -13.55111      -14.59268
H         -7.96380       -9.83935      -17.95285
H        -10.65320       -7.85691      -17.07904
H         -9.61159       -8.30826      -18.45343
H        -11.28419       -8.91702      -18.34808
H         -8.55223      -12.91449      -10.62366
C        -10.39635      -13.85830      -11.22420
```

```
H          -9.63699      -10.53183       -8.38386
H          -8.33194      -10.85223       -9.56390
H          -9.59628       -9.65043       -9.91415
H         -12.39672      -14.51018      -11.69471
H         -14.37250      -12.09854       -9.90316
H         -14.15839      -11.70289      -11.61491
H         -14.38558      -13.40137      -11.12792
C          -6.73188      -12.02821      -16.87455
C          -9.72472      -15.05593      -11.84044
H          -6.25635      -12.42284      -15.96534
H          -6.76717      -12.85134      -17.60627
H          -6.08326      -11.24580      -17.29255
H          -8.81779      -15.33850      -11.28705
H         -10.39698      -15.92475      -11.86912
H          -9.41827      -14.84291      -12.87823
```

5.3.12 H_2

```
2
H2 @ PBE-D3/def2-TZVP - Dinfh
H           0.00000        0.00000       -0.37573
H           0.00000        0.00000        0.37573
```

```
2
H2 @ B3LYP-D3/def2-TZVP - Dinfh
H           0.00000        0.00000       -0.37203
H           0.00000        0.00000        0.37203
```

```
2
H2 @ CCSD(T)/def2-TZVP - Dinfh
H           0.00000        0.00000       -0.37130
H           0.00000        0.00000        0.37130
```

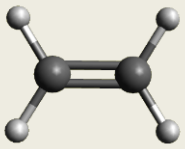
5.3.13 HC≡CH

```
4
HC≡CH @ PBE-D3/def2-TZVP - Dinfh
C           0.00000        0.00000       -0.60381
C           0.00000        0.00000        0.60381
H           0.00000        0.00000        1.67476
H           0.00000        0.00000       -1.67476
```

```
4
HC≡CH @ B3LYP-D3/def2-TZVP - Dinfh
C           0.00000        0.00000       -0.59851
C           0.00000        0.00000        0.59851
H           0.00000        0.00000        1.66139
H           0.00000        0.00000       -1.66139
```

```
4
HC≡CH @ CCSD(T)/def2-TZVP - Dinfh
C           0.00000        0.00000       -0.60491
C           0.00000        0.00000        0.60491
H           0.00000        0.00000        1.67120
H           0.00000        0.00000       -1.67120
```

5.3.14 $H_2C{=}CH_2$

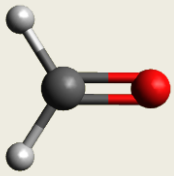


```
6
H2C=CH2 @ PBE-D3/def2-TZVP - D2h
C           0.00000        0.00000       -0.66639
C           0.00000        0.00000        0.66639
H           0.92885        0.00000       -1.24028
H          -0.92885        0.00000       -1.24028
H           0.92885        0.00000        1.24028
H          -0.92885        0.00000        1.24028
```

```
6
H2C=CH2 @ B3LYP-D3/def2-TZVP - D2h
C           0.00000        0.00000       -0.66246
C           0.00000        0.00000        0.66246
H           0.92176        0.00000       -1.23211
H          -0.92176        0.00000       -1.23211
H           0.92176        0.00000        1.23211
H          -0.92176        0.00000        1.23211
```

```
6
H2C=CH2 @ CCSD(T)/def2-TZVP - D2h
C           0.00000        0.00000       -0.66851
C           0.00000        0.00000        0.66851
H           0.92533        0.00000       -1.23633
H          -0.92533       -0.00000       -1.23633
H           0.92533        0.00000        1.23633
H          -0.92533       -0.00000        1.23633
```

5.3.15 $H_2C{=}O$

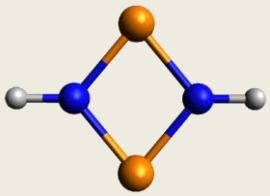


```
4
H2C=O @ PBE-D3/def2-TZVP - C2v
C           0.00000       -0.00000        0.58428
O          -0.00000        0.00000       -0.62374
H          -0.00000        0.94758        1.17925
H          -0.00000       -0.94758        1.17925
```

```
4
H2C=O @ B3LYP-D3/def2-TZVP - C2v
C           0.00000        0.00000       -0.60531
O           0.00000        0.00000        0.60419
H           0.93934        0.00000       -1.18855
H          -0.93934        0.00000       -1.18855
```

```
4
H2C=O @ CCSD(T)/def2-TZVP - C2v
C           0.00000        0.00000        0.59943
O           0.00000        0.00000       -0.59963
H           0.00000        0.93894        1.18735
H           0.00000       -0.93894        1.18735
```

5.3.16 $[P(\mu\text{-}NH)]_2$ (1H)

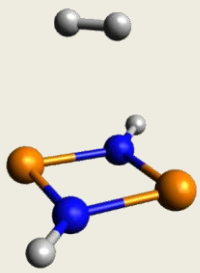


```
6
[P(μ-NH)]2 @ PBE-D3/def2-TZVP - D2h
N          1.09564        0.00000        0.00000
N         -1.09564       -0.00000        0.00000
P         -0.00000       -1.31771        0.00000
P          0.00000        1.31771        0.00000
H          2.10869        0.00000       -0.00000
H         -2.10869       -0.00000       -0.00000
```

```
6
[P(μ-NH)]2 @ B3LYP-D3/def2-TZVP – D2h
N          1.09097       -0.00000        0.00000
N         -1.09097        0.00000        0.00000
P          0.00000        1.30947        0.00000
P         -0.00000       -1.30947        0.00000
H          2.09640        0.00000        0.00000
H         -2.09640       -0.00000        0.00000
```

```
6
H2 @ CCSD(T)/def2-TZVP – D2h
N          0.00000        1.09163        0.00000
N         -0.00000       -1.09163        0.00000
P          1.31332       -0.00000        0.00000
P         -1.31332        0.00000        0.00000
H         -0.00000        2.10024        0.00000
H          0.00000       -2.10024        0.00000
```

5.3.17 $[P(\mu\text{-}NH)]_2\cdots H_2$ (vdW)



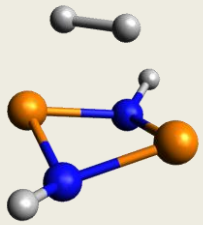
```
8
[P(μ-NH)]2···H2 (vdW) @ PBE-D3/def2-TZVP – C2v
N         -0.00000       -1.09681        0.08477
N          0.00000        1.09681        0.08477
P         -1.31191        0.00000        0.04139
P          1.31191        0.00000        0.04139
H          0.00000       -2.10860        0.03850
H         -0.00000        2.10860        0.03850
H         -0.38248        0.00000       -2.48850
H          0.38248        0.00000       -2.48850
```

```
8
[P(μ-NH)]2···H2 (vdW) @ B3LYP-D3/def2-TZVP - C2v
N         -0.00000       -1.09328        0.07959
N          0.00000        1.09328        0.07959
P         -1.30363       -0.00000        0.04408
P          1.30363        0.00000        0.04408
H          0.00000       -2.09781        0.02854
H          0.00000        2.09781        0.02854
H         -0.37726        0.00000       -2.48893
H          0.37726        0.00000       -2.48893
```

```
8
[P(μ-NH)]2···H2 (vdW) @ CCSD(T)/def2-TZVP - C2v
N          0.00000       -1.09208        0.06700
N          0.00000        1.09208        0.06700
P         -1.31044        0.00000        0.05450
P          1.31044        0.00000        0.05450
H          0.00000       -2.10042        0.06864
H          0.00000        2.10042        0.06864
H         -0.37381        0.00000       -2.67426
H          0.37381        0.00000       -2.67426
```

5.3.18 $[P(\mu\text{-}NH)]_2\cdots H_2$ (TS)

```
8
[P(μ-NH)]2···H2 (TS) @ PBE-D3/def2-TZVP - C2v
N         -0.00000       -1.11197        0.27664
N          0.00000        1.11197        0.27664
P         -1.27252        0.00000       -0.06995
P          1.27252        0.00000       -0.06995
H         -0.00000       -2.09357        0.01459
H          0.00000        2.09357        0.01459
H         -0.49551        0.00000       -1.70943
H          0.49551        0.00000       -1.70943
```

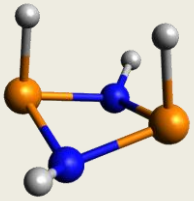


```
8
[P(μ-NH)]2···H2 (TS) @ B3LYP-D3/def2-TZVP - C2v
N          0.00000       -1.10566        0.27008
N          0.00000        1.10566        0.27008
P         -1.26638        0.00000       -0.06776
P          1.26638        0.00000       -0.06776
H          0.00000       -2.08575        0.03609
H          0.00000        2.08575        0.03609
H         -0.49843        0.00000       -1.70697
H          0.49843        0.00000       -1.70697
```

```
8
[P(μ-NH)]2···H2 (TS) @ CCSD(T)/def2-TZVP - C2v
N         -0.00000       -1.10412        0.27414
N          0.00000        1.10412        0.27414
P         -1.26876        0.00000       -0.06976
P          1.26876        0.00000       -0.06976
H          0.00000       -2.08592        0.03152
H          0.00000        2.08592        0.03152
H         -0.48710        0.00000       -1.69724
H          0.48710        0.00000       -1.69724
```

5.3.19 $[P(\mu\text{-}NH)]_2 \cdot H_2$ (addition product)

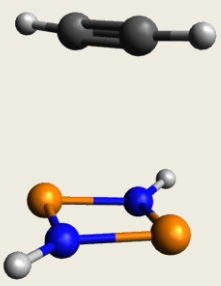
```
8
[P(μ-NH)]2·H2 @ PBE-D3/def2-TZVP - C2v
N          0.00000       -1.12692        0.29094
N          0.00000        1.12692        0.29094
P         -1.28626        0.00000       -0.07925
P          1.28626        0.00000       -0.07925
H         -0.00000       -2.08140       -0.06161
H          0.00000        2.08140       -0.06161
H         -1.12612        0.00000       -1.54602
H          1.12612        0.00000       -1.54602
```



```
8
[P(μ-NH)]2·H2 @ B3LYP-D3/def2-TZVP - C2v
N          0.00000       -1.11864        0.25278
N         -0.00000        1.11864        0.25278
P         -1.29030        0.00000       -0.06346
P          1.29030        0.00000       -0.06346
H          0.00000       -2.08165       -0.04409
H          0.00000        2.08165       -0.04409
H         -1.22171        0.00000       -1.51864
H          1.22171        0.00000       -1.51864
```

```
8
[P(μ-NH)]2·H2 @ CCSD(T)/def2-TZVP - C2v
N         -0.00000       -1.11895        0.27318
N          0.00000        1.11895        0.27318
P         -1.28727        0.00000       -0.07246
P          1.28727        0.00000       -0.07246
H          0.00000       -2.07783       -0.04978
H          0.00000        2.07783       -0.04978
H         -1.18521        0.00000       -1.51982
H          1.18521        0.00000       -1.51982
```

5.3.20 [P(μ-NH)]$_2$···HC≡CH (vdW)



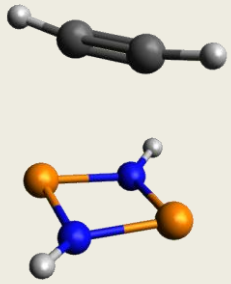
```
10
[P(μ-NH)]2···HC≡CH (vdW) @ PBE-D3/def2-TZVP - Cs
N         -1.09166        0.74147        0.00000
N          1.10559        0.70602        0.00000
P          0.00442        0.66539       -1.30809
P          0.00442        0.66539        1.30809
H         -2.10338        0.78113        0.00000
H          2.10036        0.51420        0.00000
C         -0.01772       -2.40667       -0.60698
C         -0.01772       -2.40667        0.60698
H         -0.01983       -2.47384       -1.67444
H         -0.01983       -2.47384        1.67444
```

```
10
[P(μ-NH)]2···HC≡CH (vdW) @ B3LYP-D3/def2-TZVP - Cs
N         -1.08478        0.76815        0.00000
N          1.09899        0.71025        0.00000
P          0.00588        0.70660       -1.30280
P          0.00588        0.70660        1.30280
H         -2.08888        0.81065        0.00000
H          2.09493        0.57454        0.00000
C         -0.02177       -2.52858       -0.60000
C         -0.02177       -2.52858        0.60000
H         -0.02308       -2.54724       -1.66135
H         -0.02308       -2.54724        1.66135
```

```
10
[P(μ-NH)]2···HC≡CH (vdW) @ CCSD(T)/def2-TZVP - Cs
N          -1.08433         0.78329         0.00000
N           1.10021         0.72923         0.00000
P           0.00728         0.73618        -1.30881
P           0.00728         0.73618         1.30881
H          -2.09128         0.83747         0.00000
H           2.10262         0.61818         0.00000
C          -0.02620        -2.62048        -0.60581
C          -0.02620        -2.62048         0.60581
H          -0.02760        -2.63332        -1.67167
H          -0.02760        -2.63332         1.67167
```

5.3.21 [P(μ-NH)]$_2$···HC≡CH (TS)

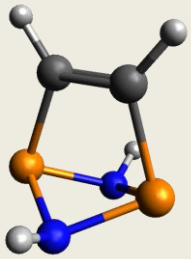
```
10
[P(μ-NH)]2···HC≡CH (TS) @ PBE-D3/def2-TZVP - C2v
N           0.00000        -1.10046         0.71447
N           0.00000         1.10046         0.71447
P          -1.30234         0.00000         0.60780
P           1.30234         0.00000         0.60780
H           0.00000        -2.10539         0.59002
H           0.00000         2.10539         0.59002
C          -0.61017         0.00000        -2.24644
C           0.61017         0.00000        -2.24644
H          -1.66457         0.00000        -2.42701
H           1.66457         0.00000        -2.42701
```



```
10
[P(μ-NH)]2···HC≡CH (TS) @ B3LYP-D3/def2-TZVP - C2v
N           0.00000        -1.09714         0.71387
N           0.00000         1.09714         0.71387
P          -1.28806         0.00000         0.55802
P           1.28806         0.00000         0.55802
H           0.00000        -2.09002         0.55737
H           0.00000         2.09002         0.55737
C          -0.60925         0.00000        -2.11459
C           0.60925         0.00000        -2.11459
H          -1.62531         0.00000        -2.42727
H           1.62531         0.00000        -2.42727
```

```
10
[P(μ-NH)]2···HC≡CH (TS) @ CCSD(T)/def2-TZVP - C2v
N          -1.09788         0.71263         0.00000
N           1.09791         0.71245         0.00000
P           0.00002         0.54180        -1.29060
P           0.00002         0.54180         1.29060
H          -2.09319         0.54807         0.00000
H           2.09330         0.54843         0.00000
C          -0.00006        -2.07137        -0.61654
C          -0.00006        -2.07137         0.61654
H          -0.00004        -2.41640        -1.62713
H          -0.00004        -2.41640         1.62713
```

5.3.22 [P(μ-NH)]$_2$ · HC≡CH (addition product)

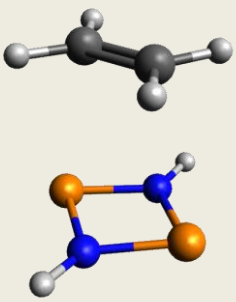


```
10
[P(μ-NH)]2·HC≡CH @ PBE-D3/def2-TZVP - C2v
N          -0.00000       -1.12705        0.82012
N           0.00000        1.12705        0.82012
P          -1.25437       -0.00000        0.28986
P           1.25437        0.00000        0.28986
H           0.00000       -2.05894        0.40082
H          -0.00000        2.05894        0.40082
C          -0.66725       -0.00000       -1.53612
C           0.66725        0.00000       -1.53612
H          -1.33540       -0.00000       -2.40002
H           1.33540        0.00000       -2.40002
```

```
10
[P(μ-NH)]2·HC≡CH @ B3LYP-D3/def2-TZVP - C2v
N          -0.00000       -1.12048        0.80670
N           0.00000        1.12048        0.80670
P          -1.25131        0.00000        0.29203
P           1.25131        0.00000        0.29203
H           0.00000       -2.05453        0.41557
H           0.00000        2.05453        0.41557
C          -0.66349       -0.00000       -1.52818
C           0.66349        0.00000       -1.52818
H          -1.32069        0.00000       -2.38948
H           1.32069        0.00000       -2.38948
```

```
10
[P(μ-NH)]2·HC≡CH @ CCSD(T)/def2-TZVP - C2v
N           0.00000       -1.11993        0.81012
N           0.00000        1.11993        0.81012
P          -1.25139        0.00000        0.28890
P           1.25139        0.00000        0.28890
H          -0.00000       -2.05214        0.40337
H           0.00000        2.05214        0.40337
C          -0.67074        0.00000       -1.52305
C           0.67074        0.00000       -1.52305
H          -1.32618        0.00000       -2.38981
H           1.32618        0.00000       -2.38981
```

5.3.23 [P(μ-NH)]$_2$···H$_2$C=CH$_2$ (vdW)

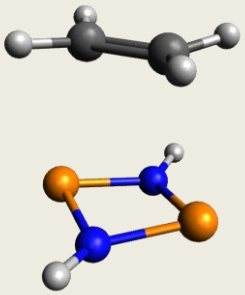


```
12
[P(μ-NH)]2···H2C=CH2 (vdW) @ B3LYP-D3/def2-TZVP - C2v
N           1.09259       -0.00000        0.75830
N          -1.09259        0.00000        0.75830
P           0.00000       -1.30099        0.69616
P           0.00000        1.30099        0.69616
H           2.09603        0.00000        0.70489
H          -2.09603       -0.00000        0.70489
C           0.00000       -0.66730       -2.34094
C           0.00000        0.66730       -2.34094
H           0.91847       -1.23870       -2.37001
H          -0.91847       -1.23870       -2.37001
H           0.91847        1.23870       -2.37001
H          -0.91847        1.23870       -2.37001
```

```
12
[P(μ-NH)]2···H2C=CH2 (vdW) @ CCSD(T)/def2-TZVP - C2v
N          1.09237        0.00000        0.77481
N         -1.09237        0.00000        0.77481
P          0.00000       -1.30846        0.74290
P          0.00000        1.30846        0.74290
H          2.10059        0.00000        0.75468
H         -2.10059        0.00000        0.75468
C          0.00000       -0.67028       -2.46621
C          0.00000        0.67028       -2.46621
H          0.92348       -1.24056       -2.48142
H         -0.92348       -1.24056       -2.48142
H          0.92348        1.24056       -2.48142
H         -0.92348        1.24056       -2.48142
```

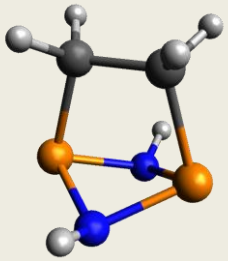
5.3.24 $[P(\mu\text{-}NH)]_2\cdots H_2C{=}CH_2$ (TS)

```
12
[P(μ-NH)]2···H2C=CH2 (TS) @ B3LYP-D3/def2-TZVP - C2v
N          1.09630        0.00000        0.74730
N         -1.09630        0.00000        0.74730
P          0.00000       -1.29041        0.59075
P          0.00000        1.29041        0.59075
H          2.09347        0.00000        0.62207
H         -2.09347        0.00000        0.62207
C          0.00000       -0.67852       -2.07874
C          0.00000        0.67852       -2.07874
H          0.91584       -1.24168       -2.19473
H         -0.91584       -1.24168       -2.19473
H          0.91584        1.24168       -2.19473
H         -0.91584        1.24168       -2.19473
```



```
12
[P(μ-NH)]2···H2C=CH2 (TS) @ CCSD(T)/def2-TZVP - C2v
N          1.09655        0.00000        0.74323
N         -1.09655        0.00000        0.74323
P          0.00000       -1.29399        0.58034
P          0.00000        1.29399        0.58034
H          2.09766        0.00000        0.62026
H         -2.09766       -0.00000        0.62026
C          0.00000       -0.68342       -2.04995
C          0.00000        0.68342       -2.04995
H          0.92031       -1.24390       -2.17714
H         -0.92031       -1.24390       -2.17714
H          0.92031        1.24390       -2.17714
H         -0.92031        1.24390       -2.17714
```

5.3.25 $[P(\mu\text{-}NH)]_2 \cdot H_2C{=}CH_2$ (addition product)



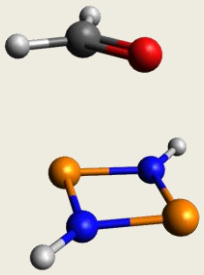
```
12
[P(μ-NH)]2·H2C=CH2 @ PBE-D3/def2-TZVP - C2v
N          -0.00000       -1.12267        0.82553
N           0.00000        1.12267        0.82553
P          -1.26125        0.00000        0.32774
P           1.26125        0.00000        0.32774
H           0.00000       -2.07677        0.46271
H           0.00000        2.07677        0.46271
C          -0.76640        0.00000       -1.51178
C           0.76640        0.00000       -1.51178
H          -1.20306       -0.88598       -1.99560
H          -1.20306        0.88598       -1.99560
H           1.20306        0.88598       -1.99560
H           1.20306       -0.88598       -1.99560
```

```
12
[P(μ-NH)]2·H2C=CH2 @ B3LYP-D3/def2-TZVP - C2v
N          -0.00000       -1.11733        0.81039
N           0.00000        1.11733        0.81039
P          -1.25734        0.00000        0.33050
P           1.25734        0.00000        0.33050
H           0.00000       -2.07337        0.48023
H           0.00000        2.07337        0.48023
C          -0.76775        0.00000       -1.50399
C           0.76775        0.00000       -1.50399
H          -1.19596       -0.87979       -1.98788
H          -1.19596        0.87979       -1.98788
H           1.19596        0.87979       -1.98788
H           1.19596       -0.87979       -1.98788
```

```
12
[P(μ-NH)]2·H2C=CH2 @ CCSD(T)/def2-TZVP - C2v
N           0.00000       -1.11605        0.81369
N           0.00000        1.11605        0.81369
P          -1.25787        0.00000        0.32763
P           1.25787        0.00000        0.32763
H          -0.00000       -2.07183        0.46941
H           0.00000        2.07183        0.46941
C          -0.77069        0.00000       -1.49971
C           0.77069        0.00000       -1.49971
H          -1.19772       -0.88377       -1.98687
H          -1.19772        0.88377       -1.98687
H           1.19772        0.88377       -1.98687
H           1.19772       -0.88377       -1.98687
```

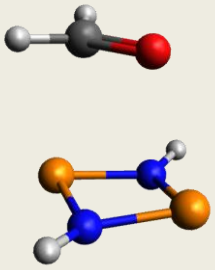
5.3.26 [P(μ-NH)]$_2$···H$_2$C=O (vdW)

```
10
[P(μ-NH)]2···H2C=O (vdW) @ CCSD(T)/def2-TZVP - Cs
N          0.73404       -0.06546       -1.09282
P          0.53539       -1.37200       -0.00015
P          0.82843        1.22459        0.00005
H          0.68715       -0.05076       -2.10026
N          0.73308       -0.06552        1.09274
C         -2.22316       -0.38825        0.00023
O         -2.04687        0.81906        0.00006
H          0.68643       -0.05095        2.10019
H         -2.34520       -0.96137       -0.93544
H         -2.34465       -0.96118        0.93609
```



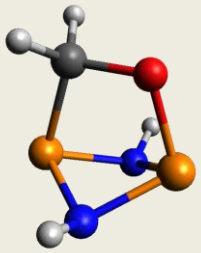
5.3.27 [P(μ-NH)]$_2$···H$_2$C=O (TS)

```
10
[P(μ-NH)]2···H2C=O (TS) @ CCSD(T)/def2-TZVP - Cs
N          0.69983        0.18379       -1.09569
P          0.87888       -1.12875       -0.00002
P          0.27954        1.39400       -0.00001
H          0.58643        0.17072       -2.09812
N          0.70000        0.18382        1.09566
C         -1.76391       -1.06578        0.00004
O         -1.99589        0.15134        0.00007
H          0.58616        0.17066        2.09804
H         -1.76175       -1.65143       -0.93340
H         -1.76178       -1.65147        0.93346
```



5.3.28 [P(μ-NH)]$_2$ · H$_2$C=O (addition product)

```
10
[P(μ-NH)]2·H2C=O @ PBE-D3/def2-TZVP - Cs
N          0.81994        0.22254       -1.11881
P          0.67586       -1.13572        0.00000
P         -0.07335        1.23605        0.00000
H          0.47207        0.12726       -2.07506
N          0.81994        0.22254        1.11881
C         -1.22939       -1.04074        0.00000
O         -1.53042        0.37235        0.00000
H          0.47207        0.12726        2.07506
H         -1.65306       -1.51565       -0.89874
H         -1.65306       -1.51565        0.89874
```



```
10
[P(μ-NH)]2·H2C=O @ B3LYP-D3/def2-TZVP - Cs
N          0.80344        0.21919       -1.11287
P          0.67929       -1.13022       -0.00000
P         -0.07539        1.23397       -0.00000
H          0.48384        0.13051       -2.06970
N          0.80344        0.21919        1.11287
C         -1.22203       -1.04190       -0.00000
O         -1.51193        0.37089       -0.00000
H          0.48384        0.13051        2.06970
H         -1.64738       -1.50630       -0.89192
H         -1.64738       -1.50630        0.89192
```

```
10
[P(μ-NH)]2·H2C=O @ CCSD(T)/def2-TZVP - Cs
N           0.80701         0.22059        -1.11285
P           0.67754        -1.13033        -0.00000
P          -0.07834         1.23039        -0.00000
H           0.46987         0.12630        -2.06765
N           0.80701         0.22059         1.11285
C          -1.21642        -1.04109        -0.00000
O          -1.51160         0.37519        -0.00000
H           0.46987         0.12630         2.06765
H          -1.64669        -1.50391        -0.89477
H          -1.64669        -1.50391         0.89477
```

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