Chemical Communications

**Supporting information**

# A neutral diphosphene radical: synthesis, electronic structure and white phosphorus activation

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# Contents

# 1 Experimental Section

## 1.1 General Remarks

All manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified nitrogen or argon, respectively. All glassware was oven-dried at 160 °C prior to use. Dry, oxygen-free solvents such as $CH_2Cl_2$, $C_6H_5F$, $CH_3CN$, *n*-pentane, *n*-hexane, THF, $Et_2O$, Toluene, Benzene (distilled from potassium or $CaCH_2$ (for $CH_2Cl$ and $CH_3CN$)) were employed. All distilled and deuterated solvents were stored over 4 Å molecular sieves, except for $CD_3CN$ and $CH_3CN$, which were store over 3 Å molecular sieves.

Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Nitrogen atmosphere.

EPR measurements were recorded using a ca. 0.5 mM solution of **1**$^{\cdot}$ in dry and degassed $CH_3CN$ in a sealed glass capillary. EPR spectra were performed using a CW X-band EMXplus spectrometer with a premiumX microwave bridge (Bruker) and a high sensitivity resonator (ER 4119 HS, Bruker). The EPR spectra were registered at 100 kHz modulation at room temperature. For the precise determination of g-values, an NMR teslameter (ER036TM, Bruker) was used. The simulation of the EPR spectrum was done using the SpinFit module incorporated in the Xenon software of the spectrometer.

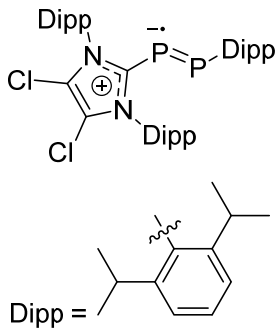
Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Elemental analyses were performed on a Vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS mode.

NMR spectra were measured on a Bruker AVANCE III HD Nanobay 400 MHz Ultrashield ($^1$H = 400.13 MHz, $^{13}$C = 100.61 MHz, $^{19}$F = 376.50 Hz, $^{31}$P = 161.98 MHz) or Bruker AVANCE III HDX 500 MHz Ascend ($^1$H = 500.13 MHz, $^{13}$C = 125.75 MHz, $^{19}$F = 470.59 MHz, $^{31}$P = 202.45 MHz) and analyzed using the software Topspin v3.2 (Bruker). Chemical shifts $\delta$ are referenced to the external standards tetramethylsilane ($^1$H, $^{13}$C) trichlorofluoromethane ($^{19}$F), or phosphoric acid 85 % ($^{31}$P) and are given in ppm. Coupling constants over n bonds $^nJ$ are given in Hz. Unless stated otherwise, all spectra were measured at 300 K. Reported numbers assigning atoms in the $^{13}$C spectra were deduced from 2D correlation experiments (HSQC, HMBC). The multiplicity of peaks is described using the following abbreviations: (br.) s – (broad) singlet, d – dublet, t – triplet, q – quartet, m – multiplet. NMR at various temperatures (250 to 350 K, in 10 K increments) were performed using a BCU II temperature control unit (Bruker) in combination with a liquid nitrogen evaporator for low temperatures.

**3**[1] and **2**[OTf][2], $Im_4P_4[OTf]_4$[3] and $Cy_4P_4$[4] were prepared according to literature procedures.

## 1.2 Preparation of ($^{CL}$IM$^{DIPP}$)P-P(DIPP) 1$^{\cdot}$




To an orange solution of **2**[OTf] (100 mg, 0.12 mmol, 1 eq.) in 3 mL THF a black solution of $CoCp_2$ (22.79 mg, 0.12 mmol, 1 eq.) in 3 ml THF was added dropwise. The reaction mixture was stirred for 12 h at RT and turned intensely dark red. The reaction mixture was dried under reduced pressure and 5 mL of *n*-pentane was added to the residue. $CoCp_2$[OTf] was removed by filtration and the solid was washed with *n*-pentane (3 x 2 ml). The collected filtrates were concentrated under reduced pressure and stored at -30 °C for two days. The product crystallized in form of dark red crystals, which were isolated by filtration. After drying under reduced pressure, **1**$^{\cdot}$ was obtained as air sensitive crystalline solid.

**Yield:** 51 mg (62 %); **melting point:** 150 °C (decomp.); **elemental analysis:** calculated: N 4.12, C 68.82, H 7.55; found: N 4.28, C 69.11, H 7.13; **UV-vis:** $\lambda_{max}$ = 401 nm, 503 nm.

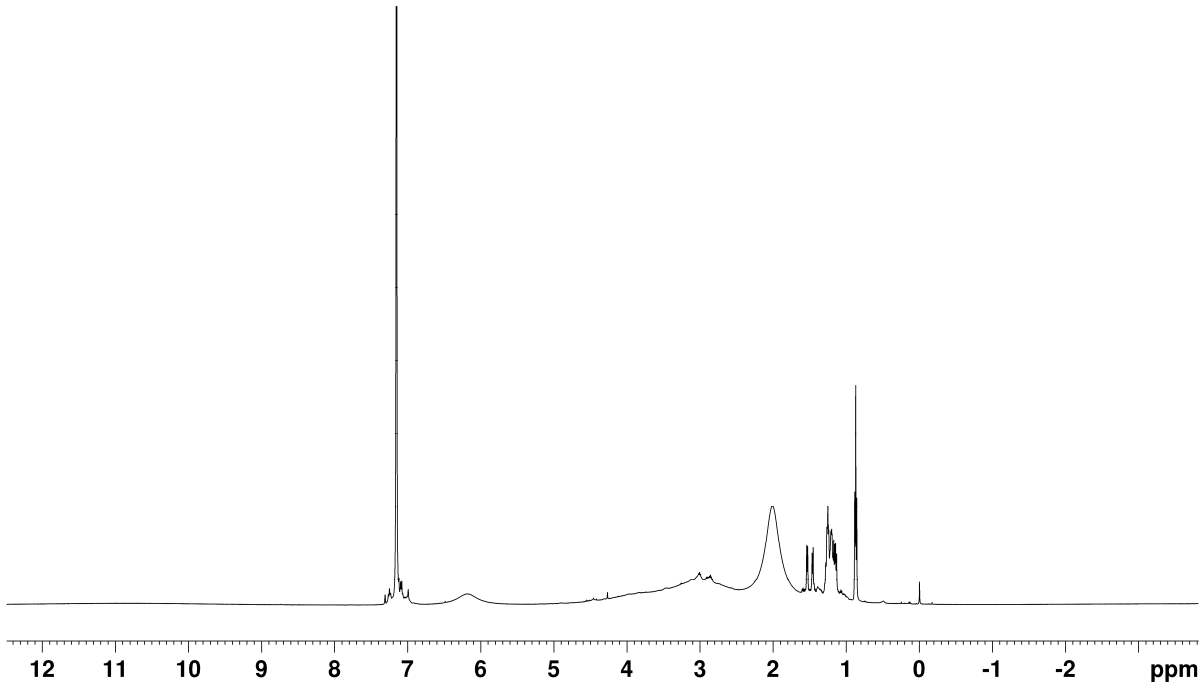



**Figure S1**: $^1$H-NMR spectrum of **1**$^{\cdot}$ ($C_6D_6$, 300 K).

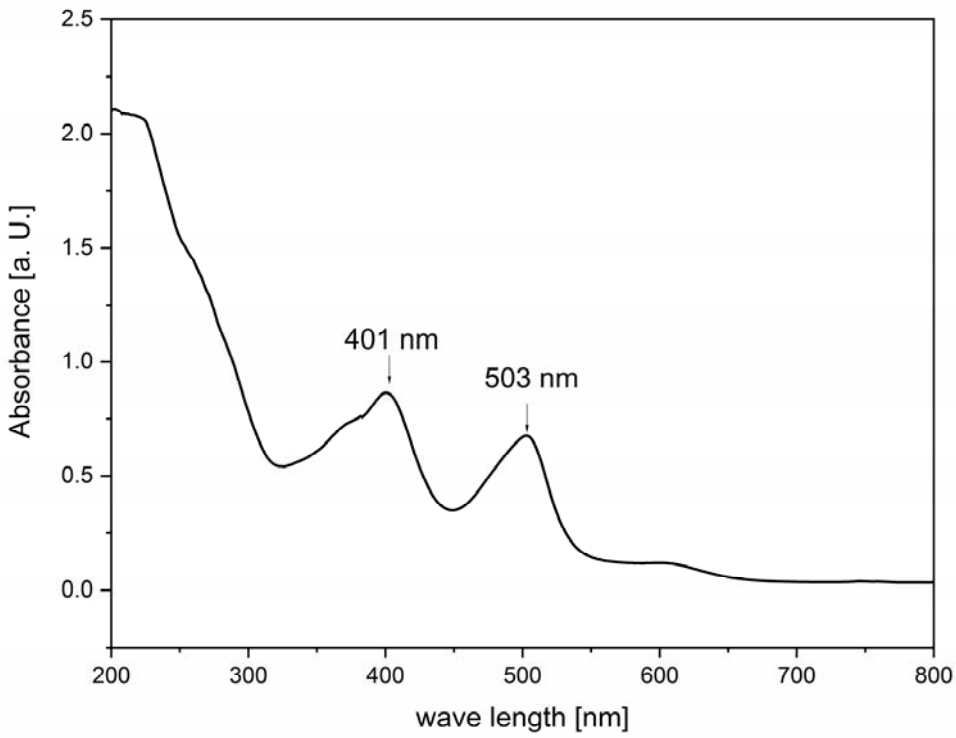



**Figure S2**: UV-vis spectrum of a 1.47*10$^{-4}$ M solution of **1**$^{\cdot}$ in *n*-pentane.

The UV-vis spectrum of **1**$^{\cdot}$ is shown in **Figure S2**. Compound **1**$^{\cdot}$ quickly reacts when exposed to atmosphere. This reaction is marked by a change in color from dark red-orange to yellow which was observed in a 1.47*10$^{-4}$ M solution of **1**$^{\cdot}$ in *n*-pentane. UV-vis spectra of the radical and the unidentified product after oxidation on atmosphere for 10 minutes are shown in **Figure S3**.

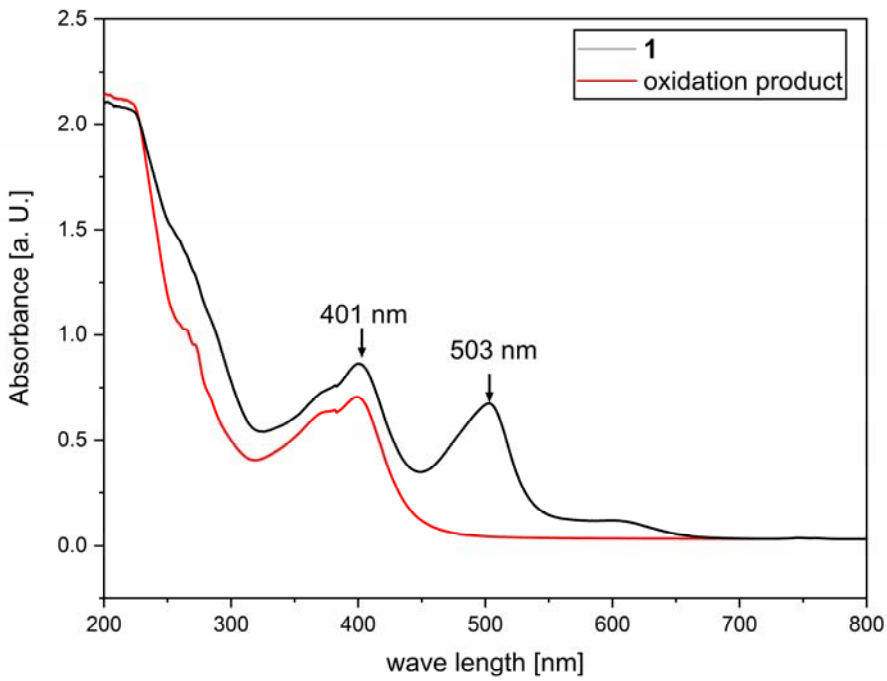



**Figure S3**: UV-vis spectrum of a 1.47*10$^{-4}$ M solution of **1**$^{\cdot}$ in *n*-pentane before (black) and after oxidation under ambient atmosphere (red).

### 1.3 Preparation of $\mathbf{1}^{\cdot}$ from 3

To a yellow suspension of **3** (100.00 mg, 0.14 mmol, 1 eq.) in 3 mL THF a solution of $CoCp_2$ (26.4 mg, 0.14 mmol, 1 eq.) in 3 mL THF is added. The reaction mixture quickly turns dark orange and is stirred at RT for 12 h. Additional $CoCp_2$ (13.2 mg, 0.07 mmol, 0.5 eq.) is added and the full conversion to $\mathbf{1}^{\cdot}$ is monitored by NMR. The dark red suspension is filtered to remove $CoCp_2Cl$ and the filtrate is dried under reduced pressure. The remaining black solid is dissolved in *n*-pentane, filtered and the filtrate is dried under reduced pressure. The product is obtained as a black solid in 90 % yield (85.5 mg).

It is worth noting that the radical $\mathbf{1}^{\cdot}$ is best handled under the total exclusion of chlorinated solvents, especially $CH_2Cl_2$. Solutions of $\mathbf{1}^{\cdot}$ in solvents like *n*-pentane slowly form **3** in the presence of $CH_2Cl_2$, which was observed in various NMR spectra.

## 1.4 Further investigation of the reactivity of of 1·

After removal of the previous gas phase, a solution of **1**· **(**15.3 mg, 0.022 mmol, 1 eq.**)** in 1 ml of THF in a *J Young* NMR Tube was charged with a 2 bar atmosphere of $H_2$ gas and vigorously shaken for several minutes. The solution was left to react at RT for 4 days. Reaction monitoring by NMR revealed no reaction. The procedure was repeated with CO gas. After another 2 days at RT, no reaction could be observed.

A suspension of $Cy_4P_4$ (31.87 mg, 0.07 mmol, 1 eq.) in 2 mL of THF is added to a solution of **1**· (47.5 mg, 0.07 mmol, 1 eq.) in 3 ml of THF and stirred overnight at RT. No Reaction was observed by NMR.

To a solution of **1**· (42.2 mg, 0.062 mmol, 1 eq.) in 2 mL of THF, a suspension of $Im_4P_4[OTf]_4$ (89.4 mg, 0.062 mmol, 1 eq.) in 3 mL of THF is added. The mixture is stirred at various temperatures and times: (i): RT, overnight; (ii): microwave, 20 min, 50 °C; (iii): microwave, 70 min, 60 °C; (iv): RT, using catalytic amounts of $PPh_3$, overnight and (v): microwave, 50 °C, using catalytic amounts of $PPh_3$, 60 min. A product could not be isolated from the resulting mixtures.

To a solution of **1**· (47.5 mg, 0.07 mmol, 1 eq.) in 2 mL of THF, a suspension of $S_8$ (2.23 mg, 0.009 mmol, 1/8 eq.) in 2 mL of THF is added. The mixture is stirred overnight at RT. The reaction is also performed with ¼ eq. of $S_8$. No product could be isolated.

Partial oxidation with trace amounts of oxygen could be observed in a sample **1**· in *n*-pentane that was stored at -30°C for several months. Crystals of the oxidation product **5** that were suitable for sc-XRD were obtained. The oxygen atom O2 is located on both P2 and P3 with a occupancy of 50 % for either. For clarity, only the latter option is depicted here (**Figure S3**).

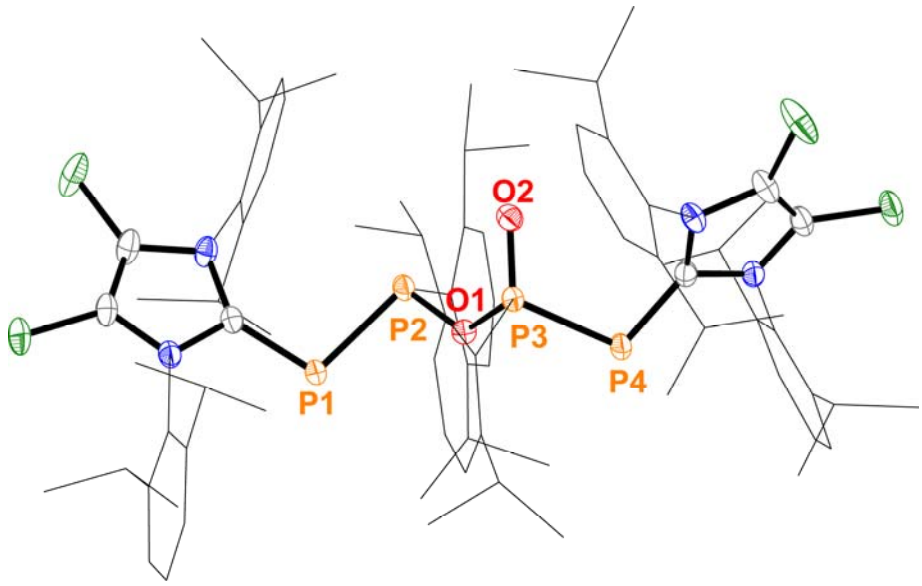
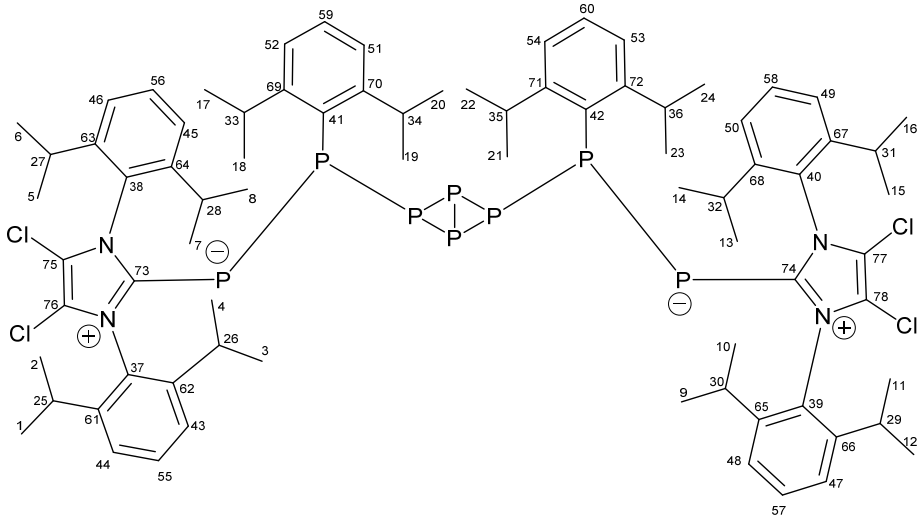



**Figure S4:** Molecular Structure of **5**, the partial oxidation product of **1**· (hydrogen atoms are omitted and Dipp substituents are shown as wireframes for clarity, thermal ellipsoids are displayed at 50 % probability), selected bond lengths in Å and angles in (°): P1–P2 = P3-P4 2.1796(5), P2-O1 = O1-P3 1.6533(7), P2-O2 = P3-O2 1.448(2), P1-P2-O1 = O1-P3-P4 96.75(4)°, P2–O1–P3 129.21(9)°.

## 1.5 Preparation of [($^{CL}$IM$^{DIPP}$)P–P(DIPP)]$_2$-P$_4$ 4



To an intensely dark red solution of **1**˙ (85.50 mg, 0.126 mmol, 1 eq.) in 3 mL *n*-pentane, a suspension of $P_4$ (7.78 mg, 0.063 mmol, 0.5 eq.) in 3 ml *n*-pentane was added dropwise. The reaction mixture was stirred for 12 h at RT and turned into a dark yellow suspension. The solution was filtered and the product was obtained by recrystallization from the filtrate at -30 °C as a yellow solid. The product is an inseparable mixture of stereoisomers.

**Yield:** 68.7 mg (73.6 %); **melting point:** 161 °C (decomposition); **Raman (100 mW, 298 K, [cm$^{-1}$]):** could not be obtained due to fluorescence; **IR (ATR, 298 K, [cm$^{-1}$]):** $\nu$ = 3045 (vw), 2961 (m), 2926 (w), 2865 (w), 1611 (w), 1589 (vw), 1464 (w), 1381 (w), 1362 (w), 1320 (w), 1301 (w), 1283 (vs), 1177 (vw), 1165 (vw), 1151 (vw), 1102 (vw), 1060 (w), 1048 (vw), 983 (vw), 936 (vw), 902 (vw), 800 (s), 776 (vw), 766 (vw), 742 (w), 732 (w), 672 (m), 654 (w), 630 (vw), 600 (vw), 542 (vw), 517 (w), 472 (w), 428 (m); **$^1$H NMR (THF-D$_8$, 300 K, in ppm):** 0.84 (3H, d, $^3J_{HH}$ = 7 Hz, CH$_3$); 0.88 (t, $^3J_{HH}$ = 7 Hz, *n*-pentane); 0.93 (3H, d, $^3J_{HH}$ = 7 Hz, CH$_3$); 0.96 (3H, d, $^3J_{HH}$ = 7 Hz, CH$_3$); 1.00 (6 H, m, CH$_3$); 1.07 (3H, d, $^3J_{HH}$ = 7 Hz, CH$_3$); 1.10 (3 H, d, $^3J_{HH}$ = 7 Hz, CH$_3$); 1.14 (18H, m, CH$_3$); 1.18-1.24 (18H, m, CH$_3$); 1.27 (6H, br. d, $^3J_{HH}$ = 7 Hz, CH$_3$); 1.32 (6H, br. d, $^3J_{HH}$ = 7 Hz, CH$_3$); 1.41 (3H, d, $^3J_{HH}$ = 7 Hz, CH$_3$); 2.56 - 3.03 (10H, m, CH); 3.28-3.28 (2 H, m, CH); 6.68-7.55 (18H, m, Phenyl-H); **$^{31}$P NMR (THF-D$_8$, 300 K, in ppm):** Mixture of two isomers in a ratio of 15/4. **minor isomer:** ABMM′XX′YZ spin system; $\delta_A$ = -326.3 (1P, ddddd, $^1J_{AB}$ = -173 Hz, $^1J_{AM}$ = -177 Hz, $^1J_{AM'}$ = -172 Hz, $^2J_{AX}$ = 84 Hz, $^2J_{AX'}$ = 87 Hz, $^3J_{AY}$ = -11 Hz, $^3J_{AZ}$ = -9 Hz), $\delta_B$ = -322.2 (1P, m, $^1J_{BM}$ = -176 Hz, $^1J_{BM'}$ = -189 Hz, $^2J_{BX}$ = 30 Hz, $^2J_{BX'}$ = 35 Hz, $^3J_{BY}$ = 6 Hz, $^3J_{BZ}$ = -4 Hz), $\delta_{M/M'}$ = -142.5 (2P, m, $^2J_{MM'}$ = -8 Hz, $^1J_{MX}$ = -90 Hz, $^3J_{MX'}$ = 138 Hz, $^2J_{MY}$ = -24 Hz, $^4J_{MZ}$ = 8 Hz, $^3J_{M'X}$ = 161, $^1J_{M'X'}$ = -81 Hz, $^4J_{M'Y}$ = 5 Hz, $^2J_{M'Z}$ = -100 Hz), $\delta_{X/X'}$ = -53.9 (1P, m, $^4J_{XX'}$ = 5 Hz, $^1J_{XY}$ = -275 Hz, $^5J_{XZ}$ = -6 Hz, $^5J_{X'Y}$ = 45 Hz, $^1J_{X'Z}$ = -277 Hz), $\delta_Y$ = -39.9 (1P, m), $\delta_Z$ = -39.8 (1P, m); **major isomer:** A$_2$MM′XX′YZ spin system; $\delta_A$ = -321.1 (2P, m, $^1J_{AM}$ = -172 Hz, $^1J_{AM'}$ = -172 Hz, $^2J_{AX}$ = 65 Hz, $^2J_{AX'}$ = 77 Hz, $^3J_{AY}$ = -8 Hz, $^3J_{AZ}$ = -8 Hz), $\delta_{M/M'}$ = -139.6 (2P, m, $^2J_{MM'}$ = 5 Hz, $^1J_{MX}$ = -101 Hz, $^3J_{MX'}$ = 91 Hz, $^2J_{MY}$ = 35 Hz, $^4J_{MZ}$ = -13 Hz, $^3J_{M'W}$ = 63 Hz, $^1J_{M'X'}$ = -156 Hz, $^4J_{M'Y}$ = -30 Hz, $^2J_{M'Z}$ = 59 Hz), $\delta_{X/X'}$ = -47.3 (2P, m, $^4J_{XX'}$ = 12 Hz, $^1J_{XY}$ = -276 Hz, $^5J_{XZ}$ = 8 Hz, $^5J_{X'Y}$ = -7 Hz, $^1J_{X'Z}$ = -282 Hz, $^6J_{YZ}$ = -4 Hz), $\delta_Y$ = -42.8 (1P, m), $\delta_Z$ = -42.9 (1P, m); **$^{31}$P{$^1$H} NMR (THF-D$_8$, 300 K, in ppm):** Mixture of two isomers in a ratio of 15/4. **minor isomer:** ABMM′XX′YZ spin system; $\delta_A$ = -326.3 (1P, ddddd, $^1J_{AB}$ = -173 Hz, $^1J_{AM}$ = -177 Hz, $^1J_{AM'}$ = -172 Hz, $^2J_{AX}$ = 84 Hz, $^2J_{AX'}$ = 87 Hz, $^3J_{AY}$ = -11 Hz, $^3J_{AZ}$ = -9 Hz), $\delta_B$ = -322.2 (1P, m, $^1J_{BM}$ = -176 Hz, $^1J_{BM'}$ = -189 Hz, $^2J_{BX}$ = 30 Hz, $^2J_{BX'}$ = 35 Hz, $^3J_{BY}$ = 6 Hz, $^3J_{BZ}$ = -4 Hz), $\delta_{M/M'}$ = -142.5 (2P, m, $^2J_{MM'}$ = -8 Hz, $^1J_{MX}$ = -90 Hz, $^3J_{MX'}$ = 138 Hz, $^2J_{MY}$ = -24 Hz, $^4J_{MZ}$ = 8 Hz, $^3J_{M'X}$ = 161, $^1J_{M'X'}$ = -81

Hz, $^4J_{M'Y}$ = 5 Hz, $^2J_{M'Z}$ = -100 Hz), $\delta_{X/X'}$ = -53.9 (1P, m, $^4J_{XX'}$ = 5 Hz, $^1J_{XY}$ = -275 Hz, $^5J_{XZ}$ = -6 Hz, $^5J_{X'Y}$ = 45 Hz, $^1J_{X'Z}$ = -277 Hz), $\delta_Y$ = -39.9 (1P, m), $\delta_Z$ = -39.8 (1P, m); **major isomer:** $A_2MM'XX'YZ$ spin system; $\delta_A$ = -321.1 (2P, m, $^1J_{AM}$ = -172 Hz, $^1J_{AM'}$ = -172 Hz, $^2J_{AX}$ = 65 Hz, $^2J_{AX'}$ = 77 Hz, $^3J_{AY}$ = -8 Hz, $^3J_{AZ}$ = -8 Hz), $\delta_{M/M'}$ = -139.6 (2P, m, $^2J_{MM'}$ = 5 Hz, $^1J_{MX}$ = -101 Hz, $^3J_{MX'}$ = 91 Hz, $^2J_{MY}$ = 35 Hz, $^4J_{MZ}$ = -13 Hz, $^3J_{M'W}$ = 63 Hz, $^1J_{M'X'}$ = -156 Hz, $^4J_{M'Y}$ = -30 Hz, $^2J_{M'Z}$ = 59 Hz), $\delta_{X/X'}$ = -47.3 (2P, m, $^4J_{XX'}$ = 12 Hz, $^1J_{XY}$ = -276 Hz, $^5J_{XZ}$ = 8 Hz, $^5J_{X'Y}$ = -7 Hz, $^1J_{X'Z}$ = -282 Hz, $^6J_{YZ}$ = -4 Hz), $\delta_Y$ = -42.8 (1P, m), $\delta_Z$ = -42.9 (1P, m); **$^{13}C\{^1H\}$ NMR (THF-$D_8$, 300 K, in ppm):** $\delta$ = 24.0 (6C, br. s, C1-24), 24.2 (6C, br. s, C1-24), 24.4 (2C, s, C1-24), 24.6 (1C, s, C1-24), 25.9 (1C, s, C1-24), 26.36 (2C, s, C1-24), 26.9 (2C, s, C1-24), 27.0 (3C, br. s, C1-24), 27.3 (1C, s, C1-24), 29.7-29.9 (4C, m, C25-36), 30.0 (1C, s, C25-36), 31.5 (1C, s, C25-36), 31.8 (1C, s, C25-36), 32.1 (2C, s C25-36), 32.4 (2C, s, C25-36), 35.5-35.9 (1C, m, C25-36), 115.8 (2C, s, C75-76), 115.6 (2C, s, C77-78), 116.6 (1C, d, $^3J_{CP}$ = 7 Hz, C51-54), 116.7 (1C, d, $^3J_{CP}$ = 7 Hz, C51-54), 121.99 (1C, d, $^3J_{CP}$ = 7 Hz, C51-54), 122.15 (1C, d, $^3J_{CP}$ = 7 Hz, C51-54), 125.3 (2C, s, C43-50), 125.4 (4C, s, C43-50), 125.5 (4C, s, C43-50), 125.7 (2C, s, C43-50), 130.6 (1C, s, C60), 130.7 (1C, s, C59), 131.9 (1C, s, C58), 131.8 (2C, br. s, C56/57), 131.6 (1C, s, C55), 140.3-140.7 (2C, m, C41/42), 147.5 - 148 (8C, m, C61-68), 152.8 (4C, dd, $^2J_{CP}$ = 32 Hz, $^3J_{CP}$ = 2 Hz, C69-72), 154.8-155.1 (4C, m, C37-40), 173.2 (2C, br. dd, $^1J_{CP}$ = -120 Hz, $^2J_{CP}$ = 20 Hz, C73/74); **elemental analysis:** calculated: N 3.77, C 63.08, H 6.92, S 0; found: N 3.57, C 62.95, H 6.42, S 0.32.

NMR studies at variable temperatures in the 350 K to 250 K range did not result in changes in the shape of the products resonances in the $^{31}P$ and $^{31}P\{^1H\}$ NMR spectra. Only slight deviations of the chemical shifts were observed (ca. 1 ppm or less, in comparison to the spectrum at 300 K).

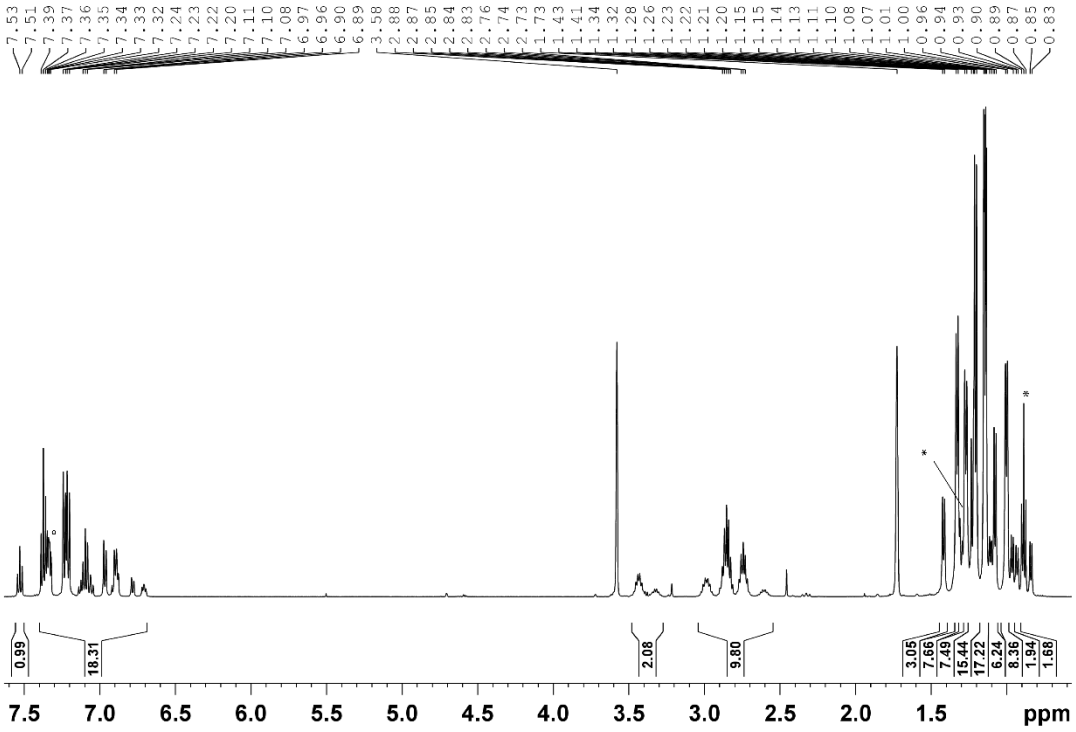



**Figure S5**: $^{1}$H NMR spectrum of **4**, *: *n*-pentane, °: benzene (THF-$D_8$, 300K).

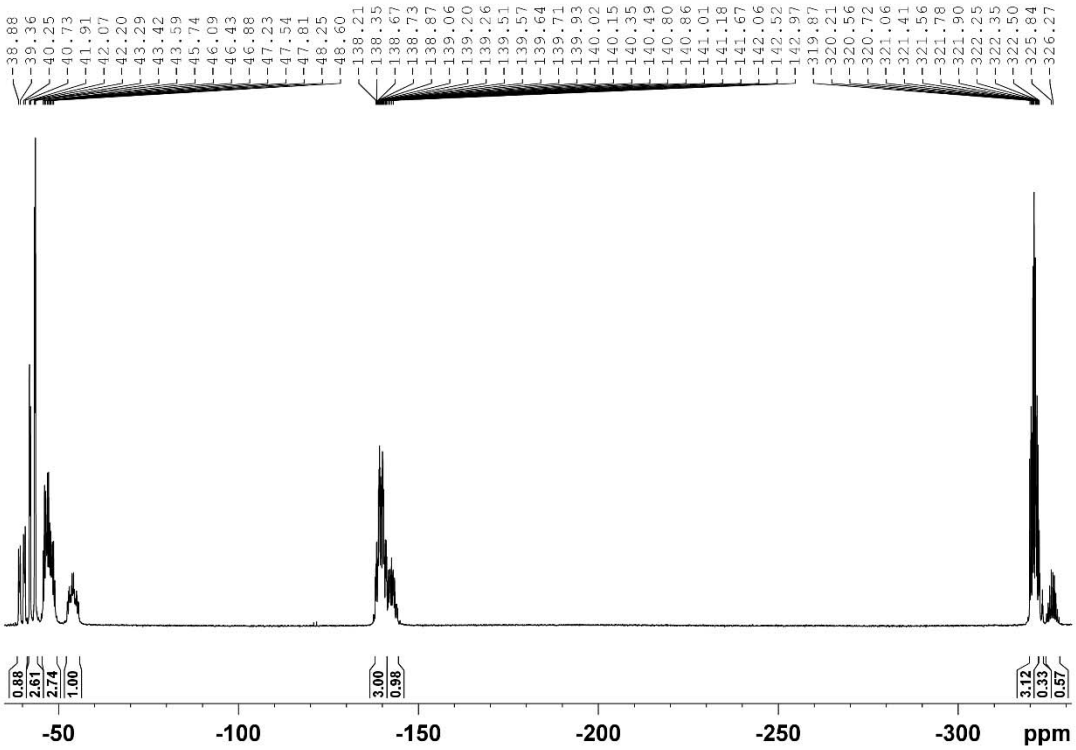



**Figure S6**: $^{31}$P NMR spectrum of **4** (THF-$D_8$, 300K).

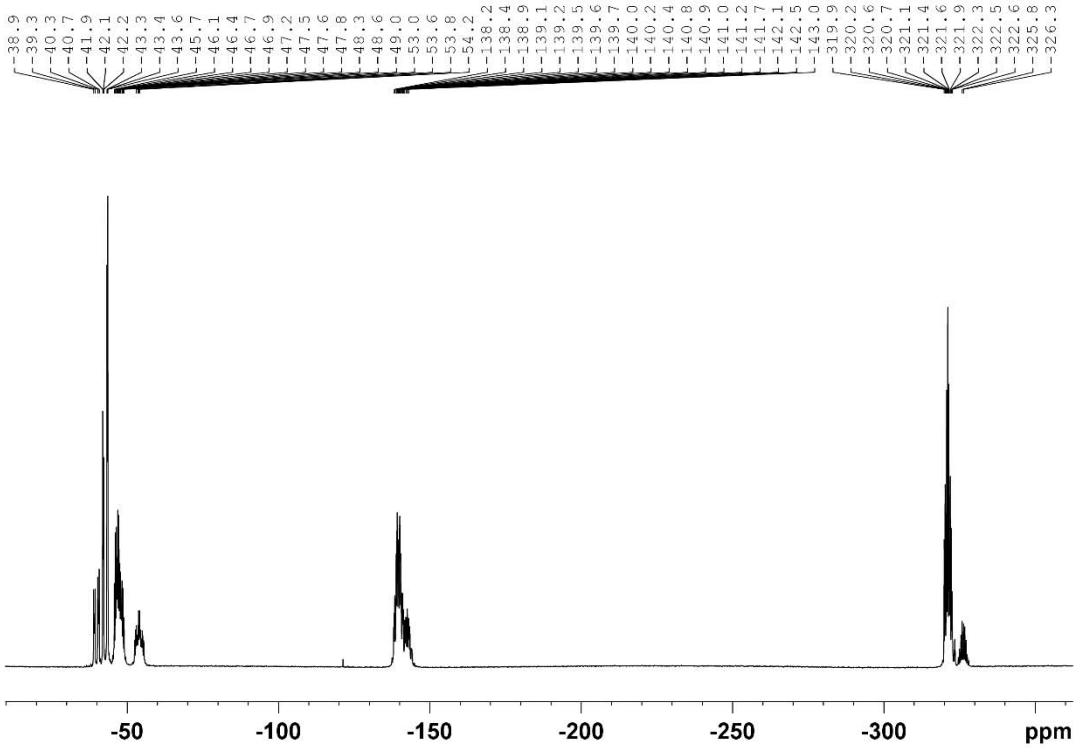



**Figure S7**: $^{31}P\{^{1}H\}$ NMR spectrum of **4** (THF-$D_8$, 300K).

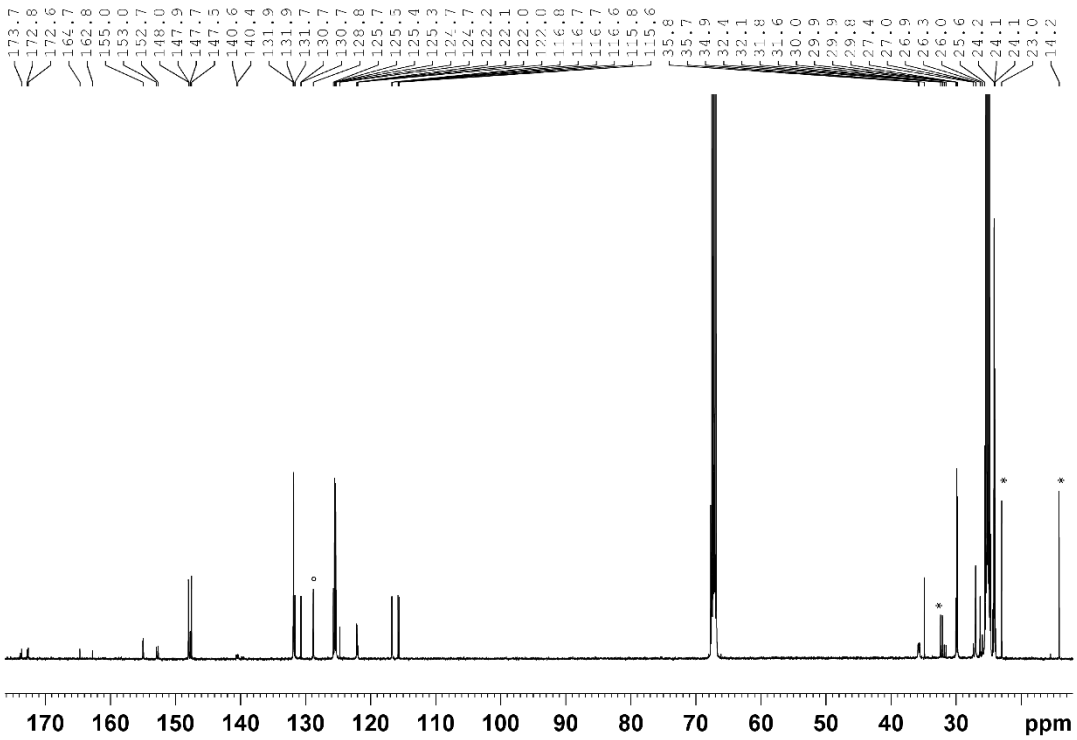



**Figure S8**: $^{13}C\{^{1}H\}$ NMR spectrum of **4**, *: *n*-pentane, °: benzene (THF-$D_8$, 300K).

## 1.6 Preparation of 4 from 3 in a stoichiometric ratio with $P_4$

To a yellow solution of **3** (44.00 mg, 0.06 mmol, 1 eq.) in 3 mL THF a solution of $CoCp_2$ (11.61 mg, 0.06 mmol, 1 eq.) in 3 mL THF was added. The reaction mixture quickly turns dark orange and is stirred at RT for 30 minutes. Then, a suspension of $P_4$ (3.8 mg, 0.03 mmol, 0.5 eq.) in 3 ml THF is added dropwise. The reaction mixture is stirred for 12 h at RT. The reaction mixture is filtered and the yellow filtrate dried under reduced pressure, dissolved in ca. 10 mL of *n*-pentane, and filtered again. The product precipitates from the *n*-pentane filtrate at -30 °C and is obtained as a yellow solid in 28.5 % yield (13 mg).

## 1.7 Preparation of 4 from 3 in a 1 to 1 ratio with $P_4$

To a yellow solution of **3** (20.00 mg, 0.03 mmol, 1 eq.) in 2 mL THF a solution of $CoCp_2$ (5.31 mg, 0.03 mmol, 1 eq.) in 2 mL THF is added. The reaction mixture quickly turns dark orange and is stirred for 3 h at RT. Then, a suspension of $P_4$ (3.46 mg, 0.03 mmol, 1 eq.) in 3 ml THF is added dropwise. The reaction mixture is stirred for 12 h at RT. The reaction mixture is filtered and the yellow filtrate contains product **4** and $P_4$ (**Figure S8**). Apparently, no further addition of radical to the $P_8$ moiety is possible under these conditions.

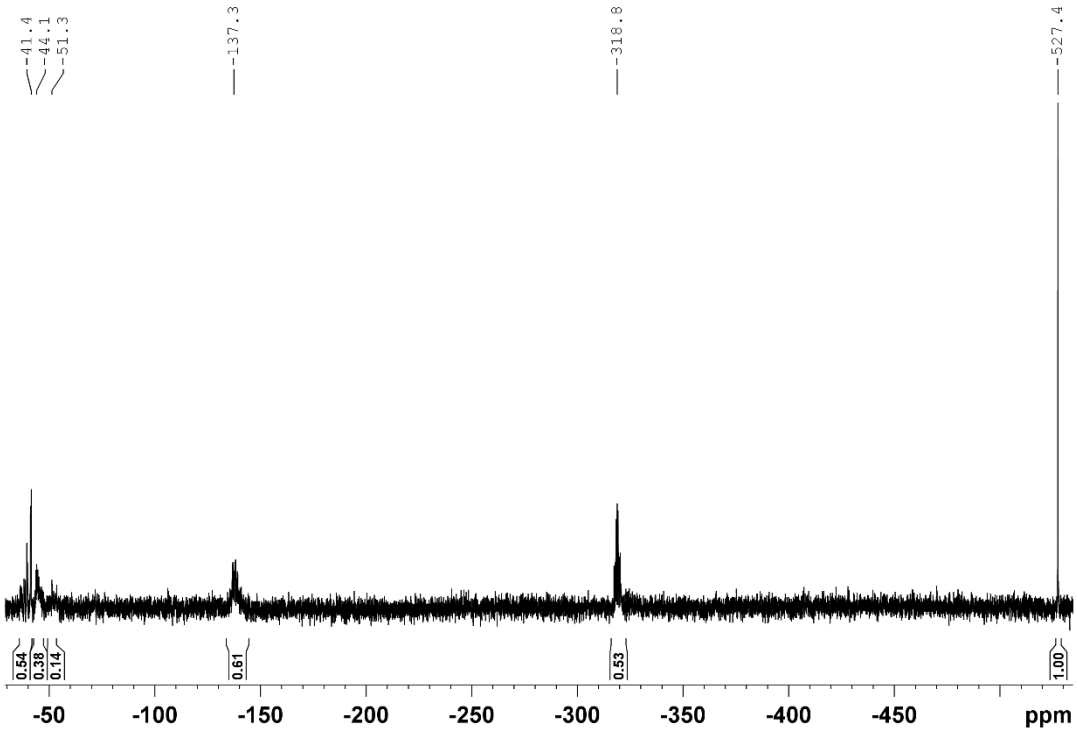



**Figure S9**: $^{31}P$ NMR spectrum of the filtrate ($C_6D_6$-capillary, *n*-pentane, 300 K).

## 1.8 Investigation of the ratio of isomers of 4

Room temperature NMR spectra of **4** were also recorded in the solvents THF-$D_8$, *n*-hexane, *n*-pentane, and $CH_3CN$. A $C_6D_6$-Capillary was used for non-deuterated solvents. In all spectra, the shifts are changed slightly, but the splitting pattern remains unchanged.

The appearance of two sets of signals in the $^{31}P\{^1H\}$ NMR (Toluene-$D_8$, 300 K - 250 K and 300 K - 350 K, in 10 K increments) was investigated using high and low temperature NMR in the temperature range from 250 K to 350 K. Only slight changes of the chemical shifts were observed and the splitting pattern remained virtually unchanged, compared to the room temperature spectra.

It appears that the energetic barrier of conversion of one isomer to the other is too high as to be affected in this temperature range. In an attempt to influence the ratio of isomers (as indicated by the integral intensity of the respective resonances in the $^{31}P$ NMR spectra) during the formation of the product, the reaction of **1** and $P_4$ was conducted at high and low temperatures.

### 1.8.1 Reaction of **1**$^{\cdot}$ and $P_4$ at low temperatures

$P_4$ (6.37 mg, 0.05 mmol, 0.5 eq.) is suspended in ca. 3 mL of *n*-pentane and cooled in an ethanol/liquid $N_2$ cooling bath at -114 °C. A strongly colored solution of **1**$^{\cdot}$ (70.0 mg, 0.10 mmol, 1 eq.) in ca. 2 mL of *n*-pentane is slowly added and the reaction mixture is stirred and allowed to slowly heat up to RT overnight. The reaction mixture is filtered, the filter residue is washed with a small amount of *n*-pentane and dried under reduced pressure to obtain the product as a yellow solid in 75.3 % yield (57.5 mg).
Compared to the reaction conducted at RT, the reaction at low temperatures yielded a similar ratio of both isomers, as indicated by the integral intensity of the signal groups in the $^{31}P$ NMR.

### 1.8.2 Reaction of **1**$^{\cdot}$ and $P_4$ at elevated temperatures

$P_4$ (3.86 mg, 0.03 mmol, 0.5 eq.) is suspended in ca. 7 mL of *n*-hexane and refluxed at ca. 69 °C. A strongly colored solution of **1**$^{\cdot}$ (42.4 mg, 0.06 mmol, 1 eq.) in ca. 5 mL of *n*-hexane is added and the reaction mixture is stirred and refluxed for 1 h. Afterwards, the reaction mixture is allowed to cool and stirred at RT overnight. The yellow reaction mixture is reduced under reduced pressure and filtered to remove a very small amount of brown solid. NMR analysis of the brown-yellow filtrate shows white phosphorus, traces of **4** and the decomposition of **1**.

## 2 Iteration of NMR spectra

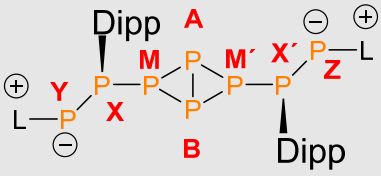
The $^{31}P$ $\{^{1}H\}$ NMR spectrum of **4** (THF-$D_8$, 300 K) was iteratively fitted using the software *gNMR* v5.0.6 (Ivorysoft). Both isomers were iterated simultaneously, as the signals partially overlap. The fitted parameters are given in **Tables S1-4.** The relative concentration of both isomers (15/4) was also confirmed by iteration.

**Table S1:** Minor product (ABMM´XX´YZ spin system), chemical shifts and widths.

| Title | multiplicity | Shift [ppm] | Width |
|---|---|---|---|
| A | 1 | -326.29 | 12.47 |
| B | 1 | -322.15 | 4.89 |
| M | 1 | -142.55 | 13.35 |
| M´ | 1 | -142.55 | 4.91 |
| X | 1 | -53.95 | 11.46 |
| X´ | 1 | -53.95 | 35.12 |
| Y | 1 | -39.85 | 9.2 |
| Z | 1 | -39.84 | 6.89 |

**Table S2:** Minor product (ABMM´XX´YZ spin system), shifts and widths.

| | A | B | M | M´ | X | X´ | Y | Z |
|---|---|---|---|---|---|---|---|---|
| A | - | | | | | | | |
| B | $^{1}J_{AB}$ -172.9 | - | | | | | | |
| M | $^{1}J_{AM}$ -176.61 | $^{1}J_{BM}$ -175.92 | - | | | | | |
| M´ | $^{1}J_{AM'}$ -171.61 | $^{1}J_{BM'}$ -188.66 | $^{2}J_{MM'}$ -7.85 | - | | | | |
| X | $^{2}J_{AX}$ 83.96 | $^{2}J_{BX}$ 30.40 | $^{1}J_{MX}$ -89.88 | $^{3}J_{M'X}$ 160.52 | - | | | |
| X´ | $^{2}J_{AX'}$ 87.23 | $^{2}J_{BX'}$ 35.00 | $^{3}J_{MX'}$ 137.73 | $^{1}J_{M'X'}$ -80.53 | $^{4}J_{XX'}$ 4.60 | - | | |
| Y | $^{3}J_{AY}$ -11.01 | $^{3}J_{BY}$ 5.76 | $^{2}J_{MY}$ -24.16 | $^{4}J_{M'Y}$ 4.37 | $^{1}J_{XY}$ -275.23 | $^{5}J_{X'Y}$ 44.69 | - | |
| Z | $^{3}J_{AZ}$ -9.25 | $^{3}J_{BZ}$ -3.86 | $^{4}J_{MZ}$ 7.81 | $^{2}J_{M'Z}$ -100.37 | $^{5}J_{XZ}$ -5.63 | $^{1}J_{X'Z}$ -276.94 | $^{6}J_{YZ}$ 0 | - |



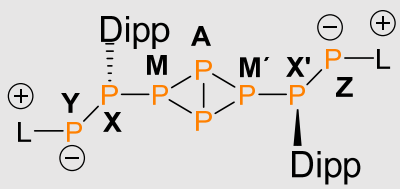

minor product

**Table S3:** Major product ($A_2MM'XX'YZ$ spin system), chemical shifts and widths.

| Title | multiplicity | Shift [ppm] | Width |
|---|---|---|---|
| A | 2 | -321.12 | 13.82 |
| M | 1 | -139.64 | 10.99 |
| M´ | 1 | -139.63 | 21.39 |
| X | 1 | -47.26 | 200.43 |
| X´ | 1 | -47.26 | 16.7 |
| Y | 1 | -42.87 | 5.8 |
| Z | 1 | -42.86 | 10.56 |

**Table S4:** Major product ($A_2MM'XX'YZ$ spin system), coupling constants.

| | A | M | M´ | X | X´ | Y | Z |
|---|---|---|---|---|---|---|---|
| A | - | | | | | | |
| M | $^1J_{AM}$ -171.36 | - | | | | | |
| M´ | $^1J_{AM'}$ -171.66 | $^2J_{MM'}$ 4.47 | - | | | | |
| X | $^2J_{AX}$ 65.45 | $^1J_{MX}$ 102.98 | $^3J_{M'X}$ 62.77 | - | | | |
| X´ | $^2J_{AX'}$ 77.48 | $^3J_{MX'}$ 90.75 | $^1J_{M'X'}$ -155.87 | $^4J_{XX'}$ 12.02 | - | | |
| Y | $^3J_{AY}$ -8.30 | $^2J_{MY}$ 35.03 | $^4J_{M'Y}$ -30.00 | $^1J_{XY}$ -276.56 | $^5J_{X'Y}$ -6.64 | - | |
| Z | $^3J_{AZ}$ -8.12 | $^4J_{MZ}$ -13.23 | $^2J_{M'Z}$ 58.72 | $^5J_{XZ}$ 7.65 | $^1J_{X'Z}$ -282.29 | $^6J_{YZ}$ -3.88 | - |




major product

## 3 Electrochemical procedures and Data

All electrochemical (EC) measurements such as cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed in a Glovebox Pure Lab HE GP-1 SR (Innovative Technology, USA) in an atmosphere of purified nitrogen (< 0.1 ppm $O_2$; < 0.1 ppm $H_2O$). The glovebox was equipped with military grade BNC feedthroughs in a custom-made gas tight flange for low noise electrical connection of the electrochemical cells inside. EC cells were connected to a PGSTAT302 (Metrohm Autolab, Utrecht, The Netherlands) E = ±10 V, U = ±35 V. NOVA Software (Metrohm Autolab) Version 1.11.2 was used to control the potentiostat and magnetic stirring. Data analysis of the electrochemical data was performed using OriginPro 2019 (OriginLab Cooperation, Northampton, MA, USA).

EC measurements were performed in 10 mL electrochemical cells using platinum disk electrodes (1.6 mm diameter, ALS Co. Ltd., Japan) as working electrodes. The electrodes were polished with 1 µm Diamond polishing paste and then 0.05 µm polishing alumina on separate polishing pads prior to use. A Pt wire coil (200 mm length, 0.5 mm width) was used as counter electrode without separation. A reference electrode, consisting of a silver wire in a solution of 0.01 M $AgNO_3$ in 0.1 M [$Bu_4N$][OTf] supporting electrolyte solution (in $CH_2Cl_2$) and separated from the substrate solution by a Vycor Frit, was used. Ferrocene was used to reference the potentials obtained in CV and SWV experiments to a potential of $E_{1/2}$ = 0 V according to IUPAC convention.

[*n*$Bu_4N$][OTf] was pre-dried at least 5 times by dissolving in $CH_2Cl_2$ and evaporating the solvent to high vacuum at 80 °C. Final drying and removal of HOTf traces was achieved by dissolving in dry benzene and refluxing this solution in a Soxhlet apparatus for 5 days with vacuum activated molecular sieves in the extraction thimble renewed every day. Prior to each measurement, the electrolyte stock solution is passed through a Pasteur pipette with an activated ($1 \cdot 10^{-3}$ mbar, 350 °C, 24 h) aluminum oxide bed (D = 5 mm; L = 70 mm) in the glove box before the substrate is added.

In the second cycle CV of **2**[OTf] (**Figure 2** in the paper, black), a reversible one-electron reduction is observed at $E_{1/2}$ = -0.862 V (vs. $E_{1/2}$ ($FeCp_2/FeCp_2^+$)). SWV measurements of the reversible process shows its formal potential of $E_p$ = -0.859 V. The reversibility was proven using the Randles–Ševčík equation (**Figure S9**). Cobaltocene, which has a formal potential of -1.33 V (vs. $E_{1/2}$ ($FeCp_2/FeCp_2^+$))[5] in $CH_2Cl_2$, was chosen as a suitable reduction agent. Based on experimental results following the chemical reduction of **2**[OTf] with cobaltocene, the reduction process observed above was assigned to the formation of **1**.

The isolated radical **1**$^{\cdot}$ was also analyzed using the same methods (**Figure 2** in the paper, red). The CV reveals a reduction process at a potential of $E_{1/2}$ = -0.913 V (vs. $E_{1/2}$ ($FeCp_2/FeCp_2^+$)). The SWV shows the same process at a potential of $E_p$ = -0.917 V (vs. $E_{1/2}$ ($FeCp_2/FeCp_2^+$)). This process is assigned to the oxidation and re-reduction of radical **1**.

Although this process fulfills the Randles–Ševčík equation (**Figure S10**), the CV curve is noticeably broadened and slightly deformed, with the peak-to-peak separation of 125.4 mV strongly exceeding the expected range for reversible processes (57 mV)[6] and the separation observed in the CV of **2**[OTf] (62 mV). Therefore, it is designated as pseudo-reversible.

The broadening of a CV Curve may be indicative of a deviation from a fully diffusion-controlled process. This could be caused by a different coefficient of diffusion of the radical. Its heightened reactivity could also cause side reactions with the products that form during the CV process. These would not directly be visible in the CV as a chemical follow-up reaction requires no electron-exchange with the electrode, but could, for example, change the concentration of **2**$^+$ that is available for re-reduction. Both of these effects could contribute to a broadened CV curve.

We suspect that when starting the measurement with the radical species **1**, the effects of these properties (coefficient of diffusion and reactivity) are more pronounced due to the high initial concentration of the radical. In contrast, the shape of the CV curve is not broadened for the measurement of **2**$^+$, possibly because only small amounts of the radical are produced and re-oxidized near the electrode.

Please note that both CVs still fulfill the Randles–Ševčík equation which is a criterium for reversibility and indicates a diffusion controlled process.

A reversible oxidation of **2**[OTf] to a "**2**$^+$" species was not observed in the potential range of -2 V to 2 V.

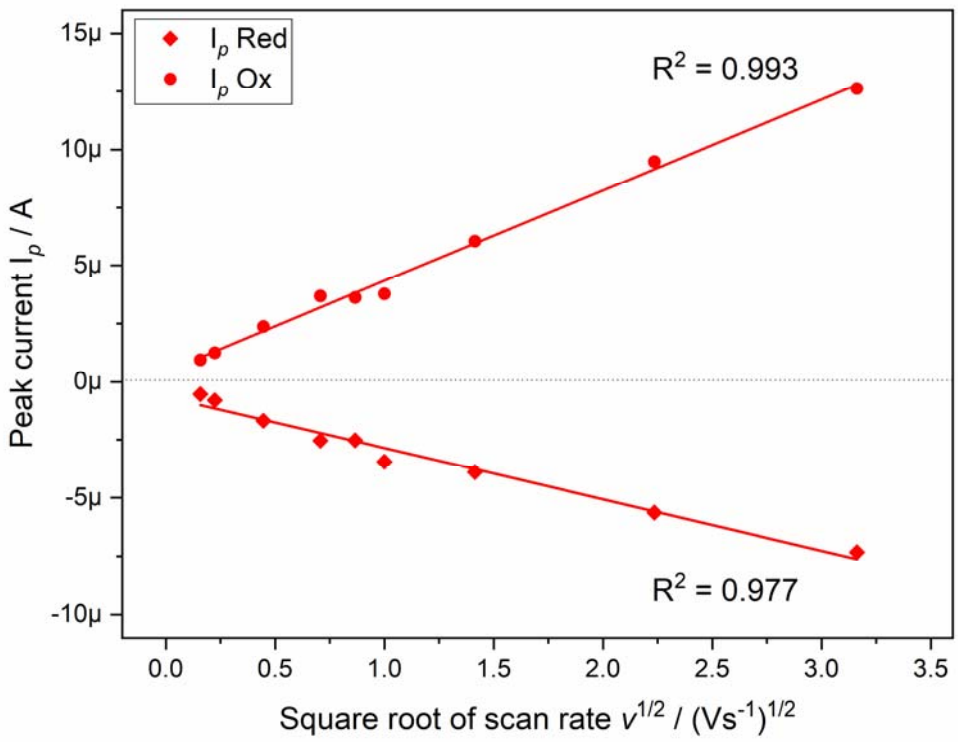



**Figure S10**: Randles–Ševčík plot for the reversible reduction and oxidation of **1**$^{\cdot}$ in $CH_3CN$ at a 1.6 mm Pt disc electrode, scan rate v = 0.2 V/s.

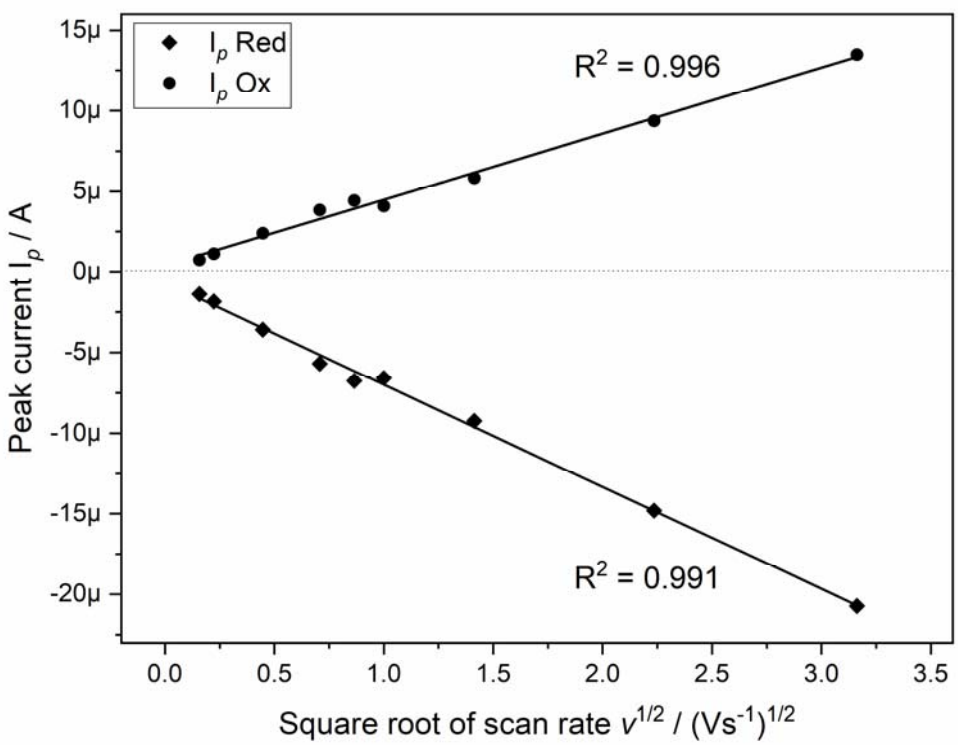



**Figure S11**: Randles–Ševčík plot for the reversible reduction and oxidation of **2**[OTf] in $CH_3CN$ at a 1.6 mm Pt disc electrode, scan rate v = 0.2 V/s.

## 4 DFT calculation of molecular orbitals and spin density and computational details

### 4.1 Computational methods

The geometries and energies of the radical included in this study were fully optimized at the RI-UBP86-D3/def2-TZVP level of theory. For comparison, some calculations have been also done using the X-ray coordinates. The calculations have been performed by using the program TURBOMOLE version 7.0[7]. For the calculations we have used the BP86[8] functional with the D3 correction for dispersion[9]. In order to reproduce solvent effects, we have used the conductor-like screening model COSMO[10], which is a variant of the dielectric continuum solvation models. The minimum nature of the complexes and compounds have been confirmed by doing frequency calculations. The Wiberg bond index[11] calculations were performed using the NBO7.0 program[12].

### 4.2 Discussion of the frontier orbitals and spin density

In **Figure S12** the plots of HOMO, SOMO and LUMO for **1**$^{\cdot}$ are represented. It can be observed that the HOMO has π-character and it is mostly localized at the P atoms (P=P double bond) with some participation of the five membered ring (5R). The SOMO corresponds to the combination of antibonding π*(P=P) and bonding π(P=C) with some participation of the five-membered ring. Finally, the LUMO is localized at the π-systems of the bis-(isopropyl)phenyl rings. The DFT and X-ray distances are very similar, giving reliability to the level of theory (RI-PB86-D3/def2-TZVP).

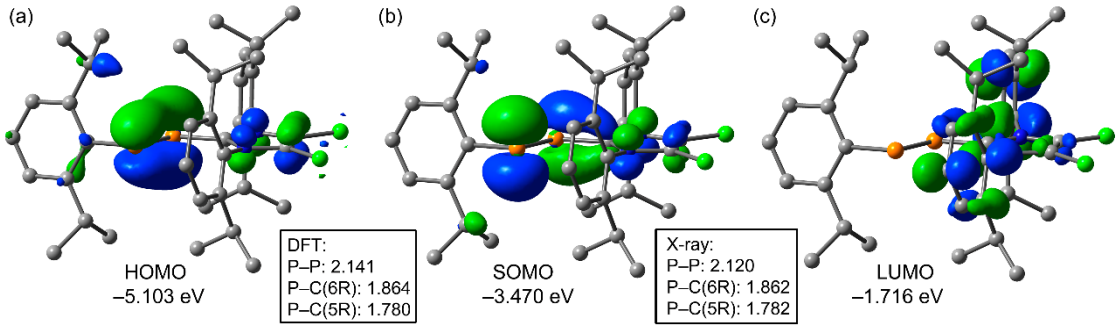



**Figure S12**: MOs computed for **1**$^{\cdot}$ and their energies at the RI-BP86-D3/def2-TZVP level of theory. Distances in Å.

The spin density plot is given in **Figure S13** along with the Wiberg bond indices for the C–P–P–C system. It can be observed that the spin is basically localized at the P atom (65%) bonded to the six membered ring (6R). Some spin is delocalized to the other P atom (8%) and the five membered ring (21%). The WBIs confirm that the bond order is higher than 1 in the P–P and P–C(5R) bonds, disclosing some double bond character, in line with the HOMO and SOMO orbitals. In contrast, the P–C(6R) WBI is 0.94, confirming its single bond character.

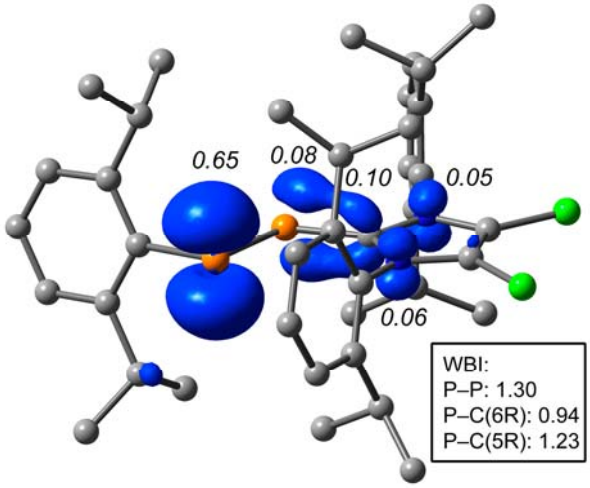



**Figure S13**: Spin density plot of **1**˙ with indication of the spin density values (in italics) for some atoms at the RI-BP86-D3/def2-TZVP level of theory. The P–P and P–C WBIs are also indicated.

## 4.3 Mechanistic Studies

The mechanistic study for the formation of **4** reveals a two-step mechanism involving the formation of a non-covalent complex in the first step. Initially, one molecule of **1**˙ interacts with $P_4$, resulting in a supramolecular assembly [**1**···$P_4$]˙ that is well pre-organized for subsequent P–P bond formation, with a P···P distance of 2.948 Å, as illustrated in Figure S14. This process is exergonic (ΔG = –4.2 kcal/mol). The second step, which is barrierless (see energy profile in Figure S15) and significantly more exergonic (ΔG = –37.6 kcal/mol), involves the coupling of the supramolecular radical [**1**···$P_4$]˙ with a second molecule of **1**˙, leading to the formation of compound 4.

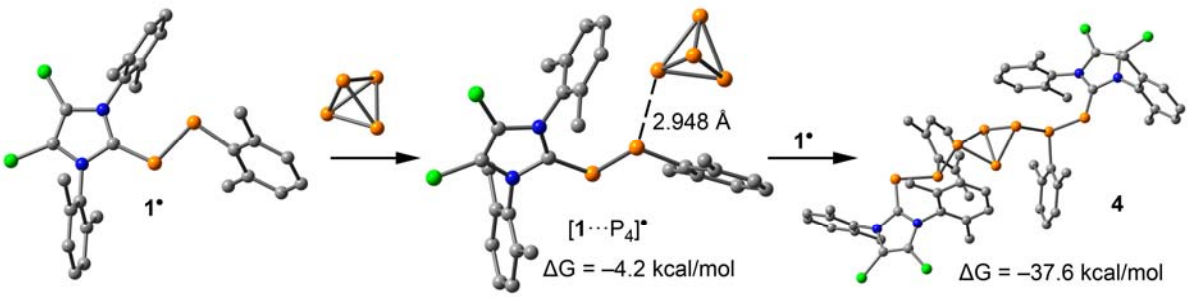



**Figure S14**: Optimized geometries and Gibbs energies involved in the transformation of **1**˙ and $P_4$ into **4**.

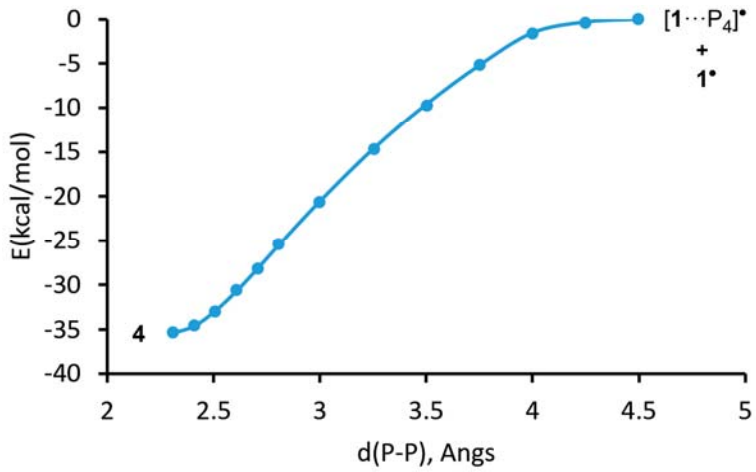



**Figure S15:** Energy profile for the transformation of [**1**···$P_4$]$^{\cdot}$ + **1**$^{\cdot}$ and $P_4$ into **4**. The y-axis shows relative energies references to the starting material.

## 4.3 Cartesian Coordinates of the optimized radical:

| | | | |
|---|---|---|---|
| Cl | 13.62891824 | 10.49030607 | 14.08203367 |
| Cl | 13.57158983 | 10.61067431 | 10.53467229 |
| P | 14.51398571 | 4.42106848 | 13.77380486 |
| P | 14.47477209 | 5.39377193 | 11.86735386 |
| N | 13.99701923 | 7.99671597 | 11.11552475 |
| N | 14.00108701 | 7.90315214 | 13.31438111 |
| C | 14.91967522 | 2.76939621 | 13.00915643 |
| C | 13.89210984 | 1.93687287 | 12.49713723 |
| C | 12.43256596 | 2.37193647 | 12.48306852 |
| H | 12.39943999 | 3.39571824 | 12.89056940 |
| C | 11.56835919 | 1.49027796 | 13.39773129 |
| H | 11.54646501 | 0.44743206 | 13.04714395 |
| H | 10.53191845 | 1.85960717 | 13.42195173 |
| H | 11.95924496 | 1.49135431 | 14.42522311 |
| C | 11.86989497 | 2.43484030 | 11.05485617 |
| H | 12.47596749 | 3.10370712 | 10.42795258 |
| H | 10.83641074 | 2.81265275 | 11.06407973 |
| H | 11.86038883 | 1.44136188 | 10.58118062 |
| C | 14.22898355 | 0.67323782 | 11.99331286 |
| H | 13.44296218 | 0.02521741 | 11.59951503 |
| C | 15.54970889 | 0.23123670 | 11.98199587 |
| H | 15.79500265 | -0.75294884 | 11.57878504 |
| C | 16.55792120 | 1.05083224 | 12.48796023 |
| H | 17.59114560 | 0.69943950 | 12.47241301 |
| C | 16.26535973 | 2.31671947 | 13.01011583 |
| C | 17.39055302 | 3.20510065 | 13.52416231 |
| H | 16.91569317 | 3.97325223 | 14.16215693 |
| C | 18.41685843 | 2.45866281 | 14.38752346 |
| H | 17.92573432 | 1.90249117 | 15.19817380 |
| H | 19.12403080 | 3.17172386 | 14.83670869 |
| H | 19.00858390 | 1.74371577 | 13.79630230 |
| C | 18.07139882 | 3.94535242 | 12.36053700 |
| H | 18.52783484 | 3.23004025 | 11.65905805 |
| H | 18.86114295 | 4.61598933 | 12.73259517 |
| H | 17.34200048 | 4.54961410 | 11.80223648 |
| C | 14.14388444 | 7.11437112 | 12.18231592 |
| C | 13.81719369 | 7.56975354 | 9.75581810 |
| C | 14.94961130 | 7.42905748 | 8.93683852 |
| C | 16.34909304 | 7.71003526 | 9.45654032 |
| H | 16.28177640 | 7.82510168 | 10.54864204 |
| C | 17.30480196 | 6.53737583 | 9.18617361 |
| H | 16.88985503 | 5.60031511 | 9.58024979 |
| H | 18.27328788 | 6.71695213 | 9.67484975 |
| H | 17.49496393 | 6.40789198 | 8.11045310 |
| C | 16.88677416 | 9.03077647 | 8.87745001 |
| H | 16.97500283 | 8.96926174 | 7.78255900 |
| H | 17.88309215 | 9.25498147 | 9.28594098 |
| H | 16.21689927 | 9.86883925 | 9.11597666 |
| C | 14.73440868 | 7.01951980 | 7.61526067 |
| H | 15.58698995 | 6.90088567 | 6.94550643 |
| C | 13.44804863 | 6.75207415 | 7.14914283 |
| H | 13.30264819 | 6.42922682 | 6.11710484 |
| C | 12.34668578 | 6.88541888 | 7.99453100 |
| H | 11.34763618 | 6.66057993 | 7.61869080 |
| C | 12.50548129 | 7.29780459 | 9.32261032 |
| C | 11.30802091 | 7.40820737 | 10.25451580 |
| H | 11.64604770 | 7.85756035 | 11.19959250 |
| C | 10.75198369 | 6.01412060 | 10.59267805 |
| H | 10.37716797 | 5.50730109 | 9.69125318 |
| H | 9.91975562 | 6.09772426 | 11.30729171 |
| H | 11.53184331 | 5.38105580 | 11.03845061 |
| C | 10.21874447 | 8.33079139 | 9.68485966 |
| H | 10.62392597 | 9.32611188 | 9.45514805 |
| H | 9.40402794 | 8.44925672 | 10.41385265 |
| H | 9.78304903 | 7.91858666 | 8.76319588 |
| C | 13.78925313 | 9.29026595 | 11.58112400 |
| C | 13.79494602 | 9.23906487 | 12.94434545 |
| C | 13.95336052 | 7.43664483 | 14.67202132 |
| C | 12.76320331 | 6.83249428 | 15.12672481 |
| C | 11.57182530 | 6.64128190 | 14.19874477 |
| H | 11.97512186 | 6.45719701 | 13.19145905 |
| C | 10.70439319 | 7.91104959 | 14.13056557 |
| H | 10.26722505 | 8.13521754 | 15.11485431 |
| H | 9.88189140 | 7.77221623 | 13.41318220 |
| H | 11.28405924 | 8.78887315 | 13.81488595 |
| C | 10.72017378 | 5.41563595 | 14.55175521 |
| H | 11.34595975 | 4.51898955 | 14.66035191 |

| | | | |
|---|---|---|---|
| H | 9.99210368 | 5.22917082 | 13.75013740 |
| H | 10.15265129 | 5.56070248 | 15.48332466 |
| C | 12.74099216 | 6.40293941 | 16.45791093 |
| H | 11.84778541 | 5.91952805 | 16.85164897 |
| C | 13.85679361 | 6.55667334 | 17.28019416 |
| H | 13.81983587 | 6.20199334 | 18.31126693 |
| C | 15.02235942 | 7.14600110 | 16.79348127 |
| H | 15.88988837 | 7.24265903 | 17.44591872 |
| C | 15.09610027 | 7.60562382 | 15.47330257 |
| C | 16.38182159 | 8.19135372 | 14.90905304 |
| H | 16.12116317 | 8.79509257 | 14.02651292 |
| C | 17.09413174 | 9.12640833 | 15.89609932 |
| H | 16.41455279 | 9.90587372 | 16.26824163 |
| H | 17.94441586 | 9.61673815 | 15.40149269 |
| H | 17.49404210 | 8.57905860 | 16.76208677 |
| C | 17.31334447 | 7.06228632 | 14.42781079 |
| H | 17.58655445 | 6.40342255 | 15.26506445 |
| H | 18.23713184 | 7.48086341 | 14.00160667 |
| H | 16.82409629 | 6.44316111 | 13.66395560 |

**1· (with methyl groups instead of isopropyl)**

| | | | |
|---|---|---|---|
| Cl | -6.93928203503680 | 1.05668962912075 | 3.90736293296254 |
| Cl | -9.59910365492644 | 0.31943470843590 | 1.63252744147006 |
| P | -4.94122102058425 | 0.06206319690868 | -1.26234780524042 |
| P | -3.02038508488643 | 0.86621058356886 | -0.69151261456430 |
| N | -5.69552937156856 | 0.66314979259021 | 1.50714945596487 |
| N | -7.34378945809954 | 0.19403026700924 | 0.11415406326730 |
| C | -5.95888891396918 | 0.34144697828824 | 0.17835469562436 |
| C | -4.39212200432858 | 0.76211654306941 | 2.09995963469212 |
| C | -3.69151433096238 | -0.43367278493455 | 2.37097318997542 |
| C | -2.39877328346348 | -0.31462234851672 | 2.91416371823271 |
| H | -1.82030014433011 | -1.22750209815730 | 3.12346619199019 |
| C | -1.84531039273539 | 0.94648262756069 | 3.17740123812723 |
| H | -0.83010245991762 | 1.02027782283644 | 3.59601952898365 |
| C | -2.57036507462250 | 2.11531669039594 | 2.90226962773758 |
| H | -2.12225051081307 | 3.10214004710176 | 3.09412974548292 |
| C | -3.86188634054801 | 2.04590229903975 | 2.35018358964376 |
| C | -6.89367899691543 | 0.70742105761559 | 2.23694173703699 |
| C | -7.91542106013926 | 0.41332107034316 | 1.36842958844899 |
| C | -8.06453947510151 | -0.12529805112336 | -1.08509781250109 |
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**[1···$P_4$]·**

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| H | 10.89074262019669 | 20.59888640800471 | 5.35805551499351 |
| C | 12.14839113039905 | 12.31080019114051 | 5.54739528170533 |

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| H | 14.38649727548382 | 17.20294289677429 | 8.17427367540329 |
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| H | 15.32984484438053 | 17.44189956747066 | 2.10220789838729 |
| C | 13.82367645567129 | 12.22933410332017 | 1.82495092509893 |
| H | 12.84242141084937 | 12.65213451446827 | 2.12011730261204 |
| H | 13.65286260128414 | 11.42761788149492 | 1.07988938051816 |
| H | 14.25057690644590 | 11.76764998274503 | 2.74020704089691 |
| C | 16.52408198955219 | 9.83575248593690 | 1.92231586106533 |
| H | 16.71989981971812 | 10.92573795887913 | 1.83514159398954 |
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| H | 15.76250573001620 | 9.56035919505815 | 1.16640908414053 |
| C | 17.20663335776850 | 9.45747102302966 | 7.00417769067045 |
| H | 16.58101148894642 | 9.35252922189794 | 7.91169560865844 |
| H | 18.02063068899454 | 8.70419414115711 | 7.05583147647033 |
| H | 17.69859376016111 | 10.45305783616948 | 7.03368456351519 |
| C | 20.20039180405706 | 9.31046295604358 | 0.71295150456612 |
| H | 21.17779904245831 | 8.89261278197149 | 0.39331920357291 |
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| H | 20.60788254858801 | 4.78820855371489 | 4.08436673009591 |
| C | 23.71282537599152 | 9.05445197824605 | 6.88356611488194 |
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| H | 22.97981697887676 | 9.86261200521449 | 6.67804766212522 |
| H | 24.12236887736399 | 9.20690302459550 | 7.89985198846308 |
| C | 21.94514883547201 | 12.40498245005911 | 4.31213228596530 |
| H | 21.40578880609111 | 11.90381295900812 | 5.14772652530994 |
| H | 22.95438678763950 | 11.94627673758796 | 4.26096950999440 |
| H | 22.05480765123017 | 13.47578810033724 | 4.56567663690411 |

$P_4$:

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| P | 2.49943940854460 | 8.58433727984623 | 24.43725668079501 |
| P | 0.77518733810494 | 8.02128768351791 | 25.73698208828669 |
| P | 2.14812686730802 | 9.66774902244945 | 26.35616928387375 |

# 5 Crystallography

## 5.1 General Remarks

Suitable single crystals were coated with Paratone-N oil or Fomblin Y25 PFPE oil, mounted using a glass fiber and frozen in the cold nitrogen stream. X-ray diffraction data were collected at 100 K on a Rigaku Oxford Diffraction SuperNova diffractometer using either Cu $K_\alpha$ radiation ($\lambda$ = 1.54184 Å) generated by micro-focus sources. The data reduction and absorption correction was performed using CrysAlisPro[13], respectively. Using Olex2[14], the structures were solved with SHELXT[15] by direct methods and refined with SHELXL[16] by least-square minimization against $F^2$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions using the riding model. Images of the structures were produced with the Olex2[13] software.

## 5.2 Crystallographic data

**Table S5**: Crystallographic Data for selected structures.

| **Compound** | **1·** | **4** | **5** |
|---|---|---|---|
| Empirical formula | $C_{39}H_{51}Cl_2N_2P_2$ | $C_{84}H_{107}Cl_4FN_4P_8$ | $C_{88}H_{126}Cl_4N_4O_2P_4$ |
| Formula weight [g/mol] | 680.66 | 1581.29 | 1537.60 |
| Temperature [K] | 99.96(12) | 100.00(10) | 100.01(10) |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | P-1 | $P2_1/c$ | C2/c |
| a [Å] | 10.8940(3) | 22.39630(10) | 14.63850(10) |
| b [Å] | 11.6371(3) | 24.84720(10) | 34.7552(3) |
| c [Å] | 17.3041(2) | 15.60040(10) | 18.1897(2) |
| a [°] | 86.498(2) | 90 | 90 |
| β [°] | 73.235(2) | 96.9330(10) | 109.1670(10) |
| γ [°] | 66.584(2) | 90 | 90 |
| Volume [$Å^3$] | 1923.91(8) | 8617.92(8) | 8741.26(14) |
| Z | 2 | 4 | 4 |
| $\rho_{calc}$ [$g/cm^3$] | 1.175 | 1.219 | 1.168 |
| μ [$mm^{-1}$] | 2.508 | 3.008 | 2.278 |
| F(000) | 726.0 | 3344.0 | 3304.0 |
| Crystal size [$mm^3$] | 0.545 × 0.441 × 0.377 | 0.2 × 0.15 × 0.03 | 0.16 × 0.08 × 0.06 |
| Radiation (λ in Å) | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection [°] | 5.344 to 154.58 | 5.334 to 153.744 | 5.086 to 153.594 |
| Index ranges | $-13 \leq h \leq 13$, $-13 \leq k \leq 14$, $-21 \leq l \leq 21$ | $-28 \leq h \leq 23$, $-31 \leq k \leq 28$, $-19 \leq l \leq 19$ | $-16 \leq h \leq 18$, $-43 \leq k \leq 43$, $-22 \leq l \leq 22$ |
| Reflections collected | 21226 | 89080 | 53294 |
| Independent reflections | 8000 [$R_{int}$ = 0.0228, $R_{sigma}$ = 0.0203] | 18007 [$R_{int}$ = 0.0386, $R_{sigma}$ = 0.0280] | 9164 [$R_{int}$ = 0.0396, $R_{sigma}$ = 0.0263] |
| Data/restraints/parameters | 8000/0/418 | 18007/547/1030 | 9164/90/499 |
| Goodness-of-fit on $F^2$ | 1.053 | 1.022 | 1.041 |
| Final R indexes (I>=2σ (I)) | $R_1$ = 0.0421, $wR_2$ = 0.1139 | $R_1$ = 0.0474, $wR_2$ = 0.1241 | $R_1$ = 0.0415, $wR_2$ = 0.0930 |
| Final R indexes (all data) | $R_1$ = 0.0426, $wR_2$ = 0.1143 | $R_1$ = 0.0542, $wR_2$ = 0.1290 | $R_1$ = 0.0455, $wR_2$ = 0.0954 |
| Largest diff. peak/hole [$e/Å^3$] | 0.68/-0.30 | 0.82/-0.83 | 0.31/-0.73 |
| CCDC Number | 2351433 | 2351435 | 2351434 |

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