Electronic Supplementary Information

Access to 1,2,3-triphospholide ligands by reduction of di-*tert*-butyldiphosphatetrahedrane

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Table of Contents

1 Synthetic Procedures

1.1 General Synthetic Methods

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H_2O and <0.1 ppm O_2). (*t*BuCP)$_2$ (**A**).[1] [Cp*FeCl(tmeda)][2], [Cp*RuCl(cod)][3] and [H(Et$_2$O)$_2$BAr$^F_4$][4] were prepared according to procedures previously reported (tmeda = tetramethylethylenediamine, cod = cycloocta-1,5-diene, BAr_4^F = B{C$_6$H$_3$(CF$_3$)$_2$}$_4$).

Solvents except DME were dried and degassed with a MBraun SPS800solvent purification system. DME was distilled from a sodium/benzophenone mixture. All dry solvents except *n*-hexane and *n*-pentane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane and *n*-pentane were stored over potassium mirrors.

1.2 Analytical Techniques

NMR spectra were all recorded on Bruker Avance 400 spectrometers except for the ^{1}H and ^{13}C{^{1}H} NMR spectra of **13**, which were recorded on a Bruker Avance III 600 HD spectrometer with a 5 mm TCI cryo probe. All spectra were recorded at 300 K, except when specified otherwise, and referenced to residual solvent resonances (^{1}H NMR: THF-d_8: 1.72 ppm, CD_3CN: 1.94 ppm, C_6D_6: 7.16 ppm, ^{13}C{^{1}H} NMR: THF-d_8: 25.31 ppm, CD_3CN: 118.26 ppm, C_6D_6: 128.06 ppm). Chemical shifts (δ) are given in ppm referring to external standards of tetramethylsilane (^{1}H, ^{13}C{^{1}H}), 85% phosphorus acid (^{31}P{^{1}H}) and 1.0 M solution of LiCl in D_2O (^{7}Li{^{1}H}). ^{13}C NMR signals were assigned based on 2D NMR spectra (^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC, ^{1}H,^{31}P-HSQC, ^{31}P,^{31}P-COSY). UV-Vis spectra were recorded on a Varian Cary 50 spectrometer. Mass spectra were recorded on a Jeol AccuTOF GCX device by the analytical department of the University of Regensburg, which also determined elemental analysis.

For compound **1, 3, 11, 12** and **13** the ^{31}P{^{1}H} NMR spectrum was processed with the software gNMR by Cherwell Scientific.[5] The full line shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum. ^1J(^{31}P^{31}P) coupling constants were set to negative values and all other signs of the coupling constants were obtained accordingly. The designation of the spin system was performed by convention.

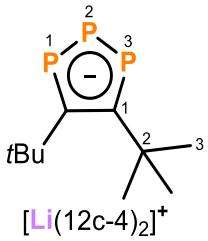
1.3 Synthesis of Compounds

[Li([12]crown-4)$_2$][1,2,3-P$_3$C$_2$*t*Bu$_2$] (1):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in alumium foil. No precautions for excluding light were taken during work-up.*

A piece of lithium (4.0 mg, 0.58 mmol, 1.0 eq.) in 2 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.56 mL, 0.55 mol/L, 0.87 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight (^{31}P{^{1}H} NMR spectrum of the crude reaction mixture see figure S1). The orange-red reaction mixture was filtered through a filter pipette in the glove box and [12]crown-4 (0.19 mL, 203 mg, 1.15 mmol, 2.0 eq.) was added. After stirring for 1.5 h at room temperature all volatiles were removed *in vacuo*. Subsequently, the orange solid was washed with *n*-hexane (1.5 mL) and toluene (2 x 0.5 mL). The dried residue was dissolved in THF (1.0 mL) and layered with diethyl ether (1.5 mL). Yellow needles were formed after 4 days at room temperature which were washed with diethyl ether (2 x 0.6 mL) and dried *in vacuo*.

Single crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane in a concentrated THF solution at ambient temperature.



$C_{26}H_{50}LiO_8P_3$, MW = 590.54 g/mol

Yield: up to 16.8 mg (0.0284 mmol, 5%)

^{1}H NMR (400 MHz, 300 K, THF-d_8): δ = 1.74 (overlapping s, 18H, H_3C^3), 3.63 (s, 32H, $H^{(12c\text{-}4)}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, THF-d_8): δ = 38.9 (m, C^3), 40.6 (m, C^2), 70.1 (s, $C^{(12c\text{-}4)}$), 185.4 (m, C^1) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, THF-d_8): (AA'X spin system) δ = 224.0 ($^{1}J_{AX}$ = −463.8 Hz, $^{1}J_{A'X}$ = −465.5 Hz 1P, P^{2}), 316.2 ($^{1}J_{AX}$ = −463.8 Hz, $^{1}J_{A'X}$ = −465.5 Hz, $^{2}J_{AA'}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm

Coupling constants and chemical shifts are taken from the simulation (Figure S7 and Table S1).

$^{7}Li\{^{1}H\}$ NMR (156 MHz, 300 K, THF-d_8): δ = −0.34 ppm.

UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [$L \cdot mol^{-1} \cdot cm^{-1}$]): 270 (8000), 345 (3000).

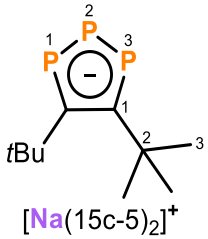
Elemental analysis calcd. C 52.88, H 8.53; found C 53.17, H 8.00

Mixture of [Na([15]crown-5)$_2$][1,2,3-P_3C_2*t*Bu$_2$] (2) and [Na([15]crown-5)$_2$][1,3-P_2C_3*t*Bu$_3$] (7):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in alumium foil. No precautions for excluding light were taken during work-up.*

A piece of sodium (6.8 mg, 0.39 mmol, 1.0 eq.) in 1 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.0 mL, 0.43 mol/L, 0.44 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [15]crown-5 (0.12 mL, 130 mg, 0.59 mmol, 2.0 eq.) was added. After stirring for 1.8 h at room temperature all volatiles were removed *in vacuo*. The orange solid was taken up in 0.5 mL toluene and 0.2 mL THF. *n*-Hexane (4 mL) was added to facilitate precipitation. The supernatant was decanted, and the residue washed with 2 mL of diethyl ether. 92.6 mg of orange solid were afforded after drying *in vacuo*.

Analytical data for **2:**

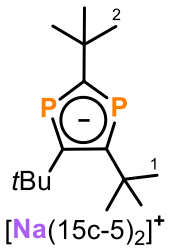


$C_{30}H_{58}NaO_{10}P_3$, MW = 694.70 g/mol

^{1}H NMR (400 MHz, 300 K, MeCN): δ = 1.68 (overlapping s, 18H, H_3C^{3}), 3.54 (s, 20H, $H^{(15c-5)}$) ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, THF-d_8): δ = 224.8 ($^{1}J_{PP}$ = 458.8 Hz, $^{1}J_{PP}$ = 473.8 Hz, 1P, P^{2}), 314.9 ($^{1}J_{PP}$ = 466.7 Hz, $^{2}J_{PP}$ = 6.8 Hz, 2P, $P^{1,3}$) ppm.

Analytical data for **7**:[6]



$C_{35}H_{67}NaO_{10}P_2$, MW = 732.85 g/mol

^{1}H NMR (400 MHz, 300 K, THF-d_8): δ = 1.38 (s, 9H, H_3C^{2}), 1.52 (s, 18H, H_3C^{1}), 3.54 (s, 20H, $H^{(15c-5)}$) ppm.

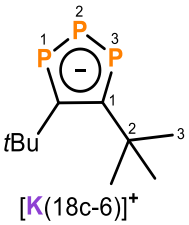
$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, THF-d_8): δ = 186.1 (s, 2P).

Mixture of [K([18]crown-6)][1,2,3-P_3C_2*t*Bu_2] (3) and [K([18]crown-6)][1,3-P_2C_3*t*Bu_3] (8):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in alumium foil. No precautions for excluding light were taken during work-up.*

A piece of potassium (21.8 mg, 0.56 mmol, 1.0 eq.) in 2.6 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.8 mL, 0.48 mol/L, 0.84 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [18]crown-6 (148 mg, 0.56 mmol, 1.0 eq.) was added. After stirring for 1.8 h at room temperature all volatiles were removed *in vacuo*. The orange solid was taken up in 0.5 mL toluene and 0.3 mL THF. *n*-Hexane (4 mL) was added to facilitate precipitation. The supernatant was decanted, and the residue washed with diethyl ether (2 x 1 mL). 130 mg of orange solid were afforded after drying *in vacuo*.

Analytical data for **3**:



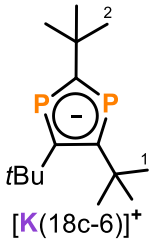
$C_{22}H_{42}KO_6P_3$, MW = 534.59 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.93 (overlapping s, 18H, H_3C^3), 3.76 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): (AA'X spin system) δ = 226.6 ($^1J_{AX}$ = −465.6 Hz, $^1J_{A'X}$ = −467.5 Hz 1P, P^2), 317.2 ($^1J_{AX}$ = −465.6 Hz, $^1J_{A'X}$ = −467.5 Hz, $^2J_{AA'}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S18 and Table S2).

Analytical data for **8**:



$C_{27}H_{51}KO_6P_2$, MW = 572.74 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.60 (s, 9H, H_3C^2), 1.75 (s, 18H, H_3C^1), 3.76 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): δ = 186.6 (s, 2P).

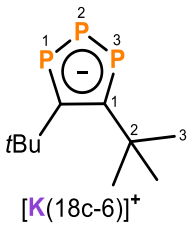
[K([18]crown-6)][1,2,3-P_3C_2*t*Bu_2] (3):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in alumium foil. No precautions for excluding light were taken during work-up.*

A piece of potassium (20.5 mg, 0.52 mmol, 1.0 eq.) in 2.6 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (2.0 mL, 0.39 mol/L, 0.79 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [18]crown-6 (138 mg, 0.52 mmol, 1.0 eq.) was added. After stirring for 1.3 h at room temperature all volatiles were removed *in vacuo*. Subsequently, the orange solid was washed with *n*-hexane (1.5 mL) and toluene (3 x 0.3 mL). The dried residue was dissolved in THF (0.5 mL) and layered with diethyl ether (1.0 mL). Yellow needles were formed after 7 days at room temperature, which were dried

in vacuo. A second crop of crystals was obtained by removing the solvent from the toluene extract, redissolving the residue in THF (0.5 mL) and layering the solution with diethyl ether (1.0 mL).

Single crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane in a concentrated toluene solution at ambient temperature.



$C_{22}H_{42}KO_6P_3$, MW = 534.59 g/mol

Yield: up to 114 mg (two crops of crystals, 0.213 mmol, 32%)

Isolated yields varied due to the crystallization properties of the compound.

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.75 (overlapping s, 18H, H_3C^{3}), 3.57 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, THF-d_8): δ = 38.9 (m, C^{3}), 40.5 (m, C^{2}), 71.2 (s, $C^{(12c\text{-}4)}$), 183.4 (m, C^{1}) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, THF-d_8): (AA'X spin system) δ = 224.8 ($^{1}J_{AX}$ = −465.6 Hz, $^{1}J_{A'X}$ = −467.5 Hz 1P, P^{2}), 314.5 ($^{1}J_{AX}$ = −465.6 Hz, $^{1}J_{A'X}$ = −467.5 Hz, $^{2}J_{AA'}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S18 and Table S2.

UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [$L \cdot mol^{-1} \cdot cm^{-1}$]): 270 (10000), 345 (4000).

Elemental analysis calcd. C 49.43, H 7.92; found C 50.15, H 7.85

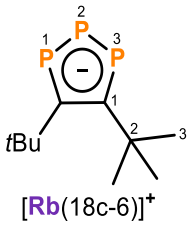
Mixture of [Rb([18]crown-6)][1,2,3-P_3C_2*t*Bu_2] (4) and [Rb([18]crown-6)][1,3-P_2C_3*t*Bu_3] (9):

Due to the light-sensitivity of ***A****, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in alumium foil. No precautions for excluding light were taken during work-up.*

A piece of rubidium (63.0 mg, 0.74 mmol, 1.0 eq.) in 3 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.3 mL, 0.85 mol/L, 1.1 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature while stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [18]crown-6 (195 mg, 0.74 mmol, 1.0 eq.) was added. After stirring for 30 min at room temperature all volatiles were removed *in vacuo*. The orange solid was washed with 1 mL *n*-hexane, taken up in 0.5 mL THF and crystalized over 2 weeks to give 5 mg of yellow crystals which were washed with toluene (4 x 0.5 mL) and dried *in vacuo*.

Single crystals suitable for X-ray analysis of both **4** and **9** were obtained from the same batch, grown by slow diffusion of *n*-hexane (2 mL) in a concentrated THF solution at ambient temperature.

Analytical data for **4**:

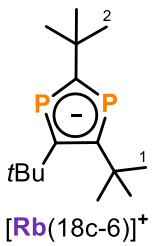


$C_{22}H_{42}RbO_6P_3$, MW = 580.96 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.77 (overlapping s, 18H, H_3C^3), 3.58 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): δ 236.6 ($^1J_{PP}$ = 457.4 Hz, $^1J_{PP}$ = 471.2 Hz, 1P, P^2), 323.0 ($^1J_{PP}$ = 466.6 Hz, $^2J_{PP}$ = 4.8 Hz, 2P, $P^{1,3}$) ppm.

Analytical data for **9**:



$C_{27}H_{51}RbO_6P_2$, MW = 619.11 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.46 (s, 9H, H_3C^2)1.61 (s, 18H, H_3C^1), 3.58 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

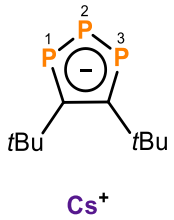
$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, CD_3CN): δ 193.6 (s, 2P).

Mixture of Cs[1,2,3-P_3C_2*t*Bu_2] (5) and Cs[1,3-P_2C_3*t*Bu_3] (10):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in alumium foil. No precautions for excluding light were taken during work-up.*

Caesium (19.5 mg, 0.15 mmol, 1.0 eq.) in 1 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (0.26 mL, 0.85 mol/L, 0.22 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature while stirring overnight. An orange reaction mixture was formed whose $^{31}P\{^{1}H\}$ NMR signals indicate the formation of **5** and **10.**

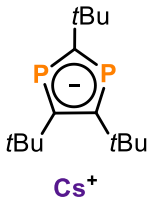
Analytical data for **5**:



$C_{10}H_{18}CsP_3$, MW = 354.08 g/mol

$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, THF with C_6D_6 capillary): δ = 238.8 ($^{1}J_{PP}$ = 455.7 Hz, $^{1}J_{PP}$ = 467.8 Hz, 1P, P^2), 328.6 ($^{1}J_{PP}$ = 461.3 Hz, $^{2}J_{PP}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Analytical data for **10**:



$C_{10}H_{18}CsP_3$, MW = 402.23 g/mol

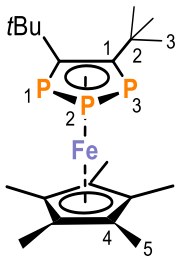
$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, THF with C_6D_6 capillary): δ 198.8 (s, 2P).

[Cp*Fe(η^5-1,2,3-P_3C_2*t*Bu_2)] (11):

A solution of triphospholide **3** (20.0 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL) at −30 °C was added dropwise to a cooled (−30 °C) solution of [Cp*FeCl(tmeda)] (13.4 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL). The mixture turned brown immediately and was left to warm to room

temperature while stirring for 1.5 h. The volatiles were removed *in vacuo* and the residue extracted in *n*-hexane to give a purple solution. The mixture was filtered through a pad of silica gel (1 cm) and washed with *n*-hexane (3 x 1 mL). The solvent was removed and the purple solid dried *in vacuo*.

Single crystals suitable for X-ray analysis were grown from *n*-hexane at ambient temperature.



$C_{22}H_{39}FeP_3$, MW = 453.32 g/mol

Yield: 9.1 mg (0.020 mmol, 54%)

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 1.65 & 1.66 (overlapping s, 18H, H_3C^3), 1.68 (s, 15H, H_3C^5) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ = 12.6 (m, C^5), 38.4 (m, C^3), 39.2 (m, C^2), 86.8 (s, C^4), 134.6 (m, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): (AA'X spin system) δ = −17.8 ($^1J_{AX}$ = −397.1 Hz, $^1J_{A'X}$ = −396.2 Hz 1P, P^2), 116.3 ($^1J_{AX}$ = −397.1 Hz, $^1J_{A'X}$ = −396.2 Hz, $^2J_{AA'}$ = 3.4 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S26 and Table S3).

UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [$L \cdot mol^{-1} \cdot cm^{-1}$]): 240 (14000), 280 (16000), 470 (200), 575 (200).

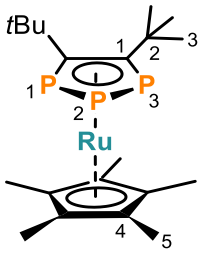
Elemental analysis calcd. C 56.89, H 7.88; found C 56.76, H 7.82

[Cp*Ru(η^5-1,2,3-P_3C_2*t*Bu$_2$)] (12):

A solution of triphospholide **3** (20.0 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL) at −30 °C was added dropwise to a cooled (−30 °C) solution of [Cp*RuCl(cod)] (14.8 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL). The mixture was left to warm to room temperature while stirring for 1 h. A color change from yellow to red was observed. The volatiles were removed *in vacuo* and

the residue extracted in *n*-hexane. Orange red crystals were formed upon storing at room temperature for 13 days. These were taken up in *n*-hexane (0.2 mL). Subsequently, the mixture was filtered through a pad of silica gel (1 cm) and washed with *n*-hexane (3 x 1 mL). The solvent was removed and the orange solid dried *in vacuo*.

Single crystals suitable for X-ray analysis were grown from *n*-hexane at ambient temperature.



$C_{22}H_{39}RuP_3$, MW = 497.55 g/mol

Yield: up to 5.9 mg (0.012 mmol, 32%)

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 1.59 (s, 18H, H_3C^3), 1.78 (s, 15H, H_3C^5) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ = 12.4 (m, C^5), 38.3 (m, C^3), 38.8 (m, C^2), 93.8 (s, C^4), 130.5 (m, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): (AA'X spin system) δ = −39.1 ($^1J_{AX}$ = −393.4 Hz, $^1J_{A'X}$ = −393.9 Hz 1P, P^2), 87.5 ($^1J_{AX}$ = −393.4 Hz, $^1J_{A'X}$ = −393.9 Hz, $^2J_{AA'}$ = 0.6 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S30 and Table S4).

UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [$L \cdot mol^{-1} \cdot cm^{-1}$]): 230 (37000).

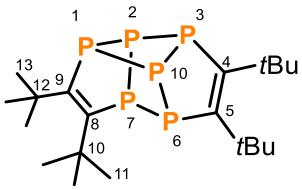
Elemental analysis calcd. C 51.39, H 7.12; found C 51.60, H 7.15

***t*Bu$_4$C$_4$P$_6$ (13)**:

To a solution of triphospholide **3** (83.0 mg, 0.155 mmol, 1.0 eq.) in THF (1.5 mL) at −30 °C was added a solution of $[H(Et_2O)_2BAr^F{}_4]$ (176 mg, 0.174 mmol, 1.1 eq.) in THF (1.5 mL). The mixture was left to warm to room temperature whilst stirring for 3 h and turned from colorless to pale yellow. The solvent was removed *in vacuo*, and the product was extracted with *n*-hexane (10x1 mL) and filtered. The compound was recrystallized from *n*-pentane (0.4 mL). Pale yellow

crystals of **13** were obtained by storing the solution at −30 °C for twelve days. A second batch of crystals was isolated after storage of the supernatant at −30 °C for three weeks.

Crystals suitable for X-ray analysis were grown from *n*-pentane at −30 °C.



$C_{20}H_{36}P_6$, MW = 462.12 g/mol

Yield: 7.8 mg (two crops of crystals, 0.017 mmol, 22%)

^{1}H NMR (600 MHz, 300 K, C_6D_6): δ = 1.08 (s, 18H, H_3C^{13}), 1.53 (s, 18H, H_3C^{11}) ppm.

^{13}C{^{1}H} NMR(151 MHz, 300 K, C_6D_6): δ = 32.1 (t, J_{CP} = 5.4 Hz, C^{13}), 34.2 (t, J_{CP} = 6.6 Hz, C^{11}), 41.5 (m, C^{12}), 41.7 (m, C^{10}), 165.0 (m, C^{9}), 170.5 (m, C^{8}), ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): (AA'MM'XX' spin system) δ = 64.2 ($^{1}J_{AA'}$ = –261.9 Hz, $^{2}J_{AM}$ = $^{2}J_{A'M'}$ = –3.2 Hz, $^{2}J_{A'M}$ = $^{2}J_{AM'}$ = 9.9 Hz, $^{1}J_{AX}$ = $^{1}J_{A'X'}$ = –293.9 Hz, $^{2}J_{A'X}$ = $^{2}J_{AX'}$ = 15.3 Hz, 2P, $P^{6,7}$), 15.0 ($^{2}J_{AM}$ = $^{2}J_{A'M'}$ = –3.2 Hz, $^{2}J_{A'M}$ = $^{2}J_{AM'}$ = 9.9 Hz, $^{2}J_{MM'}$ = 24.9 Hz, $^{1}J_{MX}$ = $^{1}J_{M'X'}$ = –157.7 Hz, $^{1}J_{M'X}$ = $^{1}J_{MX'}$ = –134.2 Hz, 2P, $P^{1,3}$), −63.8 ($^{2}J_{AX}$ = $^{2}J_{A'X'}$ = –293.9 Hz, $^{1}J_{A'X}$ = $^{1}J_{AX'}$ = 15.3 Hz, $^{1}J_{MX}$ = $^{1}J_{M'X'}$ = –157.7 Hz, $^{1}J_{M'X}$ = $^{1}J_{MX'}$ = –134.2 Hz, $^{2}J_{XX'}$ = 29.5 Hz, 2P, $P^{2,10}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S35 and Table S5).

HRMS (EI, toluene): m/z(%) calculated for $C_{20}H_{36}P_6$: 462.1237; found: 462.1233.

1.4 Additional Experiments

To an orange solution of triphospholide **3** and diphospholide **8** (combined 10 mg, approx. 0.04 mmol, 1.0 eq.) in DME (0.5 mL) at −30 °C was dropwise added a blue solution of $[Cp_2Fe]BAr^F_4$ (41 mg, 0.04 mmol, 1.0 eq.) in DME (0.5 mL). The mixture was left to warm to room temperature whilst stirring for 2.5 h and turned forest green. The solvent was removed *in vacuo*, and the product was extracted with *n*-hexane (5x0.5 mL) and filtered. The ^{31}P{^{1}H} NMR spectrum shows **13** as the main product (see Figure S37), side products can be attributed to the reaction of **8** with $[Cp_2Fe]BAr^F_4$ as they are similarly seen in the reaction of the mixture of **3**

and **8** with $[H(Et_2O)_2BAr^F{}_4]$ (Figure S38). Nevertheless, the isolation of **13** is hampered due to the similar solubilities of **13** and Cp_2Fe as can be seen in the ^1H NMR spectrum (Figure S36).

Reactions of triphospholide **3** with $[IPrNi(vtms)_2]$, $[Cp^*RuCl(diphos)]$, $[FeCl_2(tmeda)]_2$, $[(Ph_3P)_2NiCl_2]$, $[Cp_3Ni_2]BF_4$, $[Cp_2Fe]PF_6$, $[(PPh_3)CuCl]$ and MeI were conducted according to the same procedure, yielding the characteristic $^{31}P\{^1H\}$ NMR signals of **13** among other, so far unidentified reaction products.

2 NMR Spectra

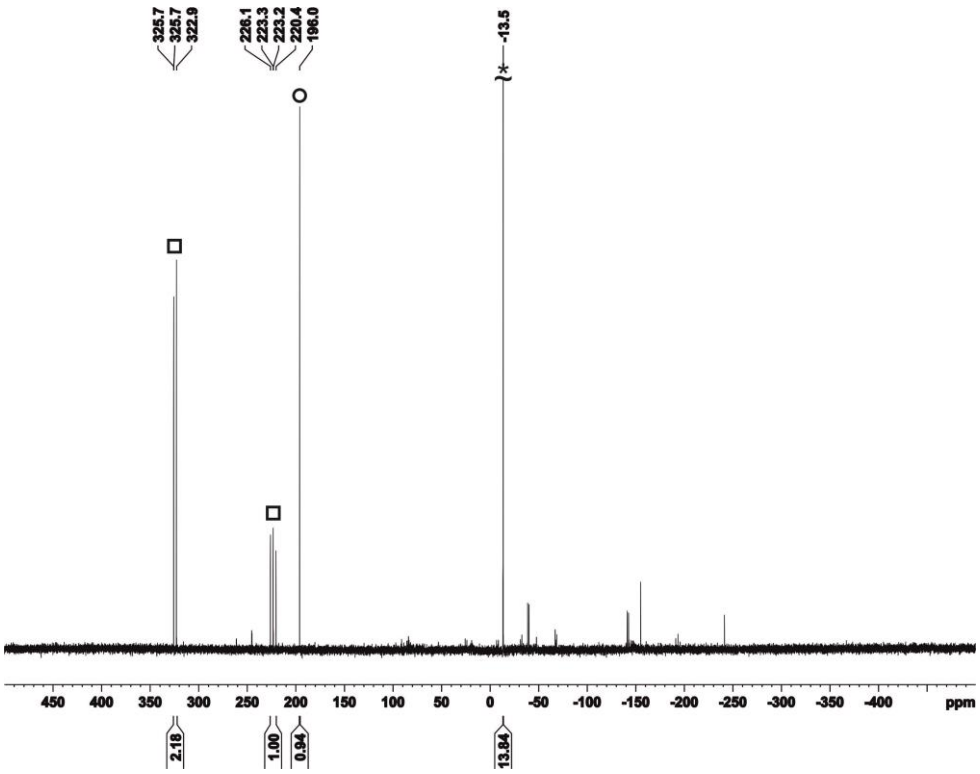


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF with C_6D_6 capillary) of the reaction mixture of 1 equiv. Li with 1.5 eqiv. **A**. **1** (□) and **6** (○). * = (*t*BuCP)$_4$.

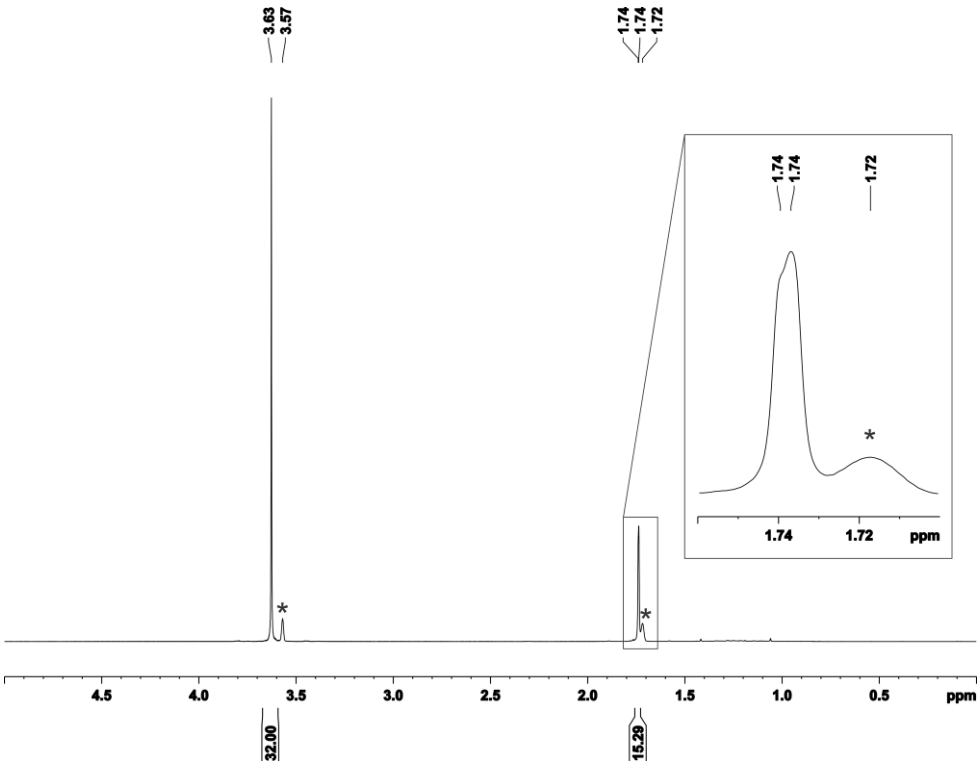


Figure S2. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **1**. *Residual proton signals of THF-d_8.

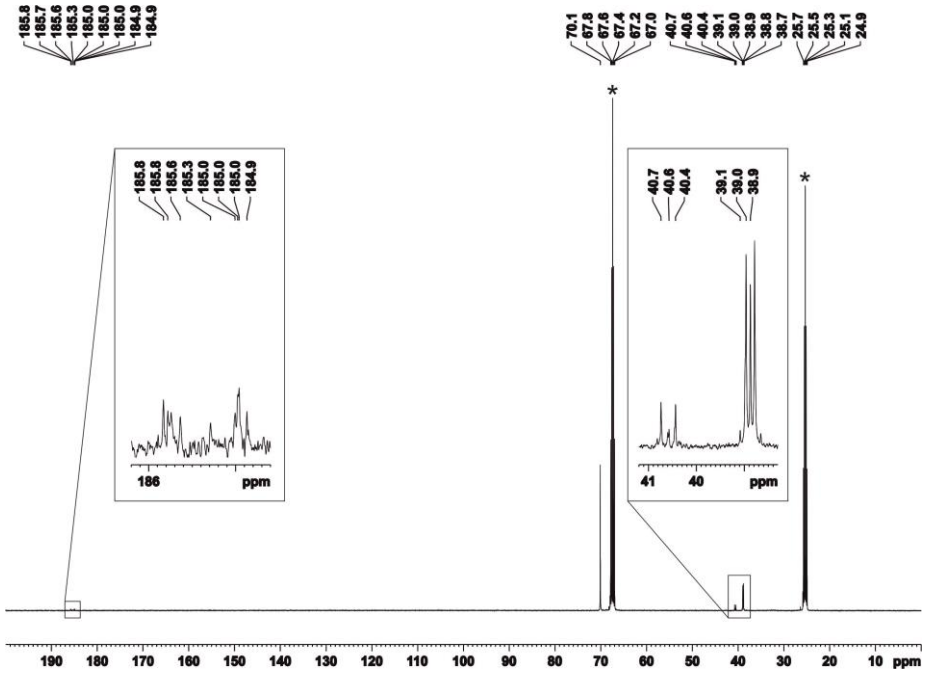


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, THF-d_8) of **1**. * = THF-d_8.

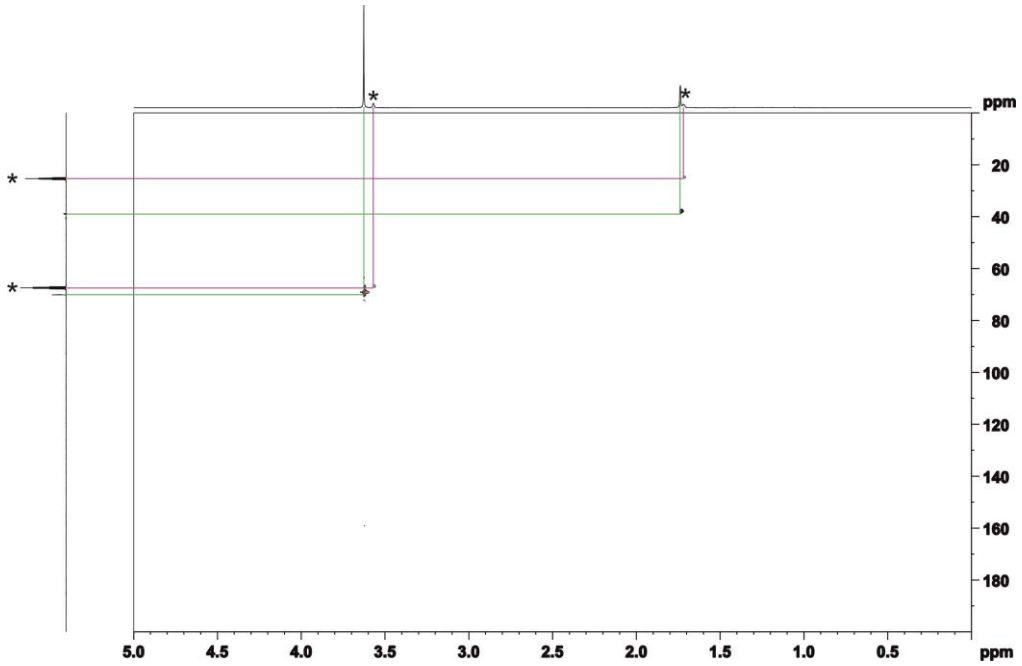


Figure S4. ^{1}H -^{13}C-HSQC NMR spectrum (100 MHz, 300 K, THF-d_8) of **1**, lines in green. * = THF-d_8, lines in purple.

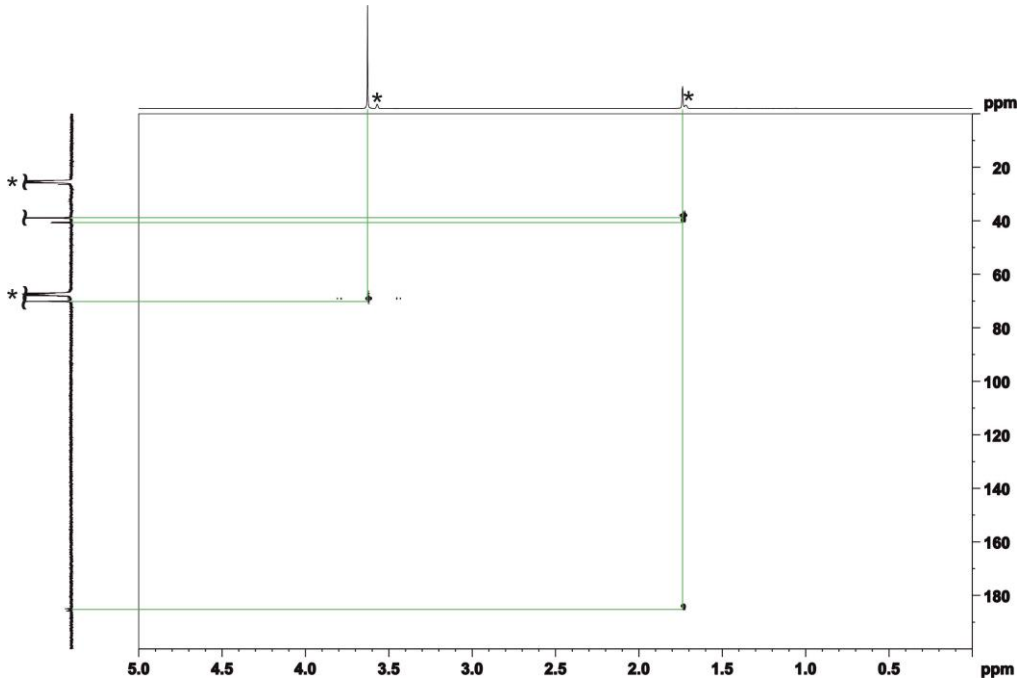


Figure S5. ^{1}H -^{13}C-HMBC NMR spectrum (100 MHz, 300 K, THF-d_8) of **1**, lines in green. * = THF-d_8.

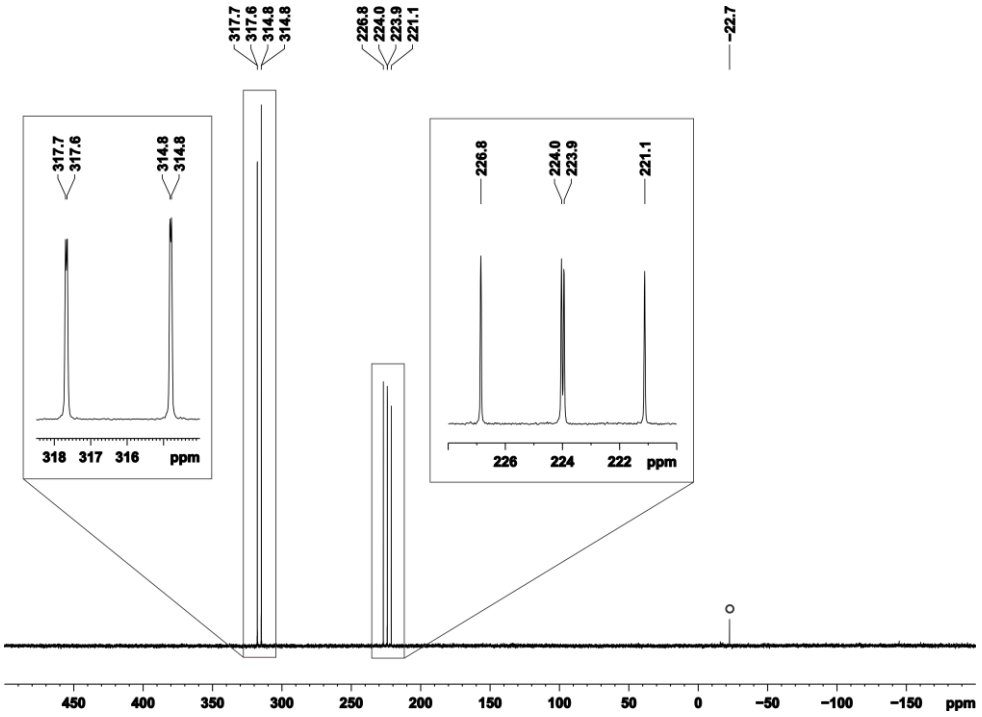


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **1**. ° = (tBuCP)$_4$.

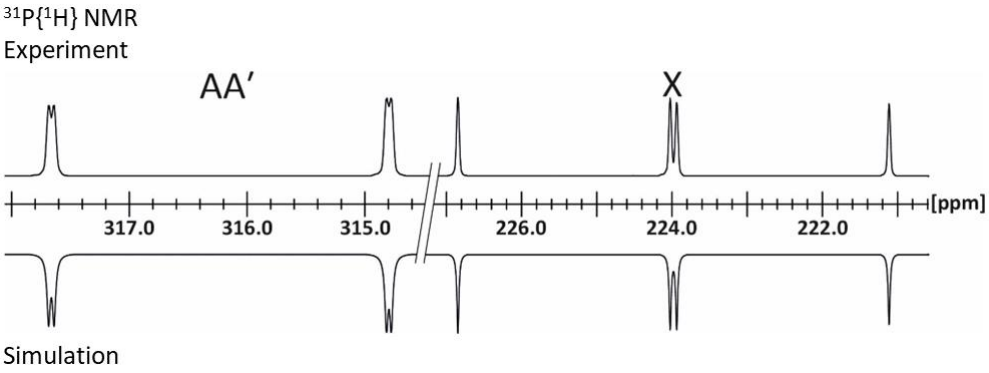
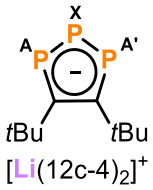


Figure S7. Section of the $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **1**; experimental (upwards) and simulation (downwards).

Table S1. Coupling constants from the iterative fit of the AA′X spin system and representation of **1**.

	$\delta(P_{AA'})$ = 316.2 ppm
	$\delta(P_X)$ = 224.0 ppm
	$^{1}J_{AX}$ = −463.8 Hz
	$^{1}J_{A'X}$ = −465.5 Hz
	$^{2}J_{AA'}$ = 4.3 Hz

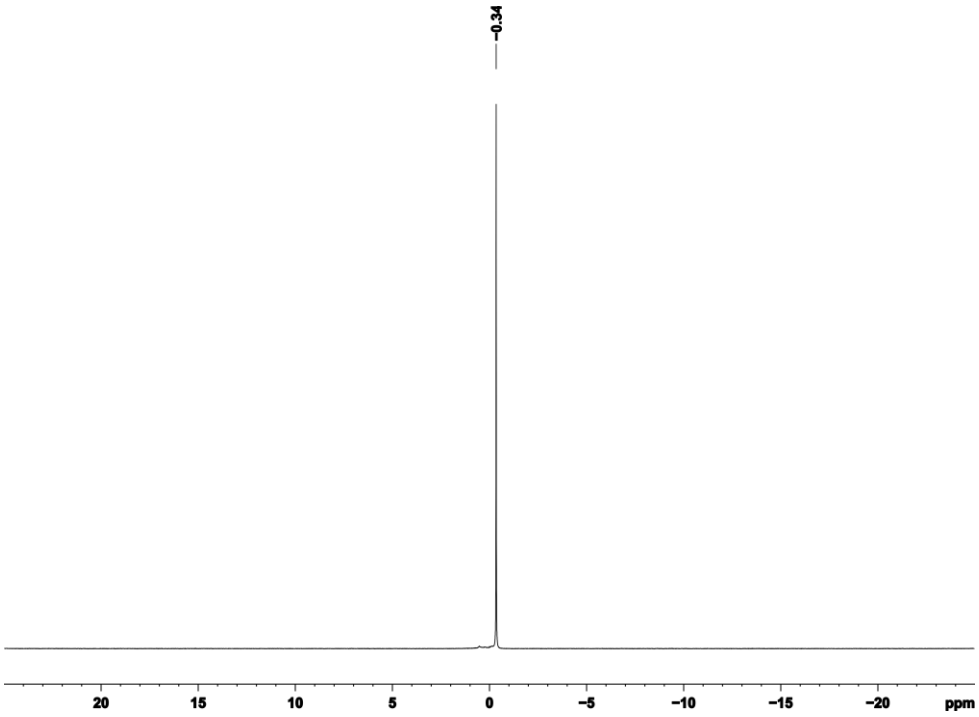


Figure S8. $^{7}Li\{^{1}H\}$ NMR spectrum (156 MHz, 300 K, THF-d_8) of **1**.

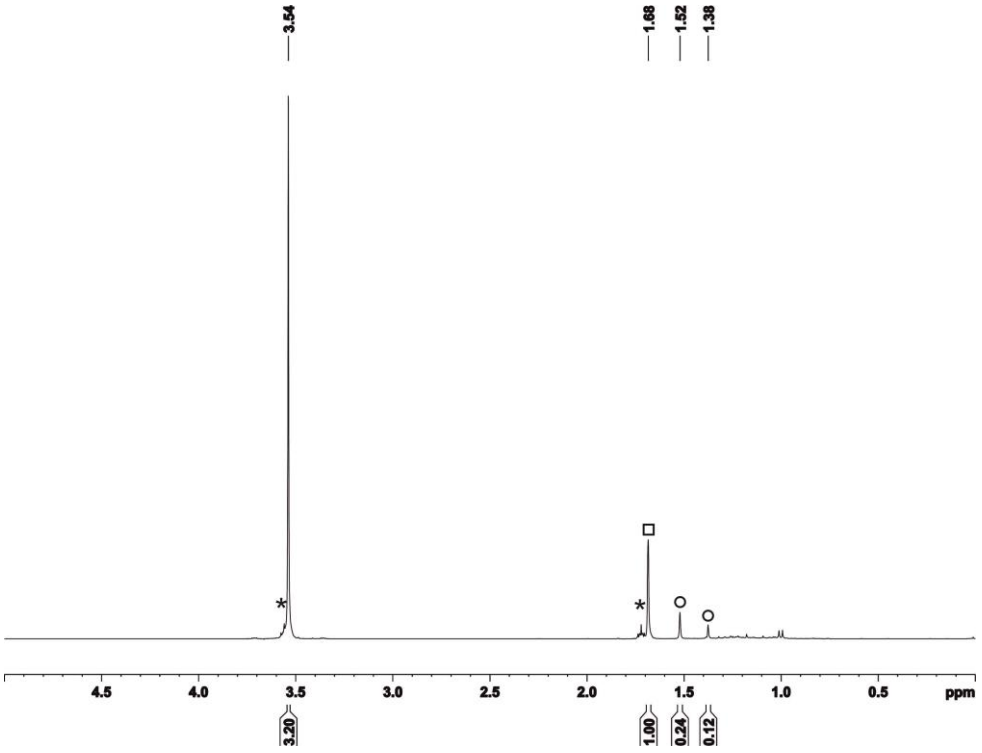


Figure S9. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of the mixture of **2** (□) and **7** (○). * = Residual proton signals of THF-d_8.

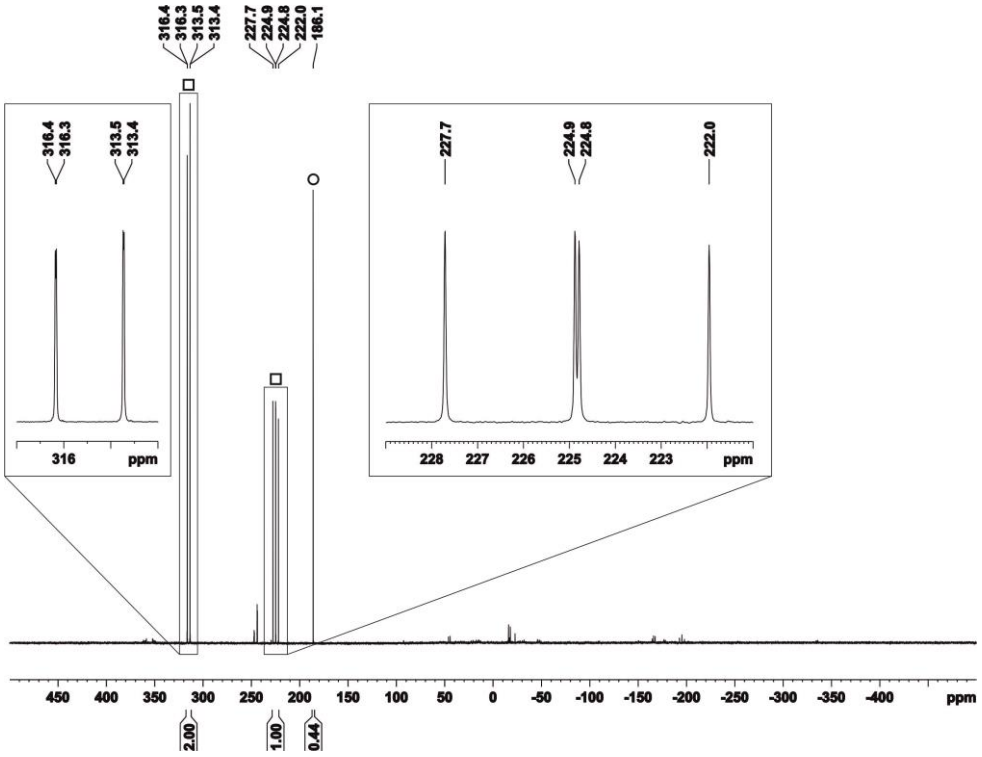


Figure S10. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, THF-d_8) of the mixture of **2** (□) and **7** (○).

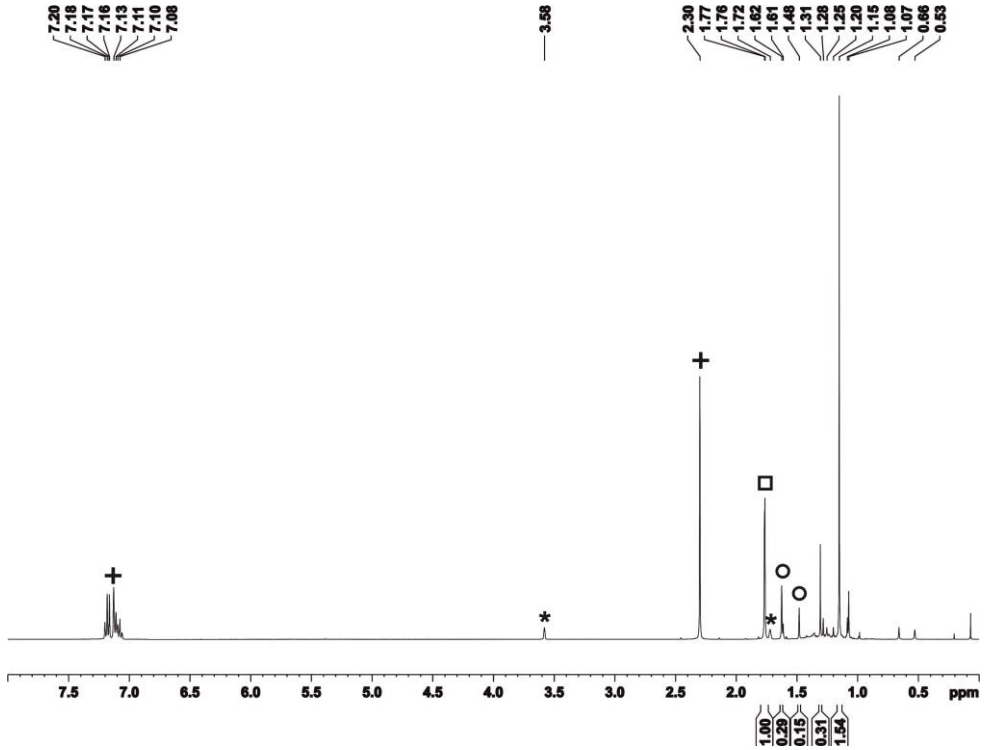


Figure S11. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of the crude reaction mixture of 1.5 eq. of **A** and 1 eq. of K in THF-d_8. **3** (□) and **8** (○). * = Residual proton signals of THF-d_8. + = toluene in which **A** is dissolved.

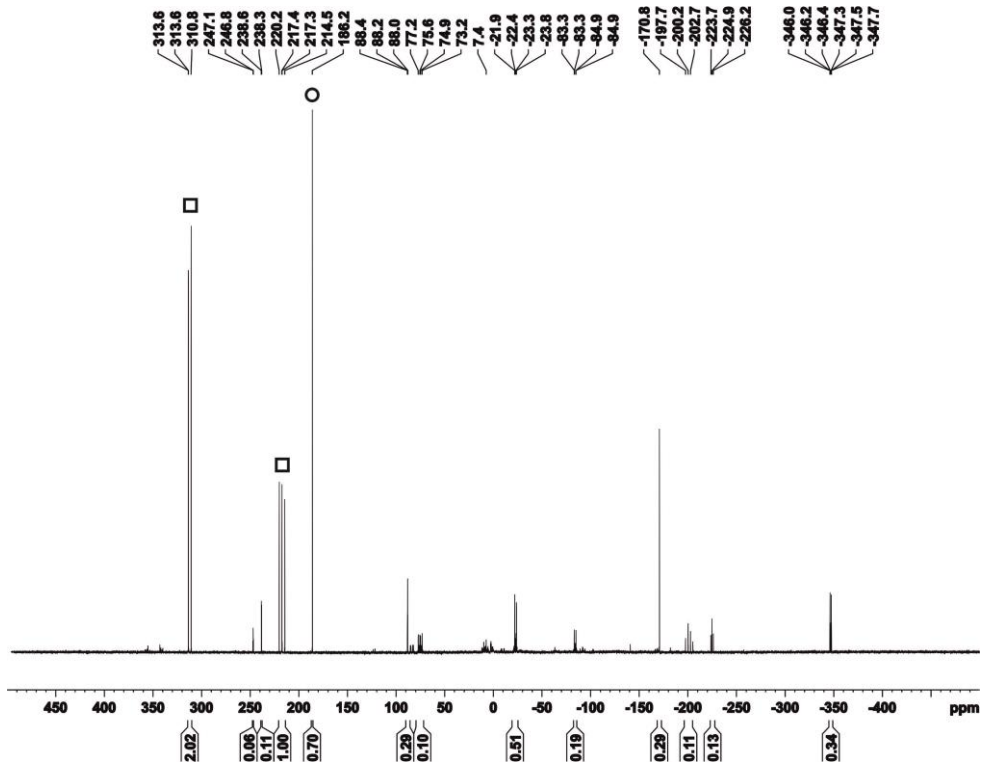


Figure S12. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, THF-d_8) of the crude reaction mixture of 1.5 eq. of **A** and 1 eq. of K in THF-d_8. **3** (□) and **8** (○).

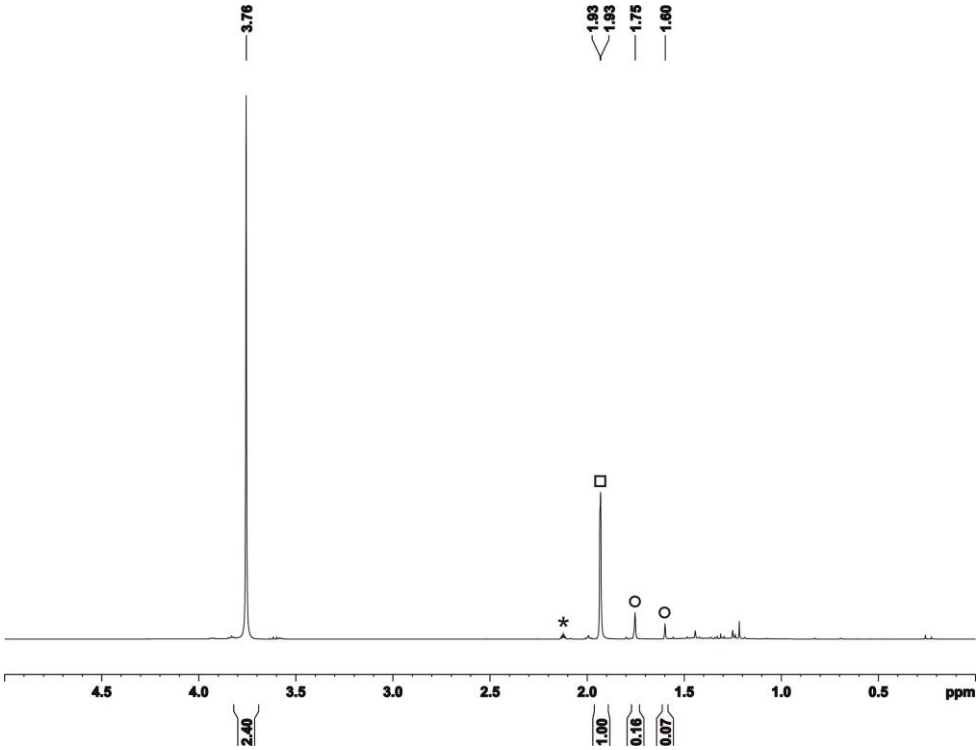


Figure S13. ^{1}H NMR spectrum (400 MHz, 300 K, CD_3CN) of the mixture of **3** (□) and **8** (○). * = Residual proton signals of CD_3CN.

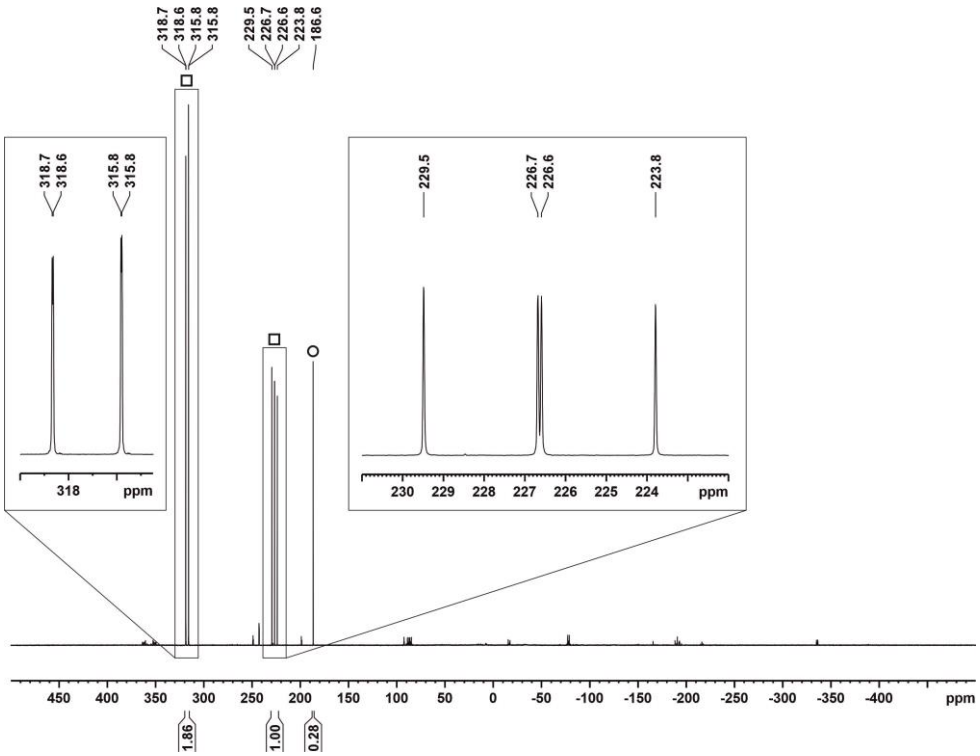


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, CD_3CN) of the mixture of **3** (□) and **8** (○).

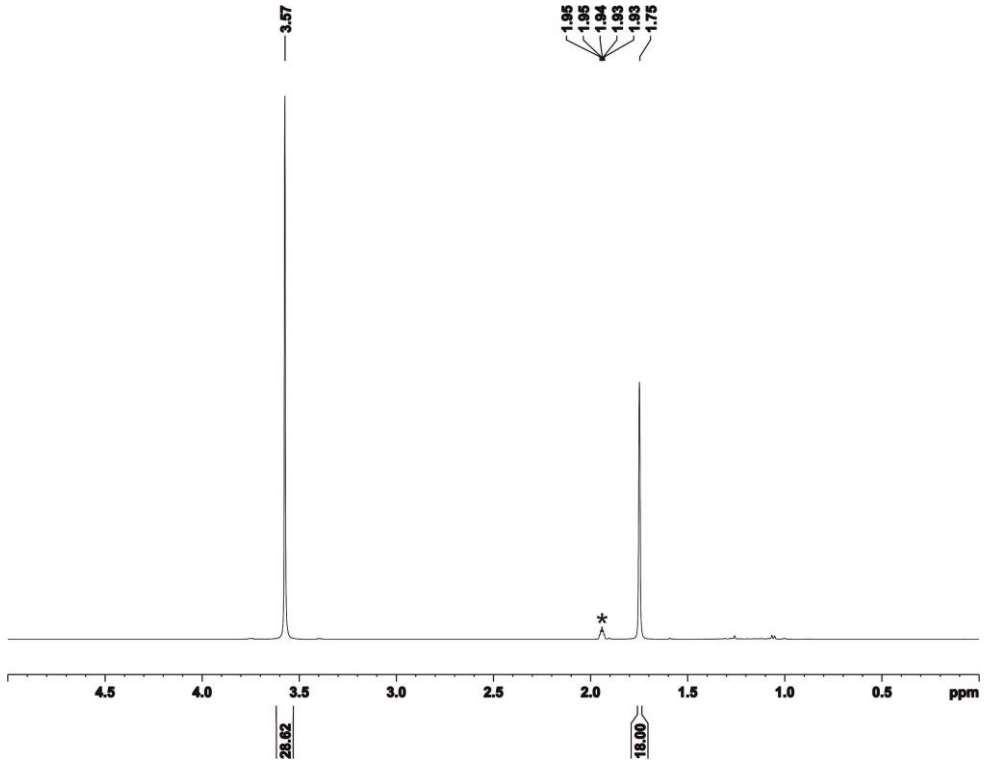


Figure S15. ^{1}H NMR spectrum (400 MHz, 300 K, CD_3CN) of **3**. * = Residual proton signals of CD_3CN.

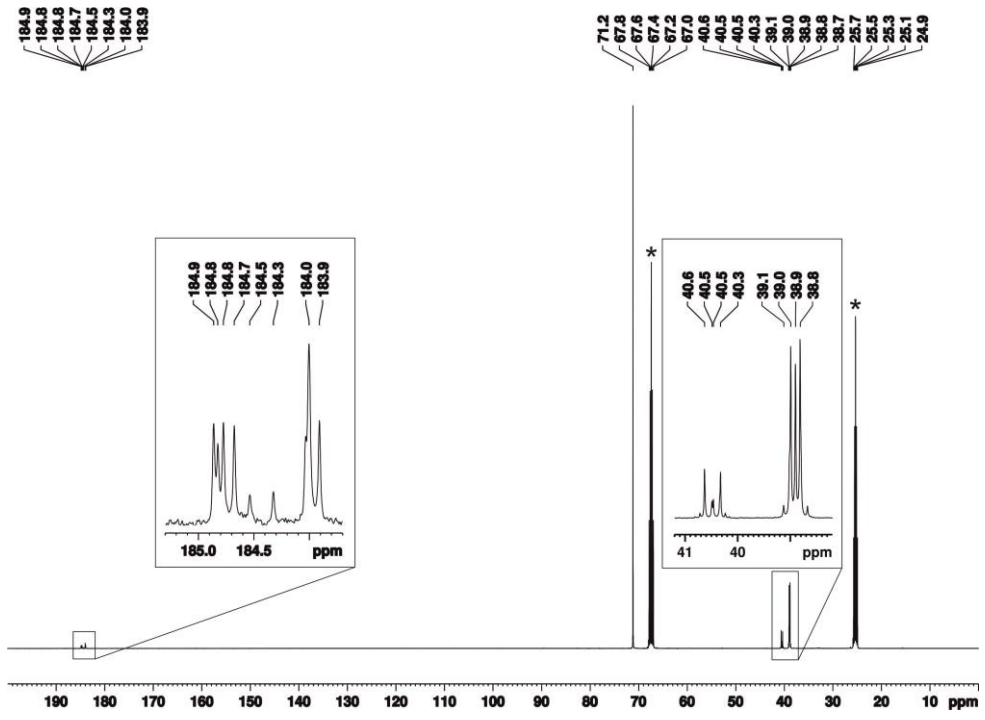


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, THF-d_8) of **3**. * = THF-d_8.

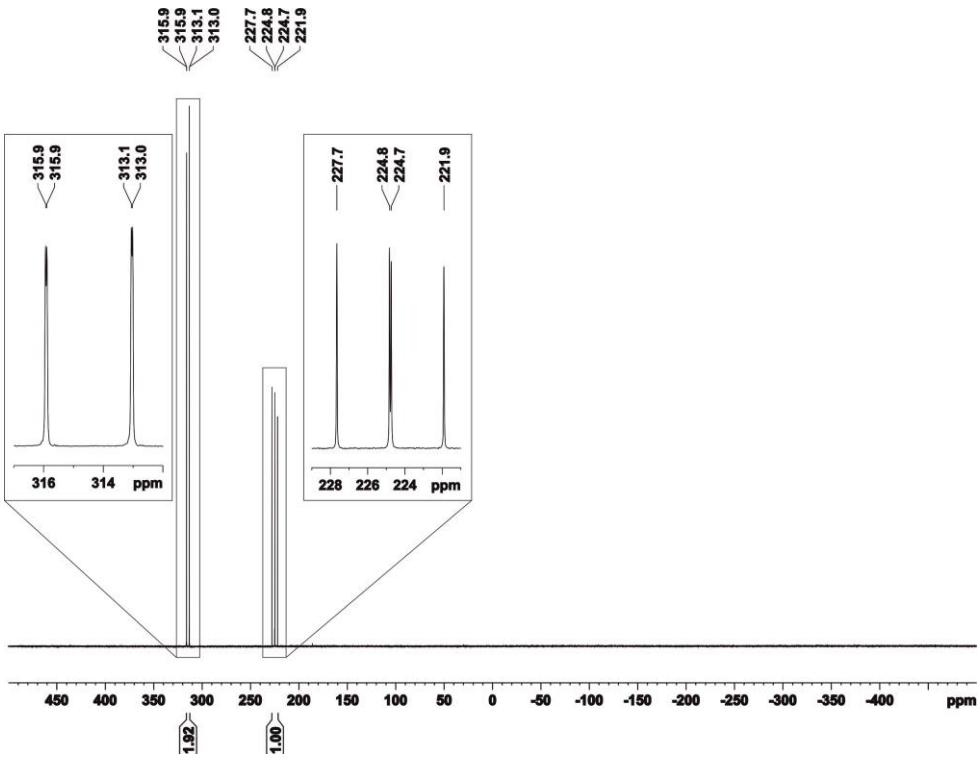


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **3**.

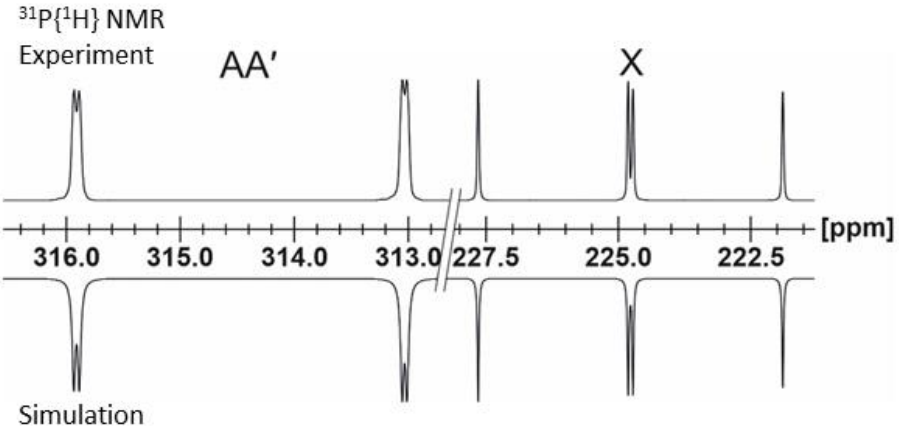
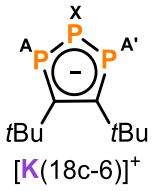


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) and simulation of **3**.

Table S2. Coupling constants from the iterative fit of the AA′X spin system and representation of **3**.

	$\delta(P_{AA'})$ = 314.4 ppm
	$\delta(P_X)$ = 224.8 ppm
	$^{1}J_{AX}$ = −465.6 Hz
	$^{1}J_{A'X}$ = −467.5 Hz
	$^{2}J_{AA'}$ = 4.3 Hz

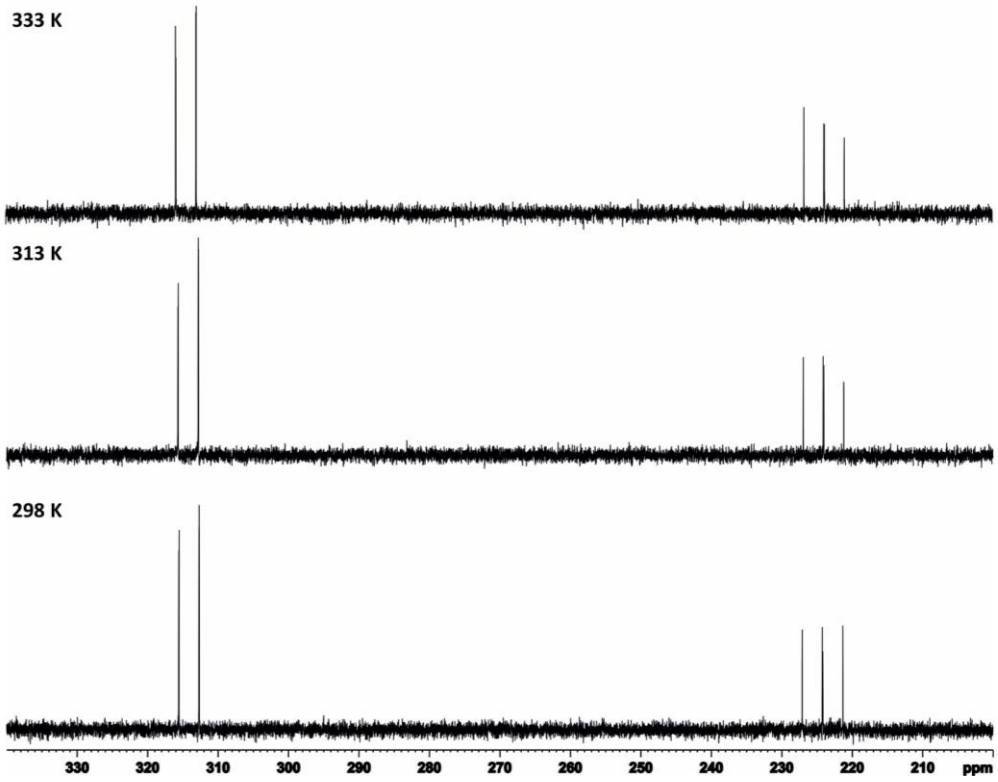


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8) of **3** at different temperatures depicted from 200 to 340 ppm.

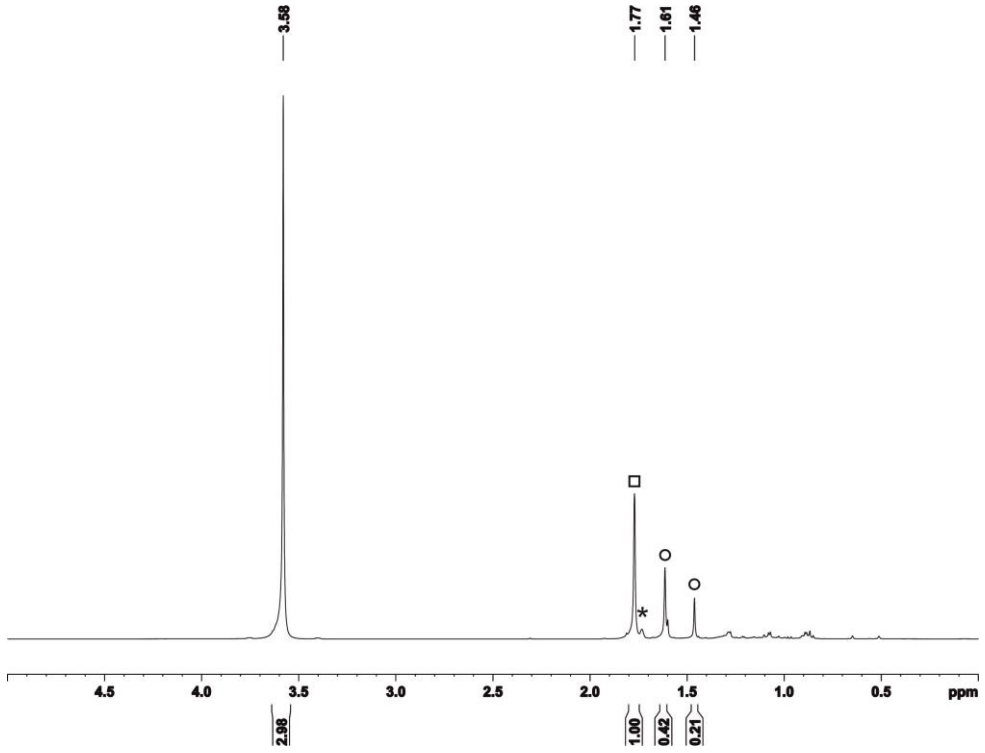


Figure S20. ^{1}H NMR spectrum (400 MHz, 300 K, CD_3CN) of the mixture of **4** (□) and **9** (○). * = Residual proton signal of THF-d_8, the other overlaps with the product signal at 3.58 ppm.

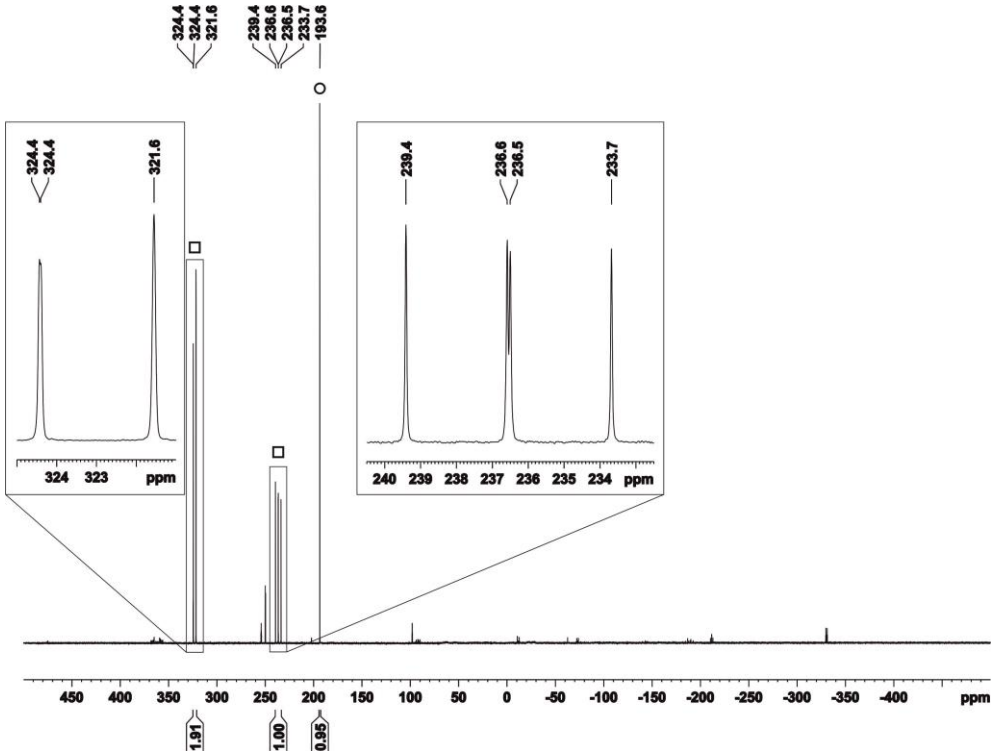


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of the mixture of **4** (□) and **9** (○).

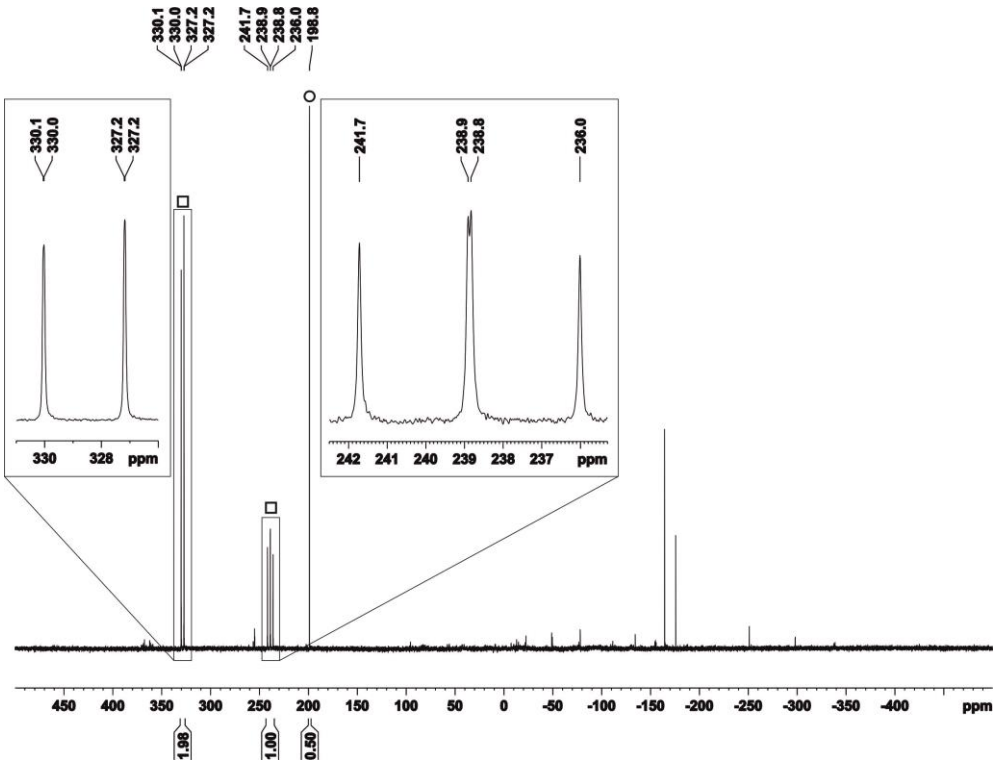


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF with C_6D_6 capillary) of the reaction of **A** with Cs yielding **5** (□) and **10** (○).

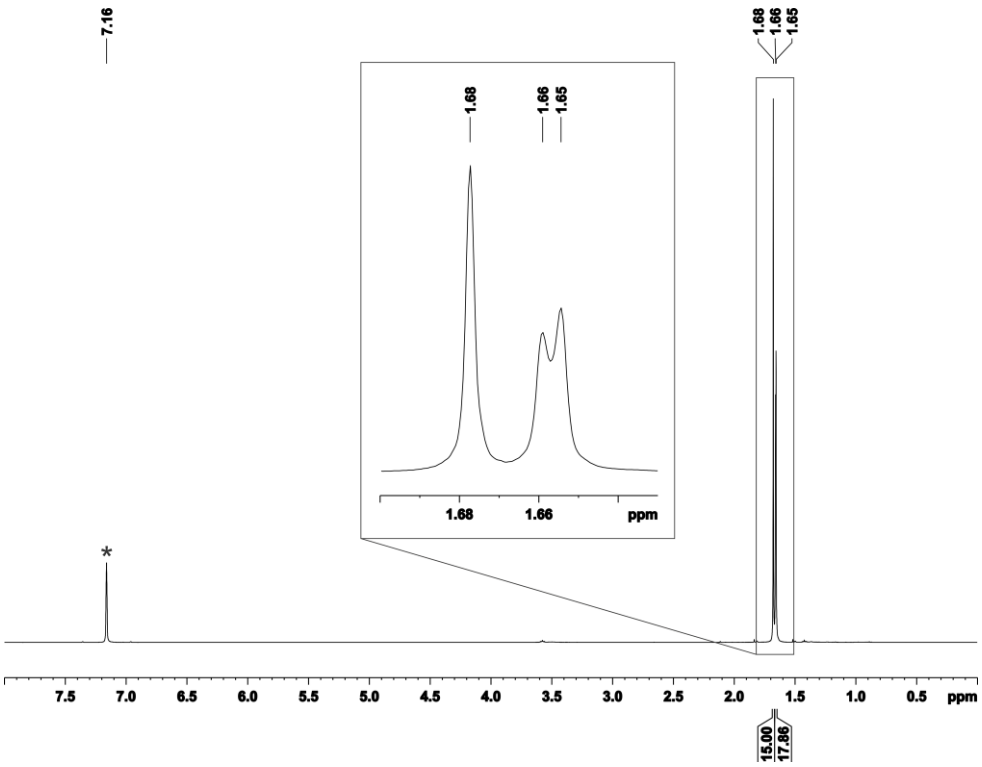


Figure S23. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **11**. * = Residual proton signals of C_6D_6.

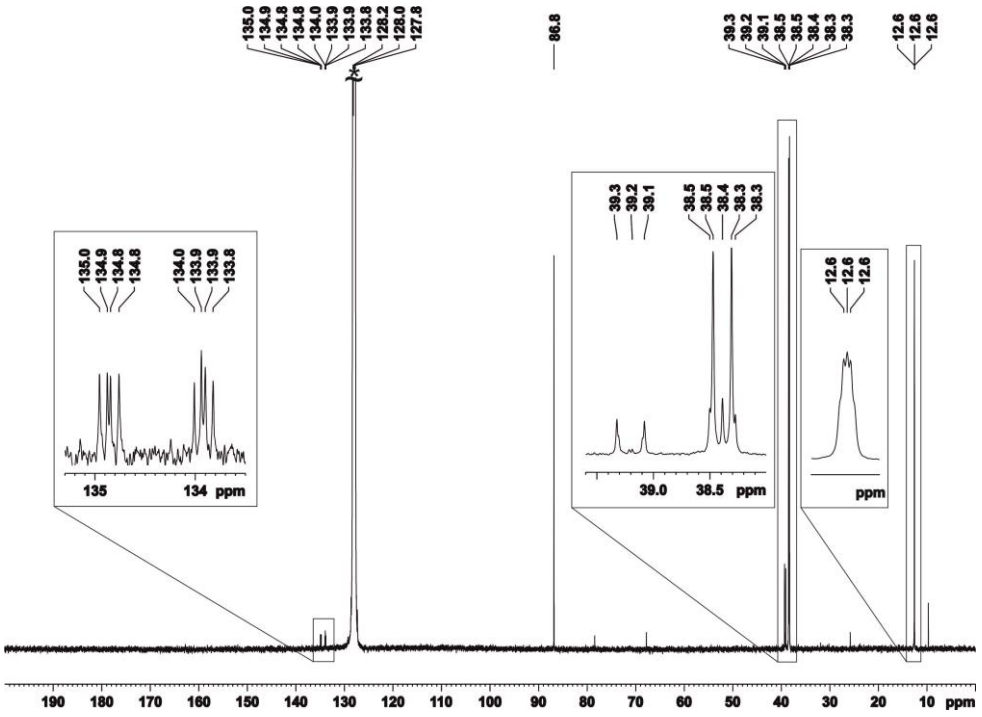


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **11**. * = C_6D_6.

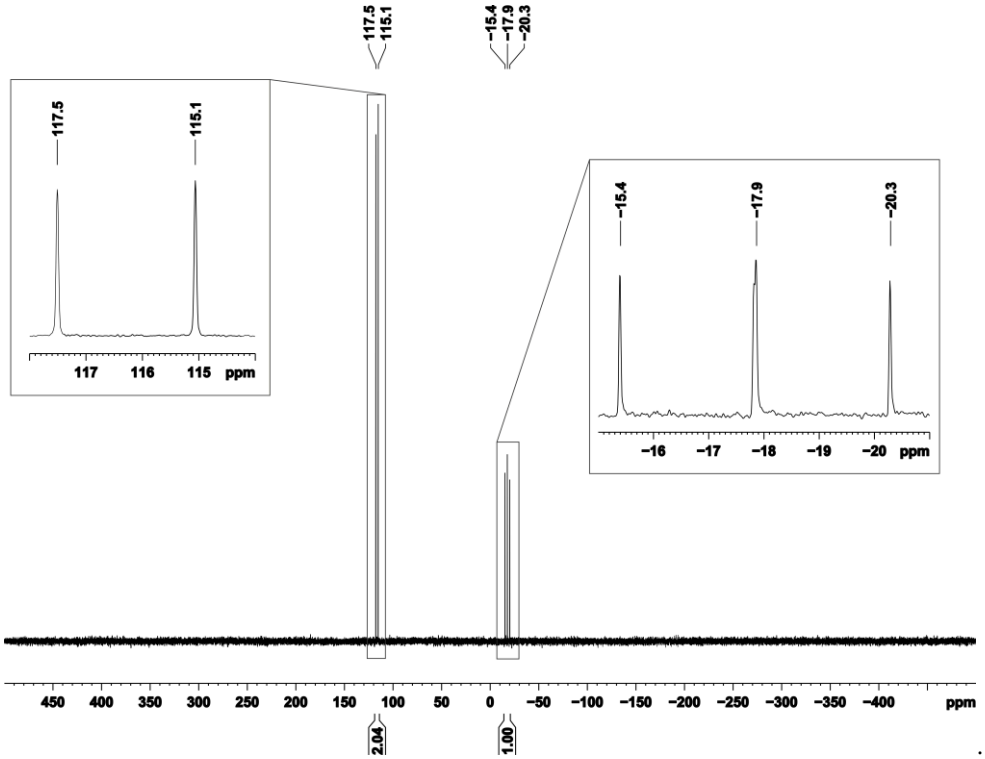


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **11**.

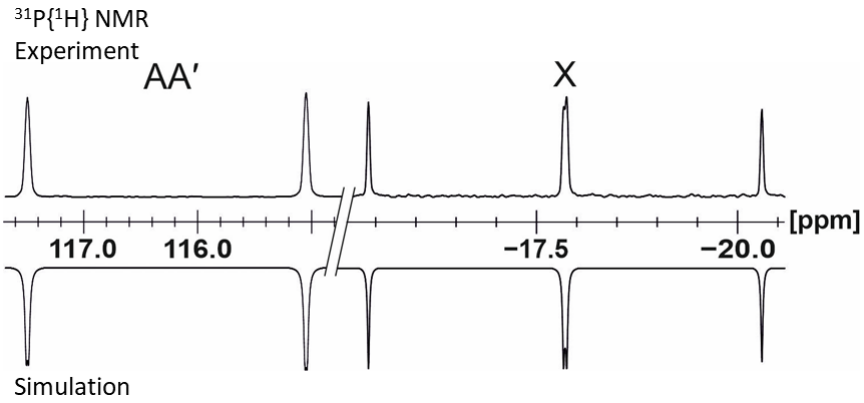
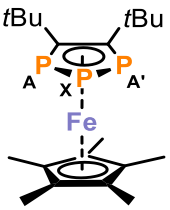


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) and simulation of **11**.

Table S3. Coupling constants from the iterative fit of the AA′X spin system and representation of **11**.

	$\delta(P_{AA'})$ = 116.3 ppm $\delta(P_X)$ = −17.8 ppm $^{1}J_{AX}$ = −397.1 Hz $^{1}J_{A'X}$ = −396.2 Hz $^{2}J_{AA'}$ = 3.4 Hz

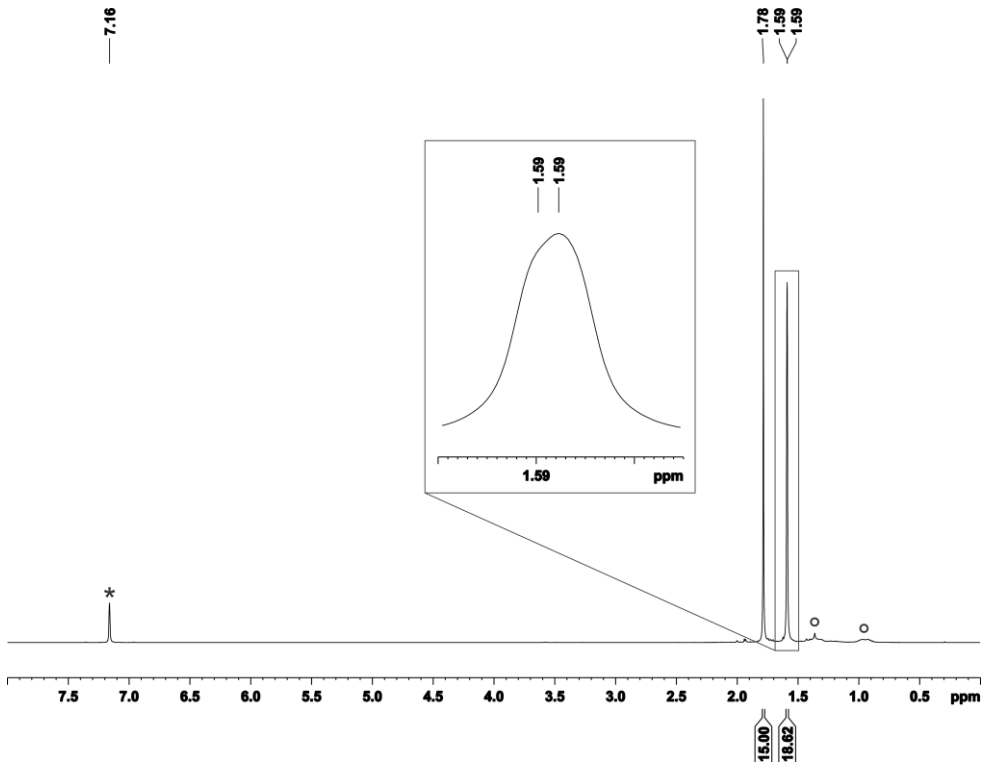


Figure S27. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **12**. * = Residual proton signals of C_6D_6 and ° = *n*-hexane.

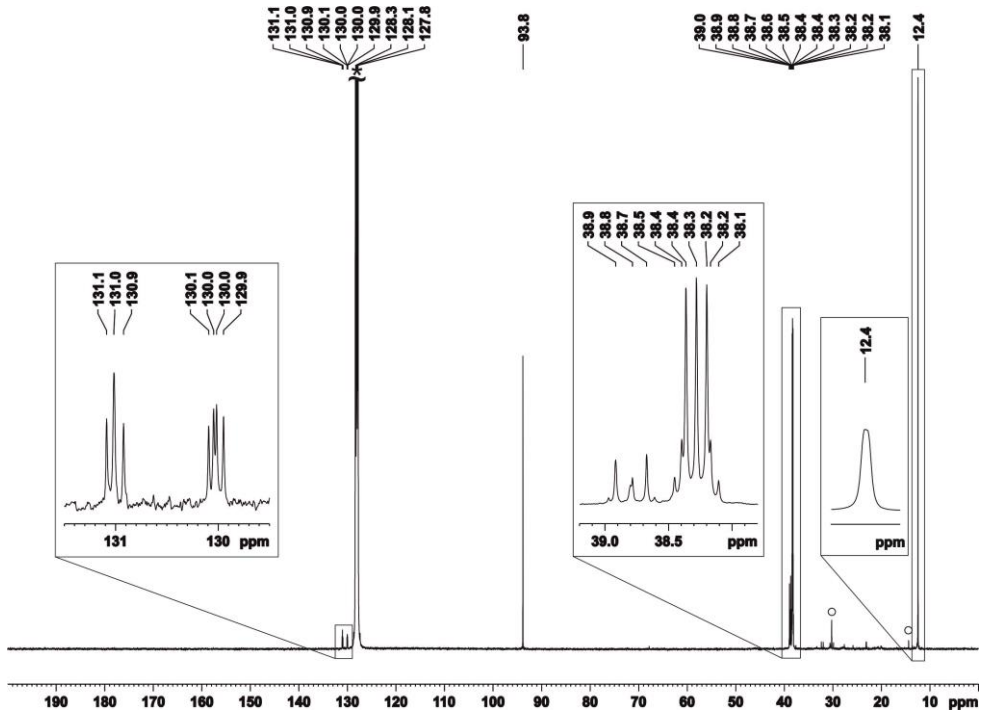


Figure S28. ^{13}C{^{1}H} NMR spectrum (100 MHz, 300 K, C_6D_6) of **12.** * = C_6D_6 and ° = *n*-hexane.

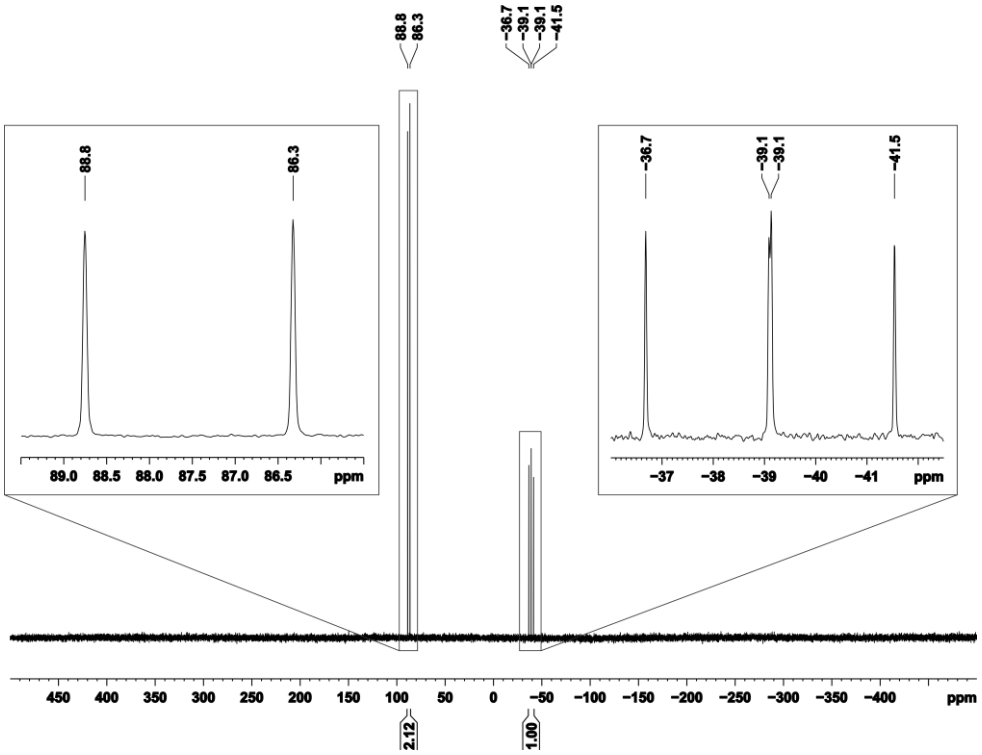


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **12**.

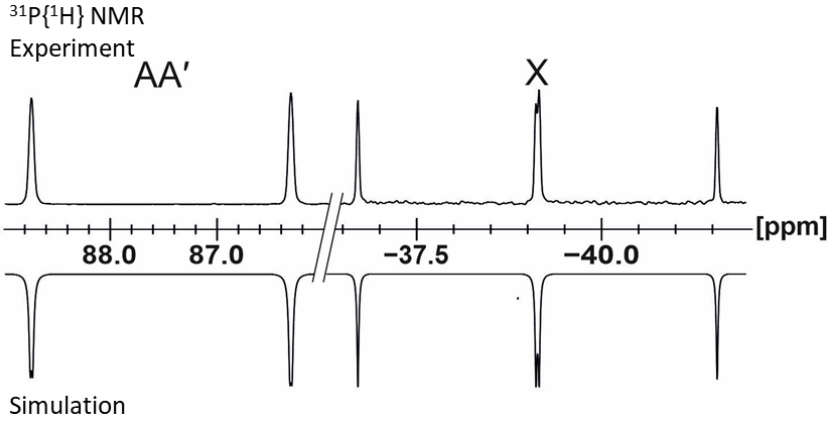
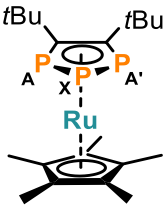


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) and simulation of **12**.

Table S4. Coupling constants from the iterative fit of the AA′X spin system and representation of **12**.

	$\delta(P_{AA'})$ = 87.5 ppm $\delta(P_X)$ = −39.1 ppm $^{1}J_{AX}$ = −393.4 Hz $^{1}J_{A'X}$ = −393.9 Hz $^{2}J_{AA'}$ = 0.6 Hz

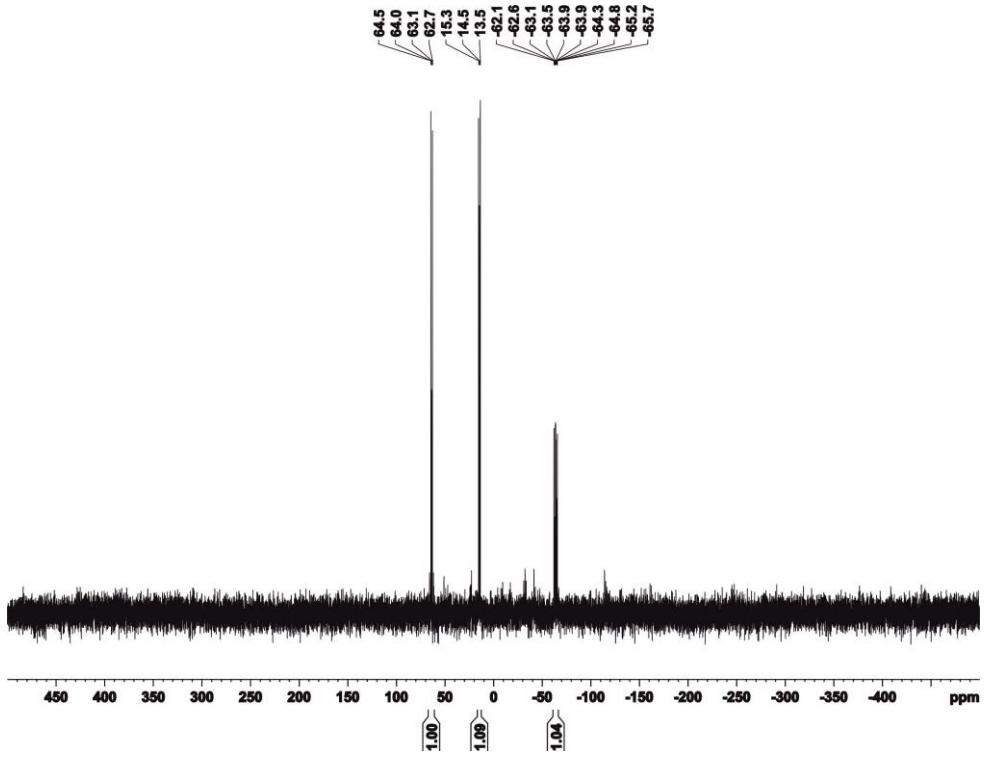


Figure S31. ^{31}P NMR spectrum (162 MHz, 300 K, THF with C_6D_6 capillary) of the crude reaction mixture of **3** and $[H(Et_2O)_2BAr^F{}_4]$.

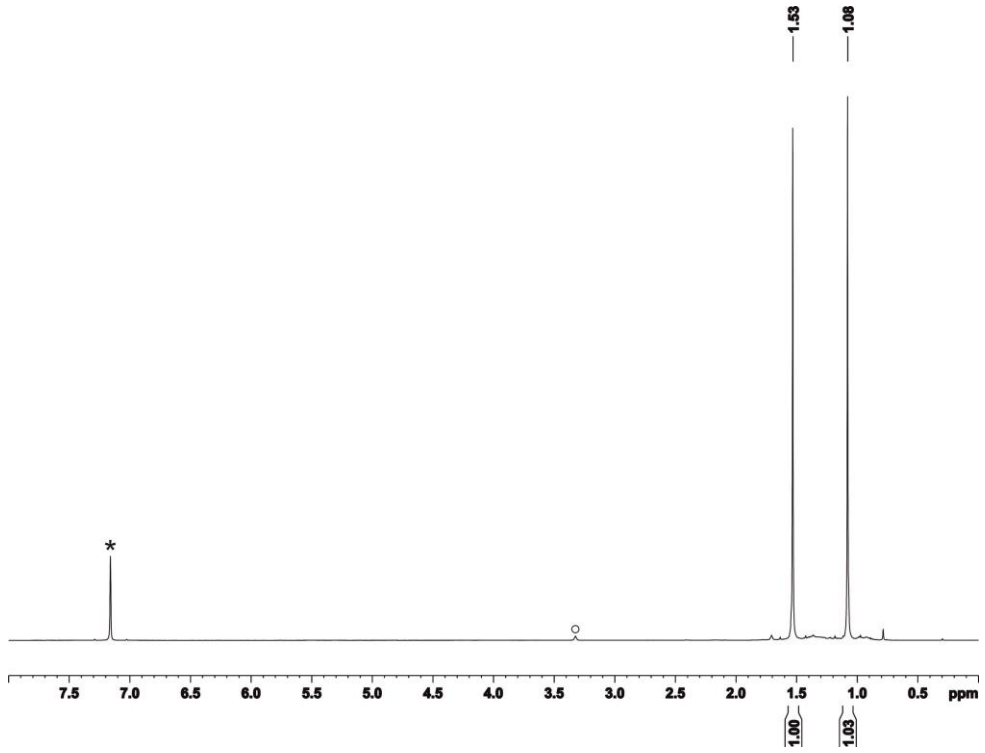


Figure S32. ^1H NMR spectrum (600 MHz, 300 K, C_6D_6) of **13**. * = Residual proton signals of C_6D_6 and ° = [18]crown-6.

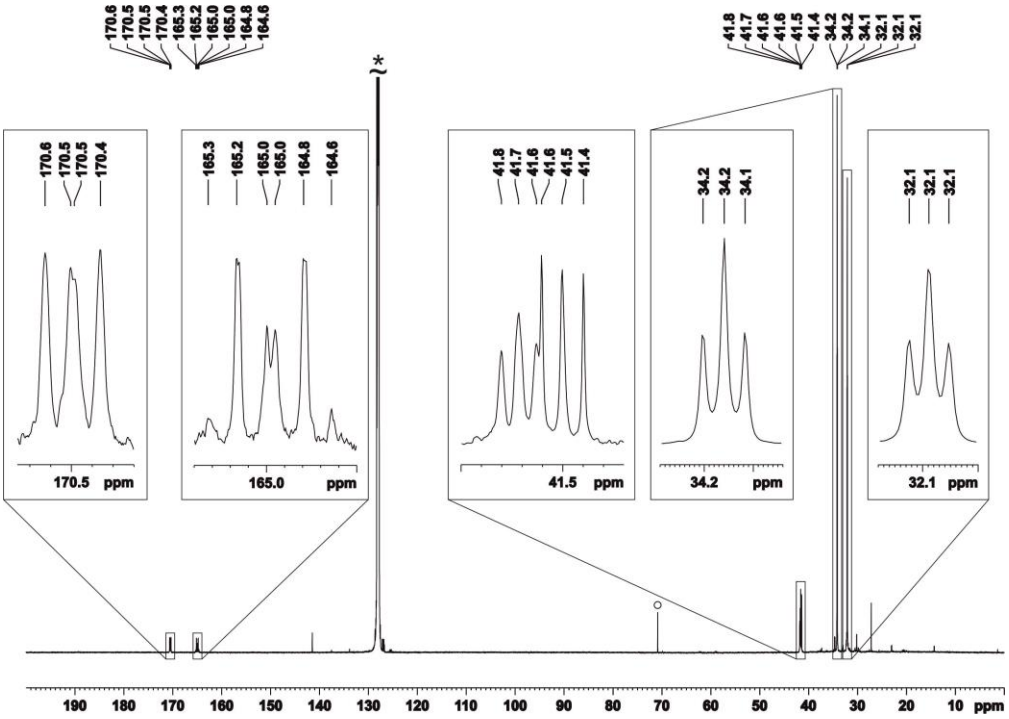


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 300 K, C_6D_6) of **13**. * = C_6D_6 and ° = [18]crown-6.

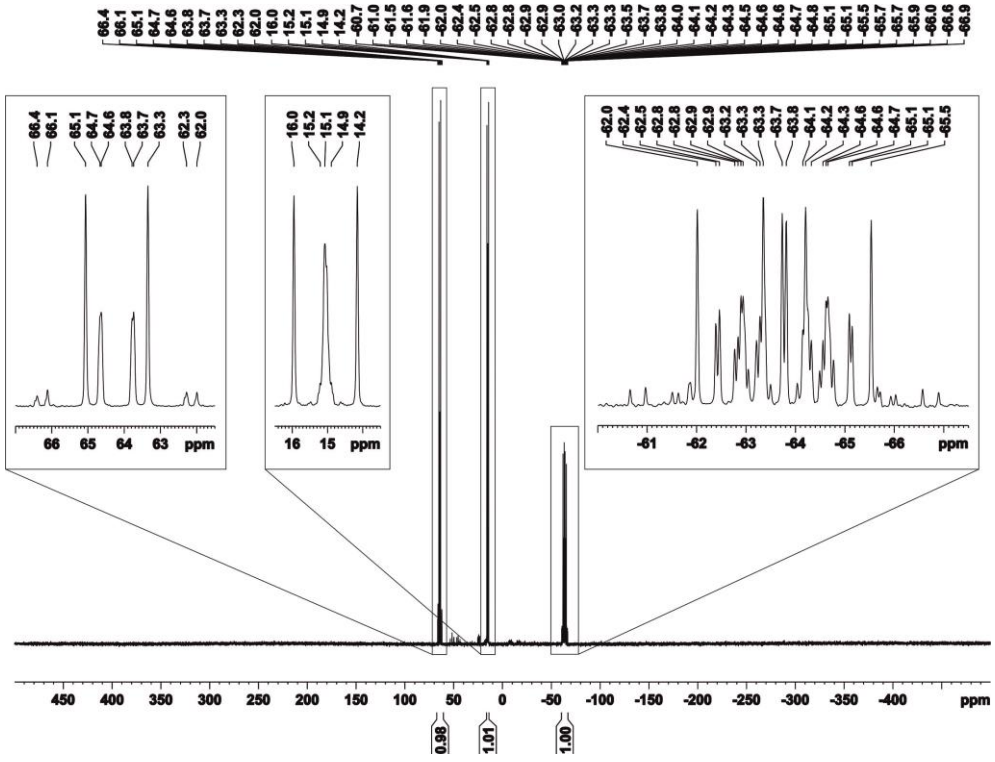


Figure S34. ^{31}P NMR spectrum (162 MHz, 300 K, C_6D_6) of **13**.

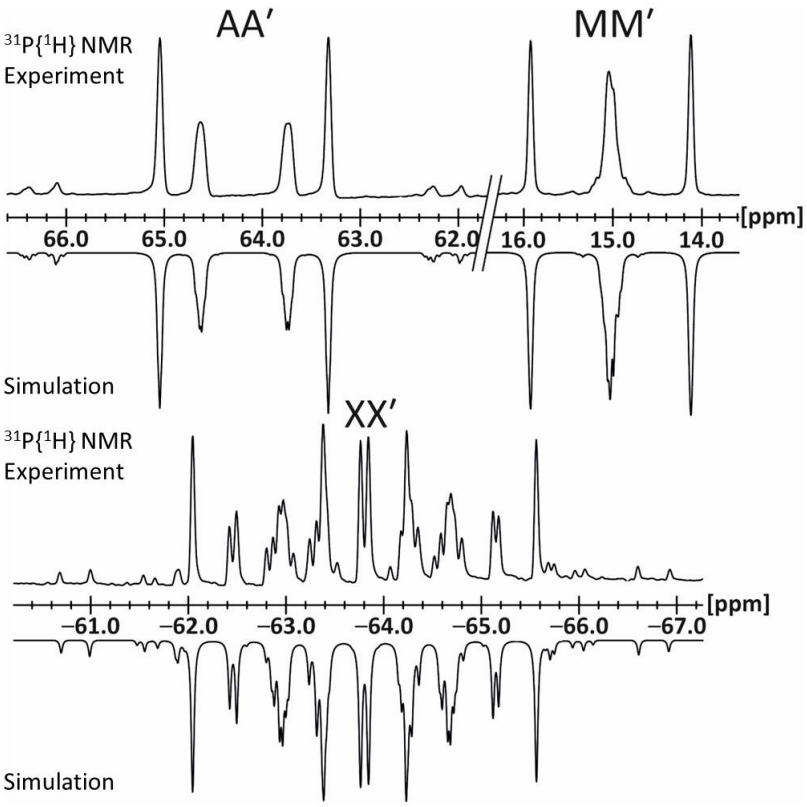
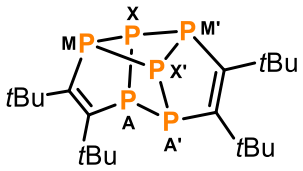


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) and simulation of **13**.

Table S5. Coupling constants from the iterative fit of the AA′MM′XX′ spin system and representation of **13**.

	$\delta(P_{AA'}) = 64.2$ ppm
	$\delta(P_{MM'}) = 15.0$ ppm
	$\delta(P_{XX'}) = -63.8$ ppm
	$^{1}J_{AA'} = -261.9$ Hz
	$^{2}J_{AM} = {}^{2}J_{A'M'} = -3.2$ Hz
	$^{2}J_{A'M} = {}^{2}J_{AM'} = 9.9$ Hz
	$^{2}J_{MM'} = 24.9$ Hz
	$^{1}J_{AX} = {}^{1}J_{A'X'} = -293.9$ Hz
	$^{2}J_{A'X} = {}^{2}J_{AX'} = 15.3$ Hz
	$^{1}J_{MX} = {}^{1}J_{M'X'} = -157.7$ Hz
	$^{1}J_{M'X} = {}^{1}J_{MX'} = -134.2$ Hz
	$^{2}J_{XX'} = 29.5$ Hz

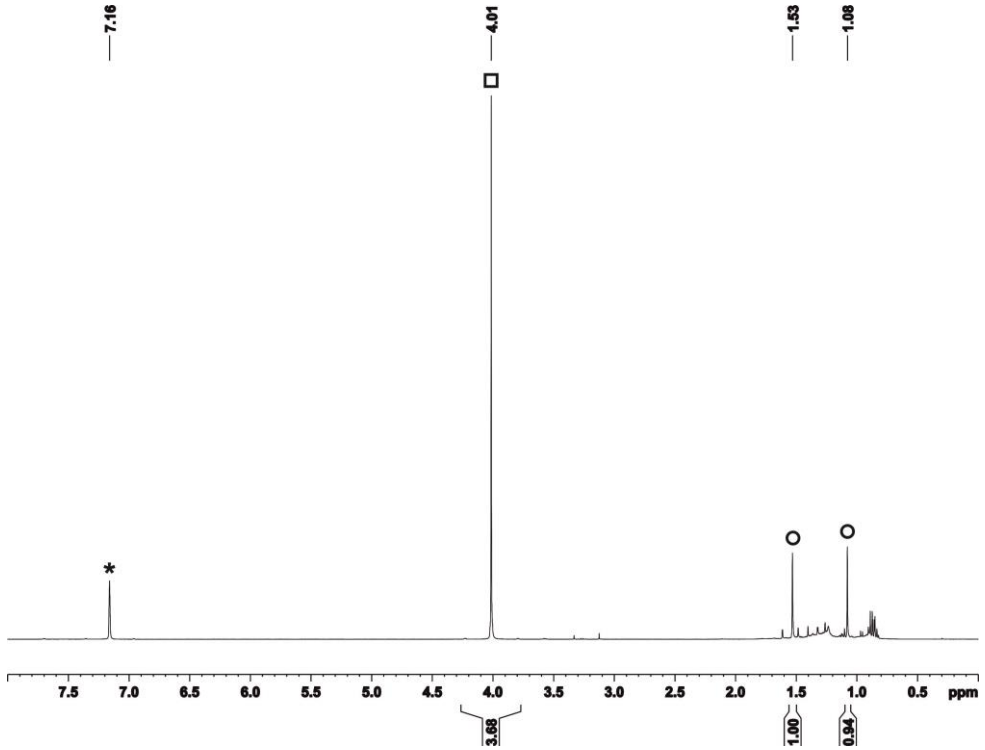


Figure S36. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of the reaction mixture of a mixture of **3** and **8** with $[Cp_2Fe]BAr^F{}_4$ after extraction. **13** (○) and Cp_2Fe (□). * = Residual proton signals of C_6D_6.

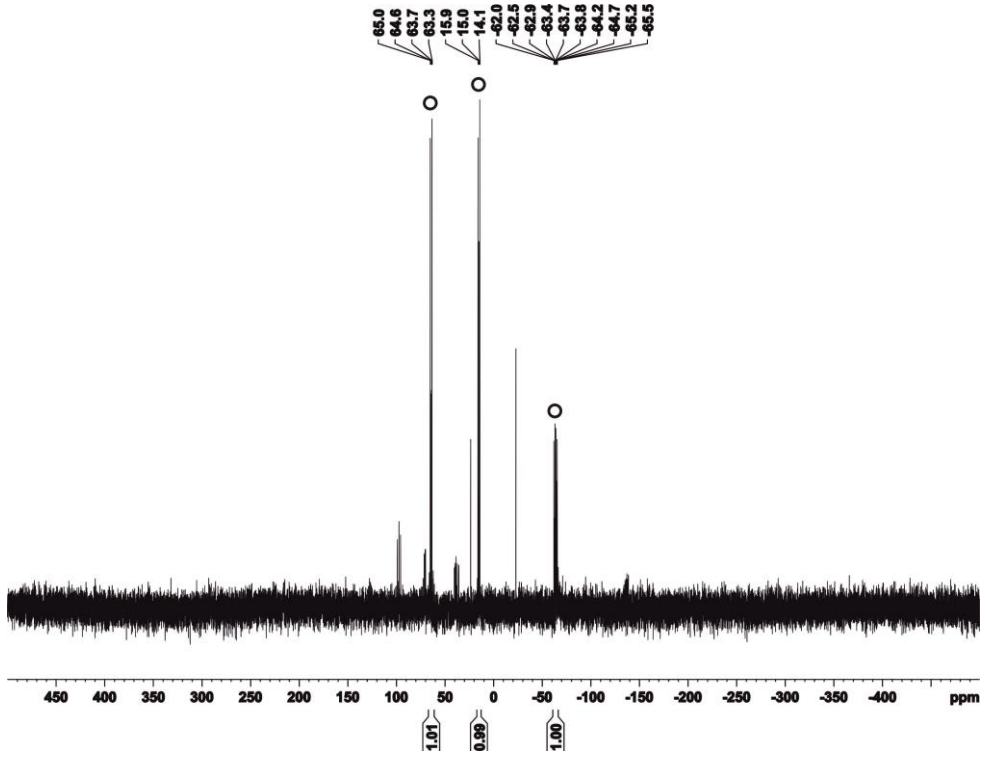


Figure S37. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction mixture of a mixture of **3** and **8** with $[Cp_2Fe]BAr^F{}_4$ after extraction. **13** (○).

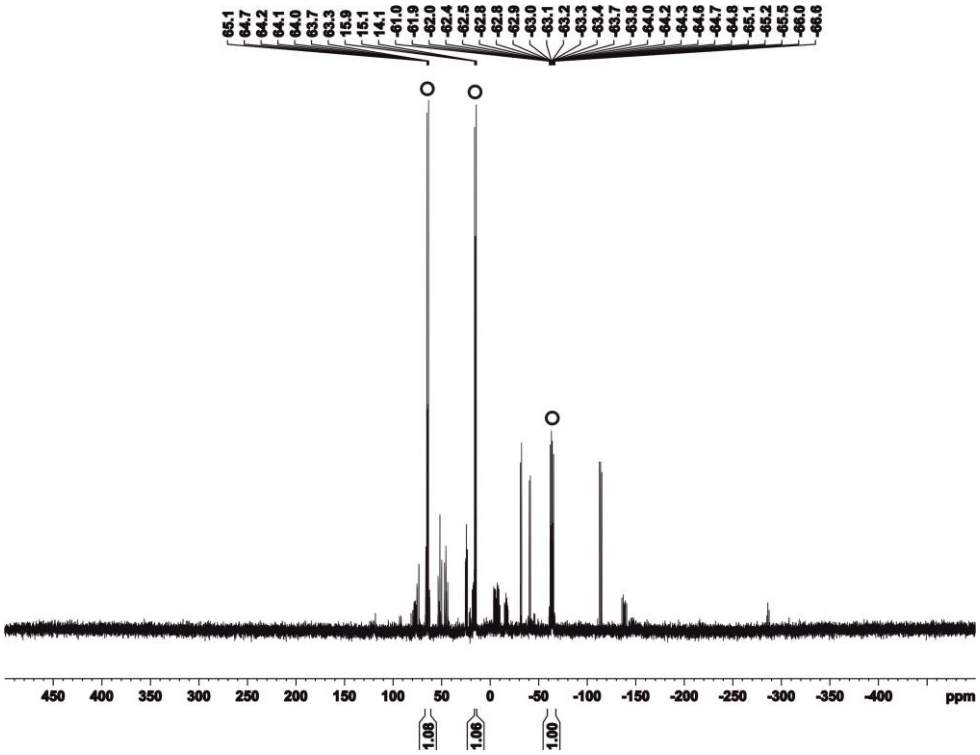


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction mixture of a mixture of **3** and **8** with $[H(Et_2O)_2BAr^F{}_4]$ after extraction with *n*-hexane. **13** (○).

3 UV-Vis Spectra

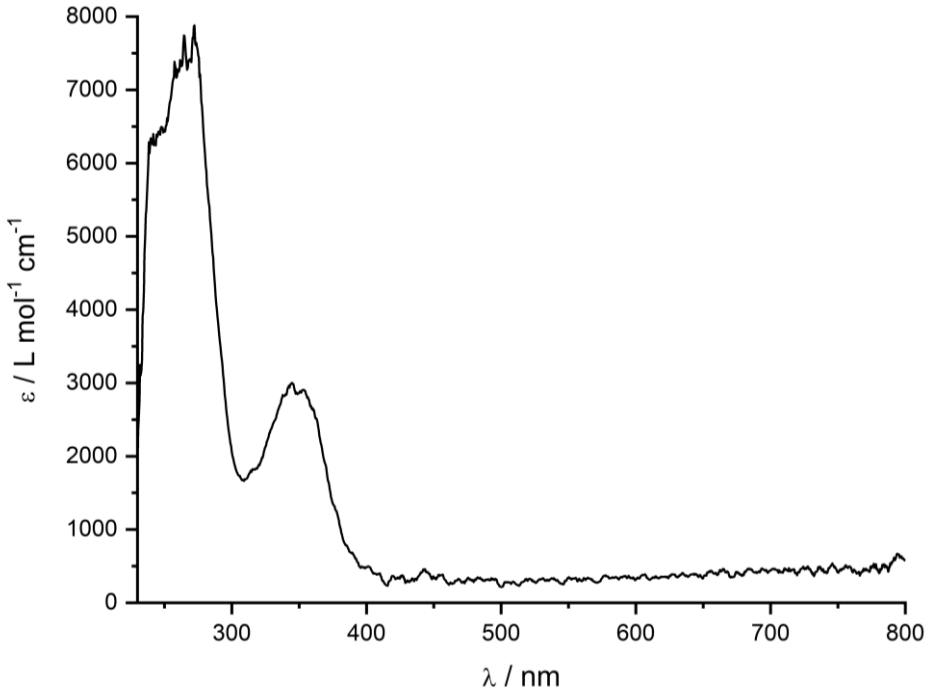


Figure S39. UV-Vis spectrum of **1** in THF.

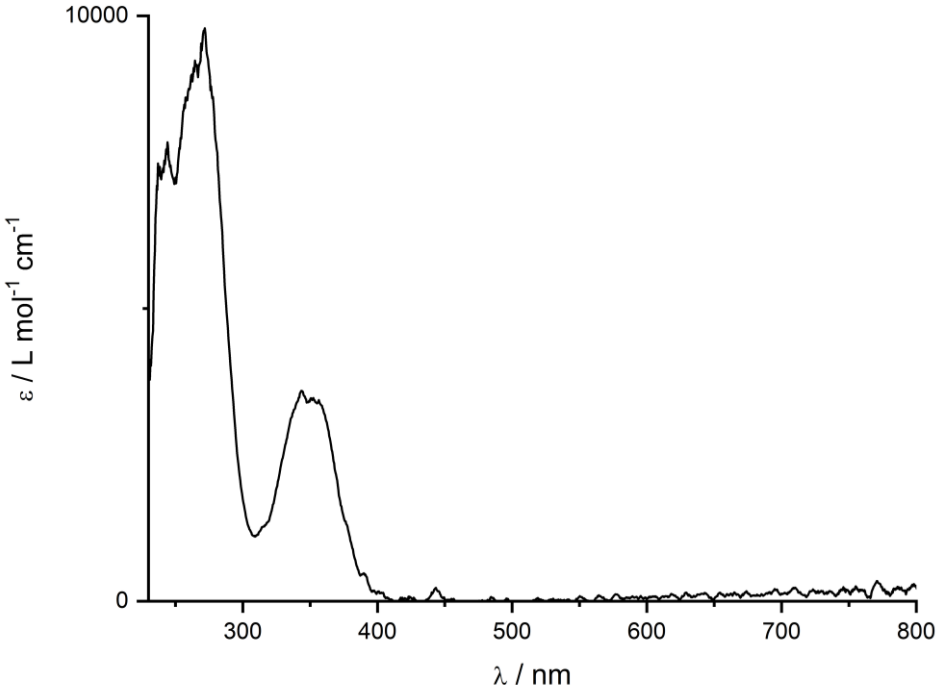


Figure S40. UV-Vis spectrum of **3** in THF.

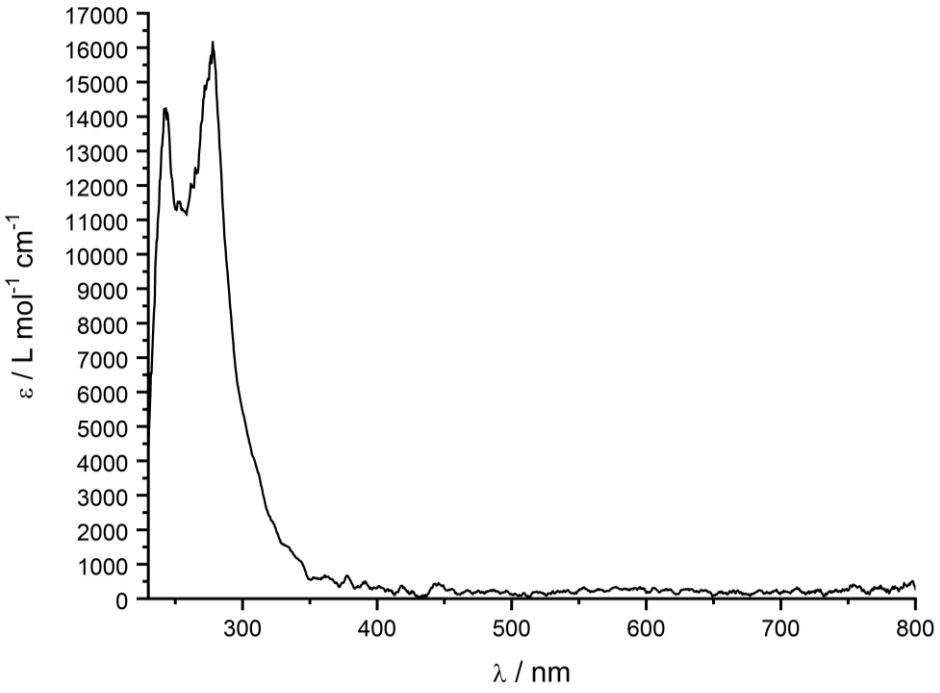


Figure S41. UV-Vis spectrum of **11** in *n*-hexane.

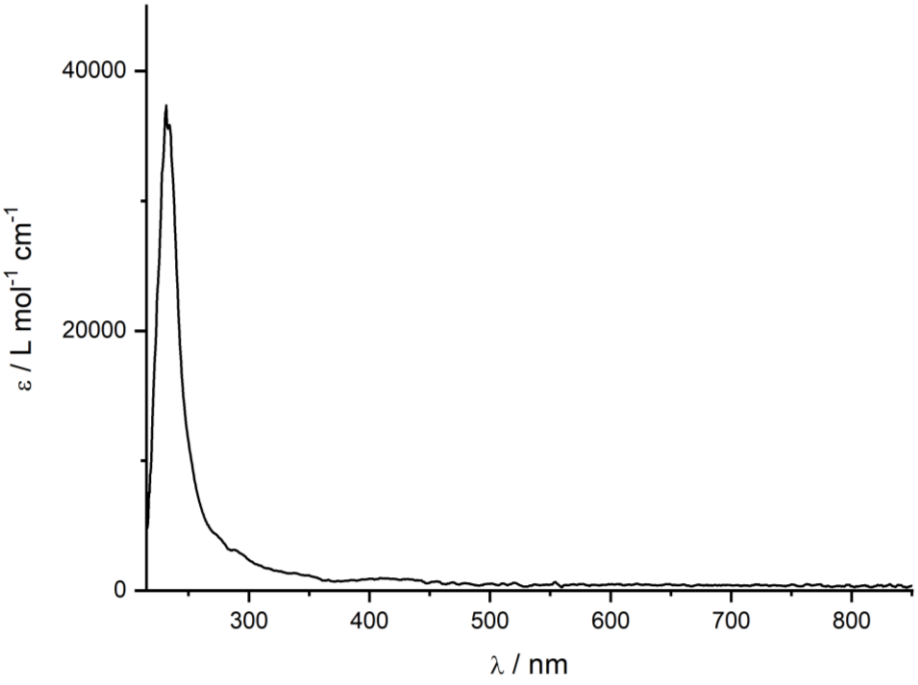


Figure S42. UV-Vis spectrum of **12** in *n*-hexane.

4 Single Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku XtaLAB Synergy DW R (DW system, HyPix-Arc 150) or GV1000 Titan diffractometers with microfocus Cu-Kα radiation (λ = 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[7] or analytical ones[8] were applied to the data. Using Olex2,[9] the structure was solved with the SHELXT[10] structure solution program using Intrinsic Phasing and refined with the SHELXL[11] refinement package using Least Squares refinements on F^2. The hydrogen atoms were located in idealized positions and refined isotropically with a riding model.

1 crystallizes in the orthorhomic space group *Pbca* with two formula units and two THF molecules in the asymmetric unit. One of these could be modeled, the other one, which is disordered over a symmetry element, was accounted for with the help of a solvent mask. The disorder of one crown ether in the crystal structure of **1** was refined with restraints (DFIX and SIMU).

CCDC 2346026 to 2346032 contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

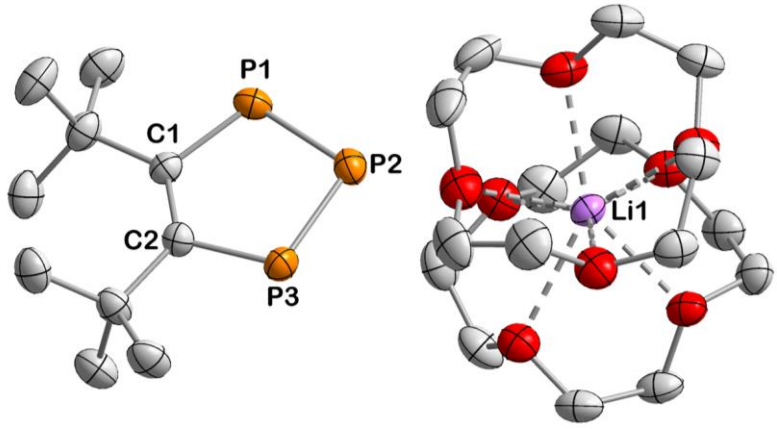


Figure S43. Solid-state molecular structure of **1**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.0748(6), P2–P3 2.0763(6), P1–C1 1.7807(14), P3–C2 1.7819(14), C1–C2 1.418(2), P1–P2–P3 97.29(2), C1–P1–P2 102.96(5), C2–P3–P2 102.79(5), C2–C1–P1 118.32(10), C1–C2–P3 118.54(10).

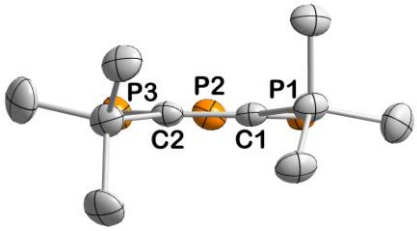


Figure S44. Solid-state molecular structure of **3**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and cation have been omitted for clarity. View from the C1–C2 bond.

4 crystallizes in the monoclinic space group $P2_1/n$ with one formula unit in the asymmetric unit.

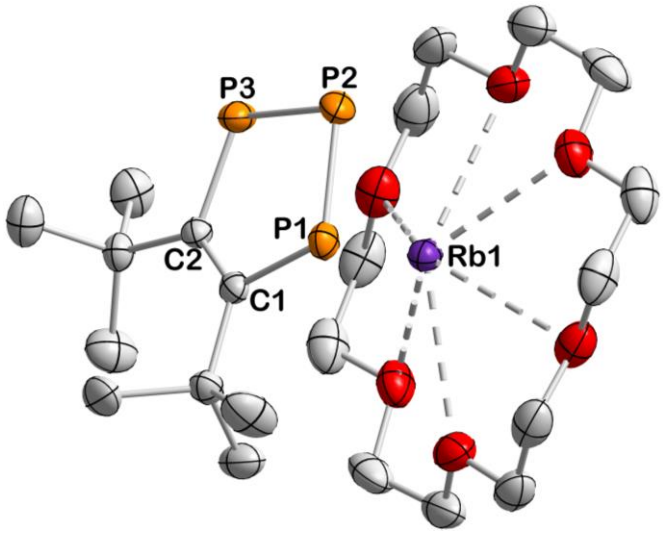


Figure S45. Solid-state molecular structure of **4**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.0789(12), P2–P3 2.0779(12), P1–C1 1.783(3), P3–C2 1.787(3), C1–C2 1.414(4), P1–P2–P3 97.06(5), C1–P1–P2 102.90(11), C2–P3–P2 103.11(11), C2–C1–P1 118.8(2), C1–C2–P3 118.1(2).

9 crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the asymmetric unit.

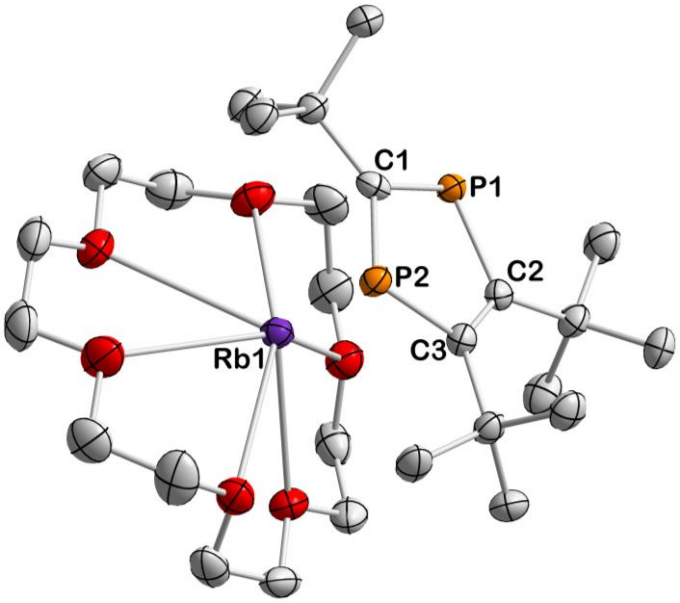


Figure S46. Solid-state molecular structure of **9**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.760(4), P2–C1 1.747(4), P1–C2 1.789(4), P2–C3 1.786(4), C2–C3 1.419(6), P1–C1–P2 112.6(2), C1–P1–C2 98.91(18), C1–P2–C3 98.93(19), P1–C2–C3 114.4(3), P2–C3–C2 115.2(3).

Table S6. Crystal data and structure refinement for **1** and **3**.

Compound	**1**	**3**
Empirical formula	$C_{28}H_{54}LiO_{8.5}P_3$	$C_{22}H_{42}KO_6P_3$
Formula Weight	662.61	534.56
Temperature [K]	123	123
Crystal System	orthorhombic	orthorhombic
Space Group	*Pbca*	$P2_12_12_1$
a [Å]	37.25924(16)	9.58810(10)
b [Å]	12.33778(5)	17.15960(10)
c [Å]	31.13083(16)	17.26040(10)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [Å^3]	14310.72(11)	2839.82(4)
Z	16	4
ρ_{calc} [g/cm^3]	1.230	1.250
μ [mm^{-1}]	1.914	3.503
F(000)	5728.0	1144.0
Crystal Size [mm^3]	0.322 × 0.181 × 0.167	0.419 × 0.287 × 0.253
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	4.744 to 143.892	7.264 to 133.652
Index ranges	$-45 \le h \le 45$, $-15 \le k \le 10$, $-38 \le l \le 38$	$-11 \le h \le 11$, $-20 \le k \le 20$, $-20 \le l \le 18$
Reflections collected	263626	53964
Independent reflections	13906 [R_{int} = 0.0529, R_{sigma} = 0.0188]	5040 [R_{int} = 0.0493, R_{sigma} = 0.0178]
Data / restraints / parameters	13906/352/851	5040/0/295
Goodness-of-fit on F^2	1.042	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0413, wR_2 = 0.1143	R_1 = 0.0236, wR_2 = 0.0632
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1178	R_1 = 0.0238, wR_2 = 0.0634
Largest diff. peak/hole [e Å^{-3}]	0.44/−0.27	0.32/−0.13
Flack parameter		−0.001(3)
CCDC number	2346026	2346027

Table S7. Crystal data and structure refinement for **4** and **9**.

Compound	**4**	**9**
Empirical formula	$C_{22}H_{42}O_6P_3Rb$	$C_{27}H_{51}O_6P_2Rb$
Formula Weight	580.93	619.08
Temperature [K]	123(1)	123(1)
Crystal System	monoclinic	triclinic
Space Group	$P2_1/n$	P-1
a [Å]	10.31930(10)	9.3862(2)
b [Å]	16.00110(10)	10.5727(2)
c [Å]	17.6998(2)	16.3426(4)
α [°]	90	90.511(2)
β [°]	106.4890(10)	98.341(2)
γ [°]	90	101.542(2)
Volume [Å^3]	2802.40(5)	1570.099(6)
Z	4	2
ρ_{calc} [g/cm^3]	1.377	1.309
μ [mm^{-1}]	4.320	3.418
F(000)	1216.0	656.0
Crystal Size [mm^3]	0.405 × 0.235 × 0.192	0.27 × 0.25 × 0.17
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.976 to 133.562	8.542 to 133.38
Index ranges	-12 ≤ h ≤ 11, -18 ≤ k ≤ 18, -14 ≤ l ≤ 21	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -18 ≤ l ≤ 19
Reflections collected	42970	42737
Independent reflections	4954 [R_{int} = 0.0518, R_{sigma} = 0.0184]	5528 [R_{int} = 0.0608, R_{sigma} = 0.0226]
Data / restraints / parameters	4954/9/295	5528/0/334
Goodness-of-fit on F^2	1.028	1.152
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1143	R_1 = 0.0518, wR_2 = 0.1228
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.1148	R_1 = 0.0523, wR_2 = 0.1230
Largest diff. peak/hole [e Å^{-3}]	1.13/-0.35	1.06/-0.47
CCDC number	2346028	2346029

Table S8. Crystal data and structure refinement for **11** and **12**.

Compound	**11**	**12**
Empirical formula	$C_{20}H_{33}P_3Fe$	$C_{20}H_{33}P_3Ru$
Formula Weight	422.22	467.44
Temperature [K]	123.0(2)	123.0(1)
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$
a [Å]	10.1779(2)	10.2485(5)
b [Å]	12.7916(2)	13.0851(5)
c [Å]	16.4260(2)	16.3300(9)
α [°]	90	90
β [°]	107.870(2)	107.637(5)
γ [°]	90	90
Volume [Å^3]	2035.35(6)	2086.96(18)
Z	4	4
ρ_{calc} [g/cm^3]	1.378	1.488
μ [mm^{-1}]	8.148	8.234
F(000)	896.0	968.0
Crystal Size [mm^3]	0.211 × 0.13 × 0.13	0.23 × 0.19 × 0.12
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.932 to 133.578	8.83 to 134.134
Index ranges	$-11 \le h \le 12$, $-15 \le k \le 14$, $-14 \le l \le 19$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-19 \le l \le 15$
Reflections collected	12907	17208
Independent reflections	3510 [R_{int} = 0.0363, R_{sigma} = 0.0268]	3671 [R_{int} = 0.0526, R_{sigma} = 0.0265]
Data / restraints / parameters	3510/0/229	3671/0/229
Goodness-of-fit on F^2	1.073	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0772	R_1 = 0.0259, wR_2 = 0.0685
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0783	R_1 = 0.0264, wR_2 = 0.0690
Largest diff. peak/hole [e Å^{-3}]	0.40/−0.30	0.66/−0.43
CCDC number	2346030	2346031

Table S9. Crystal data and structure refinement for **13**.

Compound	**13**
Empirical formula	$C_{20}H_{36}P_6$
Formula Weight	462.31
Temperature [K]	123.0(1)
Crystal System	monoclinic
Space Group	*C2/c*
a [Å]	19.2177(5)
b [Å]	12.5176(3)
c [Å]	22.1442(6)
α [°]	90
β [°]	112.755(3)
γ [°]	90
Volume [Å^3]	4912.4(2)
Z	8
ρ_{calc} [g/cm^3]	1.250
μ [mm^{-1}]	4.088
F(000)	1968.0
Crystal Size [mm^3]	0.097 × 0.072 × 0.029
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.648 to 150.8
Index ranges	$-23 \leq h \leq 24$, $-15 \leq k \leq 15$, $-27 \leq l \leq 27$
Reflections collected	39101
Independent reflections	5007 [R_{int} = 0.0389, R_{sigma} = 0.0281]
Data / restraints / parameters	5007/0/247
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.1174
Largest diff. peak/hole [e Å^{-3}]	0.95/-0.34
CCDC number	2346032

5 Cyclic Voltammogram of Di-*tert*-butyldiphosphatetrahedrane (A)

Cyclic voltammetry experiments were performed in a single-compartment cell inside a nitrogen-filled glovebox using a CH Instruments CHI600E potentiostat. The cell was equipped with a platinum disc working electrode (2 mm diameter) polished with 0.05 µm alumina paste, a platinum wire counter electrode, and a silver/silver nitrate reference electrode. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate, (nBu$_4$NPF$_6$), was dried in vacuo at 110 °C for three days. All redox potentials are reported versus the ferrocenium/ferrocene (Fc^+/Fc) couple. The scan rate is v = 100 mV·s^{-1}. To mimic the reaction conditions in the experimental setup, 29 µL of a solution of **A** in toluene (c = 0.4339 mol/L, n = 0.0126 mmol) were diluted with 10 mL THF. Similar cyclic voltammograms without any visible redox process were obtained with higher concentrations of **A**. Please note that P_4 can be reduced at the potential $E_{1/2}$ = –1.55 V (vs. bottom mercury in DMF).[12]

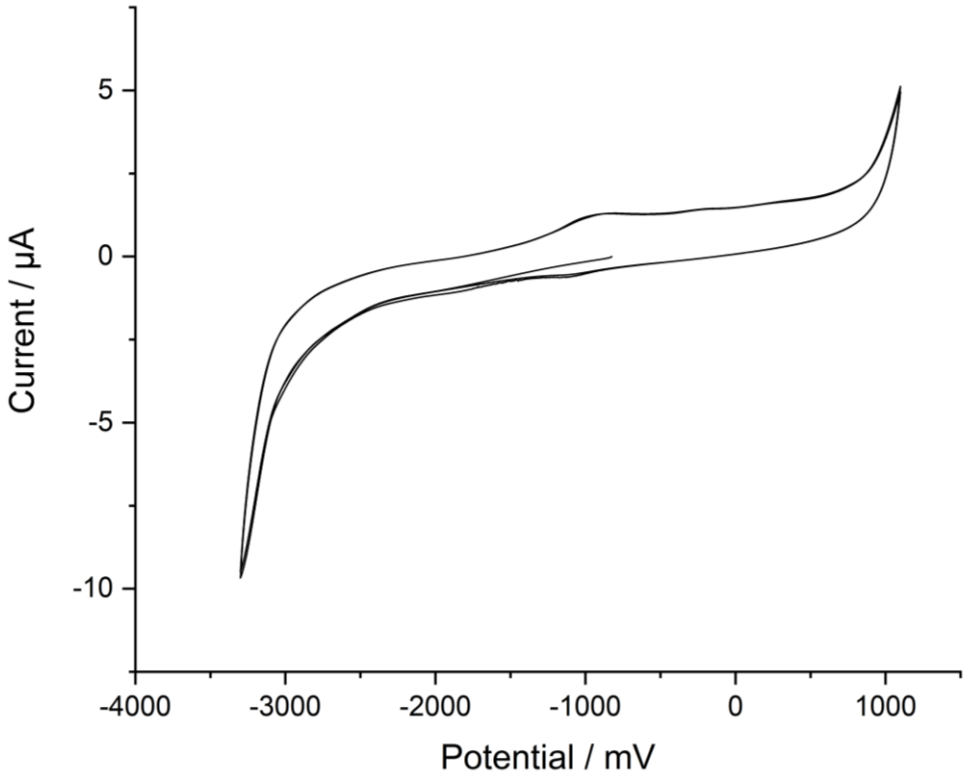


Figure S47. Cyclic voltammogram of di-tert-butyldiphosphatetrahedrane (**A**) in toluene/THF/nBu$_4$NPF$_6$; the potential is referenced vs. Cp_2Fe/Cp_2Fe^+.

6 Quantum Chemical Calculations

General Methods

All calculations were carried out with Gaussian09.[13] Geometry optimizations and frequency calculations were performed at the ωB97XD/def2-TZVPPD level of theory for all compounds except **13**, as SCF convergence could not be achieved with the diffuse function in the basis set. Thus, to calculate the thermodynamic parameters, the energies of the previously optimized geometries (at the ωB97XD/def2-TZVPPD level of theory) were calculated as single point calculations at the ωB97XD/def2-TZVPP level of theory. For compound **13**, geometry optimization and frequency calculations were performed at the ωB97XD/def2-TZVPP level of theory.[14] In all calculations, the solvent effects have been incorporated via the CPCM model using tetrahydrofuran as solvent.[15] Frequency calculations were carried out to confirm the nature of the stationary points found by geometry optimizations. All optimised geometries show no imaginary frequencies.

Spin Density Distribution of (1,2,3-$P_3C_2tBu_2$)$^{\bullet}$ (**3**$^{\bullet}$)

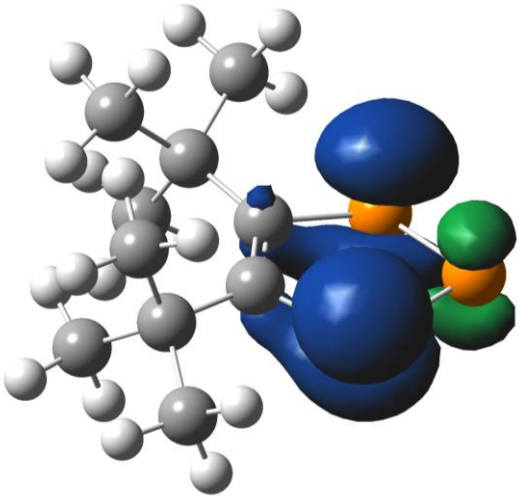
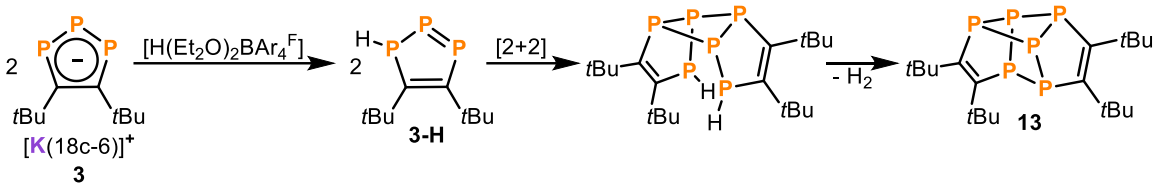


Figure S48. Calculated spin density distribution of **3**$^{\bullet}$. Surface isovalue at 0.05.

Table S10. Mulliken spin densities for selected atoms of the radical **3**$^{\bullet}$.

P1	0.597
P2	−0.135
P3	0.627
C1	−0.005
C2	−0.078

Proton Affinity



Scheme S1. Alternative proposed outline mechanisms for the formation of **13** by protonation of **3**.

Table S21. Proton affinity of selected atoms of $(1,2,3\text{-}P_3C_2tBu_2)^-$.

	P1 / P3	P2	C1 / C2
Proton Affinity [kcal/mol]	200.2	191.1	199.5

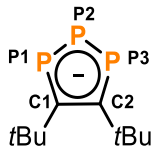
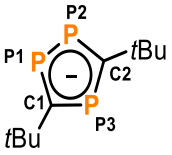


Table S32. Proton affinity of selected atoms of $(1,2,4\text{-}P_3C_2tBu_2)^-$.

	P3	P1 / P2	C1 / C2
Proton Affinity [kcal/mol]	196.5	197.6	200.3



Reaction Energies

Table S43. Reaction energies for the formation of **13** from $(1,2,3\text{-}P_3C_2tBu_2)^-$.

ΔE = −65.2 kcal/mol
ΔH = −74.5 kcal/mol
ΔS = 0.0645 kcal/mol
ΔG = −93.7 kcal/mol

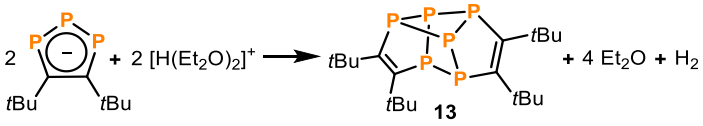


Table S54. Reaction energies for the formation of **13** from **3-H**.

ΔE = −28.7 kcal/mol
ΔH = −30.9 kcal/mol
ΔS = −0.0236 kcal/mol
ΔG = −23.9 kcal/mol

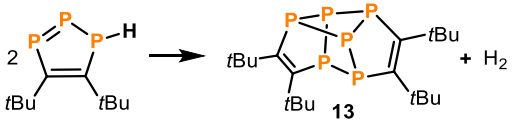
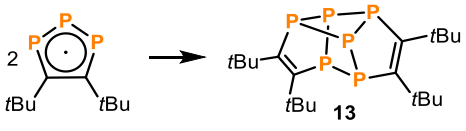


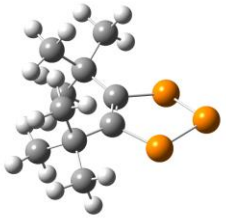
Table S65. Reaction energies for the formation of **13** from **3**•.

ΔE = −77.8 kcal/mol
ΔH = −76.5 kcal/mol
ΔS = −0.0583 kcal/mol
ΔG = −59.1 kcal/mol



Cartesian Coordinates of Optimized Structures

3•



ωB97XD/def2-TZVPPD
E = −1415.96895013 Eh
ωB97XD/def2-TZVPP
E = −1415.96701614 Eh

0 2

P	-1.15171900	1.93318000	0.01738500
P	0.60934300	2.99750500	-0.16359300
P	1.76899100	1.33162100	0.23769000
C	0.67193400	-0.09201100	0.00672000
C	1.48027900	-1.42119300	-0.03327500
C	-1.91290000	-0.76339900	0.01150600
C	-0.67508200	0.18052500	0.00413300
C	0.91113200	-2.46950400	-1.00002200
H	-0.05514500	-2.86439800	-0.71750500
H	1.60141000	-3.31274900	-1.04125200
H	0.83289700	-2.05578600	-2.00596800
C	-1.78393600	-1.91858500	1.01457100
H	-0.99668000	-2.62346300	0.78476600
H	-2.72080100	-2.47710300	1.03543900
H	-1.60706400	-1.52682400	2.01721700
C	2.90972800	-1.16704200	-0.56371800
H	2.89499200	-0.68434900	-1.54285100
H	3.41530400	-2.12667200	-0.67545200
H	3.51491100	-0.56454000	0.11136700
C	-3.19934400	-0.02662000	0.44423100
H	-3.10550300	0.41032800	1.43922100
H	-4.01354200	-0.75157500	0.46970700
H	-3.48820400	0.76108800	-0.25010500
C	1.62966900	-1.99058100	1.38764600
H	2.17400700	-1.28862400	2.02139200
H	2.19897000	-2.92141300	1.35170800
H	0.67405200	-2.19294700	1.86143800
C	-2.18334100	-1.26121600	-1.41986500
H	-2.41460500	-0.41667300	-2.07133800
H	-3.04774300	-1.92801600	-1.41701300
H	-1.34530100	-1.79311600	-1.85457800

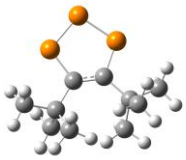
H^+

ωB97XD/def2-TZVPPD
E = −0.144243139060 Eh

1 1

H	0.00000000	0.00000000	0.00000000

(1,2,3-P_3C_2*t*Bu_2)$^-$



ωB97XD/def2-TZVPPD
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ωB97XD/def2-TZVPP
E = −1416.13002472 Eh

-1 1

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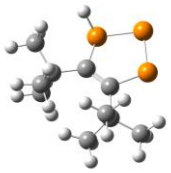
P	0.00115100	3.03702300	0.00003300
P	1.54730000	1.66499500	-0.09070800
C	0.70749000	0.10723300	-0.03685300
C	1.70778200	-1.09822000	0.02453600
C	-1.70861300	-1.09695500	-0.02453100
C	-0.70742700	0.10776400	0.03683400
C	1.39792100	-2.24905900	-0.94773800
H	0.46044400	-2.75660200	-0.76936200
H	2.18857800	-2.99898100	-0.87738800
H	1.38641200	-1.87618900	-1.97358900
C	-1.39955100	-2.24804300	0.94770300
H	-0.46249500	-2.75632500	0.76921900
H	-2.19081200	-2.99733500	0.87743300
H	-1.38763600	-1.87518800	1.97355400
C	3.14970200	-0.69614200	-0.36208800
H	3.20433800	-0.30570100	-1.37891100
H	3.78140700	-1.58554700	-0.30594800
H	3.56915700	0.05060900	0.30835200
C	-3.15023400	-0.69386000	0.36215300
H	-3.20452300	-0.30320800	1.37891400
H	-3.78251800	-1.58286700	0.30622400
H	-3.56926100	0.05304700	-0.30838000
C	1.81529600	-1.59439900	1.48039000
H	2.27970300	-0.81937100	2.09233300
H	2.44384600	-2.48765700	1.53166100
H	0.85555000	-1.82516900	1.92805000
C	-1.81654700	-1.59303600	-1.48038800
H	-2.28048000	-0.81769000	-2.09228800
H	-2.44568900	-2.48587800	-1.53163500
H	-0.85698400	-1.82443600	-1.92811300

3-H



ωB97XD/def2-TZVPPD
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ωB97XD/def2-TZVPP
E = −1416.59455789 Eh

0 1

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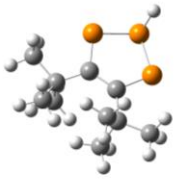
P	1.02079500	2.88419000	0.11088600
C	-0.64188600	0.24281100	0.01774100
C	-1.98903100	-0.53580800	0.03342000
C	1.28448900	-1.60905300	-0.01249200
C	0.67294200	-0.17095100	-0.01605400
C	-2.01634300	-1.68900700	1.04628100
H	-1.33328600	-2.49696300	0.82371500
H	-3.02077100	-2.11329900	1.06721200
H	-1.79105700	-1.31849300	2.04708900
C	0.58578500	-2.59858100	-0.95506600
H	-0.44047200	-2.81942700	-0.69745500
H	1.12941300	-3.54402300	-0.93778200
H	0.60625200	-2.22304500	-1.97914800
C	-3.16441300	0.36919400	0.46370900
H	-3.02384300	0.77442200	1.46600700
H	-4.07406300	-0.23118200	0.47345500
H	-3.33951500	1.19103300	-0.23056300
C	2.75182700	-1.61473200	-0.49979800
H	2.84950900	-1.19023200	-1.50021100
H	3.09445900	-2.64937200	-0.53903400
H	3.42294000	-1.07539200	0.16503200
C	-2.33561000	-1.00855500	-1.39105200
H	-2.46293800	-0.14728500	-2.04840200
H	-3.27777900	-1.55957600	-1.37223100
H	-1.57596400	-1.64663600	-1.82685800
C	1.32323200	-2.13082900	1.43521500
H	1.93599300	-1.47244800	2.05344100
H	1.77605300	-3.12411100	1.45542500
H	0.34199100	-2.19472000	1.89336100
P	-0.86070400	2.00881400	-0.24962400
H	-1.66972600	2.48151300	0.79453300

(2-H-1,2,3-P_3C_2*t*Bu_2)



ωB97XD/def2-TZVPPD
E = −1416.58191892 Eh

0 1

P	-1.42860700	1.76340400	0.15646500
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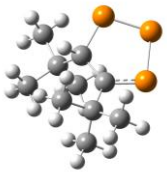
C	0.72612800	0.03634500	-0.11584500
C	1.57102200	-1.26798600	0.07994600
C	-1.81604200	-0.91636200	-0.06409000
C	-0.72546300	0.19914600	0.02660000
C	1.16023500	-2.48561000	-0.76627800
H	0.16048600	-2.85518100	-0.59291600
H	1.84685300	-3.30321200	-0.54375100

H	1.25850200	-2.25711900	-1.82846700
C	-1.68217800	-2.03033100	0.98736300
H	-0.77510000	-2.61330200	0.92344200
H	-2.51865600	-2.72199200	0.87721400
H	-1.73705000	-1.60122100	1.98912500
C	3.05642400	-1.06722400	-0.29416800
H	3.18258200	-0.80109900	-1.34470500
H	3.57624300	-2.01128100	-0.12749500
H	3.54943500	-0.31224900	0.31518100
C	-3.24193700	-0.37164700	0.16785600
H	-3.37174800	0.03380600	1.17146900
H	-3.94210200	-1.19937800	0.04719100
H	-3.52462200	0.39474700	-0.55299900
C	1.57425100	-1.59013500	1.58895400
H	2.10175700	-0.80219500	2.12821500
H	2.09806200	-2.53195400	1.76344200
H	0.58144300	-1.66915300	2.01796800
C	-1.83080100	-1.44943900	-1.51252100
H	-2.24212000	-0.68547200	-2.17375400
H	-2.46984900	-2.33221600	-1.57690900
H	-0.85115000	-1.70841200	-1.89395600
P	0.36231000	2.88295900	0.20949000
H	0.24465800	3.83561300	-0.81920200

(1,2,3-P_3HC_2*t*Bu_2)



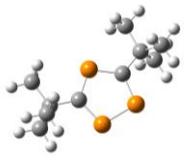
ωB97XD/def2-TZVPPD
E = −1416.59518134 Eh

0 1

P	0.43404200	-1.89952500	0.70210600
P	-1.62374200	-2.33979500	0.14574700
P	-1.99823700	-0.70646900	-0.95914000
C	-1.01368600	1.63361900	0.22732000
C	2.12957700	0.08091100	-0.19570700
C	0.66541400	-0.40900300	-0.05541300
C	-0.11458700	2.85348000	0.00421400
H	0.90621200	2.70691200	0.33607000
H	-0.51950100	3.69516900	0.56812000
H	-0.09777700	3.13822000	-1.04910100
C	2.60608700	0.77932100	1.09153300
H	1.99240800	1.62871800	1.37646900
H	3.62779000	1.13740400	0.95415200
H	2.59942700	0.07383800	1.92296500
C	-2.41385400	2.07617000	-0.23652400
H	-2.46208200	2.20176800	-1.31952400
H	-2.64466600	3.03907800	0.22101900
H	-3.19362300	1.37645500	0.06170100

C	3.07952700	-1.11413100	-0.41835100
H	3.08914200	-1.79570900	0.43105200
H	4.09555500	-0.74079900	-0.55655800
H	2.79744800	-1.67913700	-1.30737700
C	-1.07809000	1.30094700	1.71685700
H	-1.68607000	0.41415000	1.90288000
H	-1.53221100	2.13583800	2.25274900
H	-0.09024300	1.12560400	2.13961500
C	2.31387000	0.99049400	-1.41886000
H	2.00461700	0.47641200	-2.33047200
H	3.37175000	1.23435800	-1.52261200
H	1.76763200	1.92502900	-1.35419800
C	-0.50402400	0.36211700	-0.62428300
H	-0.22816300	0.76997900	-1.60235300

(1,2,4-P_3C_2*t*Bu_2)$^-$



ωB97XD/def2-TZVPPD
E = −1416.14549402 Eh

-1 1

P	-1.78545200	-0.00001600	-1.04293000
C	-0.06674300	1.24926700	-3.54206700
C	-0.07315800	-0.00012300	-1.35175200
C	0.44072400	0.00000600	-2.80397900
C	1.97198600	0.00017800	-2.89002900
C	-0.06647200	-1.24928700	-3.54220100
H	0.30440700	1.26236100	-4.57038100
H	0.27776500	-2.15583100	-3.04159400
H	2.40134200	0.88262700	-2.41386300
H	-1.15653300	1.27386500	-3.57172900
H	0.27732000	2.15583200	-3.04137900
H	-1.15625500	-1.27410500	-3.57189200
H	0.30470700	-1.26220500	-4.57050700
H	2.27764200	0.00029700	-3.93905100
H	2.40153200	-0.88225700	-2.41400800
P	1.01491100	-0.00007900	0.00000000
P	-1.78545200	-0.00001600	1.04293000
C	-0.06674300	1.24926700	3.54206700
C	-0.07315800	-0.00012300	1.35175200
C	0.44072400	0.00000600	2.80397900
C	1.97198600	0.00017800	2.89002900
C	-0.06647200	-1.24928700	3.54220100
H	0.30440700	1.26236100	4.57038100
H	0.27776500	-2.15583100	3.04159400
H	2.40134200	0.88262700	2.41386300
H	-1.15653300	1.27386500	3.57172900
H	0.27732000	2.15583200	3.04137900

H	-1.15625500	-1.27410500	3.57189200
H	0.30470700	-1.26220500	4.57050700
H	2.27764200	0.00029700	3.93905100
H	2.40153200	-0.88225700	2.41400800

(1-H-1,2,4-P_3C_2*t*Bu_2)

ωB97XD/def2-TZVPPD
E = −1416.60458195 Eh

0 1

P	-1.13741900	1.81806800	-0.12494600
C	-3.87220700	0.59060400	-0.17146100
C	-1.36988000	0.14243200	-0.03913400
C	-2.77875800	-0.46619800	0.00503100
C	-2.92938100	-1.50467700	-1.11872100
C	-2.98092700	-1.15345900	1.36604900
H	-4.85045000	0.10879100	-0.14445700
H	-2.25308900	-1.95052800	1.52278400
H	-2.78987500	-1.03973000	-2.09575500
H	-3.84536800	1.33680800	0.62366700
H	-3.77827400	1.10590100	-1.12900600
H	-2.87923300	-0.43302500	2.17881000
H	-3.97917600	-1.59192900	1.41734800
H	-3.92907700	-1.94064600	-1.08520200
H	-2.20777300	-2.31606900	-1.02127100
P	0.01017400	-1.00691300	0.00268400
C	3.66988900	0.45204500	-0.89276400
C	1.34094000	0.03321500	-0.03485700
C	2.78948700	-0.45960800	-0.02671000
C	2.89228600	-1.89060500	-0.56656300
C	3.31731300	-0.44107200	1.41883500
H	4.68379200	0.05193300	-0.93477800
H	2.72709300	-1.10414300	2.05208600
H	2.51861500	-1.95515500	-1.58939200
H	3.73325700	1.46104200	-0.48189800
H	3.28598300	0.51755900	-1.91164800
H	3.27458300	0.56259500	1.84310900
H	4.35567900	-0.77705200	1.43847600
H	3.93641900	-2.20660800	-0.56295700
H	2.32802400	-2.59321000	0.04711700
P	0.97265500	1.75702200	0.19646200
H	1.51515600	2.42475200	-0.91825600

(4-H-1,2,4-$P_3C_2tBu_2$)

ωB97XD/def2-TZVPPD
E = −1416.60293813 Eh

0 1

P	1.24766300	1.50930400	1.12949500
C	3.33604500	-1.27132500	0.39871000
C	1.40186700	0.25707600	-0.00929400
C	2.75040500	-0.21855900	-0.55891800
C	2.58551900	-0.84643500	-1.94885600
C	3.73218500	0.95384700	-0.66779300
H	4.28779400	-1.63769900	0.00935900
H	3.35201100	1.72205700	-1.34230600
H	1.97335700	-1.74974200	-1.91649800
H	3.50688600	-0.84094900	1.38566900
H	2.66044400	-2.12060700	0.50704900
H	3.92006500	1.41340400	0.30265800
H	4.68494100	0.59506500	-1.05987500
H	3.56242500	-1.13116500	-2.34161800
H	2.13101500	-0.14381800	-2.64869600
P	-0.88476500	1.51425800	1.44510800
C	-3.77104200	0.51290700	1.14317700
C	-1.36472600	0.27158400	0.39168200
C	-2.82418200	-0.07997100	0.09602400
C	-3.02941200	-1.60127900	0.06120500
C	-3.18379800	0.50800800	-1.28086700
H	-4.80153400	0.26219400	0.88775300
H	-2.56109200	0.08719400	-2.07096000
H	-2.75461600	-2.05608300	1.01340500
H	-3.69355500	1.59981100	1.18822100
H	-3.55929700	0.11423500	2.13619800
H	-3.05325800	1.59052800	-1.28379100
H	-4.22637300	0.28579700	-1.51502200
H	-4.07927200	-1.82385400	-0.13491800
H	-2.43961100	-2.07368100	-0.72607300
P	-0.05466500	-0.69667000	-0.27100500
H	-0.27001700	-0.79629700	-1.65576000

(1,2,4-$P_3HC_2tBu_2$)

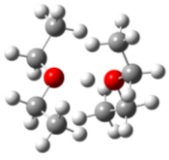
ωB97XD/def2-TZVPPD
E = −1416.60887254 Eh

0 1

P	-1.03324300	-1.85435000	-0.16315200
C	-2.61657400	0.55707000	1.61671100
C	-2.73243000	0.46722100	0.09269000

C	-3.03619200	1.85736000	-0.47976600
C	-3.89527700	-0.46083400	-0.27551600
H	-3.54766000	0.93210100	2.04432600
H	-3.98085300	-0.57707300	-1.35757200
H	-2.27711700	2.58889000	-0.20293700
H	-2.41680300	-0.42114000	2.05835400
H	-1.81606900	1.23655900	1.91576700
H	-3.78132000	-1.45155400	0.16499800
H	-4.83168200	-0.03967800	0.09355300
H	-3.99392900	2.21290400	-0.09603200
H	-3.09999200	1.82767800	-1.56919700
P	0.04376600	1.05659300	-0.36634900
P	0.96564400	-1.78757100	0.06683800
C	3.30410300	-0.02847700	1.41586300
C	1.29983900	-0.01528000	-0.08107600
C	2.75718200	0.43699700	0.05689000
C	2.90349300	1.95893700	-0.02627900
C	3.58867700	-0.19526700	-1.07111600
H	4.34376500	0.28511800	1.52310700
H	3.21742400	0.11991300	-2.04723200
H	2.34381300	2.45802900	0.76643400
H	3.27128300	-1.11421200	1.51531000
H	2.72896800	0.40686500	2.23433600
H	3.55916700	-1.28490200	-1.02853400
H	4.63056600	0.11651300	-0.98118500
H	3.95500200	2.22769400	0.08463700
H	2.55623400	2.34599900	-0.98522600
C	-1.39962600	-0.07505800	-0.51242600
H	-1.54244800	-0.10580000	-1.60879600

$[H(Et_2O)_2]^+$



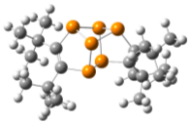
ωB97XD/def2-TZVPP
E = −467,808338514 Eh

1 1

C	1.51989500	2.03105300	0.99422000
H	0.53322700	1.95887200	1.44930300
H	1.46412900	2.67038200	0.11493900
H	2.19350200	2.49217600	1.71478400
C	2.06428400	0.67399600	0.63936400
H	2.11239700	0.00312900	1.49702200
H	3.04278600	0.73447300	0.16974300
O	1.19182300	0.05699600	-0.35774100
C	1.64475800	-1.21862900	-0.90196000
H	2.59705400	-1.00946600	-1.38228300
C	0.61717100	-1.72552800	-1.87805300
H	0.43704400	-0.99756000	-2.66741800

H	0.99524800	-2.63917400	-2.33306500
H	-0.32478000	-1.96423900	-1.38528500
H	1.80354100	-1.90467200	-0.06971700
C	-0.63913100	-1.28902500	2.18255100
H	-0.33868400	-0.41547200	2.76049900
H	0.24260500	-1.73661800	1.72260200
H	-1.05464000	-2.02401300	2.86986100
C	-1.67949700	-0.92448300	1.15399400
H	-2.58029900	-0.53112100	1.62650900
H	-1.95812900	-1.78648700	0.54224900
O	-1.15936800	0.10458600	0.29911600
C	-2.07496000	0.55272700	-0.71450500
H	-2.26267300	-0.27129400	-1.40757300
C	-1.49234300	1.75163400	-1.41983400
H	-0.56438900	1.50466500	-1.93494300
H	-2.20459900	2.10641700	-2.16313700
H	-1.30012500	2.55886200	-0.71421100
H	-3.01204100	0.80521300	-0.21719100
H	0.15812400	0.04280400	-0.05835300

***t*Bu$_4$C$_4$P$_6$ (13)**:



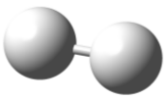
ωB97XD/def2-TZVPP
E = −2832.05804382 Eh

0 1

P	0.35221900	0.64057700	1.05453600
P	0.14969900	-1.46220100	1.56848700
P	-0.35219800	0.64061300	-1.05448900
P	1.46954500	-1.99403600	-0.10998600
P	-1.46956400	-1.99401900	0.10994900
P	-0.14971100	-1.46215100	-1.56850800
C	2.18432200	0.52053600	0.69164900
C	2.56769100	-0.50628300	-0.11019600
C	-3.79517400	-0.69887900	1.03700600
C	3.79513600	-0.69886500	-1.03704600
C	-2.56769100	-0.50624900	0.11021200
C	-2.18430000	0.52059400	-0.69159300
C	4.91894700	-1.45753700	-0.31575300
H	5.30104300	-0.91789900	0.54590600
H	5.74612000	-1.63140300	-1.00655900
H	4.55954500	-2.42862000	0.02913000
C	-2.98420100	1.69374500	-1.31074000
C	-4.91894100	-1.45754600	0.31563700
H	-5.30099900	-0.91789200	-0.54602800
H	-5.74614600	-1.63143900	1.00639700
H	-4.55951000	-2.42861600	-0.02925200
C	2.98424500	1.69367400	1.31079200

C	-3.37961200	-1.55412400	2.25513300
H	-3.07311400	-2.56340100	1.98062300
H	-4.23489900	-1.65024400	2.92406300
H	-2.57359100	-1.08076900	2.81818100
C	3.37952500	-1.55407600	-2.25518000
H	3.07303600	-2.56335900	-1.98068200
H	4.23478400	-1.65017900	-2.92414800
H	2.57348000	-1.08070600	-2.81818300
C	-4.44410800	1.33947100	-1.62537200
H	-4.48636500	0.47882200	-2.29460600
H	-4.90907200	2.18331000	-2.13654800
H	-5.05140200	1.11963900	-0.75851900
C	-4.29620700	0.61104800	1.66153100
H	-3.47608100	1.12256400	2.16718500
H	-5.05646800	0.37748900	2.40785900
H	-4.74029400	1.30295200	0.95895000
C	4.29611400	0.61109800	-1.66154100
H	3.47595400	1.12262200	-2.16713300
H	5.05634400	0.37758700	-2.40791600
H	4.74021900	1.30298100	-0.95895100
C	2.38138400	2.04744300	2.68997500
H	1.40174100	2.51237900	2.61212500
H	3.04438200	2.75294800	3.19192500
H	2.29317700	1.16240400	3.32320500
C	4.44415900	1.33939300	1.62537600
H	4.48643500	0.47872600	2.29458500
H	4.90913600	2.18321900	2.13656100
H	5.05142900	1.11958500	0.75849900
C	-2.38129400	2.04752600	-2.68989800
H	-1.40163400	2.51242000	-2.61201100
H	-3.04425200	2.75307200	-3.19184300
H	-2.29310700	1.16250200	-3.32315100
C	-2.88030400	2.94964200	-0.43261600
H	-3.34903400	2.81852700	0.53866500
H	-3.36066200	3.79178300	-0.93446900
H	-1.83379600	3.21300000	-0.26648500
C	2.88033600	2.94957600	0.43267900
H	3.34903000	2.81845800	-0.53862000
H	3.36072500	3.79170900	0.93451700
H	1.83382700	3.21295200	0.26658400

H_2



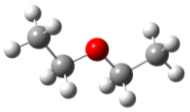
ωB97XD/def2-TZVPP
E = −1,17672716964 Eh

0 1

H	0.00000000	0.00000000	0.37187400

H	0.00000000	0.00000000	-0.37187400

Et_2O



ωB97XD/def2-TZVPP
E = −233.686444447 Eh

0 1

C	-2.37771500	0.40321800	0.00001400
H	-2.37860800	1.04025700	-0.88465700
H	-2.37864600	1.04011500	0.88478700
H	-3.29524000	-0.18537300	-0.00005200
C	-1.17477600	-0.51074400	-0.00003500
H	-1.18751300	-1.16208600	-0.88391200
H	-1.18751300	-1.16217800	0.88377300
O	0.00000000	0.26860400	0.00000500
C	1.17477600	-0.51074400	0.00001300
H	1.18751200	-1.16212400	0.88386100
C	2.37771500	0.40321800	0.00000400
H	2.37862100	1.04020300	0.88471500
H	3.29524000	-0.18537300	0.00002100
H	2.37863300	1.04016900	-0.88473000
H	1.18751400	-1.16214000	-0.88382300

7 References

[1] G. Hierlmeier, P. Coburger, M. Bodensteiner and R. Wolf, *Angew. Chem. Int. Ed.*, 2019, **58**, 16918–16922.

[2] K. Jonas, P. Klusmann and R. Goddard, *Z. Naturforsch. B*, 1995, **50**, 394–404.

[3] P. J. Fagan, W. S. Mahoney, J. C. Calabrese and I. D. Williams, *Organometallics*, 1990, **9**, 1843–1852.

[4] M. Brookhart, B. Grant and A. F. Volpe Jr., *Organometallics*, 1992, **11**, 3920–3922.

[5] P. H. M. Budelaar, *gNMR for Windows (5.0.6.0), NMR Simulation Program*, 2006, IvorySoft.

[6] a) A. H. Cowley and S. W. Hall, *Polyhedron*, 1989, **8**, 849-850.; b) R. Bartsch and J. F. Nixon, *Polyhedron*, 1989, **8**, 2407; c) R. Bartsch and J. F. Nixon, *J. Organomet. Chem*,. 1991, **415**, C15-C18.

[7] a) G. M. Sheldrick, SADABS, Bruker AXS, Madison, USA, 2007; b) SCALE3ABS, CrysAlisPro, Aglient Technologies Inc. Oxford, GB, 2015.

[8] R. C. Clark and J. S. Reid, *Acta Crystallogr. A*, 1995, **51**, 887.

[9] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

[10] G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.

[11] G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.

[12] The measurements were performed relative to the bottom mercury at r.t. Bottom mercury means that one of the electrodes is the mercury at the bottom of the CV cell. See: I. N. Brago and A. P. Tomilov, *Soviet Electrochem. (Engl. Trans.)*, 1968, **4**, 623–625.

[13] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, 2013.

[14] a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305; b) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620; c) D. Rappoport and F. Furche, *J. Chem. Phys.*, 2010, **133**, 134105; d) Basis set obtained from: B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson and T. L. Windus. *J. Chem. Inf. Model.*, 2019, **59**, 4814–4820.

[15] V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.