Electronic Supplementary Information

Reductive P-P Coupling of Primary and Secondary Phosphines mediated by N-Heterocyclic Carbenes

*Heidi Schneider, David Schmidt, and Udo Radius**

Heidi Schneider, Dr. David Schmidt, Prof. Dr. Udo Radius
Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.
* Author for correspondence. E-mail: u.radius@uni-wuerzburg.de

The Supporting Information contents:

1. Additional Figures and Tables

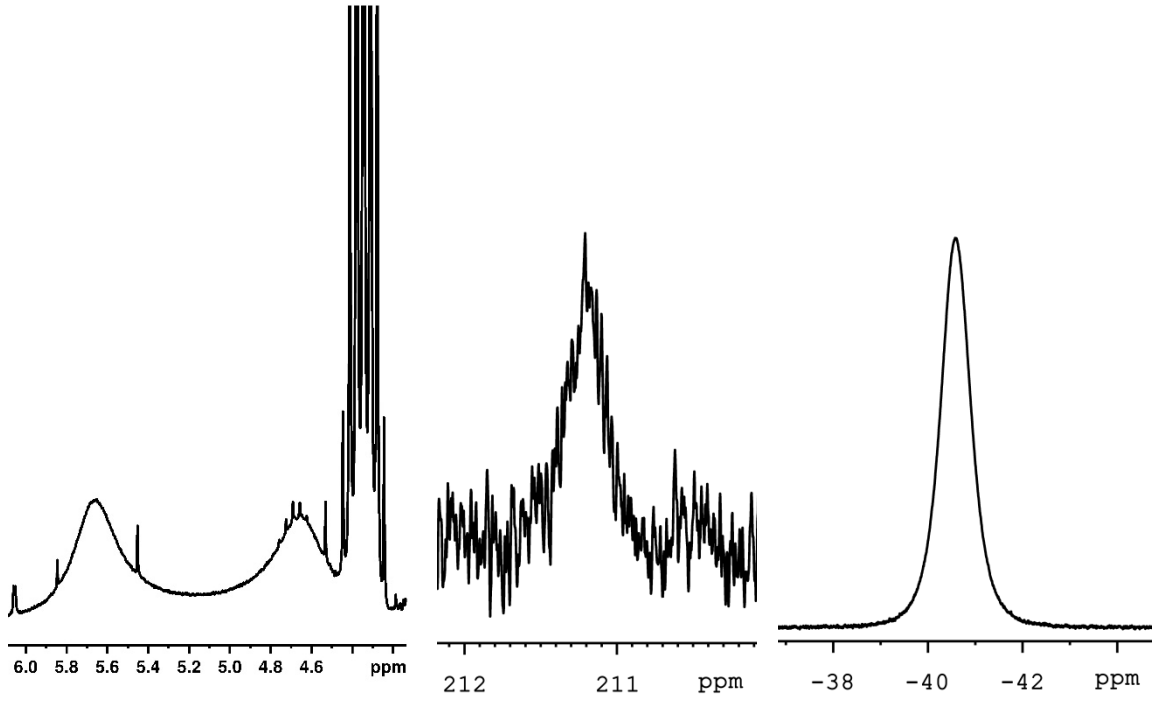

Figure S1. Segments of ^{1}H, ^{13}C and ^{31}P NMR spectra for the reaction of Ph_2PH with *i*Pr_2Im at room temperature, directly after addition in d_8-toluene.

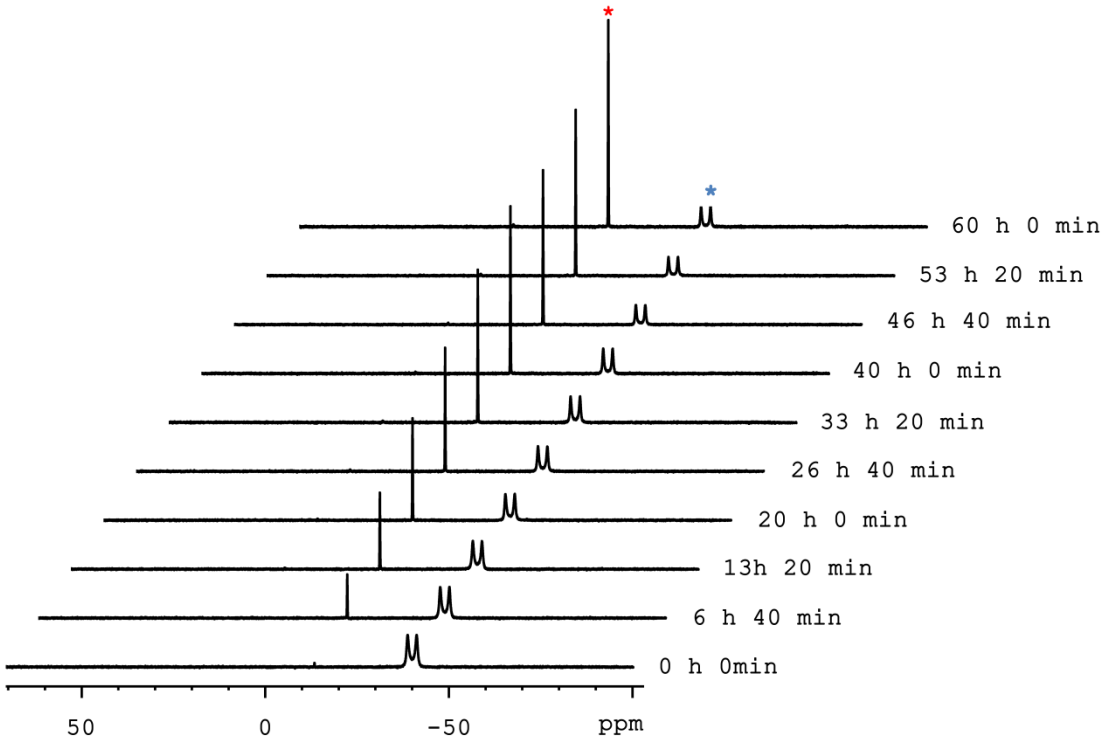

Figure S2. Time dependent ^{31}P NMR spectra for the reaction of Ph_2PH with *i*Pr_2Im to give P_2Ph_4 **2** at 95 °C in d_8-toluene (blue asterisk: Ph_2PH; red asterisk:P_2Ph_4 **2**).

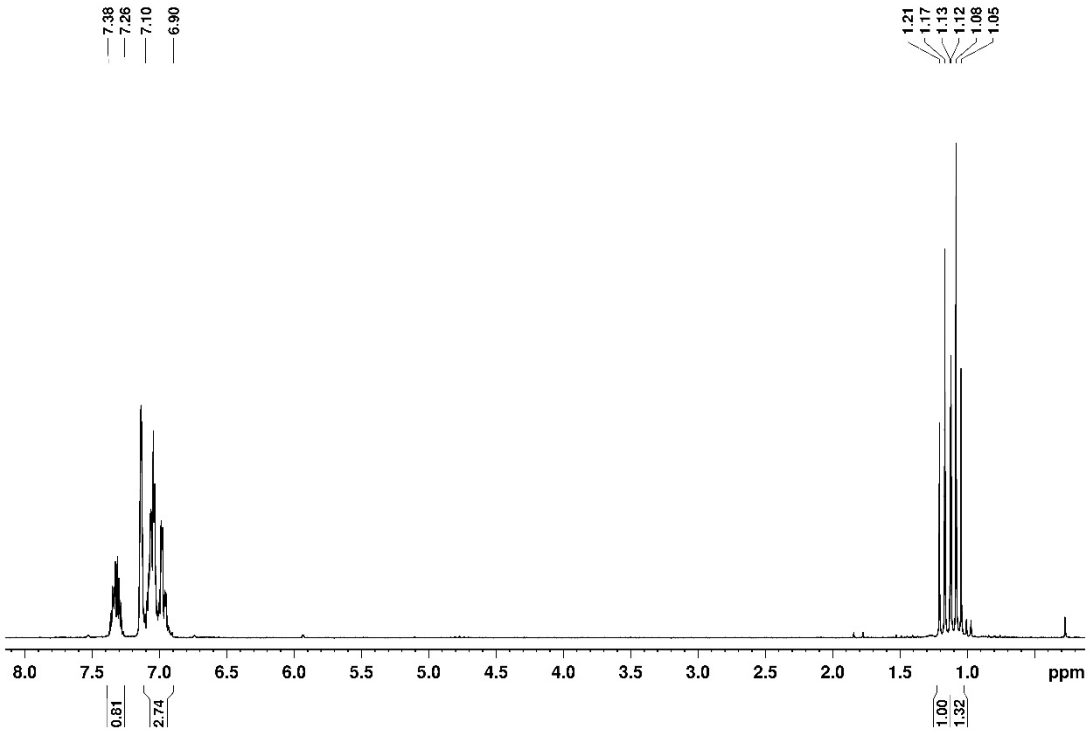

Figure S3. ^{1}H NMR spectrum of $P_2Me_2Ph_2$ **3** in C_6D_6.

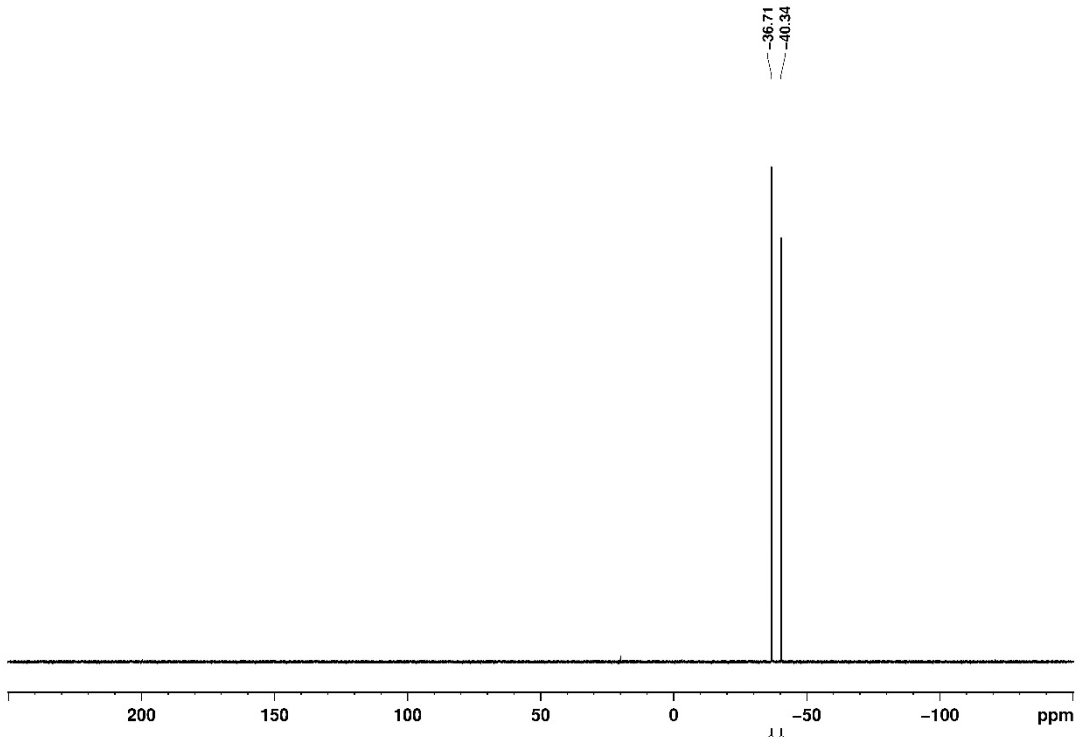

Figure S4. ^{31}P NMR spectrum of $P_2Me_2Ph_2$ **3** in C_6D_6.

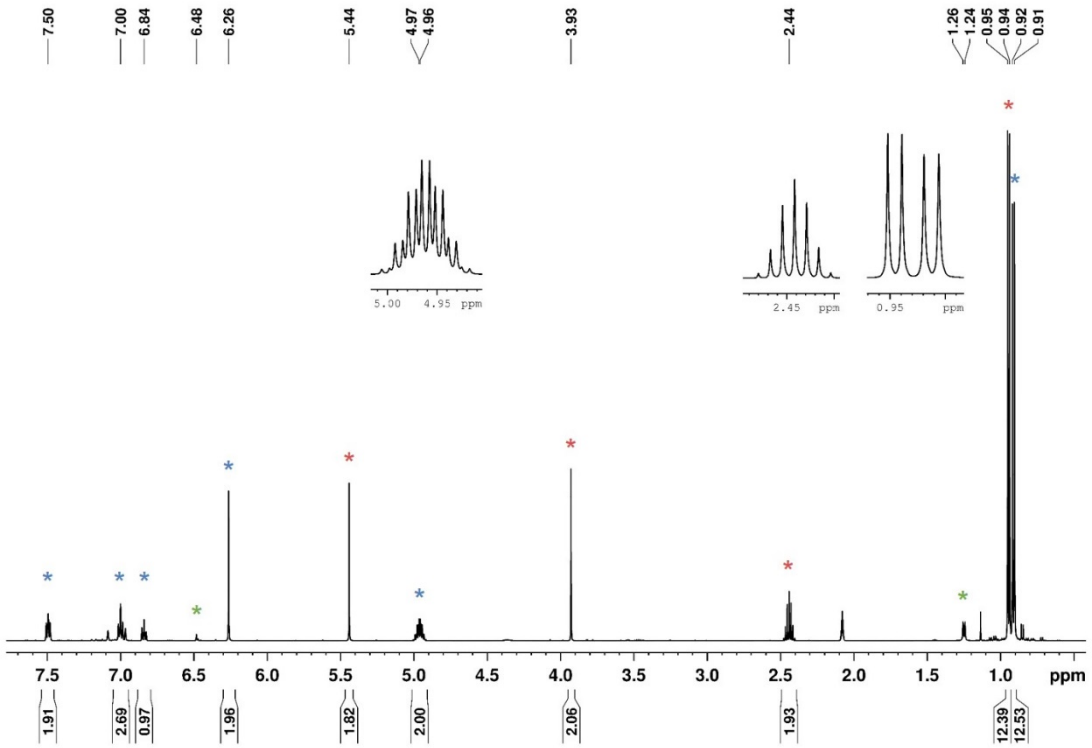

Figure S5. ^{1}H NMR spectrum for the reaction of 1 equivalent of $PhPH_2$ with 2 equivalents of *i*Pr_2Im to *i*Pr_2ImH_2 **1** and *i*Pr_2Im=PPh **4** after 5 h at 105 °C in d_8-toluene (blue asterisk: *i*Pr_2Im=PPh **6**; red asterisk: *i*Pr_2ImH_2 **1**; green asterisk: remaining *i*Pr_2Im)

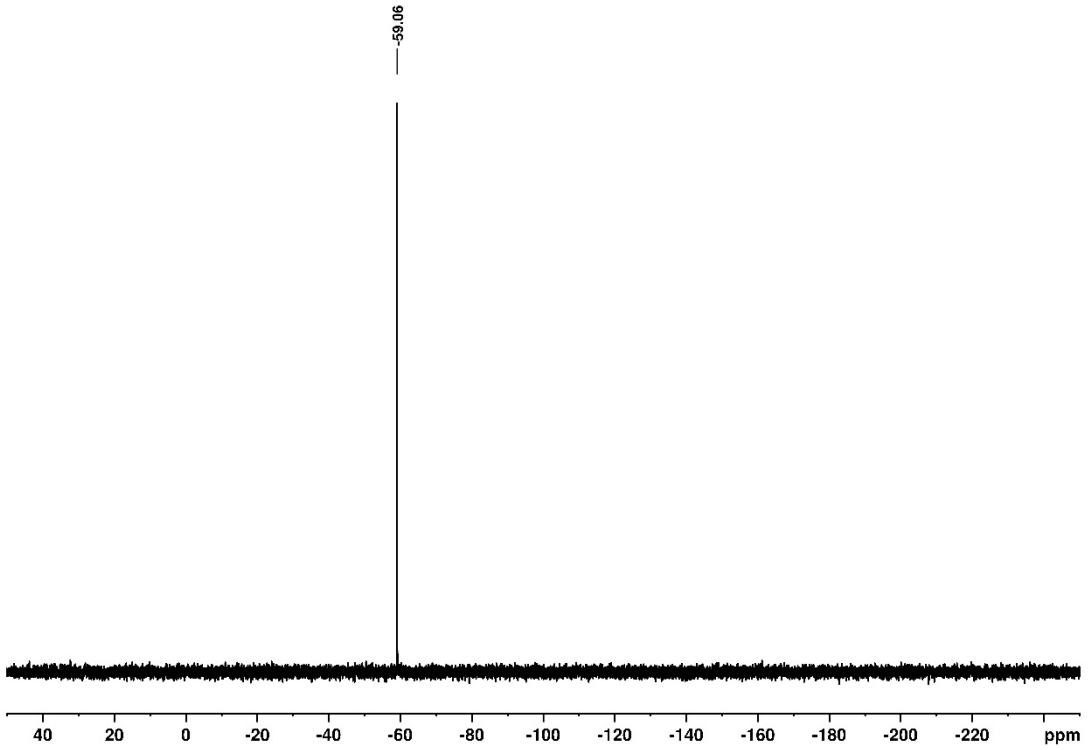

Figure S6. ^{31}P NMR spectrum for the reaction of 1 equivalent of $PhPH_2$ with 2 equivalents of *i*Pr_2Im to *i*Pr_2ImH_2 **1** and *i*Pr_2Im=PPh **4** after 5 h at 105 °C in d_8-toluene.

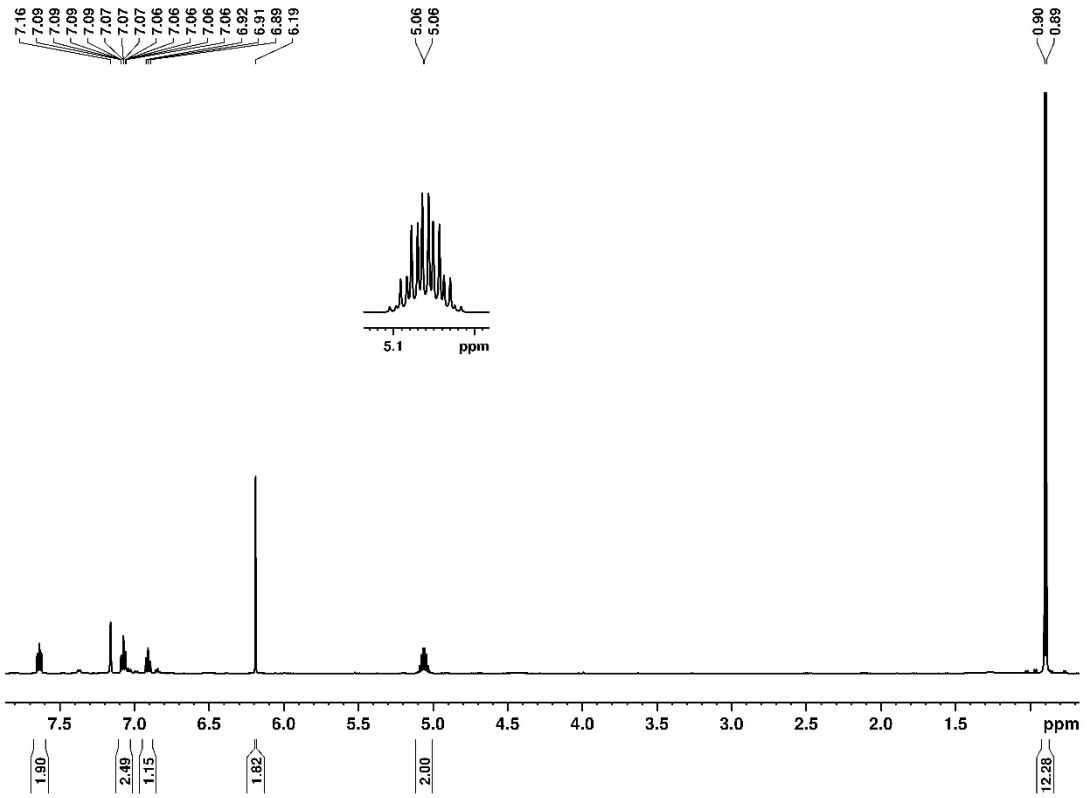

Figure S7. ^{1}H NMR spectrum of isolated *i*Pr_2Im=PPh **4** in C_6D_6.

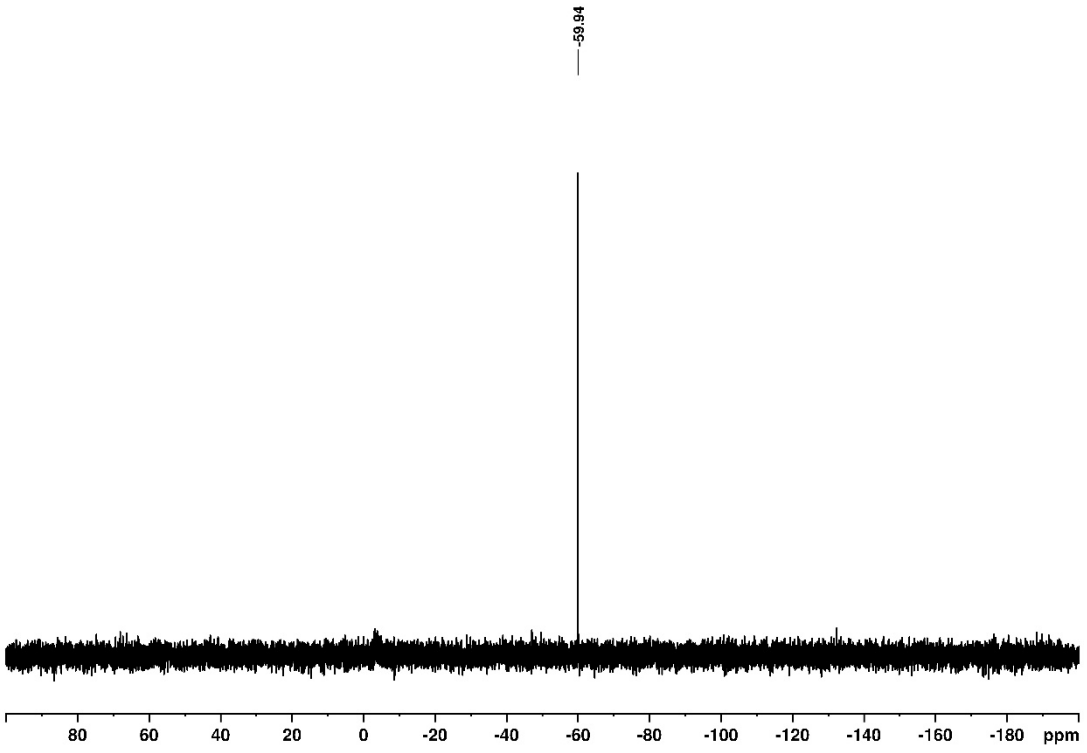

Figure S8. ^{31}P NMR spectrum of isolated *i*Pr_2Im=PPh **4** in C_6D_6.

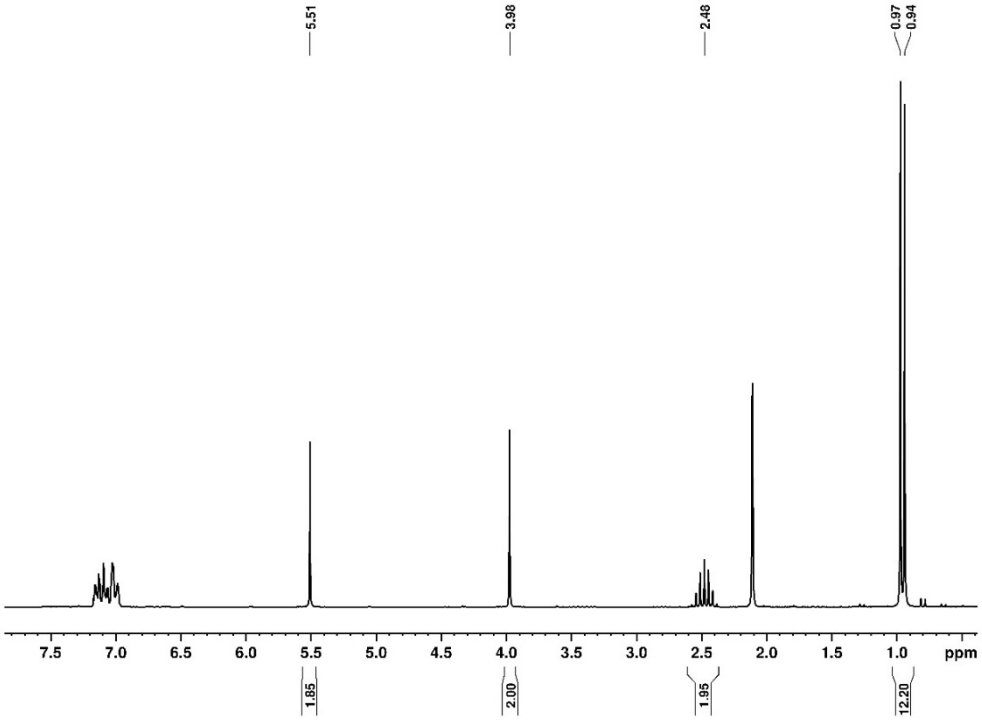

Figure S9. ^{1}H NMR spectrum of isolated *i*Pr_2ImH_2 **1** (with remaining toluene) in C_6D_6

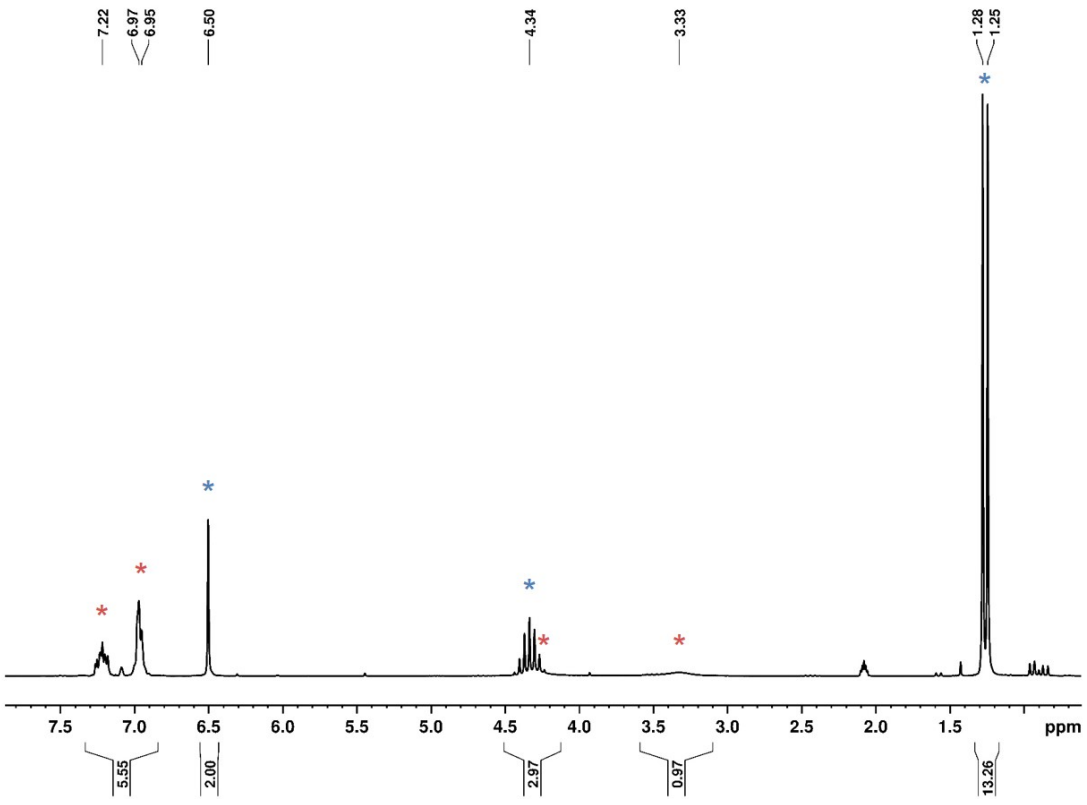

Figure S10. ^{1}H NMR spectrum of the reaction of 1 equivalent of $PhPH_2$ with 1 equivalent of *i*Pr_2Im immediately after addition at room temperature in d_8-toluene (blue asterisk: *i*Pr_2Im; red asterisk: $PhPH_2$).

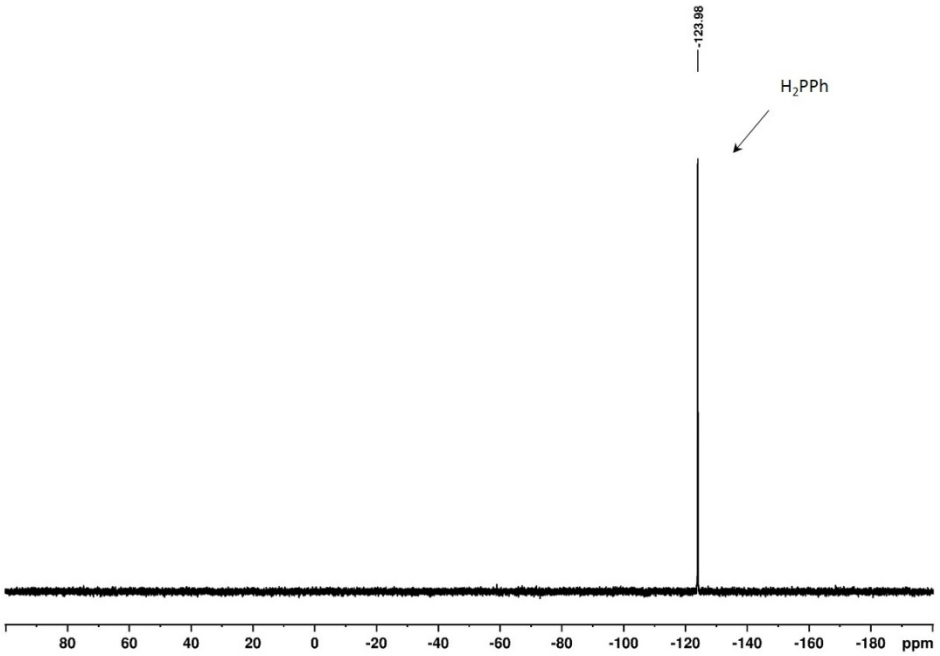

Figure S11. ^{31}P NMR spectrum of the reaction of 1 equivalent of $PhPH_2$ with 1 equivalent of *i*Pr_2Im immediately after addition at room temperature in d_8-toluene.

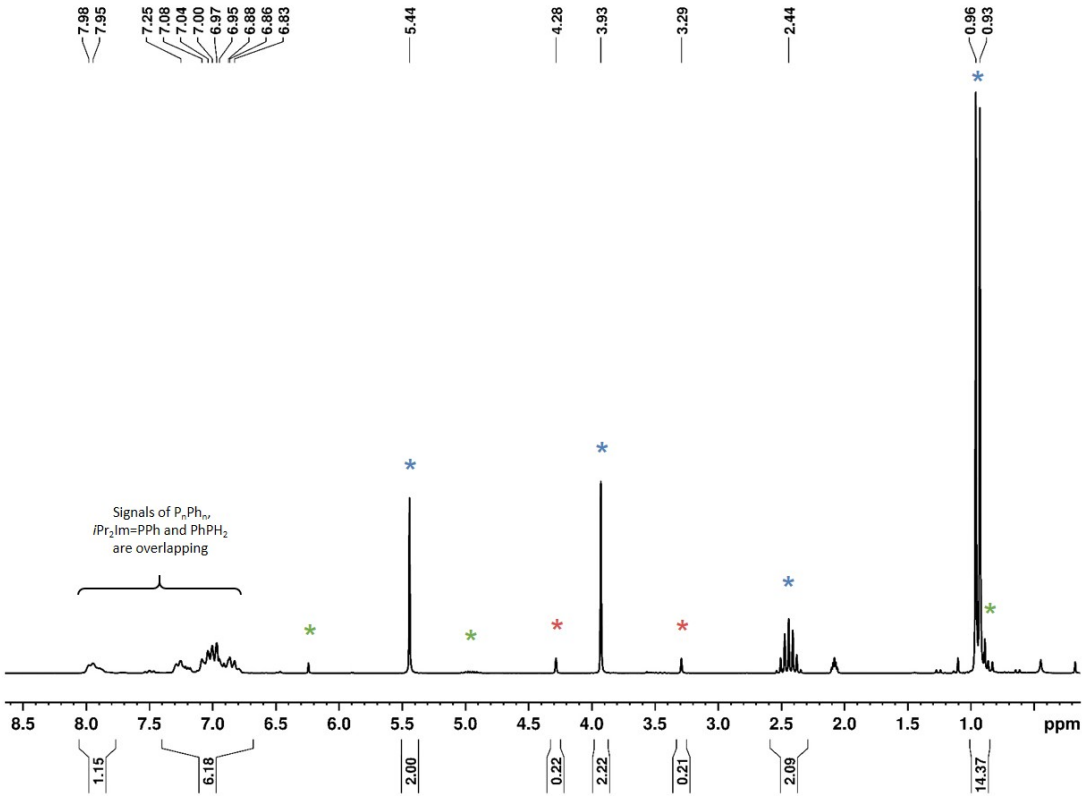

Figure S12. ^{1}H NMR spectrum of the reaction of 1 equivalent of $PhPH_2$ with 1 equivalent of *i*Pr_2Im after 2 h at 105 °C in d_8-toluene. (blue asterisk: *i*Pr_2ImH_2 **1**; red asterisk: $PhPH_2$; green asterisk: *i*Pr_2Im=PPh **4**)

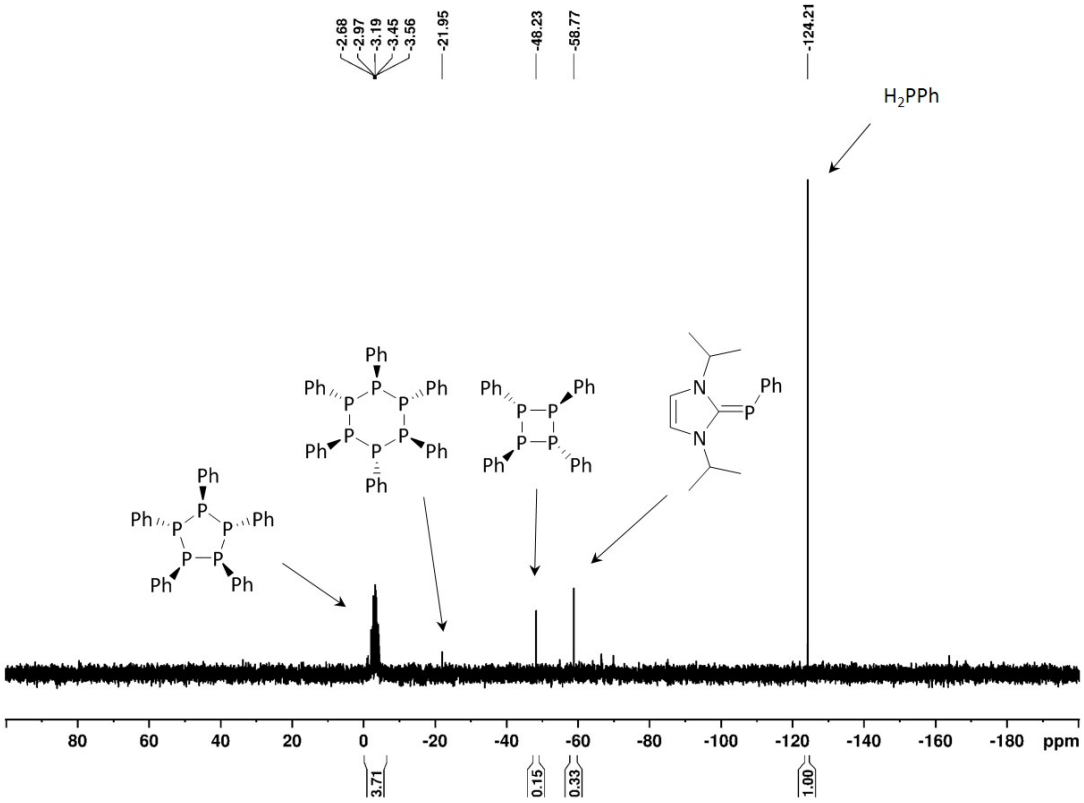

Figure S13. ^{31}P NMR spectrum of the reaction of 1 equivalent of $PhPH_2$ with 1 equivalent of *i*Pr_2Im after 2 h at 105 °C in d_8-toluene. Literature known ^{31}P NMR signals: P_4Ph_4 -48.0 [S6], P_6Ph_6 -21.2 [S5d]; P_5Ph_5 -5.0 – -2.8 [S7]

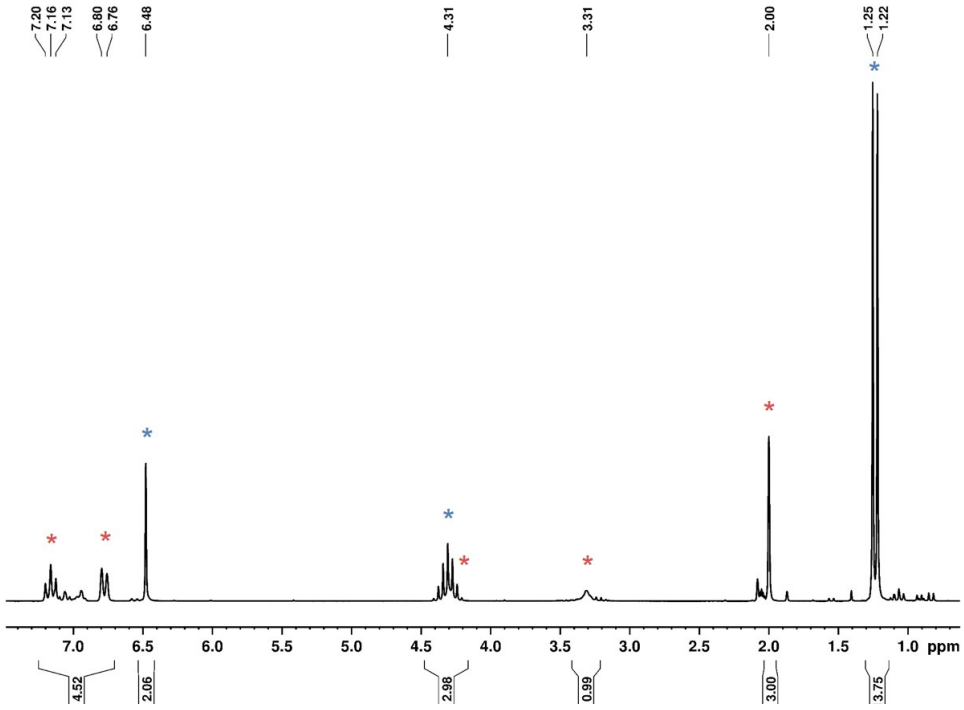

Figure S14. ^{1}H NMR spectrum of the reaction of 1 equivalent of *p*TolPH_2 with 1 equivalent of *i*Pr_2Im immediately after addition at room temperature in d_8-toluene. (blue asterisk: *i*Pr_2Im; red asterisk: *p*TolPH_2).

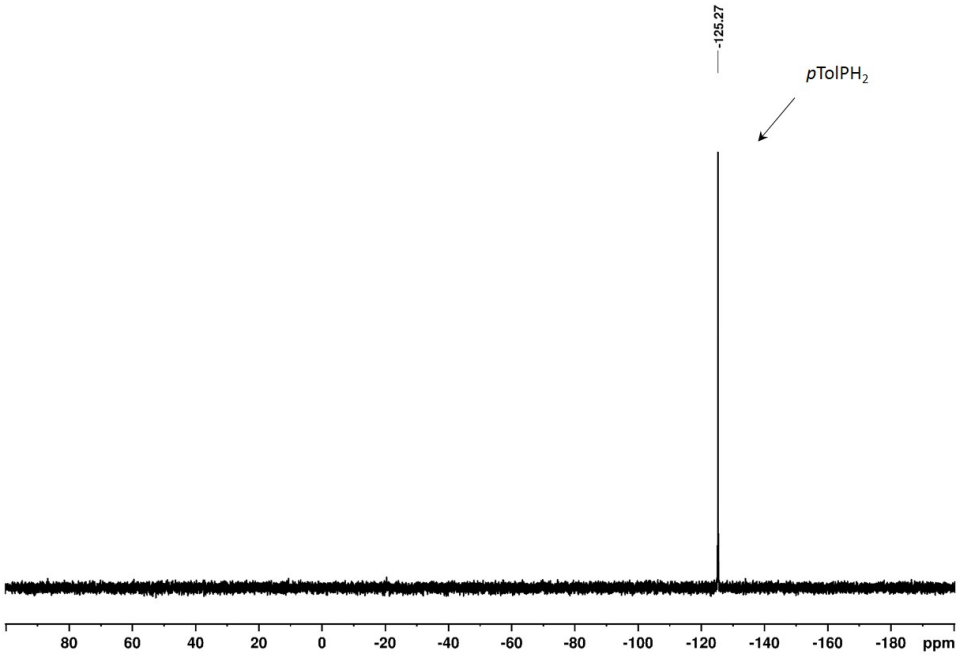

Figure S15. ^{31}P NMR spectrum of the reaction of 1 equivalent of *p*TolPH$_2$ with 1 equivalent of *i*Pr$_2$Im immediately after addition at room temperature in d_8-toluene.

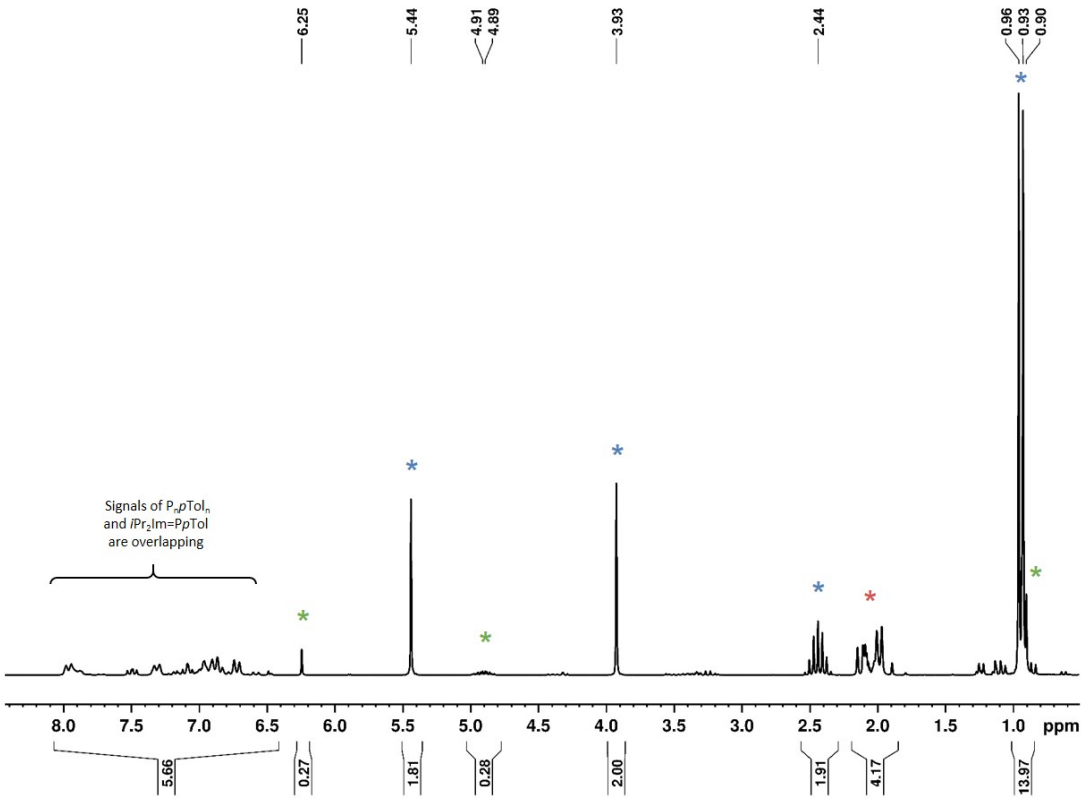

Figure S16. ^{1}H NMR spectrum of the reaction of 1 equivalent of *p*TolPH$_2$ with 1 equivalent of *i*Pr$_2$Im after 2 h at 105 °C in d_8-toluene. (blue asterisk: *i*Pr$_2$ImH$_2$ **1**; red asterisk: P$_n$(*p*Tol)$_n$; green asterisk: *i*Pr$_2$Im=P*p*Tol)

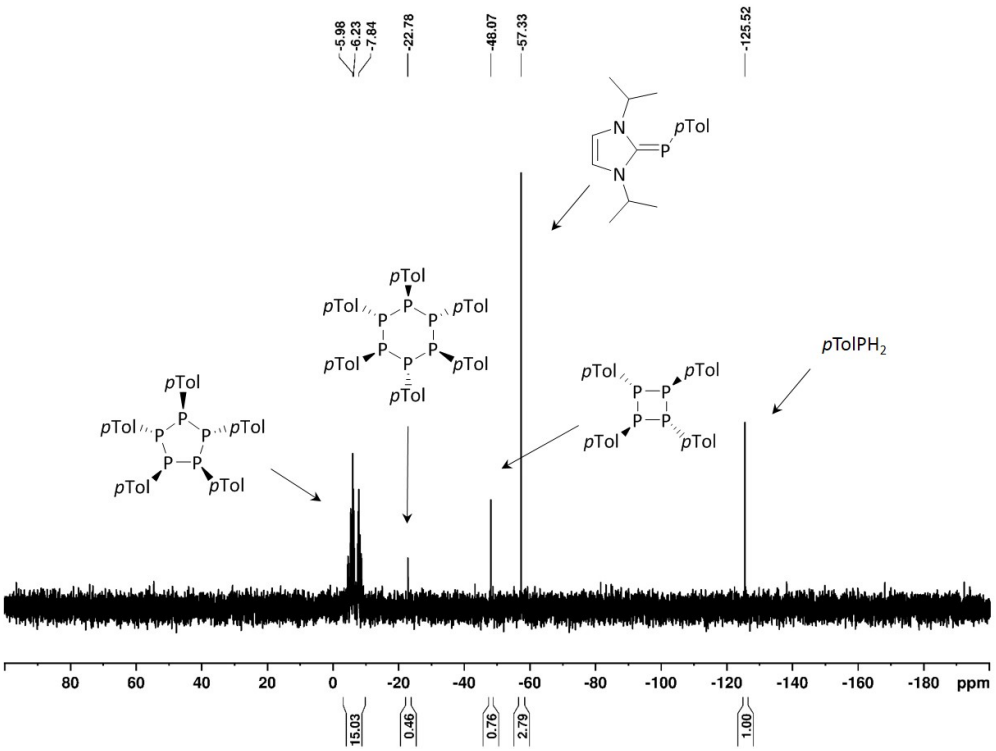

Figure S17. ^{31}P NMR spectrum of the reaction of 1 equivalent of *p*TolPH$_2$ with 1 equivalent of *i*Pr$_2$Im after 2 h at 105 °C in d_8-toluene.

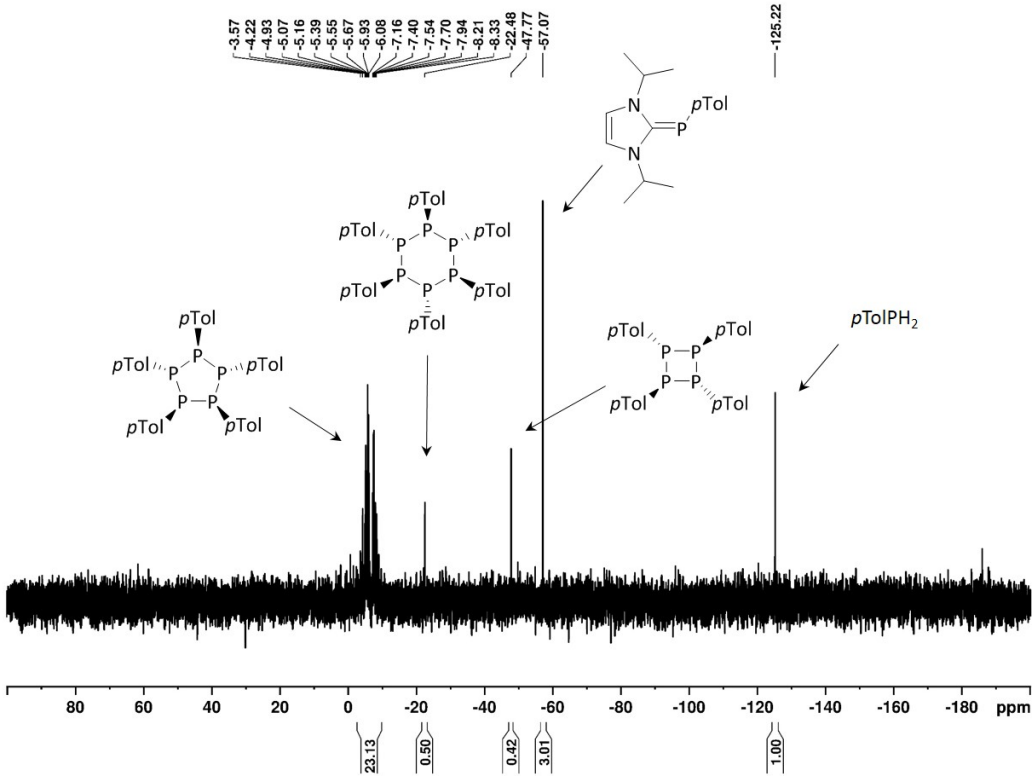

Figure S18. ^{31}P NMR spectrum of the reaction of 1 equivalent of *p*TolPH$_2$ with 1 equivalent of *i*Pr$_2$Im after 4 h at 105 °C in d_8-toluene.

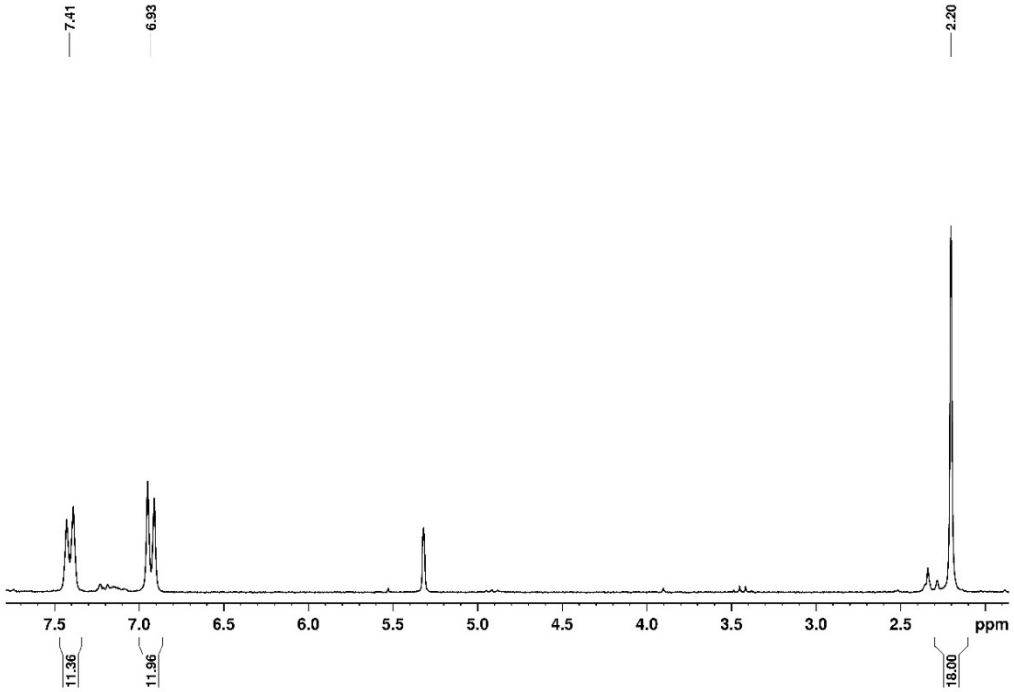

Figure S19. ^{1}H NMR spectrum of $P_6(p\text{Tol})_6$ **6** in CD_2Cl_2.

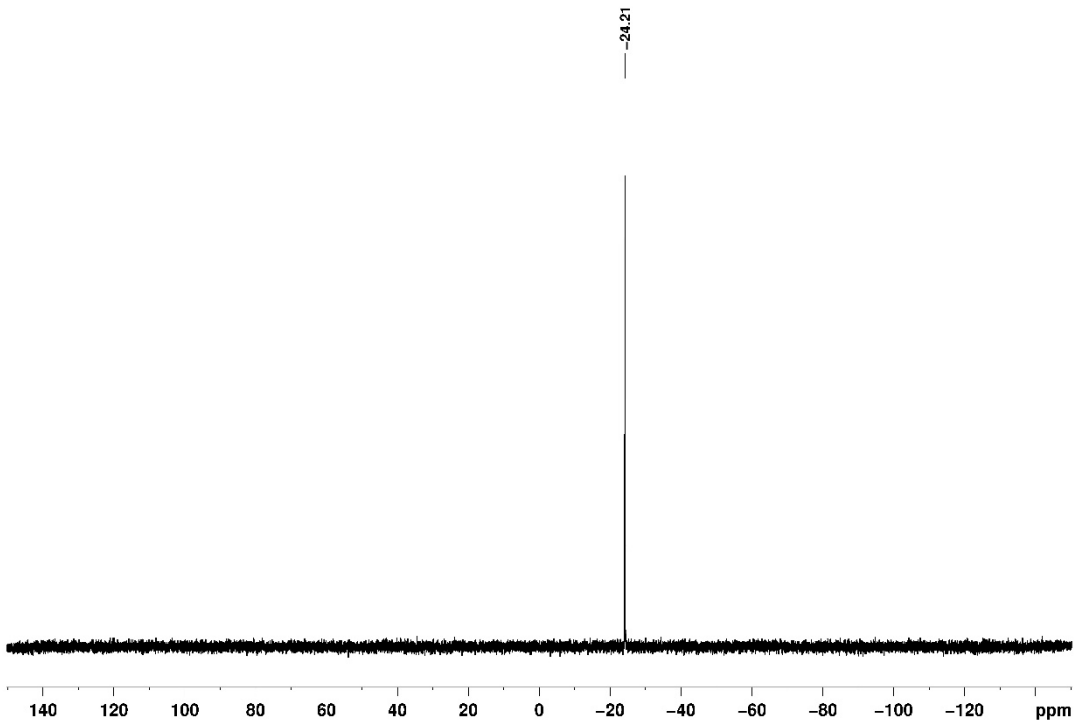

Figure S20. ^{31}P NMR spectrum of $P_6(p\text{Tol})_6$ **6** in CD_2Cl_2.

2. Experimental Details

General Considerations.

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques as reported previously. [SI1] Elemental analysis were performed in the microanalytical laboratory of the authors department with an Elementar vario micro cube. NMR spectra were recorded on a Bruker Avance 200 (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz; ^{31}P, 80.9 MHz), Bruker Avance 500 (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz), using C_6D_6, CD_2Cl_2 and toluene-d_8 as the solvent. Assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H, ^{13}C,^{1}H and ^{31}P,^{1}H correlation experiments. ^{13}C NMR spectra are broad-band proton-decoupled (^{13}C{^{1}H}). Assignment of the ^{13}C NMR data was supported by ^{13}C,^{1}H correlation experiments. Chemical shifts are listed in parts per million (ppm) and were determined relative to internal C_6D_5H (^{1}H, δ = 7.16; C_6D_6), $CDHCl_2$ (^{1}H, δ = 5.32; CD_2Cl_2) and d_7-toluene (^{1}H, δ = 2.08; d_8-toluene) or to natural-abundance carbon resonances C_6D_6 (^{13}C, δ = 128.06; C_6D_6), CD_2Cl_2 (^{13}C, δ = 53.84; CD_2Cl_2) and toluene-d_8 (^{13}C, δ = 20.43; d_8-toluene) or external 85% H_3PO_4 (^{31}P, δ = 0). Coupling constants are quoted in Hertz. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer as solids by using an ATR unit and are reported in cm^{-1}. The NHC *i*Pr$_2$Im (1,3-di-*iso*-propyl-imidazolin-2-ylidene) has been prepared according to a published procedure. [S2]

Synthesis of P_2Ph_4 2: Diphenylphosphine (2.32 g, 12.4 mmol) was added at room temperature to a solution of *i*Pr$_2$Im (945 mg, 6.21 mmol) in 10 mL of xylene and was heated to 140 °C for 3 d. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. The precipitate was filtered off, washed twice with 3 mL of *n*-hexane and dried *in vacuo* to afford 2.05 g (5.53 mmol, yield: 89 %) of a colorless powder. ^{1}H-NMR (200.1 MHz, C_6D_6, 303 K): δ = 6.86–7.02 (m, 12 H, aryl-C*H*), 7.46 – 7.63 (m, 8 H, aryl-C*H*); ^{31}P{^{1}H}-NMR (80.9 MHz, C_6D_6, 296 K): δ = -14.9; reference: -14.9 [S3]. NMR spectra of **1**: ^{1}H-NMR (200.1 MHz, d_8-toluene, 303 K): δ = 0.95 (d, 12 H, $^3J_{HH}$ = 6.4 Hz, ^{i}Pr-CH_3), 2.44 (sept, 2 H, $^3J_{HH}$ = 6.4 Hz, ^{i}Pr-C*H*), 3.93 (s, 2 H, NCH_2N), 5.44 (s, 2 H, C*H*C*H*). ^{13}C{^{1}H}-NMR (50.3 MHz, d_8-toluene, 296 K): δ = 21.0 (^{i}Pr-*C*H$_3$), 52.7 (^{i}Pr-*C*H), 73.9 (N*C*H$_2$N), 118.4 (*C*H*C*H).

Synthesis of $P_2Me_2Ph_2$ 3: Phenylmethylphosphine (2.06 g, 16.6 mmol) was added at room temperature to a solution of *i*Pr$_2$Im (1.26 g, 8.28 mmol) in 10 mL of xylene and was heated to 140 °C for 3 d. All volatiles were removed *in vacuo* and the residue was dissolved in 10 mL of *n*-hexane. The crude product was recrystallized at -80 °C, filtered, washed twice with 5 mL of -78 °C cold *n*-hexane and dried *in vacuo* to afford 367 mg (1.49 mmol, yield: 18 %) of a colorless solid containing the *S,S / R,R* and *meso* diastereomeres in the ratio 0.76 : 1.00

(ratio estimated by integration of ^{1}H NMR spectrum). $C_{14}H_{16}P_2$ [246.22 g/mol]: Calcd. (found) C 68.29 (67.91), H 6.55 (6.49). ^{1}H-NMR (200.1 MHz, C_6D_6, 296 K): δ = 1.08 (m, 3 H, CH_3), 1.17 (m, 3 H, CH_3), 6.90 – 7.10 (m, 8 H, aryl-C*H*), 7.26 – 7.38 (m, 2 H, aryl-C*H*). ^{13}C{^{1}H}-NMR (50.3 MHz, C_6D_6, 296 K): δ = 6.3 (m, *C*H_3), 6.9 (m, *C*H_3), 132.3 – 132.8 (m, aryl-*C*H). ^{31}P-NMR (80.9 MHz, C_6H_6, 298 K): δ = -40.3, -36.7; reference: -40.5, -36.9. [S4]

Synthesis of *i*Pr$_2$ImH$_2$ 1 and *i*Pr$_2$Im=PPh 4: Phenylphosphine (361 mg, 3.28 mmol) was added at room temperature to a solution of *i*Pr$_2$Im (1.00 g, 6.56 mmol) in 10 mL of toluene and was heated to 105 °C for 5 h. According to NMR spectroscopy the conversion to *i*Pr$_2$ImH$_2$ **1** and *i*Pr$_2$Im=PPh **4** is a 100 % and complete after 5 h (see Figure S5 and S6). For the isolation of both compounds all volatiles were condensed into a Schlenk tube and the remaining clear liquid was distilled to afford *i*Pr$_2$ImH$_2$ **1** (with traces of toluene). The light orange residue was suspended in 7 mL of *n*-hexane, filtered and dried *in vacuo* to afford 506 mg (1.94 mmol; 60 %) of a yellow solid. *i*Pr$_2$ImH$_2$ **1:** ^{1}H-NMR (500.1 MHz. d_8-toluene, 296 K): δ = 0.95 (d, 12 H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}Pr-CH_3), 2.44 (sept, 2 H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}Pr-C*H*), 3.93 (s, 2 H, NCH_2N), 5.44 (s, 2 H, C*H*C*H*). ^{13}C{^{1}H}-NMR (125.76 MHz, d_8-toluene, 296 K): δ = 21.0 (^{i}Pr-*C*H_3), 52.7 (^{i}Pr-*C*H), 73.9 (N*C*H_2N), 118.4 (*C*H*C*H). ^{1}H-NMR (500.1 MHz. C_6D_6, 296 K): δ = 0.96 (d, 12 H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}Pr-CH_3), 2.48 (sept, 2 H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}Pr-C*H*), 3.98 (s, 2 H, NCH_2N), 5.51 (s, 2 H, C*H*C*H*). ^{13}C{^{1}H}-NMR (125.76 MHz, C_6D_6, 296 K): δ = 21.4 (^{i}Pr-*C*H_3), 52.7 (^{i}Pr-*C*H), 73.9 (N*C*H_2N), 118.5 (*C*H*C*H). *i*Pr$_2$Im=PPh **4**: ^{1}H-NMR (500.1 MHz, d_8-toluene, 298 K): δ = 0.91 (d, 12 H, $^{3}J_{HH}$ = 6.7 Hz, ^{i}Pr-CH_3), 4.97 (sept, 2 H, $^{3}J_{HH}$ = 6.7 Hz, J_{PH} = 4 Hz, ^{i}Pr-C*H*), 6.26 (s, 2 H, C*H*C*H*), 6.84, 7.00, 7.50 (m, 5H, aryl-*H*). ^{13}C{^{1}H}-NMR (125.8 MHz, d_8-toluene, 298 K): δ = 21.7 (^{i}Pr-*C*H_3), 49.9 (d, J_{PC} = 10 Hz, *i*Pr-*C*H), 115.3 (d, J_{CP} = 3 Hz, *C*H*C*H), 122.2, 128.1 (aryl-*C*H), 132.2 (d, J_{CP} = 19 Hz, aryl-*C*H), 150.1 (d, J_{CP} = 50 Hz, aryl-*C*H), 168.5 (d, J_{CP} = 104 Hz, N*C*N). ^{31}P-NMR (202.5 MHz, d_8-toluene, 298 K): δ = -59.0, reference: -61.2 [S5]. ^{1}H-NMR (500.1 MHz, C_6D_6, 298 K): δ = 0.90 (d, 12 H, $^{3}J_{HH}$ = 6.7 Hz, ^{i}Pr-CH_3), 5.00 (sept, 2 H, $^{3}J_{HH}$ = 6.7 Hz, J_{PH} = 4 Hz, ^{i}Pr-C*H*), 6.19 (s, 2 H, C*H*C*H*), 6.91, 7.07, 7.64 (m, 5H, aryl-*H*). ^{13}C{^{1}H}-NMR (125.8 MHz, C_6D_6, 298 K): δ = 21.8 (^{i}Pr-*C*H_3), 49.9 (d, J_{PC} = 10 Hz, *i*Pr-*C*H), 115.4 (d, J_{CP} = 3 Hz, *C*H*C*H), 122.3, 128.1 (aryl-*C*H), 132.1 (d, J_{CP} = 19 Hz, aryl-*C*H), 150.2 (d, J_{CP} = 50 Hz, aryl-*C*H), 168.2 (d, J_{CP} = 104 Hz, N*C*N). ^{31}P-NMR (202.5 MHz, C_6D_6, 298 K): δ = -60.0, reference: -61.2 [S5]

NMR experiments:

Conversion of 1 equivalent of *i*Pr$_2$Im and 1 equivalent of PhPH$_2$ in d_8-toluene: Penylphosphine (16.6 mg, 151 µmol) was added at room temperature to a solution of *i*Pr$_2$Im (23.0 mg, 151 µmol) in 600 µL of d_8-toluene and was heated to 105 °C for 2 h. Identified products: **1:** ^{1}H-NMR (200.1 MHz, d_8-toluene, 296 K): δ = 0.95 (d, 12 H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}Pr-CH_3), 2.44 (sept, 2 H, $^{3}J_{HH}$ = 6.4 Hz, ^{i}Pr-C*H*), 3.93 (s, 2 H, NCH_2N), 5.44 (s, 2 H, C*H*C*H*).

iPr_2Im=PPh **4:** ^{1}H-NMR (200.1 MHz, d_8-toluene, 296 K): δ = 0.91 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, ^{i}Pr-CH_3), 4.96 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, J_{PH} = 4 Hz, ^{i}Pr-C*H*), 6.24 (s, 2 H, C*H*C*H*), 6.84, 7.00, 7.50 (m, 5H, aryl-*H*). ^{31}P-NMR (80.9 MHz, d_8-toluene, 298 K): δ = -58.8; reference: -61.2 [S5]. P_4Ph_4**:** ^{31}P-NMR (80.9 MHz, d_8-toluene, 296 K): δ = -48.23; reference: -48.0. [S6] P_6Ph_6**:** ^{31}P-NMR (80.9 MHz, d_8-toluene, 296 K): δ = -22.0; reference: -21.2. [S6d] P_5Ph_5**:** ^{31}P-NMR (80.9 MHz, d_8-toluene, 296 K): δ = -3.56 – -2:68; reference: -5.0 – -2.9. [S7]

Conversion of 1 equivalent of *i*Pr_2Im and 1 equivalent of *p*TolPH_2 in d_8-toluene: *para*-Tolylphosphine (20.7 mg, 167 µmol) was added at room temperature to a solution of *i*Pr_2Im (25.4 mg, 167 µmol) in 600 µL d_8-toluene and heated to 105 °C for 4 h. *i*Pr_2ImH_2 **1**: ^{1}H-NMR (200.1 MHz. d_8-toluene, 296 K): δ = 0.95 (d, 12 H, $^3J_{HH}$ = 6.4 Hz, ^{i}Pr-CH_3), 2.44 (sept, 2 H, $^3J_{HH}$ = 6.4 Hz, ^{i}Pr-C*H*), 3.93 (s, 2 H, NCH_2N), 5.44 (s, 2 H, C*H*C*H*). *i*Pr_2Im=P*p*Tol **4**: ^{1}H-NMR (200.1 MHz, d_8-toluene, 296 K): δ = 0.91 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, ^{i}Pr-CH_3), 4.90 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, J_{PH} = 4 Hz, ^{i}Pr-C*H*), 6.25 (s, 2 H, C*H*C*H*), 6.84, 7.00, 7.50 (m, 5H, aryl-*H*). ^{31}P-NMR (80.9 MHz, d_8-toluene, 296 K): δ = -57.3. P_4*p*Tol$_4$: ^{31}P-NMR (80.9 MHz, d_8-toluene, 298 K): δ = -48.1. P_6*p*Tol$_6$: ^{31}P-NMR (80.9 MHz, d_8-toluene, 298 K): δ = -22.8. P_5*p*Tol$_5$: ^{31}P-NMR (80.9 MHz, d_8-toluene, 298 K): δ = -8.3 – -3.6.

Synthesis of P_5Ph_5 5: Phenylphosphine (579 mg, 5.26 mmol) was added at room temperature to a solution of *i*Pr_2Im (200 mg, 1.31 mmol) in 10 mL of toluene and was heated to 105 °C for 4 d. All volatiles were removed *in vacuo* and the residue was dissolved in 10 mL of Et_2O. The crude product was recrystallized at -80 °C, filtered, washed twice with 5 mL of -78 °C cold *n*-hexane and dried *in vacuo* to afford 208 mg (385 mmol, yield: 37 %) of a colorless solid. $C_{30}H_{25}P_5$ [540.39 g/mol]: Calcd. (found) C 66.58 (66.38), H 4.66 (4.57). ^{1}H-NMR (200.1 MHz, C_6D_6, 296 K): δ = 6.79 – 7.10 (m, 15 H, aryl-C*H*), 7.36 – 7.38 (m, 4 H, aryl-C*H*), 7.97 – 8.08 (m, 6 H, aryl-C*H*). ^{13}C{^{1}H}-NMR (50.3 MHz, C_6D_6, 296 K): δ = 127.9 – 128.2 (m, aryl-*C*H), 128.8 – 129.3 (m, aryl-*C*H), 132.8 – 133.4 (m, aryl-*C*H), 134.1 –134.7 (m, aryl-*C*H). ^{31}P-NMR (80.9 MHz, C_6H_6, 298 K): δ = -5.7 – -1.0; reference: -5.0 – -2.9. [S7]

Synthesis of P_6(*p*Tol)$_6$ 6: *para*-Tolylphosphine (326 mg, 2.63 mmol) was added at room temperature to a solution of *i*Pr_2Im (400 mg, 2.63 mmol) in 10 mL of toluene and was heated to 105 °C for 4 d. All volatiles were removed *in vacuo* and the residue was dissolved in 10 mL of Et_2O. The crude product was recrystallized at -80 °C, filtered, washed twice with 5 mL of -78 °C cold *n*-hexane and dried *in vacuo* to afford 76 mg (104 mmol, yield: 20 %) of a colorless solid. $C_{42}H_{42}P_6$ [732.63 g/mol]: Calcd. (found) C 68.86 (68.82), H 5.78 (6.14). IR (ATR): $\tilde{\nu}$ = 707 (vw), 730 (w), 799 (vs), 1020 (m), 1038 (w), 1084 (m), 1103 (w), 1117 (w), 1181 (m), 1304 (w), 1393 (m), 1445 (w), 1491 (m), 1595 (w), 1904 (vw), 2862 (w, $\nu_{C\text{-}H,str}$), 2919 (w, $\nu_{C\text{-}H,str}$), 2971 (w, $\nu_{C\text{-}H,str}$), 3014 (m, aryl-$\nu_{=C\text{-}H,str}$), 3029 (w, aryl-$\nu_{=C\text{-}H,str}$), 3063 (w, aryl-$\nu_{=C\text{-}H,str}$). ^{1}H-NMR (200.1 MHz, CD_2Cl_2, 296 K): δ = 2.20 (s, 18 CH_3), 6.93 (d, 12 H, $^3J_{HH}$ =

7.7 Hz, aryl-C*H*), 6.93 (d, 12 H, $^{3}J_{HH}$ = 7.7 Hz, aryl-C*H*). $^{13}C\{^{1}H\}$-NMR (50.3 MHz, CD_2Cl_2, 296 K): δ = 21.4 (*C*H_3), 129.4 (aryl-*C*H), 135.2 (aryl-*C*H), 140.0 (aryl-*C*H). ^{31}P-NMR (80.9 MHz, CD_2Cl_2, 296 K): δ = -24.2.

3. Crystallography

Crystal data collection and processing parameters are given below. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber and transferred to a Bruker X8 Apex-2 diffractometer with CCD area detector and mirror-monochromated Mo-Kα radiation equipped with a Bruker Kryoflex^2 low-temperature device. Data were collected at 100 K. The images were processed with the Bruker software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and hydrogen atoms were included in calculated positions and refined using a riding model. Extinction corrections were applied as required. Crystallographic calculations were performed using the SHELXTL software package. [S8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 1056079 (**5**) and CCDC 1056079 (**6**). Copies of the data can be obtained free of charge on application to CCDC.

Crystal Structure Determination of P_5Ph_5 5: $C_{60}H_{51}P_{10}$, M_r = 1081.71, colorless block, 0.15 × 0.15 × 0.10 mm, triclinic space group $P\bar{1}$, a = 10.102(2) Å, b = 13.842(3) Å, c = 19.518(4), α = 90.19(3) °, β = 93.99(3) °, γ = 93.20 °, V = 2718.4(9) Å^3, T = 173 K, Z = 2, $\rho_{calcd.}$ = 1.322 g·cm^{-3}, μ = 0.355 mm^{-1}, F(000) = 1120, 11007 reflections in h(–18/18), k(–13/13), l(–28/28) measured in the range 1.05° < θ < 26.50°, completeness 99.9 %, 11007 independent reflections, 9868 observed reflections ($I > 2\sigma(I)$), 669 parameters, 0 restraints; *all data:* R_1 = 0.0673 and wR_2 = 0.1375, $I > 2\sigma(I)$*:* R_1 = 0.0589 and wR_2 = 0.1279, *Goof* 1.121, largest difference peak/hole 0.704/–0.738 e·Å^{-3}.

Crystal Structure Determination of $P_6(p\text{Tol})_6$ 6: $C_{42}H_{42}P_6$, M_r = 732.57, colorless block, 0.34 × 0.30 × 0.23 mm, trigonal space group $R\bar{3}$, a = 13.896(3) Å, b = 13.896(3) Å, c = 20.034(4), γ = 120 °, V = 3350.0(17) Å^3, T = 100 K, Z = 3, $\rho_{calcd.}$ = 1.089 g·cm^{-3}, μ = 0.266 mm^{-1}, F(000) = 1152, 7835 reflections in h(–16/17), k(–17/17), l(–24/23) measured in the range 2.6455° < θ < 25.9365°, completeness 95.6 %, 1405 independent reflections, 1184 observed reflections ($I > 2\sigma(I)$), 113 parameters, 0 restraints; *all data:* R_1 = 0.0483 and wR_2 =

0.1256, $I > 2\sigma(I)$: R_1 = 0.0423 and wR_2 = 0.1229, *Goof* 1.123, largest difference peak/hole 0.380/–0.183 e·Å^{-3}. For the molecular structure of **P_6(*p*Tol)$_6$** one diethyl ether solvent molecule could not be refined properly was subsequently removed from the model using the PLATON/SQUEEZE routine.

4. References

[S1] J. Attner, U. Radius, *Chem. Eur. J.* **2001**, *7*, 783-790.

[S2] T. Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss, *Inorg. Synth.* **2010**, *35*, 78–83.

[S3] D. L. Dodds, M. F. Haddow, A. G. Orpen, P. G. Pringle, G. Woodward, *Organometallics* **2006**, *25*, 5937-5945.

[S4] H. C. E. McFarlane, W. McFarlane, J. A. Nash, *J. Chem. Soc., Dalton Trans*. **1980**, 240-244.

[S5] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011-3015; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939-2943.

[S6] T. L. Breen, D. W. Stephan, *Organometallics* **1997,** *16,* 365-369.

[S7] (a) N. Burford, C. A. Dyker, A. Decken, *Angew. Chem. Int. Ed.* **2005**, *44*, 2364 -2367, (b) H. Goldwhite, J. Kaminski, G. Millhauser, J. Ortiz, M. Vargas, L. Vertal, M. Lappert, S. J. Smith, *J. Organomet. Chem.* **1986**, *310*. 21-25, (c) M. Scherer, D. Stein, F. Breher, J. Geier, H. Schönberg, H. Grützmacher, *Z. Anorg. Allg. Chem*. **2005**, *631*, 2770-2774, (d) R. Köster, G. Seidel R. Boese, B. Wrackmeyer, *Chem. Ber.* **1988**, *121*, 1955-1966, (e) J. Masuda, A. J. Hoskin, T. W. Graham, C. Beddie, M. C. Fermin, N. Etkin, D. W. Stephan, *Chem. Eur. J*. **2006**, *12*, 8696-8707, (f) I. Kalinina, F. Mathey, *Organometallics* **2006**, *25*, 5031-5034.

[S8] M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112-122.