Supplementary Information

Novel Synthetic Route for (Parent) Phosphetanes, Phospholanes, Phosphinanes and Phosphepanes

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1. Experimental details

General methods:

All manipulations were carried out under an inert atmosphere of dried argon using standard Schlenk and glove box techniques. 1,2-dimethoxyethane (DME) was dried and deoxygenated by distillation under argon atmosphere from sodium. *Ortho*-diflourobenze (*o*-DFB) was dried and deoxygenated by distillation under argon atmosphere from P₂O₅. All other solvents were dried using a MB SPS-800 device of the company MBRAUN and stored over molecular sieve. NMR spectra were recorded on a Bruker Avance III 400/600 MHz NMR spectrometer. Chemical shifts were measured at ambient temperature and are given in ppm; they are referenced to TMS for ¹H and 85% H₃PO₄ for ³¹P as external standard. Signal multiplicities are described using common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). LIFDI-/FD-/EI-MS spectra (LIFDI = liquid injection field desorption ionization, FD = field desorption, EI = electron ionization) were measured on a JEOL AccuTOF GCX. Elemental analysis (CHN) was determined using a Vario micro cube instrument. A glass stirring bar was used in reactions with potassium benzyl.

The compounds potassium benzyl (KBn, KC₇H₇) and $[K(dme)_2]_2[Cp*Fe(n^4-P_5)]$ (I) were synthesized according to literature procedures^{1,2}. LiAlH₄ was purified by extraction with Et₂O and filtration over diatomaceous earth. Modified Synthesis of I: Reduction of I' with KC₈ in DME or THF and used *in situ*.

Unless otherwise noted, all other materials were obtained from commercial suppliers and used without purification.

Crystals suitable for single crystal X-ray diffraction analysis were obtained as described below. The diffraction data were collected either on a Gemini Ultra diffractometer equipped with an Atlas⁵² CCD detector and with a fine-focus sealed Cu-K_{α} X-ray tube, on a XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector and a rotating-anode Cu-K_{α} X-ray tube or a GV50 diffractometer equipped with a Titan⁵² CCD detector and a micro-focus Cu-K_{α} X-ray tube. Data collection and reduction were performed with CrysAlisPro software package. The structures were solved with Olex2³, using ShelXT⁴ and a least-square refinement on *F*² was carried out with ShelXL⁴. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined with isotropic displacement parameters according to the riding model. The images of the molecular structures were made using Olex2.³ All NMR simulations were conducted with the *WinDaisy* application within the NMR software *Top Spin* 4.1.1 by *Bruker*.

Synthetic protocols:

Reaction of $[K(dme)_2]_2[Cp^*Fe(\eta^4-P_5)]$ (I) with 1,3-dibromopropane:

A solution of *in situ* generated I ([Cp*Fe(η^{5} -P₅)] (I'): 2 mmol, 691.9 mg, 1 eq; KC₈: 2.2 mmol, 593.8 mg, 2.2 eq,) in DME was slowly added to a 0.917 molar solution of 1,3-dibromopropane in DME (2 mmol, 2.2 mL, 1 eq) at -50 °C. A colour change from brown to green occurred and a colourless solid was formed. The mixture was stirred for three hours. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added, and the solvent was removed *in vacuo*. The preabsorbed reaction mixture was purified via column chromatography (SiO₂, hexane, 8 x 2 cm). Using a mixture of *n*-hexane/dichloromethane (10:1), a first green fraction of [Cp*Fe{ η^4 -P₅((CH₂)₃Br)₂]] (**1**) can be eluted, changing increasing the dichloromethane/*n*-hexane ratio to 1:1. The solvent of both fractions was removed under reduced pressure. [Cp*Fe{ η^4 -P₅((CH₂)₃Br)₂]] (**1**) can be isolated as dark green blocks after one week via layering a

dichloromethane (3 mL) solution with acetonitrile (7 mL) and stored at -30° C. [Cp*Fe{ η^{4} -P₅(C₃H₆)}] (2) can be obtained analogous as red/greenish plates.

Data for $[Cp^*Fe\{\eta^4-P_5((CH_2)_3Br)_2\}]$ (1):

Yield: 310.1 mg (0.526 mmol, 26 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 2.90 (t, 2 H, J_{H-H} = 6.20 Hz, -(CH₂)₂CH₂-Br), 2.45 (t, 2 H, J_{H-H} = 6.35 Hz, -(CH₂)₂CH₂-Br), 2.14 (m, 2 H, -(CH₂)₃-Br), 1.84 (m, 2H, -(CH₂)₃-Br), 1.61 (s, 15 H, C₅(CH₃)₅), 1.03 (m, 2 H, -(CH₂)₃-Br), 0.47 (m, 2 H, -(CH₂)₃-Br). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 136.0 (m, 1 P, P_A), 36.4 (m, 2 P, P_{M,M'}), -131.4 (m, 2 P, P_{M,M'}), -131.4 (m, 2 P, P_{XX}). For coupling constants, see Table **S1**. LIFDI-MS (toluene): m/z = 589.86 (100 %, [M]⁺). analysis (calcd., found for C₁₆H₂₇FeBr₂P₅): C (32.58, 33.09), H (4.61, 4.58).

Data for $[Cp^*Fe\{\eta^4-P_5(C_3H_6)\}]$ (2):

Yield: 232.3 mg (0.599 mmol, 30 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 2.74 (m, 2 H, -P₅(C₃H₆)), 1.58 (s, 15 H, C₅(CH₃)₅), 1.42 (m, 2 H, -P₅(C₃H₆)), 0.88 (m, 2 H, -P₅(C₃H₆)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 125.4 (m, 1 P, P_A), 43.5 (m, 2 P, P_{M,M}), -89.3 (m, 2 P, P_{X,X}). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 125.4 (m, 1 P, P_A), 43.5 (m, 2 P, P_{M,M}), -89.3 (m, 2 P, P_{X,X}). For coupling constants, see **Table S2**. **FD-MS** (toluene): *m*/*z* = 387.97 (100 %, [M]⁺). analysis (calcd., found for C₁₃H₂₁FeP₅): C (40.24, 40.39), H (5.46, 5.32).

The usage of two equivalents of 1,3-dibromopropane in the analog reaction setup does lead to complex 1 in 25 % and complex 2 in 27 % yield, respectively.

Reaction of I with 1,4-dibromobutane:

A solution of *in situ* generated I ([Cp*Fe(η^5 -P₅)] (I'): 2 mmol, 691.9 mg, 1 eq; KC₈: 2.2 mmol, 593.8 mg, 2.2 eq,) in THF was cooled to -80 °C and slowly added to a 0.9263 molar solution of 1,4-dibromobutane in DME (8 mmol, 8.6 mL, 4 eq). A colour change from brown to green occurred and a colourless solid was formed. The mixture was stirred for 12 hours. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, silica is added, and the solvent was removed *in vacuo*. The preabsorbed reaction mixture was purified via column chromatography (SiO₂, hexane, 10 x 3 cm). Using a mixture of *n*-hexane/dichloromethane (8:1), a green/brownish fraction of [Cp*Fe{ η^4 -P₅(C₄H₈)}] (**3**), followed by a very small brown one can be eluted. The solvent of the first fraction was removed under reduced pressure. Compound **3** can be isolated as dark green prism after one week via layering a dichloromethane (3 mL) solution with acetonitrile (7 mL) and stored at -30°C.

Data for $[Cp^*Fe\{\eta^4-P_5(C_4H_8)\}]$ (3)

Yield: 570.9 mg (1.42 mmol, 71 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 2.34 (m, 2 H, -P₅(C₄H₈)), 1.64 (s, 15 H, C₅(CH₃)₅), 1.14 (m, 2 H, -P₅(C₄H₈)), 0.79 (m, 2 H, -P₅(C₄H₈)), 0.43 (m, 2 H, -P₅(C₄H₈)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 145.4 (m, 1 P, P_A), 38.3 (m, 2 P, P_{M,M'}), -117.4 (m, 2 P, P_{X,X'}). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 145.4 (m, 1 P, P_A), 38.3 (m, 2 P, P_{M,M'}), -117.4 (m, 2 P, P_{X,X'}). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 145.4 (m, 1 P, P_A), 38.3 (m, 2 P, P_{M,M'}), -117.4 (m, 2 P, P_{X,X'}). For coupling constants, see **Table S3**. **FD-MS** (toluene): *m/z* = 402.04 (100 %, [M]⁺). analysis (calcd., found for C₁₄H₂₃FeP₅): C (41.82, 42.27), H (5.77, 5.73).

Reaction of I with 1,5-dibromopentane:

A solution of *in situ* generated I ([Cp*Fe(η^5 -P₅)] (I'): 2 mmol, 691.9 mg, 1 eq; KC₈: 2.2 mmol, 593.8 mg, 2.2 eq,) in THF was cooled to -80 °C and slowly added to a 1.6053 molar solution of 1,5-dibromopentane in DME (2 mmol, 1.2 mL, 1 eq). The workup is analogous to the reaction above. [Cp*Fe{ η^4 -P₅(C₅H₁₀)}] (4) can be isolated as

dark green blocks after one week via layering a dichloromethane (2 mL) solution with acetonitrile (10 mL) and stored at -30°C.

Data for [Cp*Fe{η⁴-P₅(C₅H₁₀)}] (4):

Yield: 507.6 mg (1.22 mmol, 61 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 2.08 (m, 2 H, -P₅(C₅H₁₀)), 1.64 (s, 15 H, C₅(CH₃)₅), 1.57 (m, 2 H, -P₅(C₅H₁₀)), 0.71 (m, 4 H, -P₅(C₅H₁₀))*, 0.52 (m, 2 H, -P₅(C₅H₁₀)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 127.4 (m, 1 P, P_A), 33.0 (m, 2 P, P_{M,M'}), -136.0 (m, 2 P, P_{X,X'}). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 127.4 (m, 1 P, P_A), 33.0 (m, 2 P, P_{M,M'}), -136.0 (m, 2 P, P_{X,X'}). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 127.4 (m, 1 P, P_A), 33.0 (m, 2 P, P_{M,M'}), -136.0 (m, 2 P, P_{X,X'}). For coupling constants, see **Table S4**. **LIFDI-MS** (toluene): *m*/*z* = 416.06 (100 %, [M]⁺). analysis (calcd., found for C₁₅H₂₅FeP₅): C (43.30, 42.90), H (6.06, 6.09).

* : overlay of two signals

Reaction of I with 1,6-dibromohexane:

A solution of *in situ* generated I ([Cp*Fe(η^5 -P₅)] (I'): 2 mmol, 691.9 mg, 1 eq; KC₈: 2.2 mmol, 593.8 mg, 2.2 eq,) in THF was cooled to -80 °C and slowly added to a 0.1064 molar solution of 1,6-dibromohexane in DME (2 mmol, 18.8 mL, 1 eq). The workup is analogous to the reaction above. [Cp*Fe{ η^4 -P₅(C₆H₁₂)}] (5) can be isolated as dark red plates after one week via layering a dichloromethane (2 mL) solution with acetonitrile (10 mL) and stored at -30° C.

Data for $[Cp^*Fe\{\eta^4-P_5(C_6H_{12})\}]$ (5):

Yield: 257.6 mg (0.599 mmol, 30 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 2.46 (m, 2 H, -P₅(C₆H₁₂)), 1.66 (s, 15 H, C₅(CH₃)₅), 1.52 (m, 2 H, -P₅(C₆H₁₂)), 1.14 (m, 2 H, -P₅(C₆H₁₂)), 0.87 (m, 2 H, -P₅(C₆H₁₂)), 0.75 (m, 4 H, -P₅(C₆H₁₂))*. ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 145.0 (m, 1 P, P_A), 34.8 (m, 2 P, P_{M,M'}), -128.5 (m, 2 P, P_{X,X'}). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 145.0 (m, 1 P, P_A), 34.8 (m, 2 P, P_{X,X'}). For coupling constants, see **Table S5**. **FD-MS** (toluene): *m/z* = 430.07 (100 %, [M]⁺). analysis (calcd., found for C₁₆H₂₇FeP₅): C (44.68, 44.85), H (6.33, 6.43).

* : overlay of two signals

General Synthesis of 1-Benzylphosphetane (6), 1-Benzylphospholane (7), 1-Benzylphosphinane (8) and 1-Benzylphosphepane (9):

Compound 2 (0.15 mmol, 58.2 mg, 1 eq), 3 (0.15 mmol, 60.3 mg, 1 eq), 4 (0.15 mmol, 62.4 mg, 1 eq) or 5 (0.1 mmol, 43.0 mg, 1 eq) were dissolved in THF and cooled to -80 °C. To the solution, a -80 °C cold solution of KBn (0.15 mmol / 19.5 mg for 2-4, 0.1 mmol / 13.0 mg for 5, 1 eq) in THF was added, respectively. The colour changed to dark red and rapidly back to brownish-green. The solution was stirred overnight and allowed to reach room temperature. The solvent was slowly removed under reduced pressure. The oily residue was extracted with n-pentane (3 x 5 mL) and filtered over diatomaceous earth. The solvent was removed in vacuo and compounds 6-9 can be isolated as viscous liquids.

Data for 1-Benzylphosphetane (6):

Yield: 14.8 mg (0.09 mmol, 60 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 7.06 (m, 5 H, Ph), 2.82 (d, ²J_{P-H} = 73.7 Hz, 2 H, -C<u>H₂</u>-Ph), 1.65 (m, 2 H, -P(C₃H₆)), 1.36 (m, 2 H, -P(C₃H₆)), 0.87 (m, 4 H, -P(C₃H₆))*. ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 14.1 (s). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 14.1 (m). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 128.9 (d, J_{P-C} = 5.2 Hz, Ph), 128.4 (d, J_{P-C} = 1.5 Hz, Ph), 128.3 (d, J_{P-C} = 20.4 Hz, Ph), 37.7 (d, ¹J_{P-C} = 20.9 Hz, -(CH₂)-Ph), 23.1 (d, ²J_{P-C} = 2.0 Hz, -P(C₃H₆)), 18.8 (d, ¹J_{P-C} = 5.1 Hz, -P(C₃H₆)).

* : overlay of two signals

Data for 1-Benzylphospholane (7):

Yield: 21.4 mg (0.12 mmol, 80 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 7.07 (m, 5 H, Ph), 2.42 (s, br, -C<u>H₂-Ph), 1.53 (m, 2 H, -P(C₄H₈)), 1.37 (m, 6 H, -P(C₄H₈)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = -16.3 (s). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = -16.3 (s, br). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 139.2 (d, J_{P-C} = 5.3 Hz, Ph), 129.1 (d, J_{P-C} = 5.7 Hz, Ph), 128.4 (d, J_{P-C} = 1.3 Hz, Ph), 125.6 (d, J_{P-C} = 2.4 Hz, Ph), 35.5 (d, ¹J_{P-C} = 21.9 Hz, -(<u>C</u>H₂)-Ph), 27.5 (d, ²J_{P-C} = 4.1 Hz, -P(<u>C</u>₄H₈)), 25.1 (d, ¹J_{P-C} = 15.4 Hz, -P(<u>C</u>₄H₈)).</u>

Data for 1-Benzylphosphinane (8):

Yield: 21.1 mg (0.11 mmol, 73%). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 7.08 (m, 5 H, Ph), 2.66 (s, br, -C<u>H</u>₂-Ph), 1.67 (m, 2 H, -P(C₅H₁₀)), 1.52 (m, 2 H, -P(C₅H₁₀)), 1.43 (m, 2 H, -P(C₅H₁₀)), 1.32 (m, 2 H, -P(C₅H₁₀)), 1.11 (m, 2 H, -P(C₅H₁₀))*. ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = -35.0 (s). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = -35.0 (s, br). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 138.5 (d, J_{P-C} = 4.9 Hz, Ph), 129.0 (d, J_{P-C} = 5.4 Hz, Ph), 128.3 (d, J_{P-C} = 1.3 Hz, Ph), 125.5 (d, J_{P-C} = 2.3 Hz, Ph), 34.4 (d, ¹J_{P-C} = 18.9 Hz, -(CH₂)-Ph), 27.8 (d, ²J_{P-C} = 2.1 Hz, -P(C₅H₁₀)), 24.2 (d, ¹J_{P-C} = 14.5 Hz, -P(C₅H₁₀)), 23.3 (d, ³J_{P-C} = 3.5 Hz, -P(C₅H₁₀)).

Data for 1-Benzylphosphepane (9):

Yield: 16.5 mg (0.08 mmol, 80 %). ¹H NMR (C₆D₆, 293 K): *δ* [ppm] = 7.07 (m, 5 H, Ph), 2.52 (s, br, -C<u>H</u>₂-Ph), 1.65 (m, 4 H, -P(C₆H₁₂)), 1.51 (m, 4 H, -P(C₆H₁₂)), 1.32 (m, 2 H, -P(C₆H₁₂)), 1.13 (m, 2 H, -P(C₆H₁₂)). ³¹P{¹H} NMR (C₆D₆, 293 K): *δ* [ppm] = -26.4 (s). ³¹P NMR (C₆D₆, 293 K): *δ* [ppm] = -26.5 (m). ¹³C{¹H} NMR (C₆D₆, 293 K): *δ* [ppm] = 138.7 (s, br, Ph), 129.1 (d, J_{P-C} = 5.4 Hz, Ph), 128.2 (d, J_{P-C} = 1.1 Hz, Ph), 125.5 (d, J_{P-C} = 2.1 Hz, Ph), 36.8 (d, ¹ J_{P-C} = 15.9 Hz, -(CH₂)-Ph), 29.0 (d, ¹ J_{P-C} = 16.1 Hz, -P(C₆H₁₂)), 28.1 (d, ² J_{P-C} = 4.5 Hz, -P(C₆H₁₂)), 25.9 (d, ³ J_{P-C} = 9.4 Hz, -P(C₆H₁₀)).

Synthesis of Phospholane (10b):

Complex **3** (0.1 mmol, 40.2 mg, 1 eq) and LiAlH₄ (0.12 mmol, 4.5 mg, 1.2 eq) were dissolved separately in 1 mL THF-d₈. LiAlH₄ is added to compound **3**. The solution was stirred overnight, resulting in a colour change from greenish/brown to red. The formed phosphine **10b** was distilled of under reduced pressure ($1\cdot10^{-3}$ mbar, 60 °C, 30 min.).

Yield: 0.068 mmol, 69 %*. ¹H NMR (THF-d₈, 293 K): δ [ppm] = 2.91 (m, 1 H, -P<u>H</u>), 2.47 (m, 2 H, HP(C₄H₈)), 1.89 (m, 2 H, HP(C₄H₈)), 1.73 (m, 13 H, HP(C₄H₈))[#], 1.41 (m, 2 H, HP(C₄H₈)). ³¹P{¹H} NMR (THF-d₈, 293 K): δ [ppm] = -70.8 (dt, ¹J_{P-H} = 180.3 Hz, ¹J_{P-H} = 21.7 Hz). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 30.1 (d, ²J_{P-C} = 5.5 Hz, HP(C₄H₈)), 19.3 (d, ¹J_{P-C} = 9.3 Hz, HP(C₄H₈)).

* according to NMR via internal standard of PPh₃ capillary in toluene-d₈ (c = 0.2 mol·L^{-1} , v = 0.07 mL).

[#] overlap of solvent- and product-signal causes wrong integral

Synthesis of secondary phosphines 10a,c,d according to previous reaction setup - Synthesis of phospholane (10b).

General Synthesis of 6'-9':

Compound 6-9 (0.15 mmol for 6-8, 1 eq; 0.1 mmol for 9, 1 eq) were synthesized according to the previous procedure *in situ*, dissolved in 5 mL of *n*-pentane, respectively, added to a solution of sulphur (0.15 mmol, 4.8 mg, 1 eq for 6-8; 0.1 mmol, 3.2 mg for 9, 1 eq) in 5 mL *n*-pentane and stirred for 2 hours at room temperature. The volume was reduced *in vacuo* and stored at -30 °C. Colourless crystals of 6'-9' were formed after one day.

Data for 6':

Yield: 21.6 mg (0.11 mmol, 73 %). ¹H NMR (C₆D₆, 293 K): *δ* [ppm] = 7.02 (m, 5 H, Ph), 2.94 (d, ²*J*_{P-H} = 13.1 Hz, 2 H, -C<u>H</u>₂-Ph), 2.06 (m, 2 H, -P(C₃H₆)), 1.87 (m, 2 H, -P(C₃H₆)), 0.88 (m, 2 H, -P(C₃H₆)). ³¹P{¹H} NMR (C₆D₆, 293 K): *δ* [ppm] = 58.2 (s). ³¹P NMR (C₆D₆, 293 K): *δ* [ppm] = 58.2 (m). ¹³C{¹H} NMR (C₆D₆, 293 K): *δ* [ppm] = 129.4 (d, *J*_{P-C} = 5.1 Hz, Ph), 128.4 (d, *J*_{P-C} = 3.1 Hz, Ph), 126.9 (d, *J*_{P-C} = 3.5 Hz, Ph), 41.5 (d, ¹*J*_{P-C} = 31.7 Hz, -(<u>C</u>H₂)-Ph), 34.2 (d, ¹*J*_{P-C} = 47.1 Hz, -P(<u>C</u>₃H₆)), 13.2 (d, ²*J*_{P-C} = 21.4 Hz, -P(<u>C</u>₃H₆)). **EI-MS** (CH₂Cl₂): *m/z* = 63.9 (100 %, [S]⁺), 191.83 (56 %, [S₆]⁺), 127.89 (24 %, [S₄]⁺). analysis (calcd., found for C₁₀H₁₃PS): C (61.20, 63.72), H (6.68, 7.74), S (16.34, 16.36).

Data for 7':

Yield: 23.1 mg (0.11 mmol, 73 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 7.03 (m, 5 H, Ph), 2.87 (d, ²*J*_{P-H} = 14.0 Hz, 2 H, -C<u>H</u>₂-Ph), 1.57 (m, 4 H, -P(C₄H₈)), 1.37 (m, 2 H, -P(C₄H₈)), 0.91 (m, 4 H, -P(C₄H₈)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 61.9 (s). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 61.9 (s, br). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 132.9 (d, *J*_{P-C} = 8.2 Hz, Ph), 129.7 (d, *J*_{P-C} = 5.1 Hz, Ph), 128.3 (d, *J*_{P-C} = 3.0 Hz, Ph), 126.9 (d, *J*_{P-C} = 3.5 Hz, Ph), 42.0 (d, ¹*J*_{P-C} = 40.3 Hz, -(<u>C</u>H₂)-Ph), 32.1 (d, ¹*J*_{P-C} = 51.7 Hz, -P(<u>C</u>₄H₈)), 25.4 (d, ²*J*_{P-C} = 6.1 Hz, -P(<u>C</u>₄H₈)). **EI-MS** (CH₂Cl₂): *m/z* = 210.06 (83 %, [M]⁺), 91.05 (100 %, [C₇H₇]⁺), 119.01 (99 %, [M-C₇H₇]⁺). analysis (calcd., found for C₁₁H₁₅PS): C (62.83, 62.80), H (7.19, 7.49), S (15.25, 15.60).

Data for 8':

Yield: 29.2 mg (0.13 mmol, 87 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 7.08 (m, 5 H, Ph), 2.84 (d, ²J_{P-H} = 14.0 Hz, 2 H, -C<u>H₂</u>-Ph), 1.81 (m, 2 H, -P(C₅H₁₀)), 1.42 (m, 2 H, -P(C₅H₁₀)), 1.24 (m, 4 H, -P(C₅H₁₀)), 1.09 (m, 1 H, -P(C₅H₁₀)), 0.70 (m, 1 H, -P(C₅H₁₀)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 36.8 (s). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 36.8 (m). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 132.0 (d, J_{P-C} = 8.0 Hz, Ph), 129.9 (d, J_{P-C} = 5.0 Hz, Ph), 128.2 (d, J_{P-C} = 3.0 Hz, Ph), 126.8 (d, J_{P-C} = 3.5 Hz, Ph), 40.2 (d, ¹J_{P-C} = 45.4 Hz, -(CH₂)-Ph), 29.9 (d, ¹J_{P-C} = 48.4 Hz, -P(C₅H₁₀)), 26.1 (d, J_{P-C} = 6.0 Hz, -P(C₅H₁₀)), 21.3 (d, J_{P-C} = 5.8 Hz, -P(C₅H₁₀)).)). EI-MS (CH₂Cl₂): *m/z* = 224.08 (66 %, [M]⁺), 91.05 (100 %, [C₇H₇]⁺), 133.02 (78 %, [M-C₇H₇]⁺), 99.05 (34 %, [P(C₅H₈)]⁺), 192.11 (23 %, [BnzP(C₅H₁₀)]⁺). analysis (calcd., found for C₁₂H₁₇PS): C (64.26, 62.80), H (7.64, 7.49), S (14.30, 15.60).

Data for 9':

Yield: 16.7 mg (0.07 mmol, 70 %). ¹H NMR (C₆D₆, 293 K): δ [ppm] = 7.08 (m, 5 H, Ph), 2.82 (d, ²J_{P-H} = 13.8 Hz, 2 H, -C<u>H</u>₂-Ph), 1.75 (m, 2 H, -P(C₆H₁₂)), 1.45 (m, 4 H, -P(C₆H₁₂)), 1.19 (m, 4 H, -P(C₆H₁₂)), 1.04 (m, 2 H, -P(C₆H₁₂)). ³¹P{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 48.9 (s). ³¹P NMR (C₆D₆, 293 K): δ [ppm] = 48.9 (s, br). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 129.9 (d, J_{P-C} = 4.8 Hz, Ph), 128.2 (d, J_{P-C} = 2.9 Hz, Ph), 126.8 (d, J_{P-C} = 3.3 Hz, Ph), 42.0 (d, ¹J_{P-C} = 45.6 Hz, -(<u>C</u>H₂)-Ph), 32.6 (d, ¹J_{P-C} = 48.1 Hz, -P(<u>C₆H₁₂</u>)), 28.4 (d, ²J_{P-C} = 0.8 Hz, -P(<u>C₆H₁₂</u>)), 21.4 (d, ³J_{P-C} = 3.7 Hz, -P(<u>C₆H₁₀</u>)). **EI-MS** (CH₂Cl₂): *m/z* = 238.09 (54 %, [M]⁺), 91.05 (100 %, [C₇H₇]⁺), 147.04 (64 %, [M-C₇H₇]⁺), 113.05 (17 %, [P(C₆H₁₀)]⁺). Elemental analysis failed after several attempts of the isolated crystals.

Synthesis of $[({C_4H_8}PH)_2PtCl_2]$ (11):

An *in situ* solution of compound **10b** (0.2 mmol, 2.67 eq) in 3 mL THF was synthesized according to the previous procedure, added to a solution of $[(PhCN)_2PtCl_2]$ (0.075 mmol, 35.4 mg, 1 eq) in 3 mL THF and stirred for 1 hour at room temperature. The volume was removed *in vacuo*, the colourless residue was dissolved in 2 mL of CH₂Cl₂, layered with 10 mL of Et₂O and stored at room temperature. Colourless crystals of **11** were formed after one day.

Yield: 0.041 mmol, 53 %. ¹H NMR (CH₂Cl₂, 293 K): δ [ppm] = 5.32 (t, br, J_{P-H} = 2.03 Hz, 1 H, -P<u>H</u>), 2.36 (m, 1 H, HP(C₄H₈))[#], 2.28 (m, 2 H, HP(C₄H₈))[#], 2.08 (m, 2 H, HP(C₄H₈))[#], 1.88 (m, 3 H, HP(C₄H₈))[#]. ³¹P{¹H} NMR (CD₂Cl₂, 293 K) = 0.01 M S = 0.01

293 K): δ [ppm] = -15.4 (s). ³¹P NMR (CD₂Cl₂, 293 K): δ [ppm] = -15.4 (d, ¹J_{P-H} = 377.1 Hz). ¹³C{¹H} NMR (C₆D₆, 293 K): δ [ppm] = 27.7 (s, HP(C₄H₈)), 21.1 (d, ¹J_{P-C} = 42.4 Hz, HP(C₄H₈)). LIFDI-MS (o-DFB): m/z = 442.00 (100 %, [M]⁺). Elemental analysis failed after several attempts of the isolated crystals due to minor unidentified side products, sticking on the crystals of **11** used for the preparation of the sample and which could not be removed by washing.

[#] overlap of solvent- and product-signal causes wrong integral

2. NMR spectroscopic characterization

¹H NMR Spectra:

 $[Cp*Fe{\eta^4-P_5((CH_2)_3Br)_2}]$ (1)



Fig. S1. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 1.

 $[Cp^*Fe{\eta^4-P_5(C_3H_6)}]$ (2)



Fig. S2. Experimental ¹H NMR (400.13 MHz, C_6D_6) spectrum of 2 (* = I').



Fig. S3. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 3.

 $[Cp^*Fe{\eta^4-P_5(C_5H_{10})}]$ (4)



Fig. S4. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 4.





Fig. S5. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 5.

PBn{(CH₂)₃} (6)



Fig. S6. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 6 (* = unknown sideproduct, not visible in ³¹P NMR).





Fig. S7. Experimental ¹H NMR (400.13 MHz, C_6D_6) spectrum of 7.





Fig. S8. Experimental ¹H NMR (400.13 MHz, C_6D_6) spectrum of 8.

PBn{(CH₂)₆} (9)



Fig. S9. Experimental ¹H NMR (400.13 MHz, C_6D_6) spectrum of 9 (* = 5).

HP{(CH₂)₄} (10b)



Fig. S10. Experimental ¹H NMR (400.13 MHz, THF-d₈) spectrum of **10b** (' = integral wrong due to solvent signal overlap with product signal).

SPBn{(CH₂)₃} (6')



Fig. S11. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 6'.

SPBn{(CH₂)₄} (7')









Fig. S13. Experimental ${}^{1}H$ NMR (400.13 MHz, C₆D₆) spectrum of 8'.





Fig. S14. Experimental ¹H NMR (400.13 MHz, C₆D₆) spectrum of 9' (* = 5).



Fig. S15. Experimental ¹H NMR (400.13 MHz, CH₂Cl₂) spectrum of **11** (* = grease; # = unidentified sideproduct(s)).

³¹P NMR Spectra:

 $[Cp*Fe{\eta^4-P_5((CH_2)_3Br)_2}]$ (1)



Fig. S16. Experimental (top) and simulated (bottom) ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of 1.

J [Hz]				δ [ppm]]
¹ J _{PA,PX}	397.93	¹ J _{PM,PX}	391.62	X, X'	-131.4
¹ J _{PA,PX} '	398.58	¹ J _{PM',PX'}	405.29		
² J _{PA,PM}	-11.40	² Ј_{РМ',РХ}	-32.39	M, M'	36.4
² J _{PA,PM} '	-12.33	² Ј_{РМ,РХ'}	-45.34		
¹ J _{PM,PM} '	379.55	² J _{PX,PX} '	-1.08	A	136.0

 $[Cp*Fe{\eta^4-P_5(C_3H_6)}]$ (2)



Fig. S17. Experimental (top) and simulated (bottom) ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of **2**.

 Table S2. Chemical shifts and coupling constants obtained from the simulation (R-factor = 2.72 %) in Figure S17.

J [Hz]				δ [ppm]
¹ J _{PA,PX}	431.20	¹ J _{PM,PX}	404.0	X, X'	-89.3
¹ Ј _{РА,РХ'}	430.90	¹ Ј _{РМ',РХ'}	412.0		
² J _{PA,PM}	15.36	² Ј _{РМ',РХ}	-35.32	M, M'	43.5
² Ј _{РА,РМ} '	16.74	² Ј _{РМ,РХ'}	-42.30		
¹ J _{PM,PM} '	388.0	² J _{PX,PX} '	9.47	A	125.4

$[Cp*Fe{\eta^4-P_5(C_4H_8)}]$ (3)



Fig. S18. Experimental (top) and simulated (bottom) ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of 3.

Table S3. Chemical shifts and coupling constants obtained for	rom the simulation (R-factor =	⁻ 3.86 %) in Figure S18.
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J [Hz]		δ [ppm]			
¹ J _{PA,PX}	403.23	¹ J _{PM,PX}	408.00	X, X'	-117.4
¹ J _{PA,PX} '	403.18	¹ J _{PM',PX'}	400.51		
² J _{PA,PM}	14.30	² J _{PM',PX}	-41.46	M, M'	38.3
2 Ј _{РА,РМ} '	13.60	² J _{PM,PX} '	-34.16		
¹ Ј _{РМ,РМ} ,	382.76	² Ј _{РХ,РХ'}	9.47	А	145.4

 $[Cp*Fe{\eta^4-P_5(C_5H_{10})}]$ (4)



Fig. S19. Experimental (top) and simulated (bottom) ${}^{31}P{}^{1}H$ NMR (161.98 MHz, C₆D₆) spectrum of 4.

Table S4. Chemica	al shifts and couplir	g constants obtained	l from the simulation	(R-factor = 3	3.86 %) in Figure S19.
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J [Hz]				δ [ppm]]
¹ J _{PA,PX}	389.10	¹ J _{PM,PX}	396.66	X, X'	-136.0
¹ J _{PA,PX} '	388.90	¹ J _{PM',PX'}	402.12		
² J _{PA,PM}	11.83	² Ј_{РМ',РХ}	-34.40	M, M'	33.0
² Ј _{РА,РМ'}	11.20	² Ј _{РМ,РХ'}	-40.48		
¹ Ј _{РМ,РМ} '	380.94	² J _{PX,PX} '	5.27	А	127.4
				i	

 $[Cp^*Fe{\eta^4-P_5(C_6H_{12})}]$ (5)



Fig. S20. Experimental (top) and simulated (bottom) ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of 5.

 Table S5. Chemical shifts and coupling constants obtained from the simulation (R-factor = 3.86 %) in Figure S20.

J [Hz]				δ [ppm]]
¹ J _{PA,PX}	384.49	¹ J _{PM,PX}	407.78	X, X'	-128.5
¹ Ј _{РА,РХ'}	384.59	¹ Ј _{РМ',РХ'}	392.43		
² Ј_{РА,РМ}	11.65	² Ј _{РМ',РХ}	-45.00	M, M'	34.8
² Ј_{РА,РМ}'	12.96	² J _{PM,PX} '	-29.61		
¹ J _{PM,PM} '	380.03	² J _{PX,PX} '	3.36	А	145.0



Fig. S21. ${}^{31}P{}^{1}H$ NMR (161.98 MHz, C₆D₆) spectrum of **6**.





Fig. S22. ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of **7**.

PBn{(CH₂)₅} (8)



Fig. S23. ³¹P{¹H} NMR 161.98 MHz, C₆D₆) spectrum of **8**.



Fig. S24. ${}^{31}P{}^{1}H$ NMR (161.98 MHz, C₆D₆) spectrum of 9 (* = 5).

HP{(CH₂)₄} (10b)



Fig. S25. ${}^{31}P{}^{1}H$ NMR (161.98 MHz, C₆D₆) spectrum of 10b (* = OHP{(CH₂)₄}).



Fig. S26. ³¹P NMR (top) and ³¹P{¹H} NMR (button) (161.98 MHz, C₆D₆) spectrum of **10b**.



Fig. S27. ${}^{31}P{}^{1}H$ NMR (161.98 MHz, C₆D₆) spectrum of **6**'.





Fig. S28. ${}^{31}P{}^{1}H$ NMR (161.98 MHz, C₆D₆) spectrum of 7'.





Fig. S29. ${}^{31}P\{{}^{1}H\}$ NMR (161.98 MHz, C_6D_6) spectrum of 8'.

SPBn{(CH₂)₆} (9')



Fig. S30. ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of **9**' (* = **5**; # = OPBnz{(CH₂)₆}).

[({C₄H₈}PH)₂PtCl₂] (11)



Fig. S31. ^{31}P (top) and $^{31}P\{^{1}H\}$ (buttom) NMR (161.98 MHz, CD_2Cl_2) spectra (zoom-in) of 11.

¹³C NMR Spectra:

PBn{(CH₂)₃} (6)



Fig. S32. Experimental $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100.61 MHz, C_6D6) spectrum of 6.

PBn{(CH₂)₄} (7)



Fig. S33. Experimental ¹³C{¹H} NMR (100.61 MHz, C₆D₆) spectrum of **7**.

PBn{(CH₂)₅} (8)



Fig. S34. Experimental $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100.61 MHz, C₆D₆) spectrum of 8.



Fig. S35. Experimental ¹³C{¹H} NMR (100.61 MHz, C₆D₆) spectrum of **8**.

HP{(CH₂)₄} (10b)



Fig. S36. Experimental ¹³C{¹H} NMR (100.61 MHz, C₆D₆) spectrum of **10b**.

SPBn{(CH₂)₃} (6')



Fig. S37. Experimental $^{13}C\{^{1}H\}$ NMR (100.61 MHz, C₆D₆) spectrum of 6'.

SPBn{(CH₂)₄} (7')



Fig. S38. Experimental ${}^{13}C{}^{1}H$ NMR (100.61 MHz, C₆D₆) spectrum of 7'.

SPBn{(CH₂)₅} (8')



Fig. S39. Experimental $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100.61 MHz, C_6D_6) spectrum of 8'.

SPBn{(CH₂)₆} (9')



Fig. S40. Experimental $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100.61 MHz, C_6D_6) spectrum of 9'.

[({C₄H₈}PH)₂PtCl₂] (11)



Fig. S41. Experimental ${}^{13}C{}^{1}H$ NMR (100.61 MHz, CH₂Cl₂) spectrum of **11**.

3. Crystallographic details

 $[Cp*Fe{\eta^4-P_5((CH_2)_3Br)_2}]$ (1): The asymmetric unit contains one molecule of 1 without any disorder. The structure in the solid state is given in Figure S42. Crystallographic and refinement data are summarized in Table S6.

 $[Cp*Fe{\eta^4}-P_5(C_3H_6)]]$ (2): The asymmetric unit contains one molecule of 2 without any disorder. The structure in the solid state is given in Figure S43. Crystallographic and refinement data are summarized in Table S6.

 $[Cp*Fe{\eta^4-P_5(C_4H_8)}]$ (3): The asymmetric unit contains two molecules of 3 without any disorder. The structure in the solid state is given in Figure S44. Crystallographic and refinement data are summarized in Table S6.

 $[Cp*Fe{\eta^4-P_5(C_5H_{10})}]$ (4): The asymmetric unit contains one molecule of 4 without any disorder. The structure in the solid state is given in Figure S45. Crystallographic and refinement data are summarized in Table S6.

 $[Cp*Fe{\eta^4-P_5(C_6H_{12})}]$ (5): The asymmetric unit contains one molecule of 5. One Cp* ligand and three carbon atoms of the *cyclo*-hexyl substituent at the phosphorus ligand are disordered over two positions with a distribution of 57:43, respectively. To describe the disorders the SIMU restrain is applied. The structure in the solid state is given in **Figure S46**. Crystallographic and refinement data are summarized in **Table S6**.

SPBn{(CH₂)₃**} (6'):** The asymmetric unit contains two molecules of **6'** without any disorder. The structure in the solid state is given in **Figure S47**. Crystallographic and refinement data are summarized in **Table S7**.

SPBn{(CH₂)₄} (7'): The asymmetric unit contains one molecule of **7'** without any disorder. The structure in the solid state is given in **Figure S48**. Crystallographic and refinement data are summarized in **Table S7**.

SPBn{(CH₂)₅**} (8'):** The asymmetric unit contains two molecules of **8'** without any disorder. Since the measured crystal was twinned, a HKLF5 refinement was applied (BASF 0.444). The structure in the solid state is given in **Figure S49**. Crystallographic and refinement data are summarized in **Table S7**.

SPBn{(CH₂)₆} (9'): The asymmetric unit contains four molecules of 9' without any disorder. Since the measured crystal was twinned, a HKLF5 refinement was applied (BASF 0.171). The structure in the solid state is given in Figure S50. Crystallographic and refinement data are summarized in Table S7.

[({C₄H₈}PH)₂PtCl₂] (11):

The asymmetric unit contains half molecule of **11**. The platinum atom is located at the inversion center and is disordered over two positions (52:48). The structure in the solid state is given in **Figure S51**. Crystallographic and refinement data are summarized in **Table S7**.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC 2232605-2232614. These data can be obtained free of charge at <u>www.ccdc.cam.ac.uk/conts/retrieving.html</u> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>)

Compound	1	2	3	л	5
Compound	1	۷.	5	-	5
CCDC	2232605	2232606	2232607	2232608	2232609
Formula	$C_{16}H_{27}Br_2FeP_5$	$C_{13}H_{21}FeP_5$	$C_{14}H_{23}FeP_5$	$C_{15}H_{25}FeP_5$	$C_{16}H_{27}FeP_5$
D (4 700	4 505	4 4/7	4 400	4 400
$D_{calc.}$ / g Cm ^o	1.738	1.505	1.467	1.422	1.433
μ/mm^{\pm}	9.596	11.350	10.697	10.036	9.800
Formula Weight	589.89	388.00	402.02	416.05	430.07
Colour	dark green	green	dark green	dark green	red
Shape	block-shaped	plate-shaped	prism-shaped	block-shaped	plate-shaped
Size/mm ³	0.69×0.28×0.22	0.31×0.23×0.08	0.80×0.26×0.20	0.15×0.13×0.07	0.25×0.17×0.07
T/K	123.2(3)	123.00(10)	123.00(10)	123.01(10)	122.99(10)
Crystal System	monoclinic	orthorhombic	triclinic	orthorhombic	orthorhombic
Flack Parameter	/	-0.010(3)	/	0.003(2)	0.011(4)
Hooft Parameter	/	-0.0120(17)	/	-0.0053(15)	0.0033(14)
Space Group	P21/c	P212121	P-1	P212121	P212121
a/Å	13.35480(10)	8.47550(10)	9.4353(2)	9.17120(10)	9.2930(3)
b/Å	14.71550(10)	8.84210(10)	13.7981(3)	14.22010(10)	14.8439(5)
c/Å	11.90660(10)	22.8473(3)	15.3668(4)	14.9030(2)	14.4562(5)
$\alpha/^{\circ}$	90	90	69.087(2)	90	90
β/°	105.4910(10)	90	77.735(2)	90	90
γ/°	90	90	89.910(2)	90	90
V/Å ³	2254.91(3)	1712.20(4)	1820.09(8)	1943.58(4)	1994.14(12)
Ζ	4	4	4	4	4
Z'	1	1	2	1	1
Wavelength/Å	1.39222	1.54184	1.54184	1.54184	1.54184
Radiation type	CuKα	CuKα	CuKα	CuKα	CuKα
$\Theta_{min}/^{\circ}$	4.121	3.870	3.161	4.297	4.269
$\Theta_{max}/^{\circ}$	75.867	73.258	73.907	74.432	74.771
Measured Refl's.	32647	8327	23461	20511	15527
Ind't Refl's	6367	3197	6987	3935	4030
Refl's with $I > 2(I)$	6143	3167	6827	3896	3953
Rint	0.0743	0.0258	0.0262	0.0303	0.0273
Parameters	222	177	371	195	329
Restraints	0	0	0	0	312
Largest Peak	1.320	0.448	0.684	0.218	0.498
Deepest Hole	-1.068	-0.422	-0.804	-0.307	-0.518
GooF	1.053	1.036	1.058	1.076	1.200
wR ₂ (all data)	0.1335	0.0739	0.0978	0.0592	0.1093
wR2	0.1321	0.0737	0.0971	0.0590	0.1091
R_1 (all data)	0.0491	0.0274	0.0362	0.0271	0.0468
R1	0.0480	0.0272	0.0355	0.0267	0.0462

 Table S6. Crystallographic details of 1-5.

Compound	mpound 6' 7' 8'		9'	11	
CCDC	2232610	2232611	2232612	2232613	2232614
Formula	$C_{10}H_{13}PS$	$C_{11}H_{15}PS$	$C_{12}H_{17}PS$	$C_{13}H_{19}PS$	$C_8H_{18}CI_2P_2Pt$
D _{calc.} / g cm ⁻³	1.302	1.282	1.252	1.245	2.277
µ/mm⁻¹	3.898	3.615	3.342	3.156	11.502
Formula Weight	196.23	210.26	224.28	238.31	442.15
Colour	colourless	colourless	colourless	colourless	colourless
Shape	plate-shaped	needle-shaped	needle-shaped	block-shaped	block-shaped
Size/mm ³	0.25×0.16×0.04	0.22×0.04×0.03	0.21×0.05×0.03	0.34×0.06×0.05	0.08×0.05×0.04
T/K	123.00(10)	122.98(10)	122.97(11)	100.02(10)	100.01(12)
Crystal System	monoclinic	orthorhombic	monoclinic	monoclinic	tetragonal
Flack Parameter	/	-0.04(5)	-0.01(3)	0.171(15)	-0.013(3)
Hooft Parameter	/	-0.101(13)	-0.009(5)	-0.003(4)	0.0048(16)
Space Group	P21/c	Pna21	Рс	P21	I-4c2
a/Å	16.77790(10)	16.0552(8)	19.0300(5)	12.92590(10)	11.67740(10)
b/Å	10.42680(10)	10.9392(5)	6.1666(2)	9.99760(10)	11.67740(10)
c/Å	11.69300(10)	6.2040(3)	10.2233(2)	19.73260(10)	18.9131(2)
$\alpha/^{\circ}$	90	90	90	90	90
β/°	101.7780(10)	90	97.346(2)	94.2160(10)	90
γ/°	90	90	90	90	90
V/Å ³	2002.50(3)	1089.61(9)	1189.86(6)	2543.10(3)	2579.02(5)
Ζ	8	4	4	8	8
Ζ'	2	1	2	4	0.5
Wavelength/Å	1.54184	1.54184	1.54184	1.54184	0.71073
Radiation type	CuKα	CuKα	CuKα	CuKα	ΜοΚα
$\Theta_{min}/^{\circ}$	2.690	4.892	2.341	2.245	2.467
$\Theta_{max}/^{\circ}$	74.370	74.471	74.906	74.952	32.546
Measured Refl's.	34643	8454	6716	54571	192001
Ind't Refl's	4062	1811	6716	10219	2350
Refl's with I > 2(I)	3934	1706	6045	9952	2300
Rint	0.0226	0.0444	•	0.0377	0.0693
Parameters	217	118	254	542	69
Restraints	0	1	2	1	0
Largest Peak	0.455	0.535	1.014	0.603	1.857
Deepest Hole	-0.293	-0.465	-0.408	-0.452	-0.412
GooF	1.049	1.108	1.057	1.027	1.081
wR2 (all data)	0.0751	0.1467	0.1704	0.1018	0.0499
wR ₂	0.0746	0.1439	0.1648	0.1013	0.0495
R₁ (all data)	0.0279	0.0539	0.0654	0.0364	0.0200
R ₁	0.0272	0.0514	0.0599	0.0358	0.0195

Table S7. Crystallographic details of 6'-9' and 11.



Fig. S42. Molecular structure of **1** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
Br1	C13	1.954(3)	P1	C11	1.825(3)
Br2	C16	1.967(3)	P4	P5	2.1509(10)
P2	P1	2.1451(8)	P4	P3	2.1540(10)
P2	P3	2.1478(9)	P1	C14	1.822(3)
P1	P5	2.1423(8)			

Table S8. Selected bond lengths of 1.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
P3	P4	Fe1	62.62(3)	C11	P1	P2	106.44(9)
P1	P5	Fe1	86.71(3)	C11	P1	P5	109.93(9)
P1	P5	P4	96.93(3)	P5	P4	Fe1	62.09(2)
P4	P5	Fe1	62.98(3)	P5	P4	P3	105.06(4)
P2	P3	Fe1	62.65(3)	P4	P3	Fe1	62.60(3)
P2	P3	P4	104.37(4)				

 $[Cp^*Fe{\eta^4-P_5(C_3H_6)}]$ (2)



Fig. S43. Molecular structure of **2** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

 Table S10.
 Selected bond lengths of 2.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
P2	P1	2.1261(12)	C11	C12	1.524(6)
P2	P3	2.1358(12)	C13	C12	1.536(5)
P1	P5	2.1384(12)	P4	P5	2.1396(12)
P1	C11	1.865(3)	P3	P4	2.1392(12)
P1	C13	1.835(4)			

Table S11. Selected angles of 2.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
P1	P2	P3	102.31(5)	C13	P1	P5	107.67(13)
P2	P1	P5	101.66(4)	C13	P1	C11	78.86(17)
C11	P1	P2	126.19(14)	P2	P3	P4	106.16(5)
C11	P1	P5	126.09(14)	C12	C11	P1	88.9(2)
C13	P1	P2	111.56(13)	C12	C13	P1	89.7(2)
C11	C12	C13	100.3(3)				

[Cp*Fe{η⁴-P₅(C₄H₈)}] (3):



Fig. S44. Molecular structure of **3** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. **Table S12.** Selected bond lengths of **3**.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
P5	P4	2.1385(8)	C14	C13	1.536(3)
P5	P1	2.1383(8)	C11	C12	1.526(3)
P4	P3	2.1498(9)	C13	C12	1.527(3)
P1	P2	2.1388(8)	P1	C11	1.843(2)
P1	C14	1.841(2)	P2	P3	2.1434(9)

Table S13. Selected angles of 3	3.	•
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Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C13	C14	P1	105.91(16)	C14	P1	C11	94.84(11)
C12	C11	P1	104.40(16)	C11	C12	C13	106.9(2)
C12	C13	C14	107.25(19)				

$[Cp^*Fe{\eta^4-P_5(C_5H_{10})}]$ (4)



Fig. S45. Molecular structure of **4** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
P1	P5	2.1409(12)	P2	P3	2.1465(13)
P1	P2	2.1360(12)	P4	P3	2.1529(17)
P1	C15	1.816(3)	C15	C14	1.534(5)
P1	C11	1.816(4)	C11	C12	1.533(5)
P5	P4	2.1380(14)	C14	C13	1.517(6)
C12	C13	1.518(7)			

 Table S14. Selected bond lengths of 4.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C14	C15	P1	111.3(3)	P2	P1	P5	98.92(5)
C12	C11	P1	110.6(2)	C15	P1	P5	106.82(13)
C13	C14	C15	113.3(4)	C15	P1	P2	109.28(13)
C13	C12	C11	112.0(3)	C11	P1	P5	119.20(13)
C14	C13	C12	113.9(4)	C11	P1	P2	119.99(13)
C11	P1	C15	102.05(18)				

Table S15. Selected angles of 4.

 $[Cp^*Fe{\eta^4-P_5(C_6H_{12})}]$ (5)



Fig. S46. Molecular structure of **5** (left part) in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. The disorder is highlighted blue (Part 1) and green (Part 2) (right part).

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
	Part 1 - :	5		Part 2 - :	5
C12	C13A	1.40(4)	C13B	C14B	1.49(4)
C14A	C15A	1.51(3)	C15B	C14B	1.54(2)
C14A	C13A	1.59(4)	C16	C15B	1.61(2)
C16	C15A	1.46(2)	C12	C13B	1.60(3)
P1	P5	2.139(3)	C12	C11	1.538(11)
P1	C16	1.819(7)	P3	P4	2.153(3)
P1	C11	1.823(7)	P5	P4	2.140(3)
P2	P3	2.143(3)	P1	P2	2.143(2)

Table S16. Selected bond lengths of 5.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
	P	Part 1 – 5			F	Part 2 – 5	
C15A	C16	P1	119.0(11)	C15B	C16	P1	113.4(9)
C13A	C12	C11	122.0(14)	C11	C12	C13B	112.3(13)
C15A	C14A	C13A	115.1(17)	C14B	C13B	C12	118(2)
C16	C15A	C14A	115.8(17)	C14B	C15B	C16	113.7(13)
C12	C13A	C14A	115(2)	C13B	C14B	C15B	114.4(14)
C12	C11	P1	112.4(5)	-T			

Table S17. Selected angles of 5.

SPBn{(CH₂)₃} (6')



Fig. S47. Molecular structure of 6' in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S18	. Selected	bond	lengths	of 6' .
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Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
P1	S1	1.9538(5)	C8	C9	1.554(2)
P1	C1	1.8273(13)	C10	C9	1.560(2)
P1	C10	1.8251(14)	P1	C8	1.8232(14)

Table S19. Selected angles of 6'.									
Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]		
C1	P1	S1	115.06(5)	C8	C9	C10	99.23(11)		
C10	P1	S1	120.94(5)	C9	C8	P1	89.43(9)		
C10	P1	C1	106.73(6)	C9	C10	P1	89.18(8)		
C8	P1	S1	120.30(5)	C8	P1	C10	81.12(7)		
C8	P1	C1	107.58(7)						

SPBn{(CH₂)₄} (7')



Fig. S48. Molecular structure of **7'** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. **Table S20.** Selected bond lengths of **7'**.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
P1	S1	1.9557(16)	C10	C9	1.514(8)
P1	C8	1.831(5)	C11	C10	1.521(9)
P1	C11	1.818(7)	C8	C9	1.540(8)
P1	C1	1.826(5)			

Table	S21.	Selected	angle	es of	7	'
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Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C8	P1	S1	116.16(17)	C9	C8	P1	104.8(4)
C11	P1	S1	115.39(19)	C10	C11	P1	105.6(4)
C11	P1	C8	95.4(3)	C9	C10	C11	107.9(5)
C11	P1	C1	107.9(3)	C10	C9	C8	106.6(4)
C1	P1	C8	105.3(2)				

SPBn{(CH₂)₅} (8')



Fig. S49. Molecular structure of 8' in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S22	. Selected	bond	lengths	of	8
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Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
P2	C18	1.827(8)	C18	C19	1.508(11)
P2	C17	1.802(7)	C14	C15	1.531(11)
P2	C13	1.789(8)	C14	C13	1.507(10)
P2	S2	1.963(3)	C16	C15	1.513(11)
C16	C17	1.525(10)			

Table S23. Selected angles of 8'.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C18	P2	S2	114.2(2)	C15	C16	C17	113.2(6)
C17	P2	C18	107.0(3)	C13	C14	C15	112.5(6)
C17	P2	S2	112.8(2)	C16	C15	C14	113.8(6)
C13	P2	C18	105.6(4)	C16	C17	P2	110.0(5)
C13	P2	C17	101.9(4)	C14	C13	P2	111.6(5)
C13	P2	S2	114.3(2)	C19	C18	P2	113.3(5)





Fig. S50. Molecular structure of **9**' in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S24. Selected bond lengths of 9'.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
S4	P4	1.9673(9)	C42	C43	1.528(4)
P4	C41	1.815(3)	C45	C46	1.537(4)
P4	C47	1.825(3)	C45	C44	1.537(5)
P4	C46	1.816(3)	C43	C44	1.538(4)
C41	C42	1.532(4)			

Table S25. Selected angles of 9'.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C41	P4	S4	114.30(9)	C43	C42	C41	115.5(2)
C41	P4	C47	105.17(13)	C46	C45	C44	117.5(3)
C41	P4	C46	105.78(13)	C42	C43	C44	113.6(2)
C47	P4	S4	114.04(9)	C45	C46	P4	116.1(2)
C46	P4	S4	113.92(10)	C45	C44	C43	117.7(2)
C46	P4	C47	102.49(13)				

$[({C_4H_8}PH)_2PtCl_2](11)$



Fig. S51. Molecular structure of **11** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. **Table S26.** Selected bond lengths of **11**.

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
Pt01	P003	2.2263(14)	P003	C006	1.831(5)
Pt01	Cl02	2.3600(14)	C005	C2	1.519(9)
P003	C005	1.823(4)	C006	C1	1.529(8)
C1	C2	1.503(12)			

Table S27. Selected angles of 11.

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
Cl02 P003	Pt01 Pt01	P003 Cl02 ¹	87.30(4) 179.39(5)	C005 C006	P003 P003	C006 Pt01	95.5(2) 116.43(19)
C005	P003	Pt01	117.50(19)				

¹1-Y,1-X,1/2-Z

4. Additional Information





Fig. S52. ³¹P{¹H} NMR (161.98 MHz, C_6D_6) spectrum of the reaction of I with 1,5-dibromopentane (* = unidentified sideproduct).



Fig. S53. ³¹P{¹H} NMR (161.98 MHz, C₆D₆) spectrum of the reaction of I with 1,6-dibromohexane (* = unidentified sideproduct).







Fig. S55. ³¹P{¹H} NMR (161.98 MHz, THF-d₈) spectrum of the reaction of **3** with LiAlH₄ and distillation of the phospholane (HP{(CH₂)₄}, **10b**) (PPh₃ capillary in toluene-d₈, c = 0.2 mol/L, internal reference).



Fig. S56. ³¹P NMR (top) and ³¹P{¹H} NMR (bottom) (161.98 MHz, THF) spectrum of the reaction of **4** with LiAlH₄ and distillation of the phosphinane HP{(CH₂)₅} (PPh₃ capillary in toluene-d₈, c = 0.2 mol/L, internal reference).



Fig. S57. Cutout: ³¹P NMR (top) and ³¹P{¹H} NMR (bottom) (161.98 MHz, THF-d₈) spectrum of the reaction of **5** with LiAlH₄: Phosphepane HP{(CH₂)₆} (PPh₃ capillary in toluene-d₈, c = 0.2 mol/L, internal reference). (*, # = unidentified sideproducts).



Fig. S58. Cutout: ³¹P NMR spectrum (top) and ³¹P{¹H} NMR (bottom) (161.98 MHz, THF-d₈) spectrum of the reaction of **2** with LiAlH₄ and distillation.

5. References

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