SUPPORTING INFORMATION

Reactivity of Phospha-Wittig Reagents towards NHCs and NHOs

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This file includes:

1 Experimental

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

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
Benzene	local trade	dried over Na/benzophenone freshly distilled prior to use, stored over molecular sieves.
n-hexane	Geyer, CHROMASOLV®, for HPLC, ≥97,0% (GC)	purified with the Grubbs-type column system "Pure Solv MD-5" dried over Na/benzophenone/tetraglyme freshly distilled prior to use
n-pentane	local trade	dried over Na/benzophenone/tetraglyme freshly distilled prior to use
Toluene	Fisher Chemical, for HPLC	purified with the Grubbs-type column system "Pure Solv MD-5"
C_6D_6	euriso-top	dried over Na/benzophenone freshly distilled prior to use
C_7D_8 (toluene-d_8)	euriso-top	dried over Na/benzophenone freshly distilled prior to use
1,3-Dichlorobenzene	Acros, 98%	used as received
$^{Dip}TerPCl_2$[1]	synthesized	
$^{Dip}TerPPMe_3$	synthesized	See Chapter 2.4
$IDipCH_2$[2]	synthesized	
$IDipC_3H_4$[3]	synthesized	see Chapter 2.5
I^iPr_2[4]	synthesized	
IMe_4[5]	synthesized	

Table S1 continued.

Substance	Origin	Purification
IMes[6]		
$HNEt_2$	TCI Chemicals 98%	used as received
$^{Me}IDipCH_2$[2]		
$^{Me}IMes$[7]		
Mes*$PPMe_3$	synthesized	See Chapter 2.2
$^{Mes}TerPPMe_3$	synthesized	See Chapter 2.3
Mesityl bromide	Abcr 98%	used as received
n-Butyllithium	Acros Organics, 2.5M in hexanes	used as received
PCl_3	Sigma-Aldrich, 99%	Refluxed over P_4O_{10}, distilled prior to use
PMe_3	Strem Chemicals, 98%	used as received
1,3,5-*t*Bu_3-C_6H_3	Alfa Aesar, 97+%	used as received

NMR spectra were recorded on Bruker spectrometers (AVANCE 300, AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent (^{13}C: C_6D_6 δ_{ref} = 128.06 ppm) or to protic impurities in the deuterated solvent[8] (^{1}H: $CHDCl_2$ C_6HD_5 δ_{ref} = 7.16 ppm) or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable).

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: weak (w, 0–33%), medium (m, 33–66%), strong (s, 66–100%).

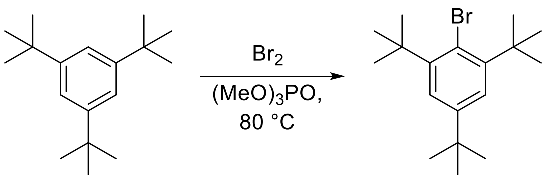
Elemental analyses were obtained using a Leco Tru Spec elemental analyzer.

Melting points (uncorrected) were determined using on a Mettler-Toledo MP 70 apparatus at a heating rate of 5 °C/min. Clearing points are reported.

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

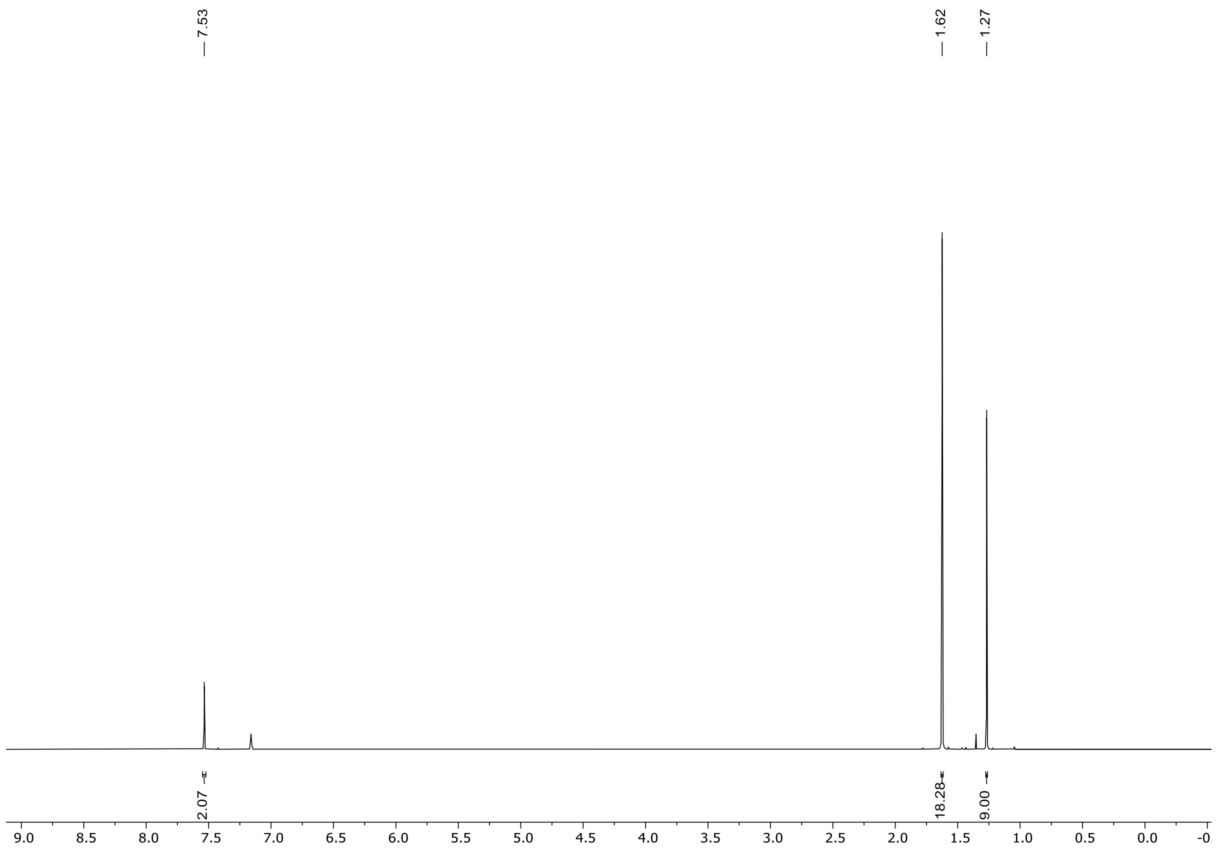
2 Syntheses of starting materials

2.1 Synthesis of Mes*Br

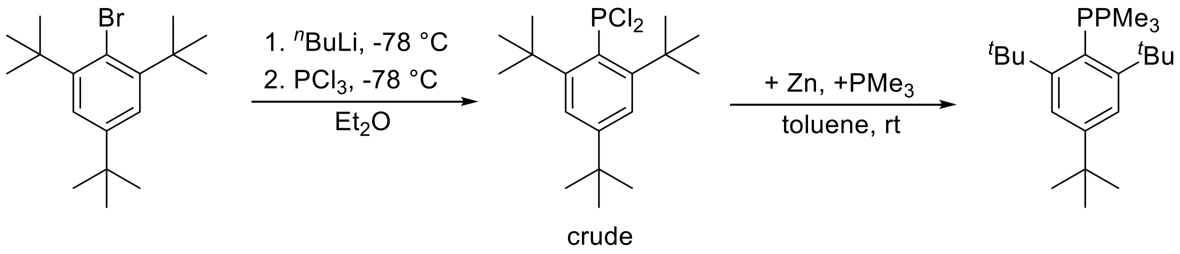


To a solution of 2,4,6-tri-*tert*-butylbenzene (75.00 g, 30.43 mmol) in 700 mL of trimethyl phosphate bromine (97.28 g, 60.87 mmol) was added portion wise at 0 °C upon the solution turned red. The reaction mixture was stirred for 72 h under reflux, then cooled to 0 °C, and kept at that temperature for four hours. The crystalline precipitate was separated by filtration, washed with cold ethanol (approx. 100 mL) and dried under vacuum to give Mes*Br as a colorless crystalline solid. Yield: 75.04 g (23.07 mmol; 76%). **^{1}H NMR** (300 MHz, C_6D_6): δ [ppm] = 7.53 (2H, Ar*H*), 1.62 (18H, o-C(C*H*$_3$)$_3$), 1.27 (18H, p-C(C*H*$_3$)$_3$).

Figure S1: ^{1}H NMR spectrum of Mes*Br (300 MHz, C_6D_6, rt).



2.2 Synthesis of Mes^*PPMe_3 (1)



n-Butyllithium (2.58 mL, 6.455 mmol; 2.5 M in hexanes) was added dropwise to a solution of Mes*Br (2.000 g, 6.148 mmol) in THF (20 mL) at −78 °C. After stirring for one hour at −78 °C, PCl_3 (1.08 mL, 12.30 mmol) was added dropwise at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for another one hour at that temperature and then heated to 80 °C for 15 minutes. All volatile components were removed under vacuum followed by addition of either benzene or toluene (30 mL). The soluble parts were filtered into a Schlenk tube containing zinc (2.010 g, 30.74 mmol). PMe_3 (3.12 mL, 30.74 mmol) was added dropwise and the suspension was stirred for two hours at room temperature (wrap flask with tin foil). The soluble parts were filtered over celite into another Schlenk tube. All volatile components were removed under vacuum to yield Mes^*PPMe_3 (**1**) as a yellow solid.

Yield: 1.748 g, 4.959 mmol (81%).

^{1}H NMR (300 MHz, C_6D_6): δ [ppm] = 7.42 (d, J = 3.0 Hz, 2H, Ar*H*), 1.89 (d, 18H, J_{PH} = 0.9 Hz, o-C(CH_3)$_3$), 1.36 (9H, p-C(CH_3)$_3$), 0.70 (dd, 9H, $^2J_{PH}$ = 11.6 Hz, $^3J_{PH}$ = 2.2 Hz, P(CH_3)$_3$). **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6): δ [ppm] = 4.03 (d, $^1J_{PP}$ = 583 Hz), −134.47 (d, $^1J_{PP}$ = 583 Hz)

Figure S2: ^{1}H NMR spectrum of Mes*PPMe$_3$ (**1**) in C_6D_6.

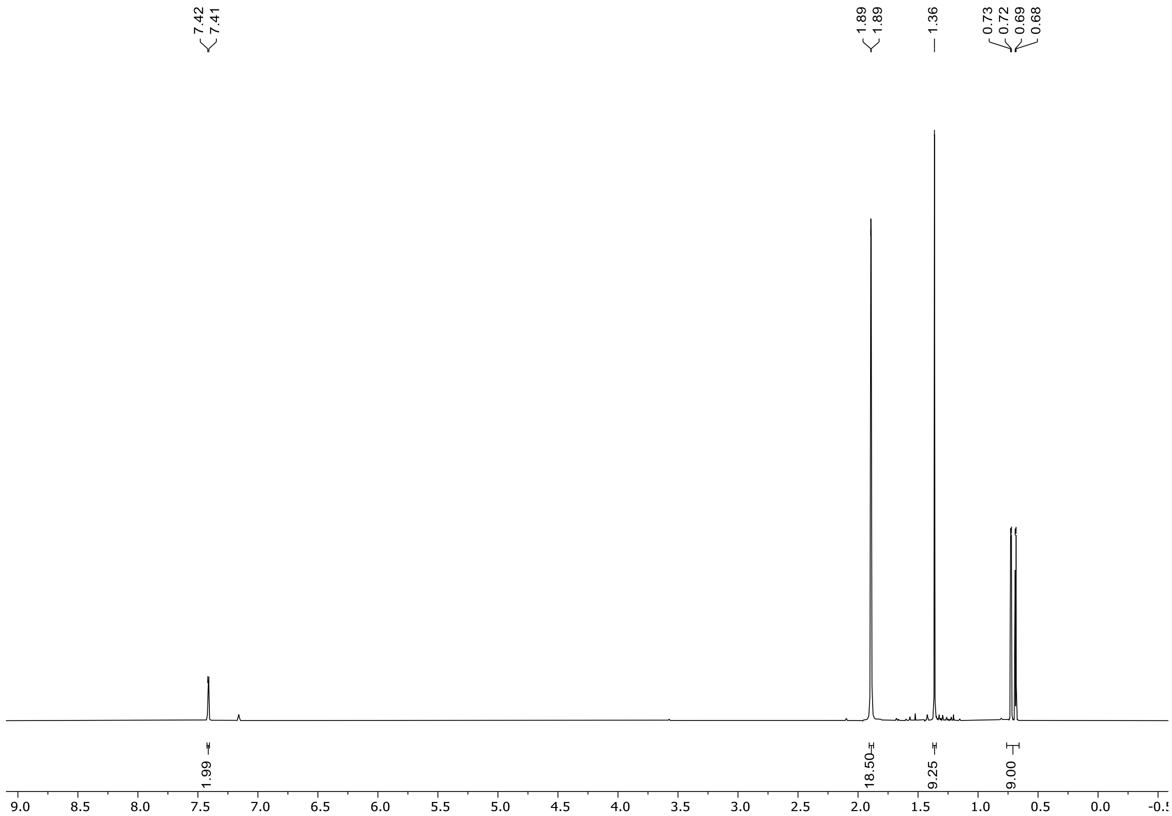
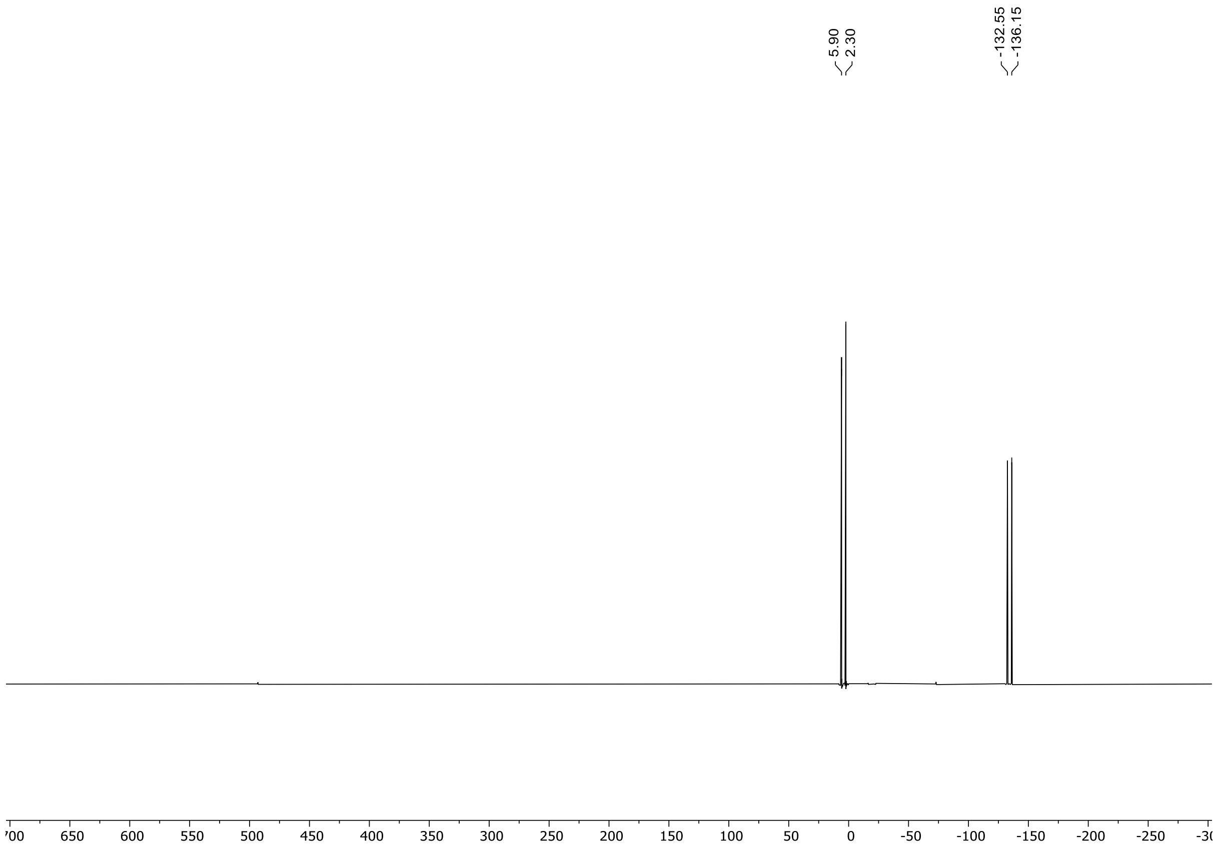


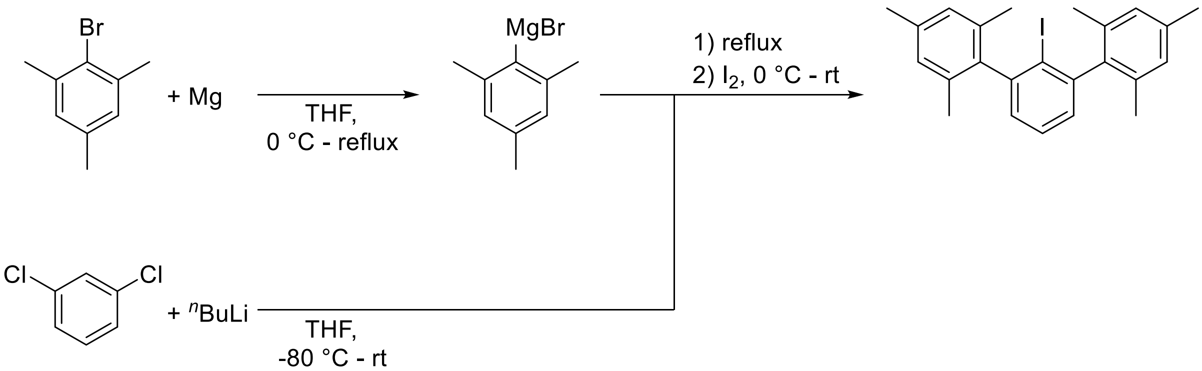
Figure S3: $^{31}P\{^{1}H\}$ NMR spectrum of Mes*PPMe$_3$ (**1**) (122 MHz, C_6D_6, rt).



2.3 Synthesis of ^{Mes}TerPPMe$_3$ (2)

^{Mes}TerPPMe$_3$ (**2**) was synthesized in a four-step synthesis according to modified literature procedures.[9] The obtained ^{1}H and ^{31}P{^{1}H} NMR spectra of the bulk material are shown for each isolated product.

2.3.1 Synthesis of ^{Mes}TerI



Mesityl bromide (50.00 g, 251.1 mmol) was added dropwise to a stirred suspension of magnesium turnings (6.716 g, 27.63 mmol) in tetrahydrofuran (200 mL) over a period of 20 min resulting in a brownish suspension followed by heating of the reaction mixture to reflux for ca. 4 h.

In the meantime *n*-butyllithium (118.6 mmol, 47.5 mL; 2.5 M in hexanes) was added dropwise to a stirred solution of 1,3-dichlorobenzene (16.61 g, 113.0 mmol) in tetrahydrofuran (300 mL) at −80 °C over a period of 20 min, which resulted in a slightly yellow solution. The solution is stirred for one hour at −80 °C, which was accompanied by the formation of a colorless solid. Subsequently, the freshly prepared and to room temperature cooled suspension of MesMgBr (described beforehand) was added dropwise at −80 °C over a period of 30 minutes to give a clear brown solution which was slowly warmed to room temperature and stirred overnight.

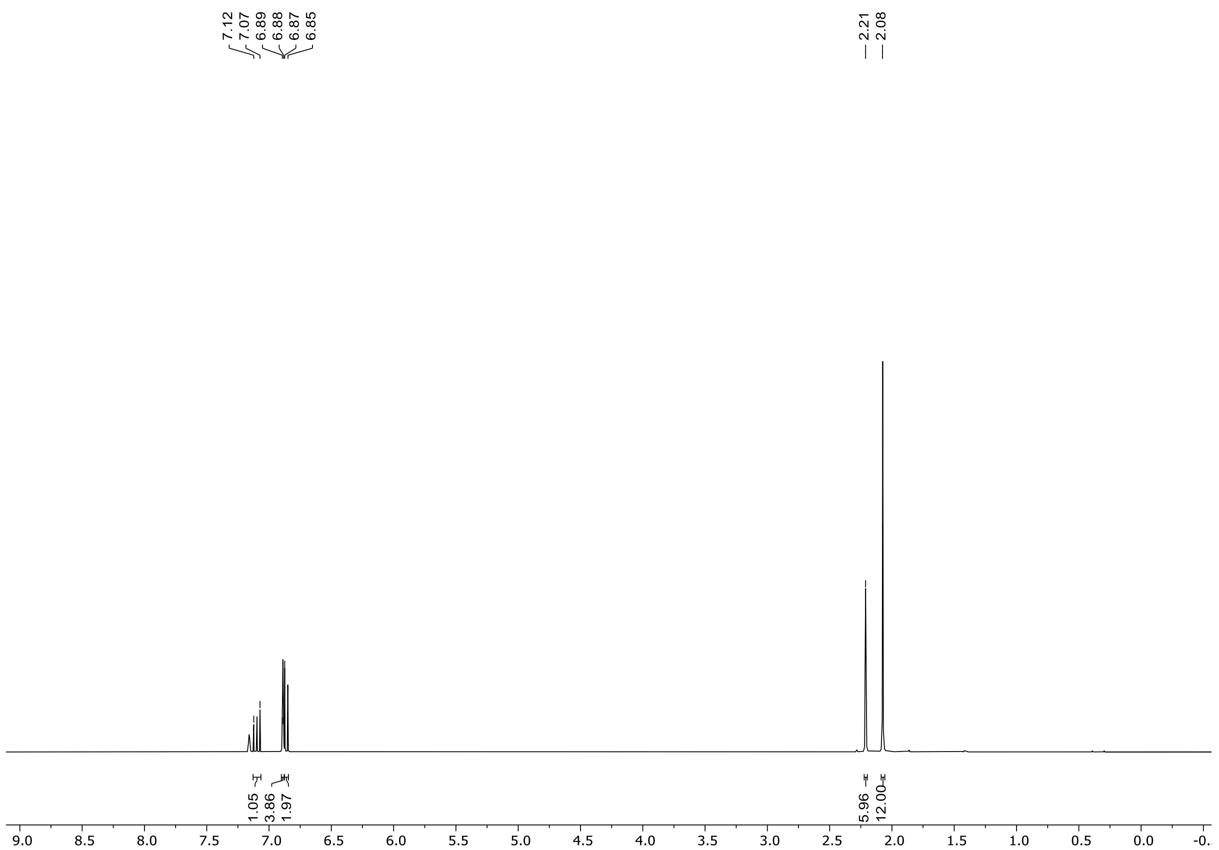
The next morning, the reaction mixture was heated to reflux (oil-bath at 90°C) for two hours. Afterwards the solution was cooled to 0 °C. Iodine (43.02 g, 16.95 mmol) in THF (100 mL) was added dropwise over a period of one hour. This addition was accompanied by a color change to red-brown and finally to purple due to using an excess of iodine. The solution is stirred for another four hours at room temperature.

An aqueous solution of Na_2SO_3 (22.25 g, 176.6 mmol, 400 mL) was then added and the yellow organic layer was separated. The aqueous layer was extracted with diethylether (3 × 200 mL) and the combined organic fractions were dried over magnesium sulfate. After filtration, the solvents were removed by rotary evaporation to give a yellowish solid. Subsequently, all volatile components were removed from the sticky yellow crude material by distillation for two hours at 140 °C in vacuo ($1 \cdot 10^{-3}$ mbar). The remaining solid was recrystallized from hot ethanol (ca. 100 mL). The hot solution was slowly cooled to ambient temperature, the solid was collected on a medium porosity frit, and washed with cold methanol to give ^{Mes}TerI as a colorless solid.

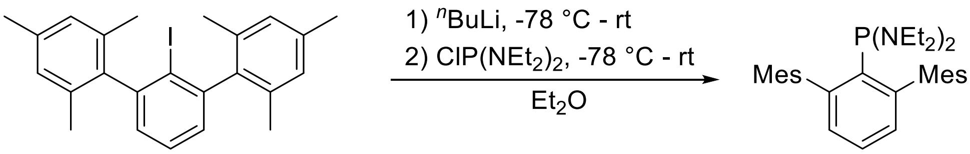
The filtrate (mother liquor) was stored at −30 °C to give a second fraction of ^{Mes}TerI.

Yield: 26.19 g, 58.47 mmol (53%).

Figure S4: ^{1}H NMR spectrum of ^{Mes}TerI (300 MHz, C_6D_6, rt).



2.3.2 Synthesis of MesTerP$(NEt_2)_2$



^{Mes}TerI (11.04 g, 25.06 mmol) was suspended in diethyl ether (100 mL). *n*-Butyllithium (11.0 mL, 27.57 mmol, 2.5 M in hexanes) was added dropwise at −78 °C, the reaction mixture was stirred for one hour at −78 °C, warmed to room temperature, and stirred for another hour at that temperature. Then, freshly prepared ClP$(NEt_2)_2$* (5.280 g, 25.06 mmol) was added dropwise at −78 °C, followed by slowly warming of the reaction mixture to room temperature. The reaction mixture was stirred overnight at room temperature. All volatile components were removed under vacuum followed by extraction of the remaining yellow solid over celite with *n*-hexane (120 mL). The volume was reduced to incipient crystallization (approx. 20 mL) and stored at −30 °C overnight, which resulted in the precipitation of ^{Mes}TerP$(NEt_2)_2$ as a colorless solid.

Yield: 7.394 g (15.13 mmol; 60%).

*Synthesis of ClP$(NEt_2)_2$[10]

Diethylamine (62.5 mL, 600 mmol) in diethyl ether (50 mL) was added dropwise to a solution of PCl_3 (13.0 mL, 150 mmol) in diethyl ether (250 mL) at 0 °C. The white suspension was stirred for additional three hours at room temperature. The supernatant was collected by filtration. After the first fraction was obtained, the remaining solids were washed with diethyl ether (300 mL) and filtered again. All volatile components were removed from the combined filtrate solutions under vacuum. The residue was distilled at 150 °C and $1 \cdot 10^{-3}$ mbar to yield ClP$(NEt_2)_2$ as a colorless liquid.

Yield: 22.96 g (109 mmol; 73%).

Figure S5: ^{1}H NMR spectrum of $ClP(NEt_2)_2$ (300 MHz, C_6D_6, rt).

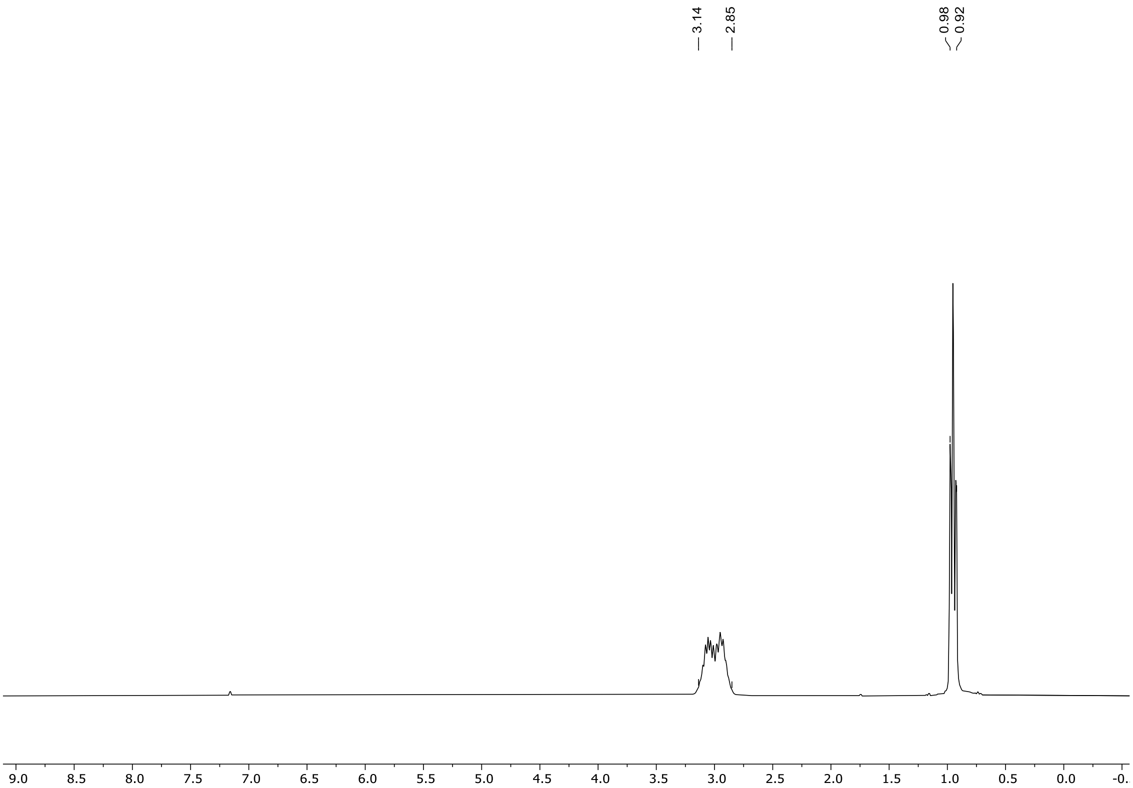


Figure S6: ^{31}P {^{1}H} NMR spectrum of $ClP(NEt_2)_2$ (122 MHz, C_6D_6, rt).

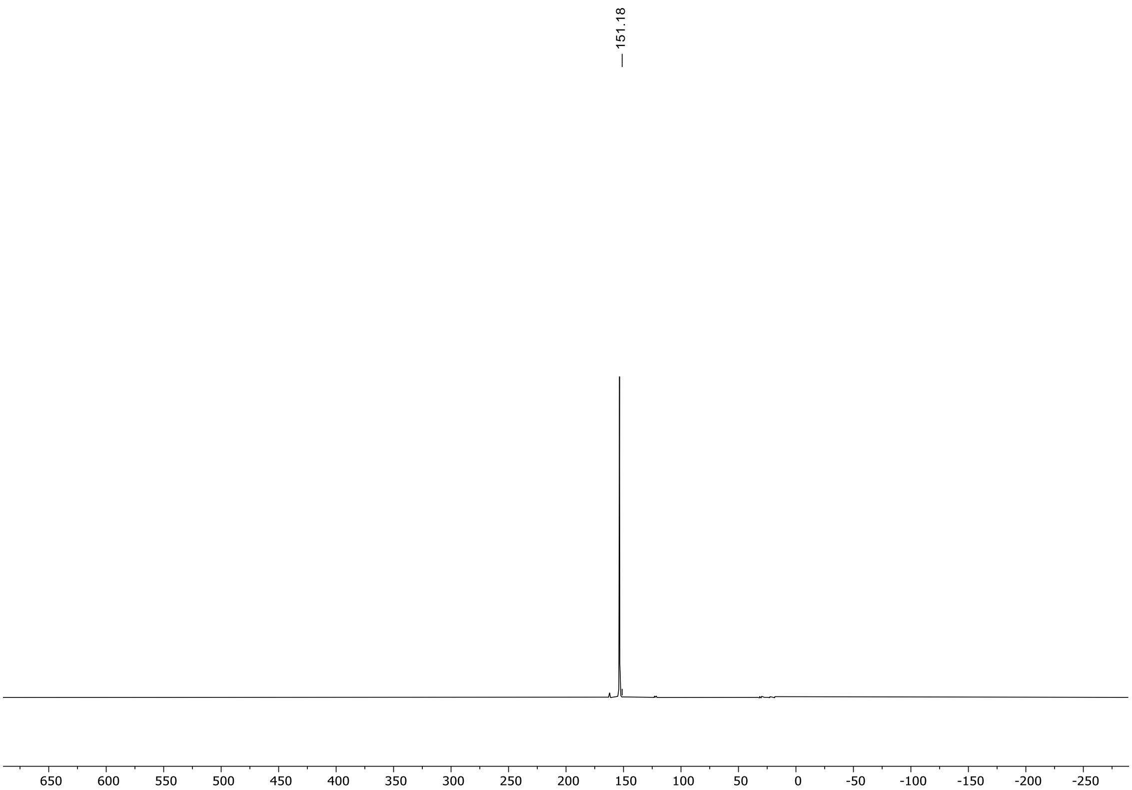


Figure S7: ^{1}H NMR spectrum of ^{Mes}TerP(NEt_2)$_2$ (300 MHz, C_6D_6, rt).

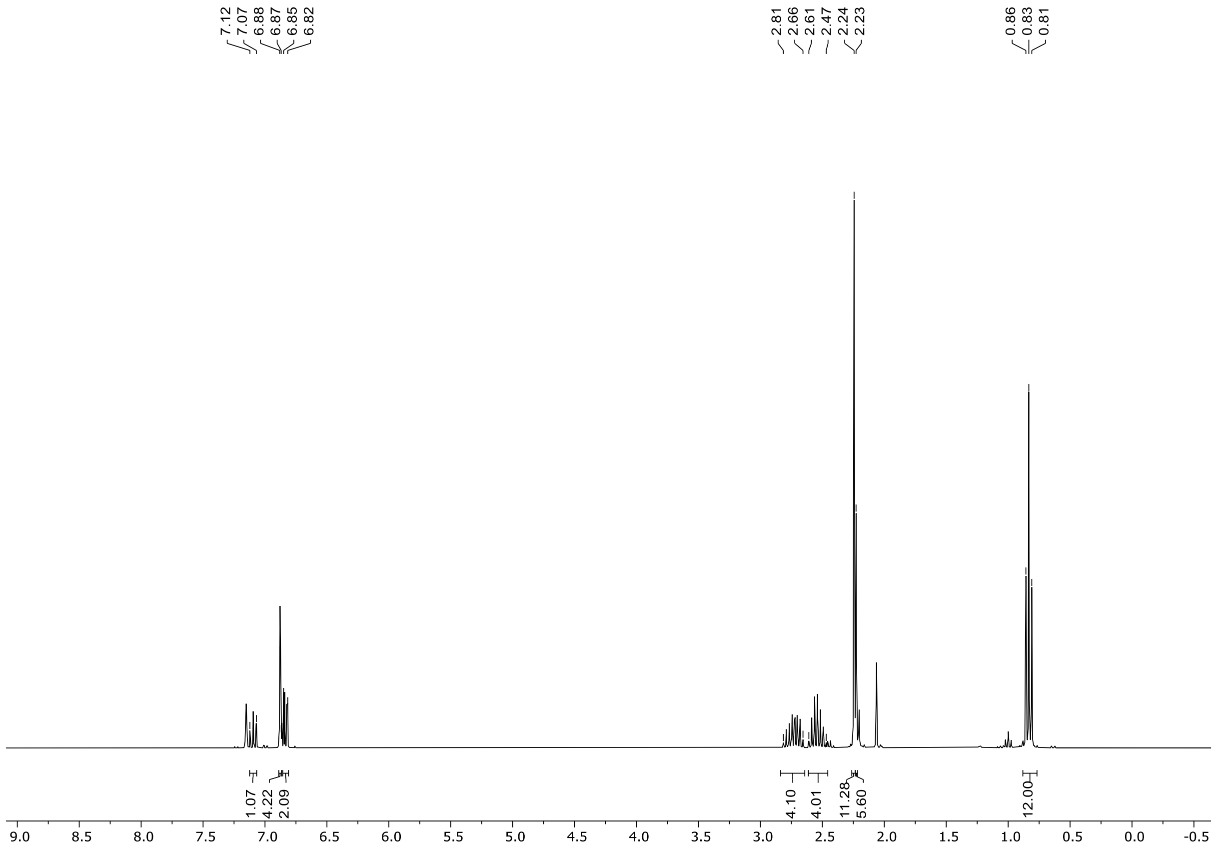
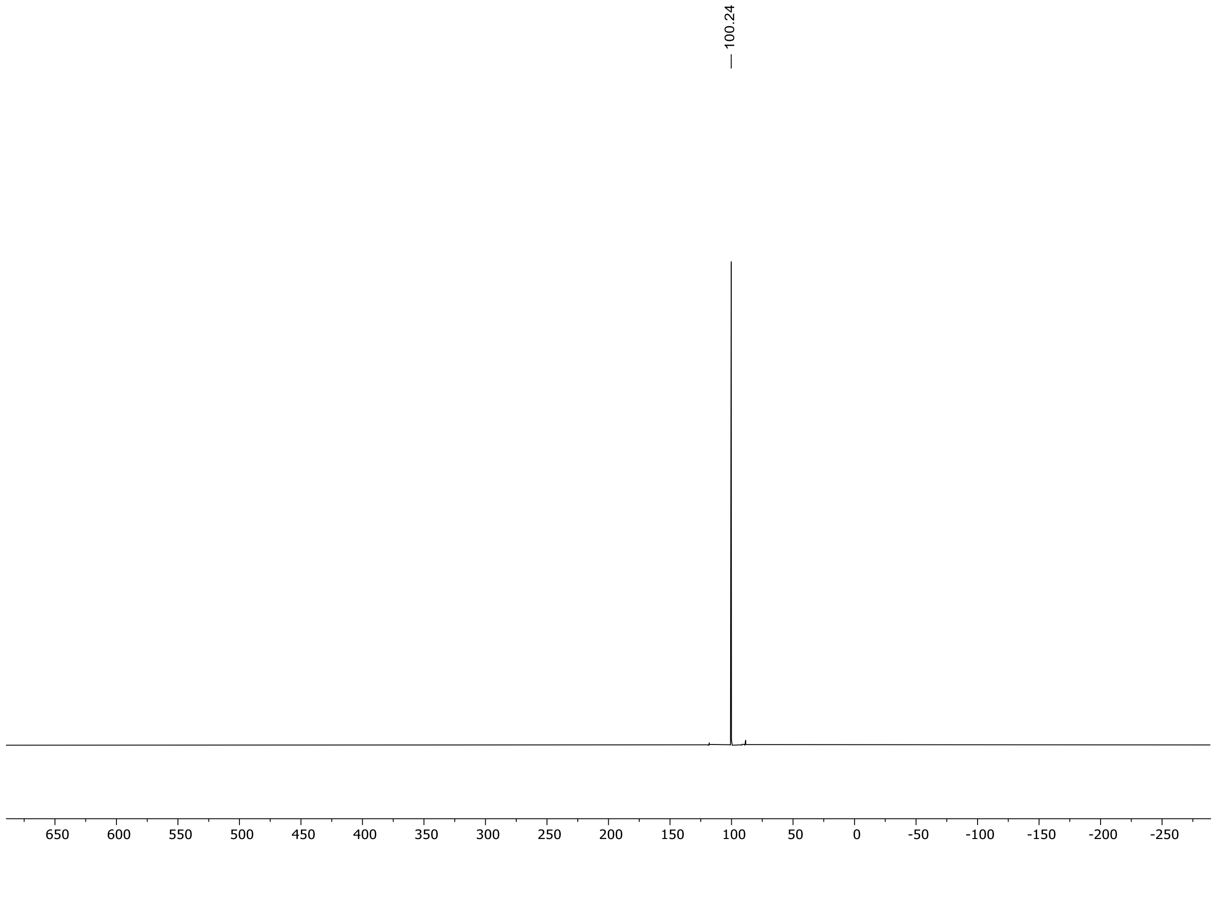
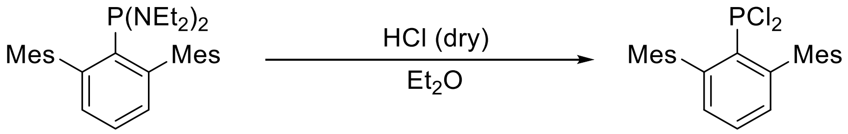


Figure S8: ^{31}P {^{1}H} NMR spectrum of ^{Mes}TerP(NEt_2)$_2$ (122 MHz, C_6D_6, rt).



2.3.3 Synthesis of ^{Mes}TerPCl$_2$



Dry HCl (generated by addition of H_2SO_4 to NaCl) was passed through a solution of ^{Mes}TerP(NEt$_2$)$_2$ (6.250 g, 12.79 mmol) in diethyl ether (100 mL) over the course of four hours. All volatile components were removed under vacuum, and the residue was extracted with toluene (approx. 50 mL). The volume was reduced to incipient crystallization (approx. 15 mL) and the solution was stored at −30 °C which resulted in the precipitation of ^{Mes}TerPCl2 as a colorless solid.

Yield: 4.126 g (9.934 mmol; 78%).

Figure S9: ^{1}H NMR spectrum of ^{Mes}TerPCl$_2$ (300 MHz, C_6D_6, rt).

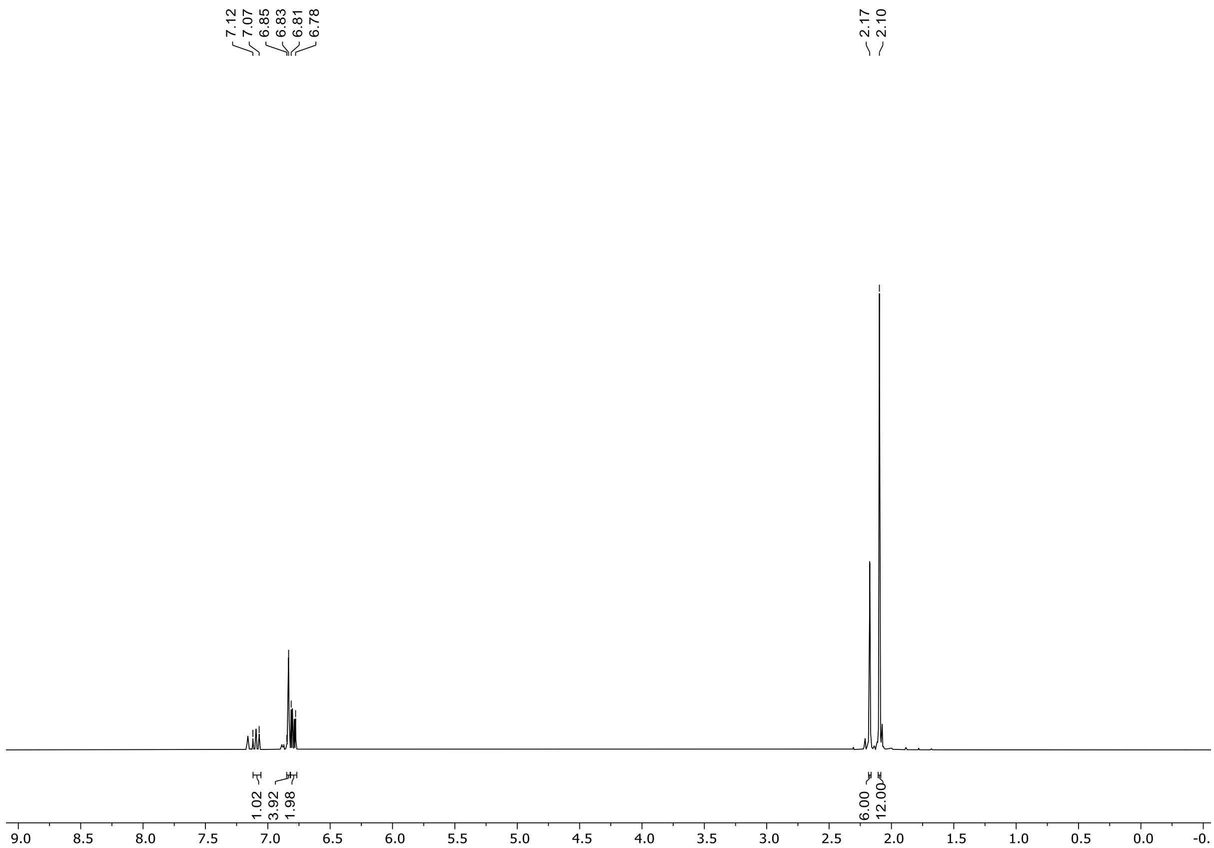
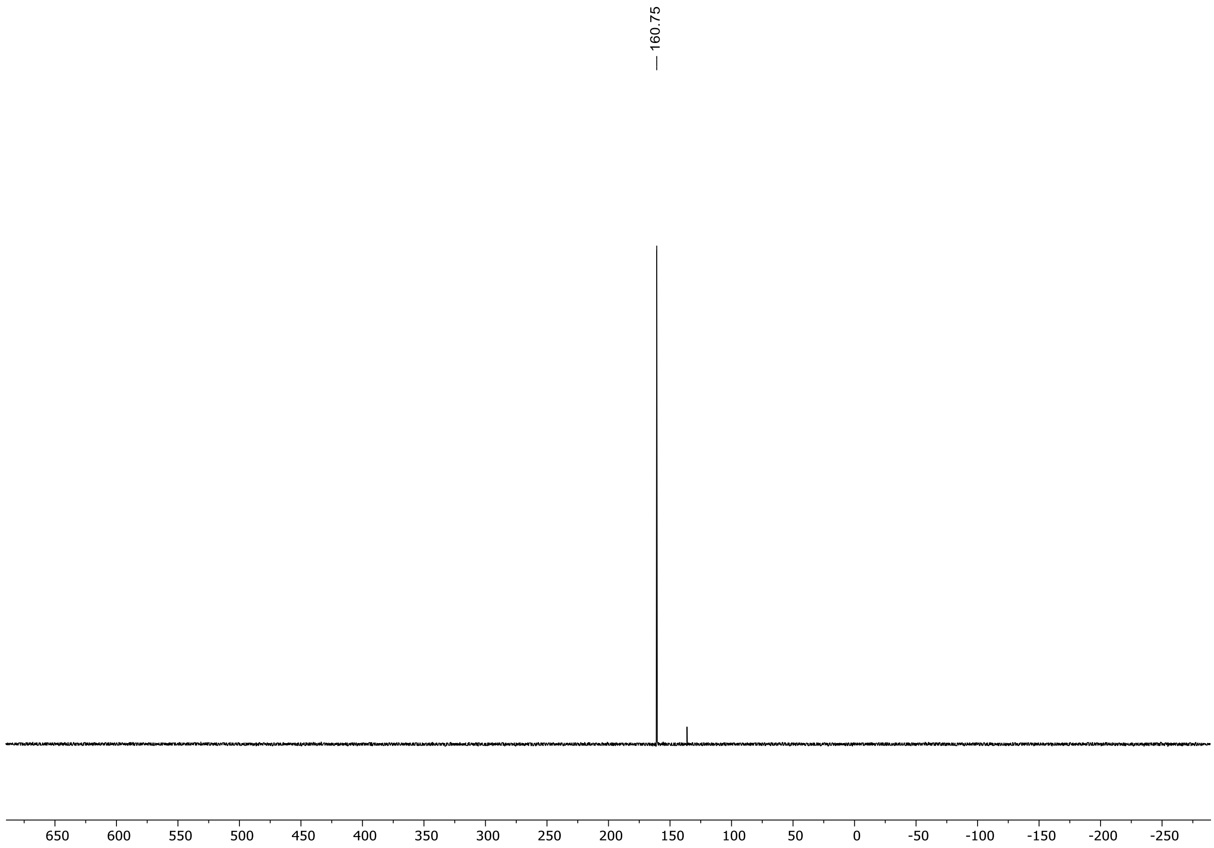
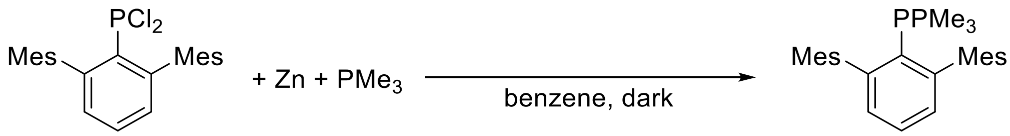


Figure S10: ^{31}P {^{1}H} NMR spectrum of ^{Mes}TerPCl$_2$ (122 MHz, C_6D_6, rt).



2.3.4 Synthesis of ^{Mes}TerPPMe$_3$ (2)



^{Mes}TerPCl$_2$ (2.500 g, 6.019 mmol) and zinc dust (1.968 g, 30.10 mmol) were suspended in either benzene or toluene (50 mL). PMe$_3$ (1.8 mL, 18.06 mmol) was added dropwise to the suspension and the reaction mixture was stirred under the exclusion of light for 16 hours at room temperature. The supernatant was collected by filtration over celite and all volatile components were removed under vacuum to yield ^{Mes}TerPPMe$_3$ (**2**) as a bright yellow solid.

Yield: 1.982 g (4.713 mmol; 78%).

^{1}H NMR (300 MHz, C_6D_6): δ [ppm] = 7.11–7.04 (m, 1H, *p*-Ar*H*), 6.98–6.93 (m, 2H, *m*-Ar*H*), 6.91 (4H, *m*-Ar*H* Mes), 2.37 (12H, o-C*H*$_3$ Mes), 2.22 (6H, p-C*H*$_3$ Mes), 0.59 (dd, 9H,

$^2J_{PH}$ = 11.8 Hz, $^3J_{PH}$ = 3.4 Hz, P(CH_3)$_3$). **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6): δ [ppm] = −3.03 (d, $^1J_{PP}$ = 576 Hz), −1114.72 (d, $^1J_{PP}$ = 576 Hz).

Figure S11: ^{1}H NMR spectrum of ^{Mes}TerPPMe$_3$ (300 MHz, C_6D_6, rt).

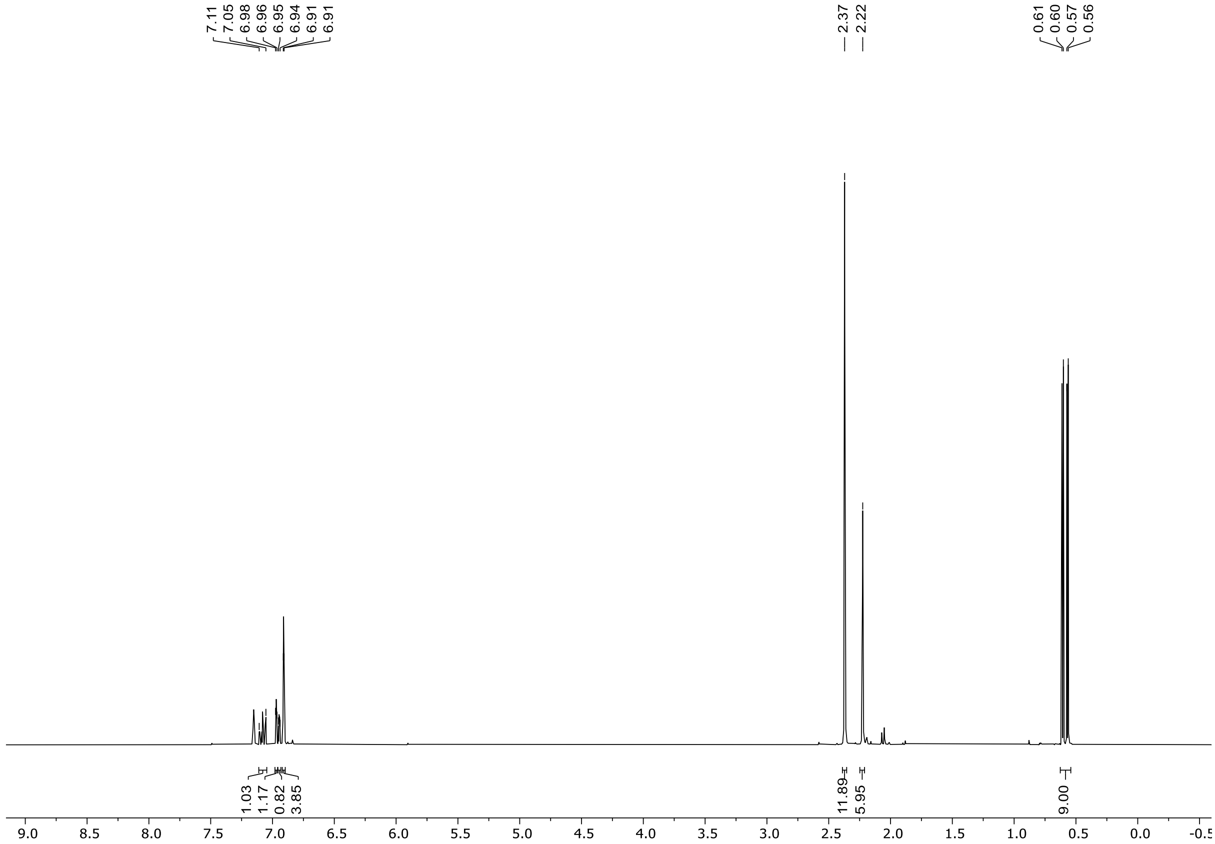
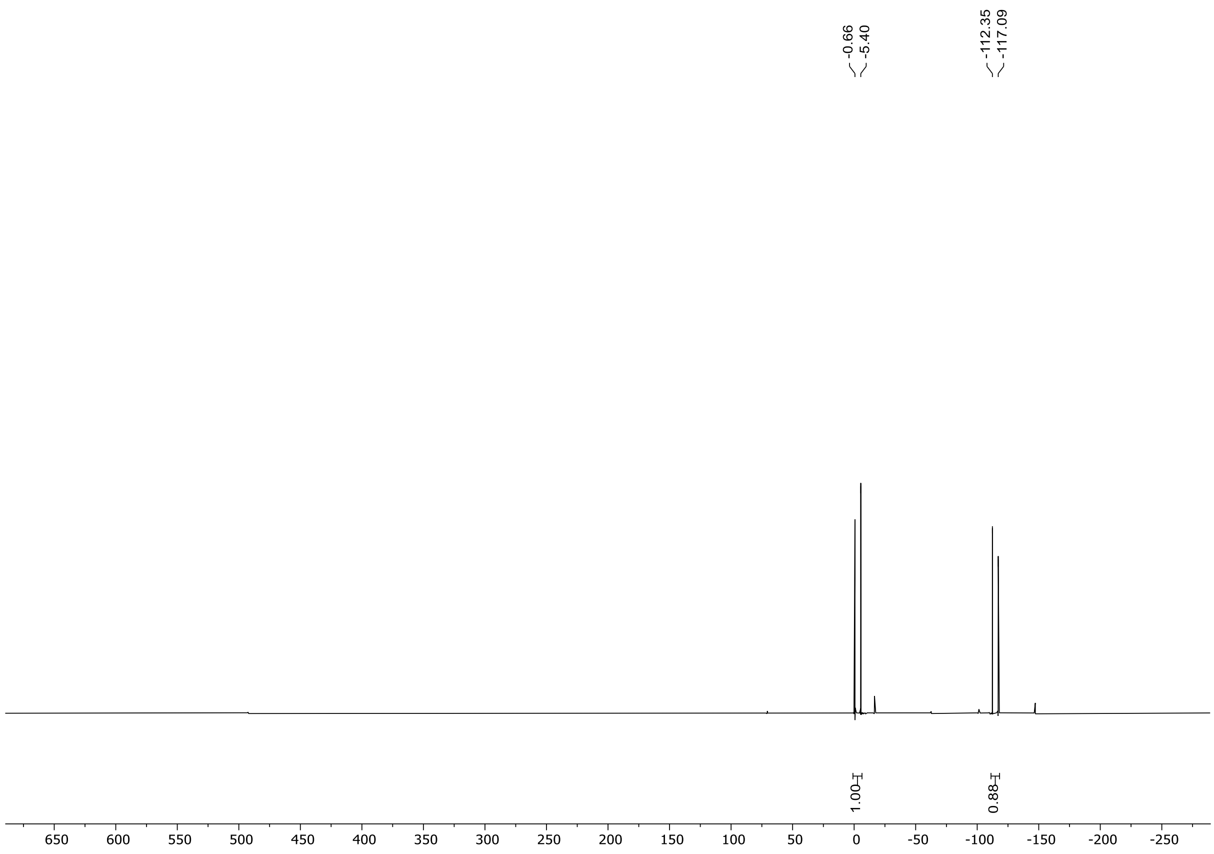
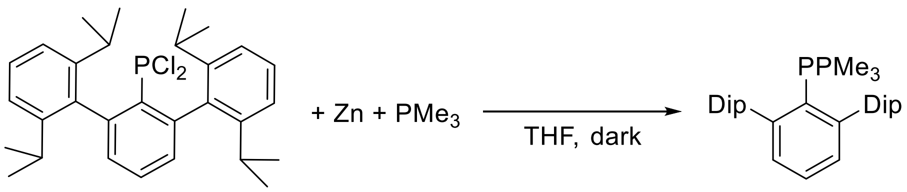


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of $^{Mes}TerPPMe_3$ (122 MHz, C_6D_6, rt).



2.4 Synthesis of $^{Dip}TerPPMe_3$ (4)



$^{Dip}TerPCl_2$ (0.500 g, 1.001 mmol) and zinc dust (0.127 g, 2.002 mmol) were suspended in 40 mL of tetrahydrofuran. PMe_3 (1.02 mL, 10.01 mmol) was added dropwise to the suspension, and the reaction mixture was stirred under the exclusion of light for 24 hours at room temperature. The supernatant was collected by filtration over celite and all volatile components were removed under vacuum to yield $^{Dip}TerPPMe_3$ (**4**) as a bright yellow solid. In the case of observable impurities in the NMR spectra, recrystallization from either *n*-hexane or *n*-pentane results in analytically pure material.

Crystals suitable for single crystal X-ray diffraction were obtained from a saturated solution of **4** in *n*-hexane at −30 °C.

Yield: 0.254 g, 0.503 mmol (50%).

CHN calc. (found) in %: for $C_{33}H_{46}P_2$: C 78.54 (78.27); H 9.19 (8.95). **^{1}H NMR** (300 MHz, C_6D_6, 298 K): δ [ppm] = 0.53 (dd, 9H, $^2J_{PH}$ = 11.9 Hz, $^3J_{PH}$ = 3.2 Hz, P(CH_3)$_3$), 1.08 (d, 12H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.35 (d, 12H, $^3J_{H,H}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 3.06 (hept, 4H, $^3J_{H,H}$ = 6.8 Hz, C*H*(CH_3)$_2$), 6.96-7.00 (m, 1H, CH_{Aryl}), 7.02-7.07 (m, 4H, CH_{Aryl}), 7.14-7.15 (m, 2H, CH_{Aryl}), 7.21-7.25 (m, 2H, CH_{Aryl}). **^{13}C{^{1}H} NMR** (75 MHz, C_6D_6, 298 K): δ [ppm] = 17.3 (dd, $^1J_{P,C}$ = 41.5 Hz, $^2J_{P,C}$ = 15.9 Hz, P(CH_3)$_3$), 24.1 (CH($\underline{C}H_3$)$_2$), 24.2 (CH($\underline{C}H_3$)$_2$), 26.0 (CH($\underline{C}H_3$)$_2$), 31.09 ($\underline{C}$H(CH_3)$_2$), 31.11 ($\underline{C}$H(CH_3)$_2$), 123.6 (CH_{Aryl}), 130.2 (CH_{Aryl}), 143.0 (d, $^3J_{P,C}$ = 4.2 Hz, *o*-$\underline{C}_{q,Aryl}$CH(CH_3)$_2$), 144.5 (dd, $^1J_{P,C}$ = 64.5 Hz, $^2J_{P,C}$ = 9.6 Hz, $C_{q,Aryl}$P), 146.4 (dd, $^2J_{P,C}$ = 14.5 Hz, $^3J_{P,C}$ = 10.6 Hz, *o*-$C_{q,Aryl}$P), 147.4 ($\underline{C}_{q,Aryl}$CH(CH_3)$_2$). **^{31}P{^{1}H} NMR** (122 MHz, C_6D_6, 298 K): δ [ppm] = −116.5 (d, $^1J_{P,P}$ = 560.1 Hz, P*P*(CH_3)$_3$), −3.1 (d, $^1J_{P,P}$ = 560.2 Hz, *P*P(CH_3)$_3$) ppm. **MS** (ESI-TOF): expected: m/z = 505.3153 [M + H]$^+$; found: m/z = 505.3151.

Figure S13: POV-ray depiction of the molecular structure of **4**. ORTEPs drawn at 50% probability, all H-atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) of **4**: P1-C1 1.8481(14), P1-P2 2.0955(7); C1-P1-P2 108.47(5).

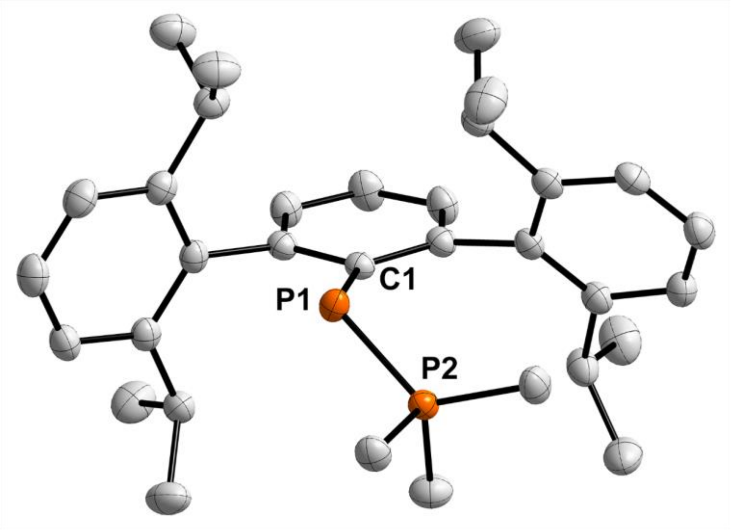


Figure S14: ^{1}H NMR spectrum of ^{Dip}TerPPMe$_3$ (**4**) of C_6D_6.

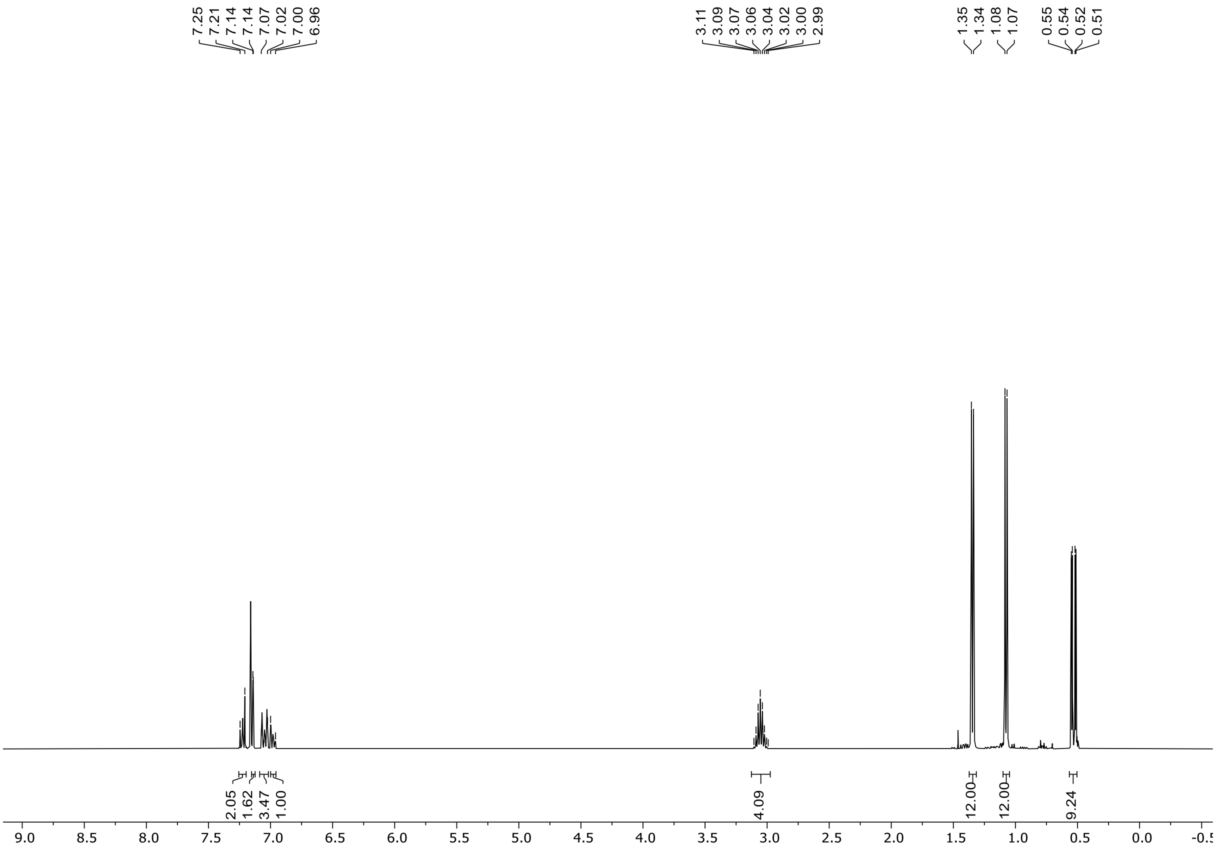


Figure S15: ^{13}C NMR spectrum of ^{Dip}TerPPMe$_3$ (**4**) (75 MHz, C_6D_6, rt).

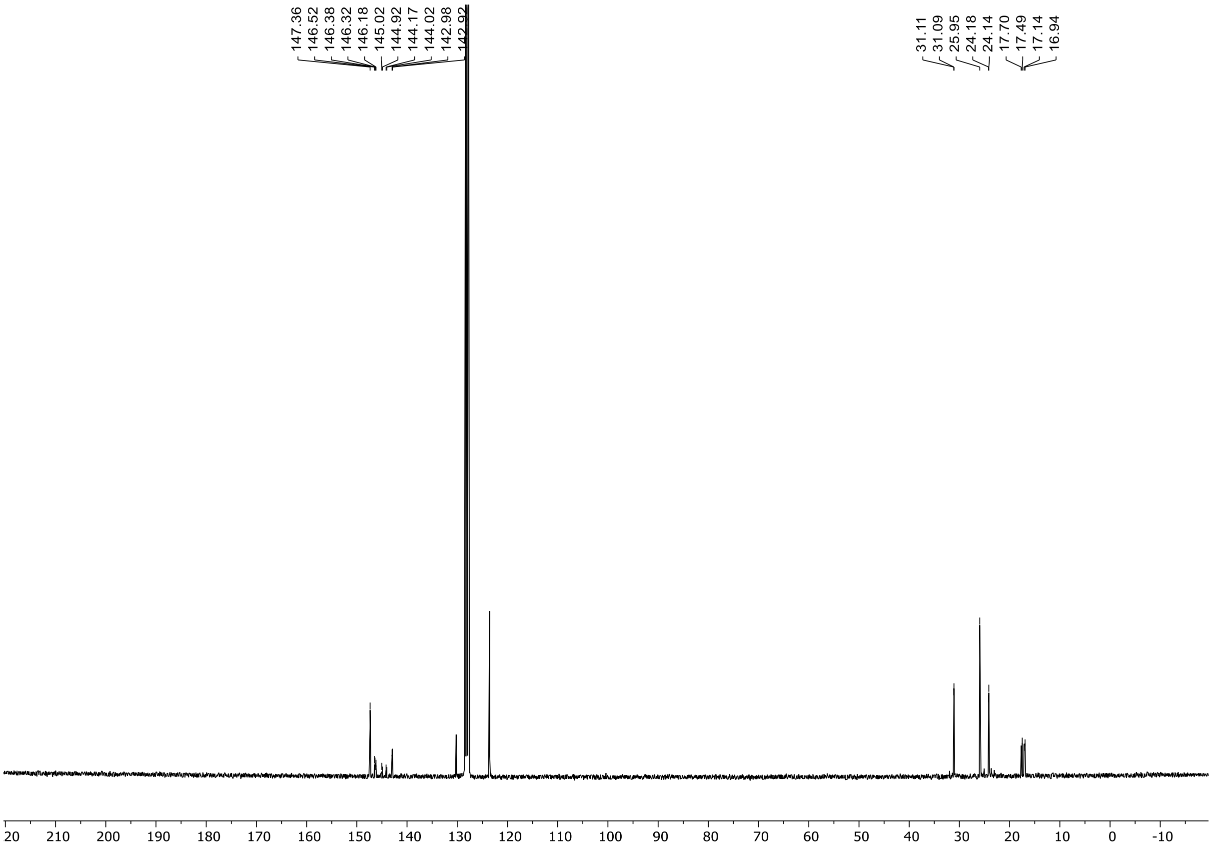
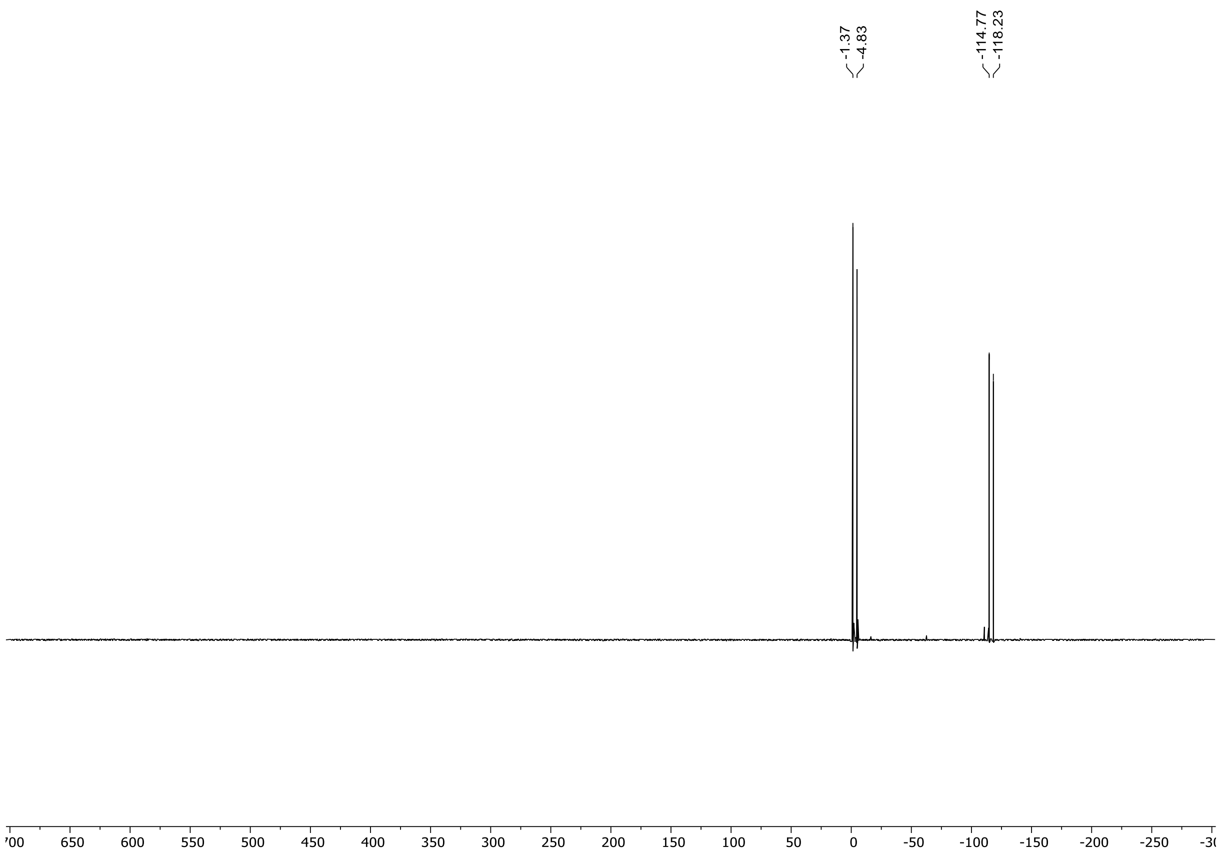
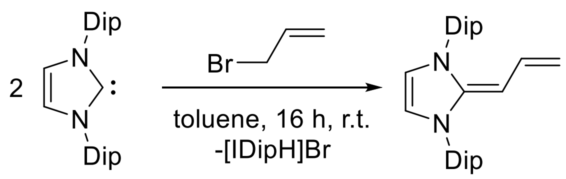


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of $^{Dip}TerPPMe_3$ (**4**) (122 MHz, C_6D_6, rt).



2.5 Synthesis of $IDipC_3H_4$[3]

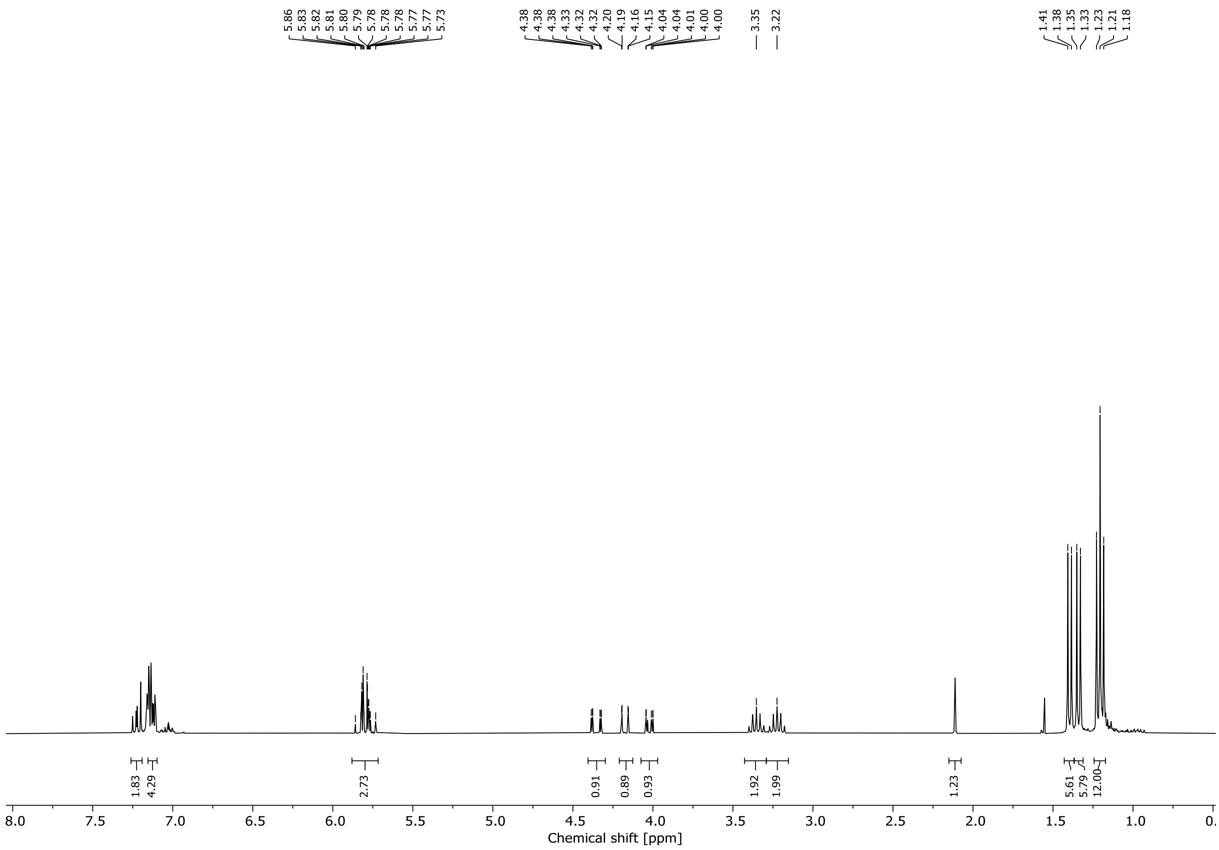


To a solution of IDip (1.24 g, 3.19 mmol) in toluene (20 mL) a solution of vinyl bromide (0.195 g, 1.60 mmol) in toluene (5 mL) was added dropwise at −78 °C. Upon complete addition the mixture turned yellow and a colorless precipitate began to form. The mixture was allowed to warm to room temperature overnight (16 h) and the volatiles were then removed *in vacuo*. The residue was then extracted with *n*-hexane (10 mL) and filtered using a canula fitted with a glass filter paper. The supernatant was then concentrated to incipient crystallization and placed in the freezer at −30 °C for 24 h.

This afforded a first crystalline crop of $IDipC_3H_4$ (0.185g, 0.43 mmol) as yellow crystalline solid. From the supernatant solution a second crop of brownish crystals was obtained. Yield: (Combined crops) 0.435 g, 1.01 mmol (63 %).

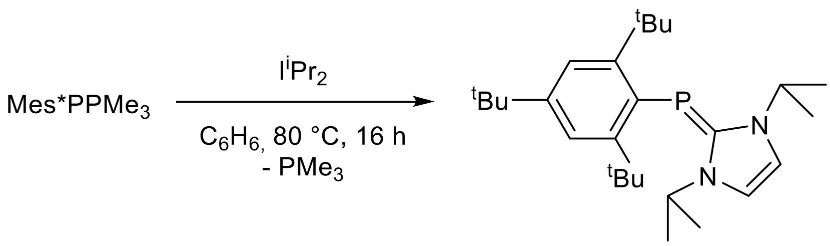
^{1}H NMR (300 MHz, C_6D_6, 298 K): δ [ppm] = δ = 7.26–7.19 (m, 2H, Ar*H*), 7.15–7.08 (m, 4H, Ar*H*), 5.87−5.72 (m, 3H), 4.35 (ddd, 1H, $^3J_{HH}$ = 16.0 Hz, J_{HH} = 2.7 Hz, J_{HH} = 0.7 Hz), 4.17 (d; 1H, $^3J_{HH}$ = 11.8 Hz), 4.02 (ddd; 1H, $^3J_{HH}$ = 10.0 Hz, J_{HH} = 2.7 Hz, J_{HH} = 0.7 Hz), 3.21 (hept; 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 3.09 (hept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.40 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.34 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.21 (2 overlapping d, 12H, CH(C*H*$_3$)$_2$).

Figure S17: ^{1}H NMR spectrum of $IDipC_3H_4$ in C_6D_6.



3 Syntheses of compounds

3.1 Synthesis of Mes*PI^{i}Pr$_2$ (5)



In a 25 ml Schlenk flask, Mes*PPMe$_3$ (0.100 g, 0.284 mmol) and I*i*Pr$_2$ (0.043 g, 0.284 mmol) were dissolved in benzene (5 mL). The orange reaction mixture was heated overnight at 80 °C. Subsequently, the solvent was removed *in vacuo* and the resulting solid was extracted using *n*-hexane. It was then filtered using a filter canula and the filtrate was concentrated to incipient crystallization and kept at −30 °C for 48 h. This resulted in the deposition of Mes*PI*i*Pr$_2$ (**5**) as deep yellow crystalline solid. Yield: 0.070 g, 0.163 mmol (58%).

Mp. 138 °C. **CHN** calc. (found) in %: for $C_{27}H_{45}N_2P$: C 75.66 (75.73); H, 10.58 (10.34), N 6.54 (6.36). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 7.51 (d, 2H, $^4J_{PH}$ = 1.8 Hz, Ar-*H*), 6.04–6.10 (m, 1H, (*H*CN*i*Pr)$_2$C), 5.89–5.96 (m, 1H, (*H*CN*i*Pr)$_2$C), 4.82– 5.02 (m, 1H, C*H*(CH$_3$)$_2$), 2.59 (hept, 1H, $^3J_{HH}$ = 6.6 Hz, , CH$_3$-CH of NHC^{IiPr2}), 1.92 (d, 18H, J_{PH} = 1.1 Hz, *o*-C(C*H*$_3$)$_3$), 1.36 (s, 9H, *p*-C(C*H*$_3$)$_3$ of Mes*), 1.05 (d, 6H $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$) ,0.74 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 21.5 (2C, CH(*C*H$_3$)$_2$), 23.5 (2C, CH(*C*H$_3$)$_2$), 31.9 (3C, *p*-C(CH$_3$)$_3$), 33.5 (d, 6C, J_{PC} = 9.8 Hz, *o*-C(CH$_3$)$_3$), 35.0 (1C, *p*-*C*(CH$_3$)$_3$), 38.95 (d, 2C, J_{PC} = 1.3 Hz, *o*-C(CH$_3$)$_3$), 46.3 (1C, *C*H(CH$_3$)$_2$), 47.6 (d, 1C, J_{PC} = 30.2 Hz, *C*H(CH$_3$)$_2$), 112.7 (d,1C, J_{PC} = 5.3 Hz, (H*C*N*i*Pr)$_2$C), 113.2 (d, J_{PC} = 2.1 Hz, (HN*i*Pr)$_2$C), 121.1 (2C, ArH) 137.5 (d, 1C, $^1J_{PC}$ = 60.3 Hz, P*C*$_{ipso}$), 147.8 (1C, ArC$_{quat}$), 158.3 (d, 2C, $^2J_{PC}$ = 5.1 Hz, ArC$_{quat}$), 167.5 (d, 1C, $^1J_{PC}$ = 115.0 Hz, PC$_{NHC}$). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = -50.67. **IR** (ATR, 32 scans, cm^{-1}): ν = 2951 (m), 2903 (m), 2868 (m), 1586 (w), 1521 (w), 1477 (w), 1462 (w), 1417 (m), 1401 (m), 1385 (m), 1367 (m), 1358 (m), 1314 (m), 1273 (s), 1250 (m), 1236 (m), 1207 (s), 1168 (w), 1115 (m), 1081 (w), 1033 (m), 983 (w), 921 (w), 903 (w), 875 (m), 775 (w), 758 (m), 690 (s), 642 (w), 599 (w), 583 (w), 545 (w), 465 (w), 434 (w), 420 (w). **MS** (ESI-TOF): expected: m/z = 429.3398; found: m/z = 429.3403.

X-Ray quality crystals of 5 were obtained from saturated n-hexane solutions at −30 °C. However, the dataset obtained from a twinned crystal just confirmed the connectivity of **5**.

Figure S18: POV-ray depiction of the molecular structure of **5**. ORTEPs drawn at 50% probability, all H-atoms (except H1 and H4) are omitted for clarity. Selected bond lengths (Å) and angles (°) of **5**: P1-C20 1.772(2), P1-C1 1.862(2), C20−P1−C1 102.82(10).

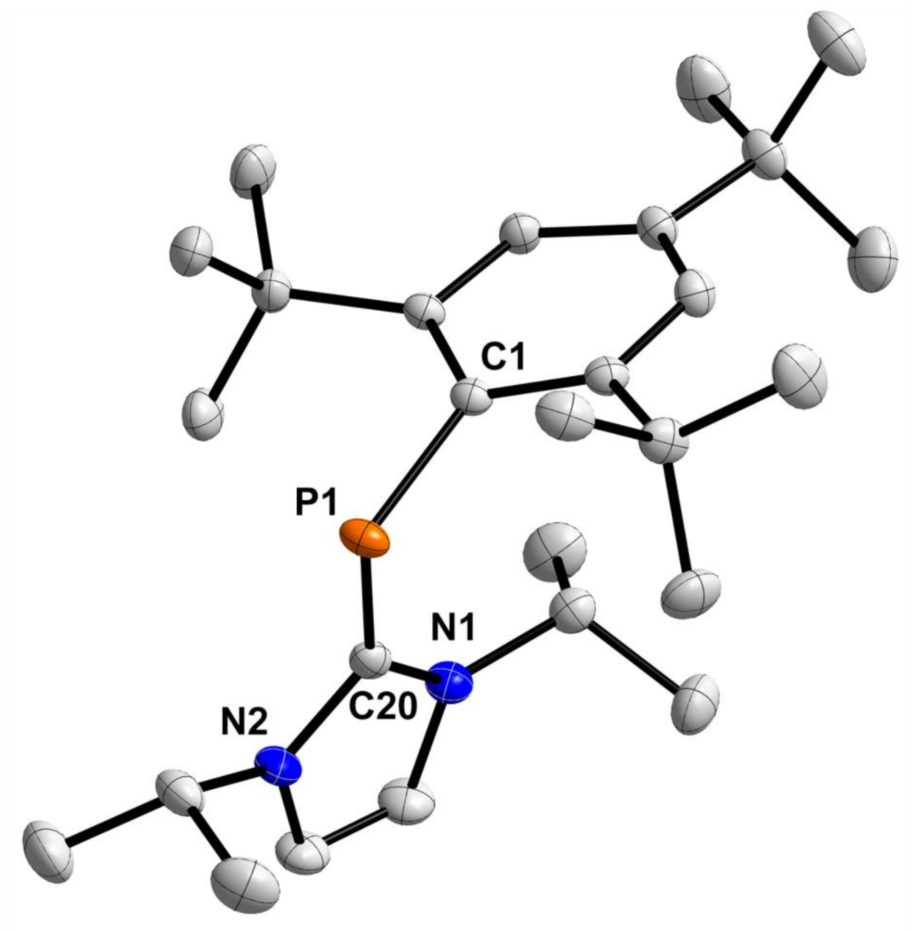


Figure S19: ^{1}H NMR spectrum of Mes*P$I^{i}Pr_2$ (**5**) in C_6D_6.

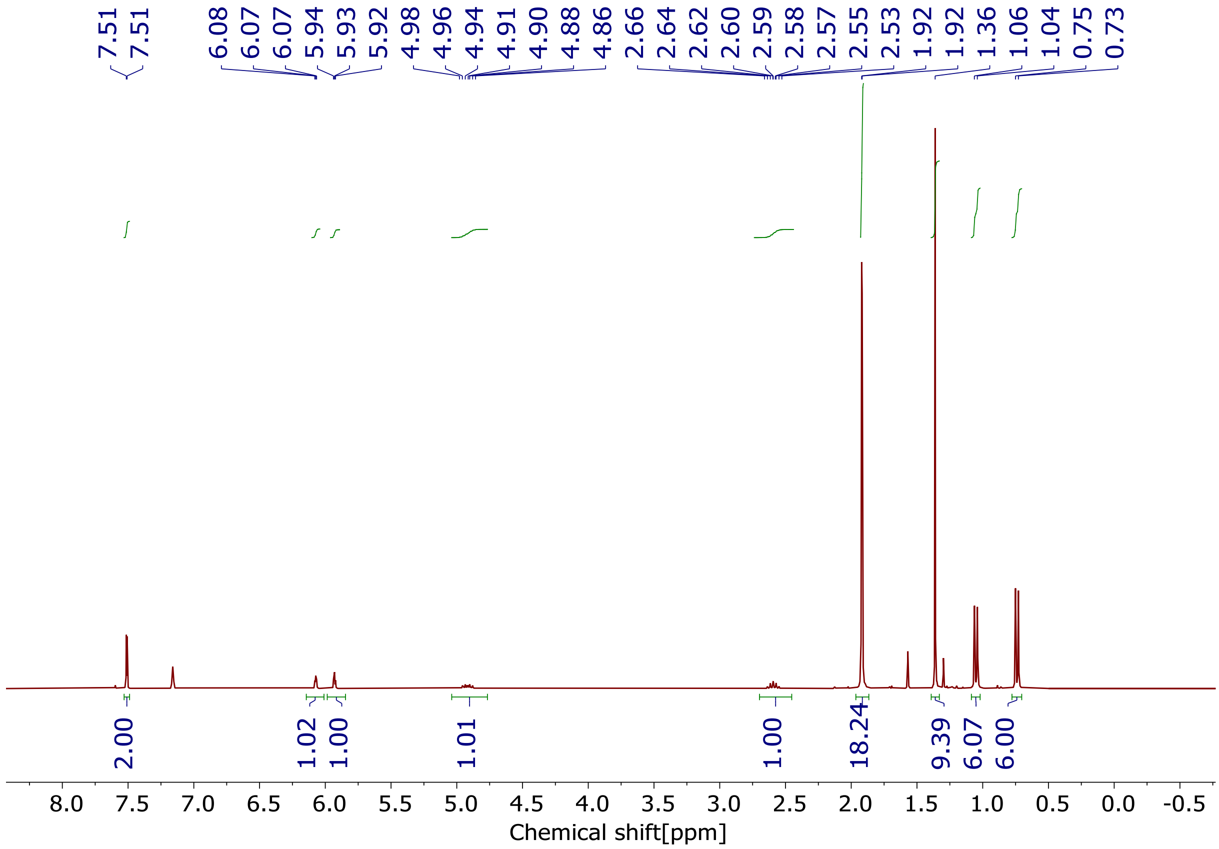


Figure S20: ^{13}C NMR spectrum of Mes*P$I^{i}Pr_2$ (**5**) in C_6D_6.

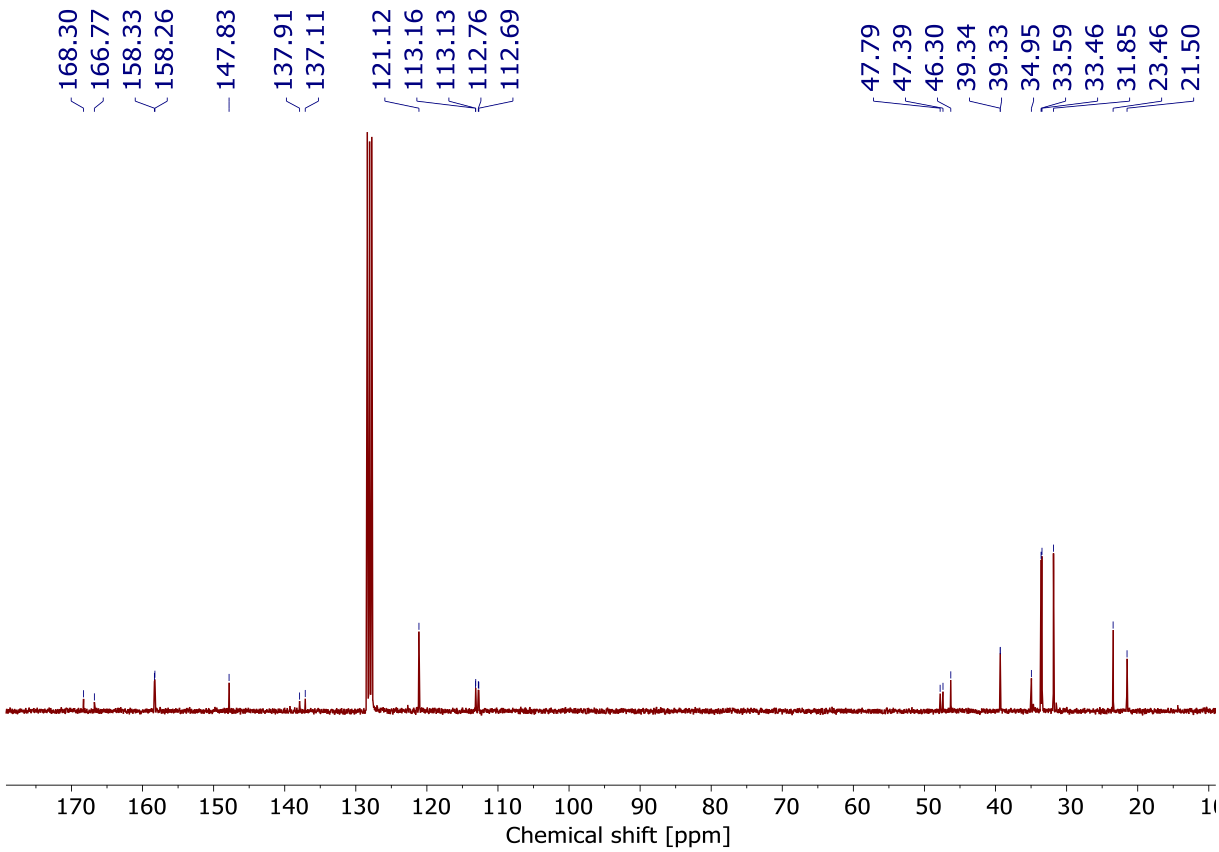
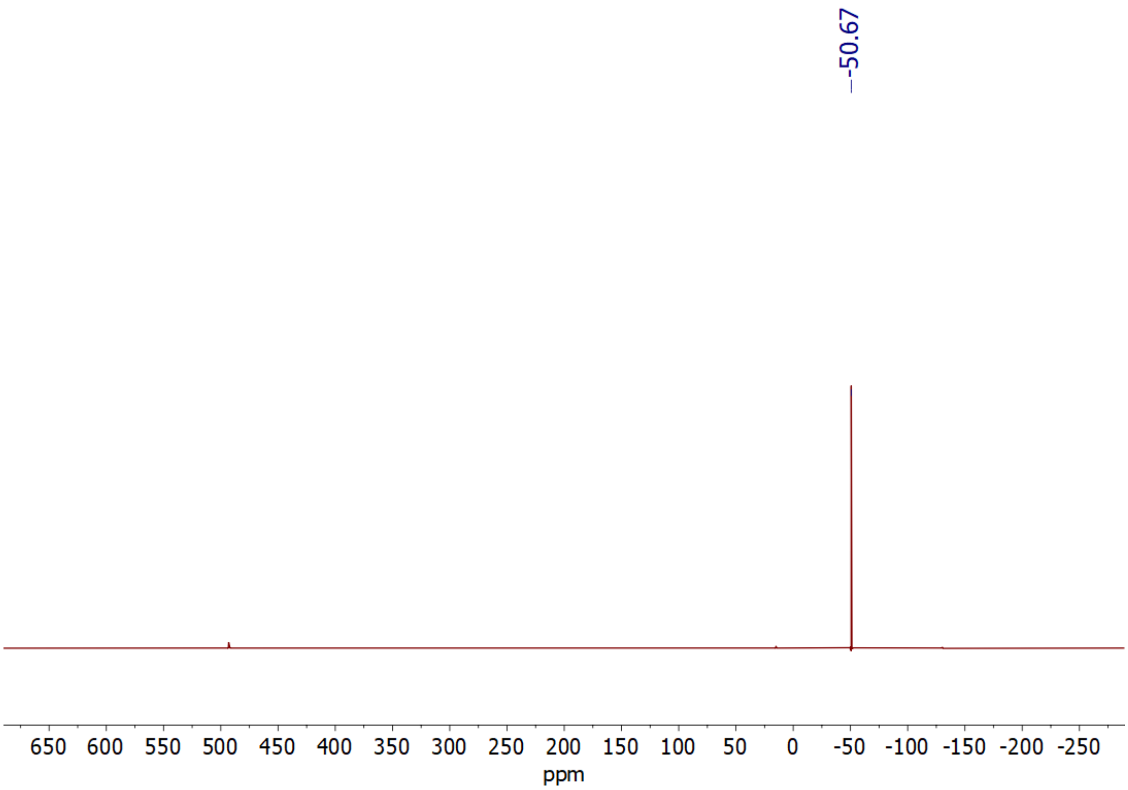
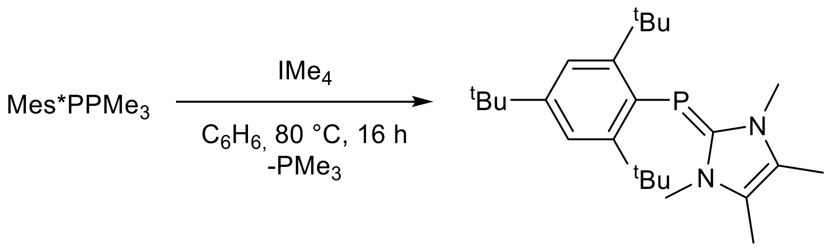


Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of Mes*PI$^{i}Pr_2$ (**5**) in C_6D_6.



3.2 Synthesis of Mes*PIMe$_4$ (6)



Mes*PPMe$_3$ (0.078 g, 0.221 mmol) was combined with IMe$_4$ (0.0274 g, 0.221 mmol) in benzene (5 ml) and was stirred overnight at 80 °C. Afterwards the solvent was evaporated and the residue was extracted with *n*-hexane, filtered using a canula fitted with a glass microfiber filter and concentrated to incipient crystallization and was then placed in the freezer at −30 °C for a period of 48 h. This afforded Mes*PIMe$_4$ (**6**) as yellow crystalline solid. Yield: 0.0587 g, 0.146 mmol (66.2%).

Mp. 141 °C. **CHN** calc. (found) in % for $C_{25}H_{41}N_2P$: C 74.96 (74.79), H 10.30 (10.33), N 6.99 (5.94). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 7.61 (d, $^{4}J_{PH}$ = 1.8 Hz, Ar*H*), 3.00 (d, J_{PH}

= 2.6 Hz, NCH_3), 2.17 (d, J_{PH} = 1.2 Hz, NCH_3), 1.97 (d, J_{PH} = 1.2 Hz, *o*-C(CH_3)$_3$), 1.41 (s, 9H, *p*-C(CH_3)$_3$), 1.26 (s, 3H, (H_3CCCMe)$_2$C), 1.24 (s, 3H, (H_3CCCMe)$_2$C). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 8.4 (1C, (H_3CCNMe)$_2$C), 8.5 (1C, (H_3CCNMe)$_2$C), 30.4 (1C, NCH_3), 30.9 (1C, J_{PC} = 30.5 Hz, NCH_3), 30.74 (CH_3-C of Mes*), 31.8 (*p*-C(CH_3)$_3$), 33.6 (d, J_{PC} = 9.6 Hz, *o*-C(CH_3)$_3$), 35.1 (1C, *p*-*C*(CH_3)$_3$), 39.5 (2C, o-*C*(CH_3)$_3$), 119.6 (1C, (H_3CCNMe)$_2$C), 119.9 (d, 1C, J_{CP} = 5.8 Hz, (H_3CCNMe)$_2$C)), 120.9 (2C, Ar*C*H), 137.3 (d, 1C, $^1J_{PC}$ = 58.2 Hz, PC_{ipso}), 148.6 (1C, ArC_{quat}), 159.5 (d, 2C, $^2J_{PC}$ = 5.2 Hz, ArC_{quat}), 167.6 (d, 1C, $^1J_{PC}$ = 108.3 Hz, PC_{NHC}). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −47.47. **IR** (ATR, 32 scans, cm^{-1}): ν = 2956 (s), 2917 (m), 2902 (m), 2870 (m), 2850 (m), 1693 (w), 1667 (w), 1589 (w), 1523 (w), 1474 (m), 1432 (m), 1398 (m), 1382 (s), 1360 (s), 1331 (s), 1282 (w), 1237 (m), 1206 (m), 1179 (m), 1163 (m), 1124 (w), 1096 (s), 1057 (w), 1037 (m), 920 (w), 903 (w), 875 (m), 852 (m), 756 (m), 716 (w), 647 (w), 602 (w), 542 (w), 496 (w), 460 (w), 430 (w), 415 (w). **MS** (ESI-TOF): expected: m/z = 401.3086; found: m/z = 401.3075.

Single crystals suitable for X-ray diffraction of **6** can be grown from saturated *n*-hexane solution at −30 °C.

Figure S22: ^{1}H NMR spectrum of Mes*PIMe$_4$ (**6**) in C_6D_6.

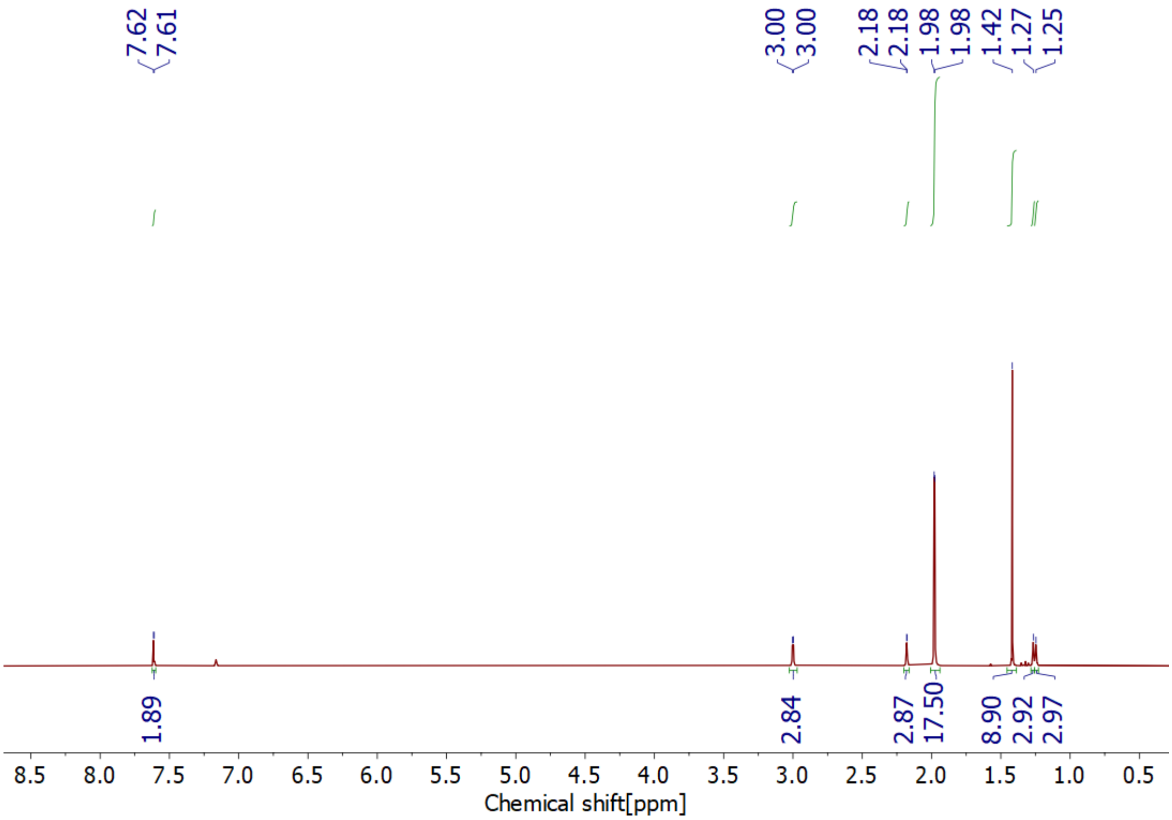


Figure S23: ^{13}C NMR spectrum of Mes*PIMe$_4$ (**6**) in C_6D_6.

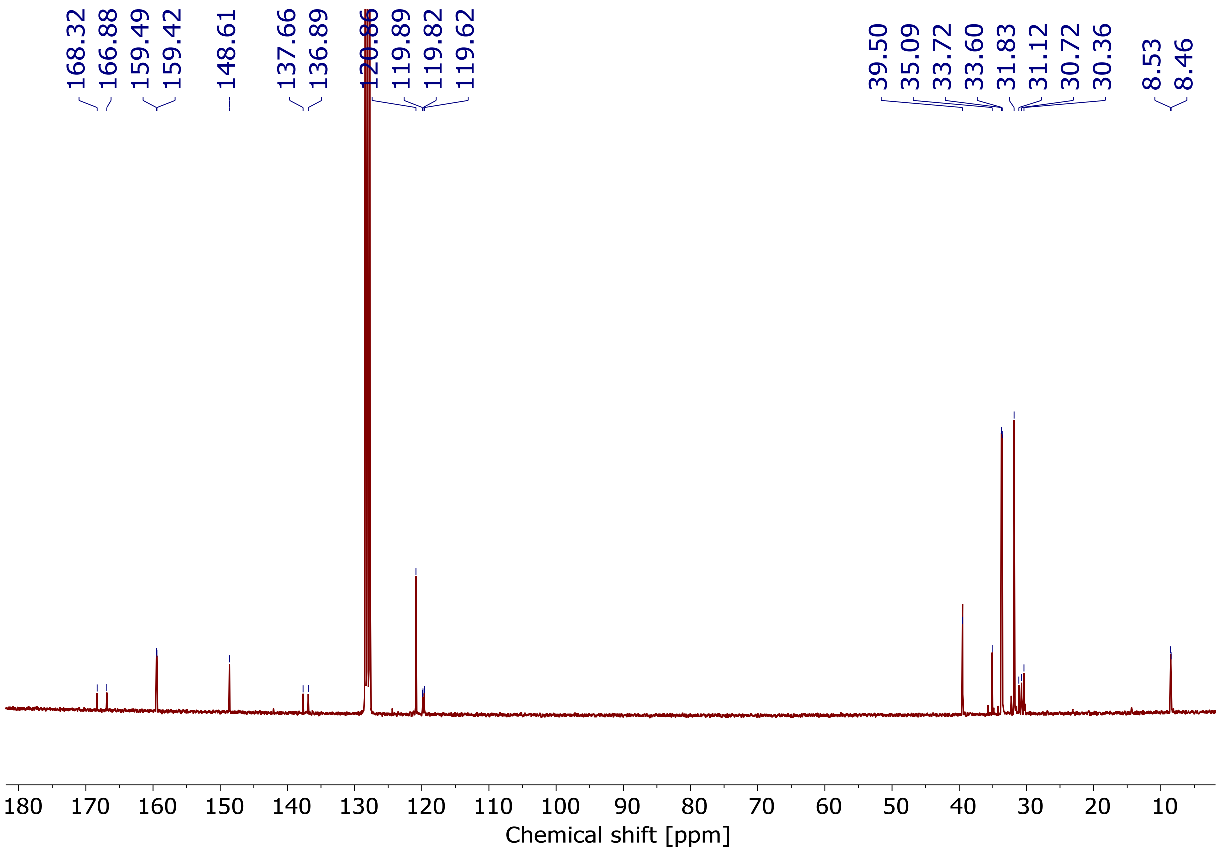
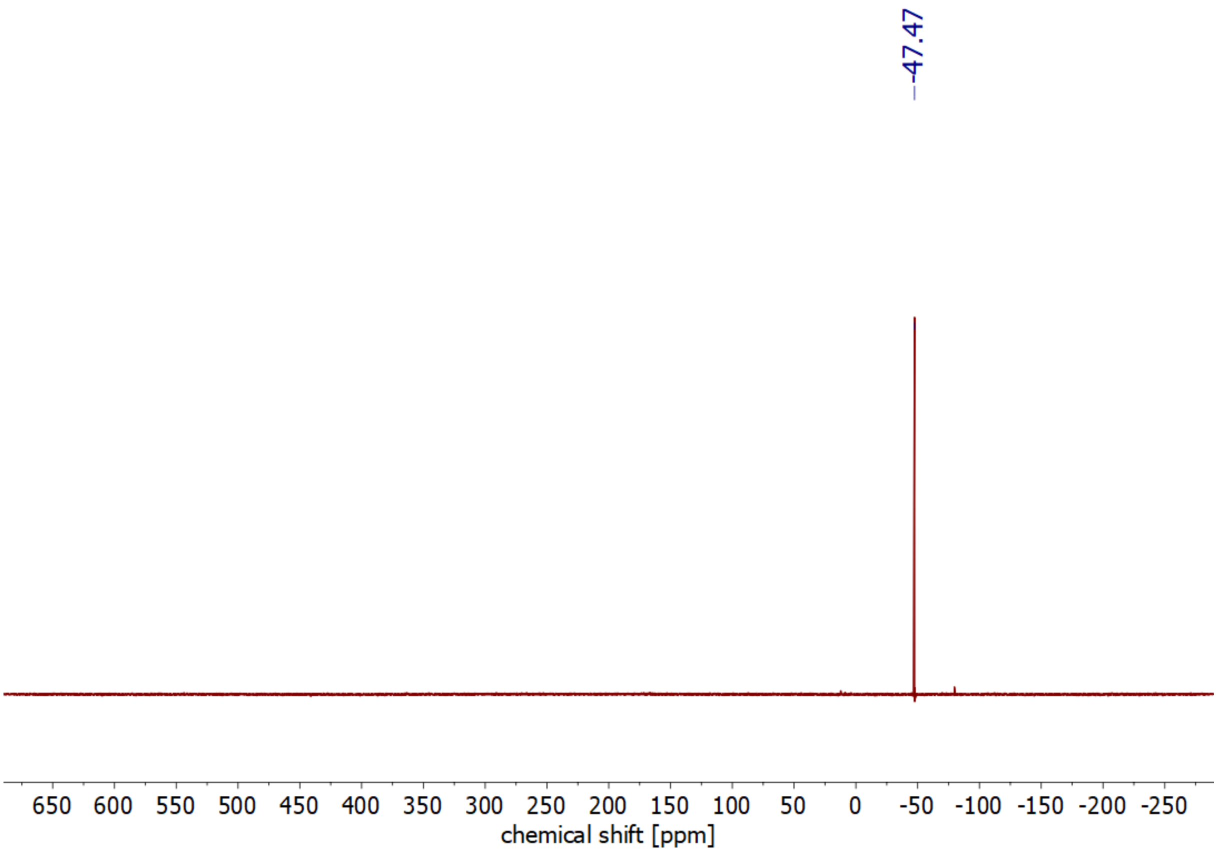
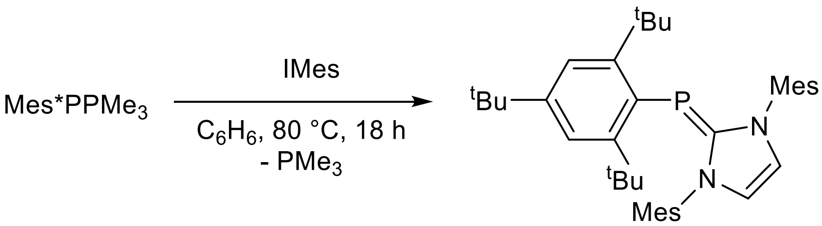


Figure S24: $^{31}P\{^1H\}$ NMR spectrum of Mes*PIMe$_4$ (**6**) in C_6D_6.



3.3 Synthesis of Mes*PIMes (7)



In a round-bottomed flask Mes*PPMe$_3$ (0.100 g, 0.283 mmol) and IMes (0.0865 g, 0.283 mmol) were suspended in benzene (5mL) and stirred for 18 h at 80 °C. Later, the solvent was evaporated *in vacuo* and the remaining solid was extracted with *n*-hexane. It was then filtered using filter canula and dried again to obtain an amorphous yellow solid of Mes*PIMes (**7**). Yield: 0.120 g, 0.206 mmol (73%)

Mp. 163 °C. **CHN** calc. (found) in % for $C_{39}H_{53}N_2P$: C 80.65 (80.61), H 9.20 (9.01), N 4.82 (3.83). ^{1}**H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.37 (s, 9H, *p*-C(CH_3)$_3$), 1.75 (d, 18H, J_{PH} =

1.1 Hz, *o*-$C(CH_3)_3$), 2.05 (s, 6H, CH_3 of NMes), 2.08 (d, 6H, J_{PH} = 3.6 Hz, CH_3 of NMes), 2.45 (s, 6H, CH_3 of NMes), 5.53−5.56 (m, 1H, (*H*CNMes)$_2$C), 5.84−5.87 (m, 1H, (*H*CNMes)$_2$C), 6.48 (d, 2H, J_{PH} = 0.6 Hz, Ar*H* NMes), 6.81 (d, 2H, J_{PH} = 0.7 Hz, Ar*H* NMes), 7.10 (d, 2H, J_{PH} = 2.1 Hz, Ar*H*). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 19.5 (d, 2C, J_{CP} = 6.9 Hz, CH_3 of NMes), 19.9 (2C, CH_3 of NMes), 21.0 (d, 2C, J_{CP} = 9.1 Hz, CH_3 of NMes), 32.0 (3C, *p*-C(CH$_3$)$_3$), 34.6 (d, 6C, J_{CP} = 9.5 Hz, *o*-C(CH$_3$)$_3$), 34.7 (1C, *p*-*C*(CH$_3$)$_3$), 39.07 (d, 2C, J_{CP} = 1.3 Hz, *o*-*C*(CH$_3$)$_3$), 118.7 (d, 1C, JPC = 1.4 Hz, (H*C*NMes)C), 119.25 (d, 2C, J_{CP} = 5.5 Hz, (H*C*NMes)C), 129.5 (2C, Ar*C*H), 130.0 (2C, Ar*C*H), 134.8 (1C, ArC_{quat}), 134.9 (1C, ArC_{quat}), 135.4 (d, 1C, $^1J_{PC}$ = 60.3 Hz, PC_{ipso}), 136.1−136.5 (4C, ArC_{quat}), 136.6 (1C, ArC_{quat}), 138.4 (1C, ArC_{quat}), 146.7 (1C, ArC_{quat}), 156.9 (d, 2C, $^2J_{PC}$ = 5.0 Hz, ArC_{quat}), 170.6 (d, 1C, $^1J_{PC}$ = 110.9 Hz, PC_{NHC}). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −29.77. **IR** (ATR, 32 scans, cm^{-1}): ν = 2950 (m), 2905 (w), 2866 (w), 1609 (w), 1588 (w), 1476 (m), 1382 (m), 1354 (m), 1310 (s), 1277 (s), 1254 (m), 1234 (m), 1207 (w), 1162 (w), 1111 (m), 1079 (w), 1033 (w), 915 (w), 871 (w), 847 (m), 806 (w), 775 (w), 754 (m), 692 (m), 662 (w), 646 (w), 623 (w), 598 (w), 579 (w), 516 (w), 497 (w), 471 (w), 439 (w). **MS** (ESI-TOF): expected: m/z = 581.4025; found: m/z = 581.4031. X-ray quality crystals of **7** could not be grown.

Figure S25: ^{1}H NMR spectrum of Mes*PIMes (**7**) in C_6D_6.

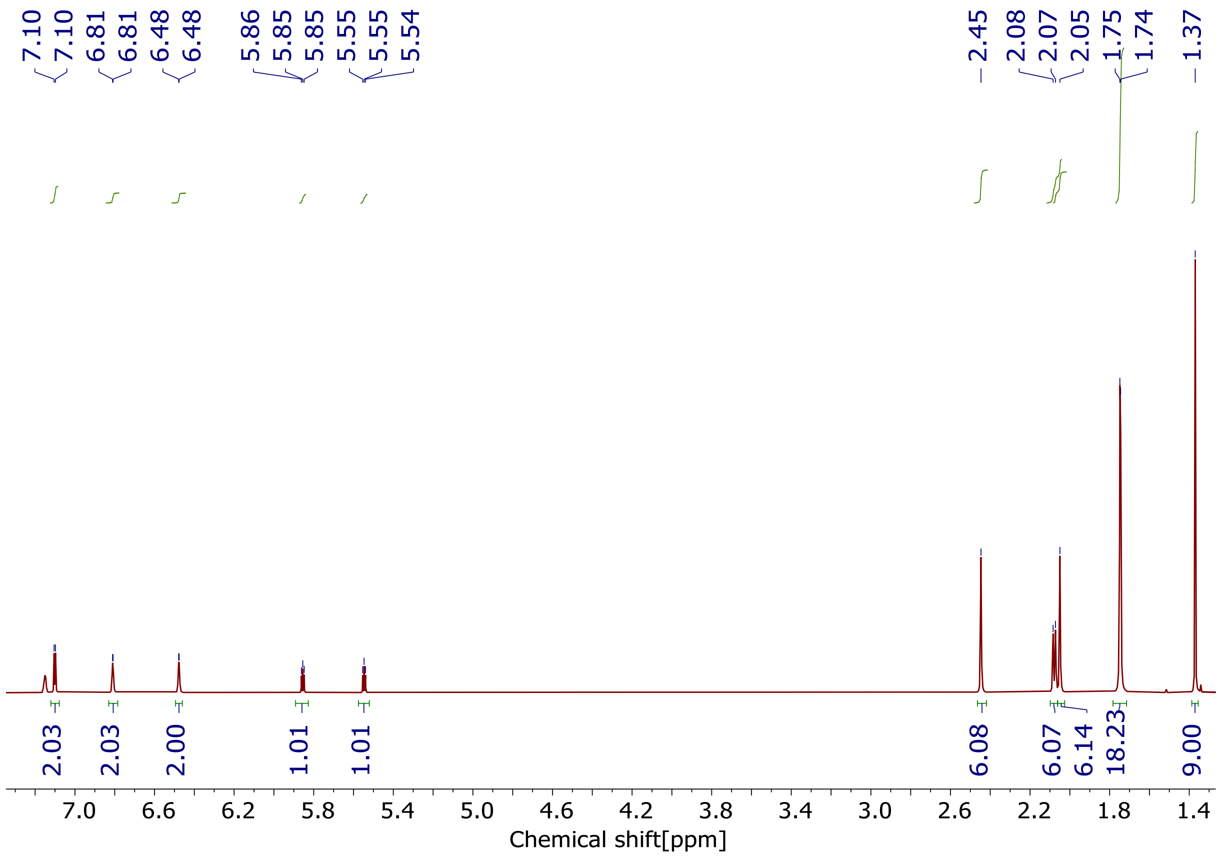


Figure S26: ^{13}C NMR spectrum of Mes*PIMes (**7**) in C_6D_6.

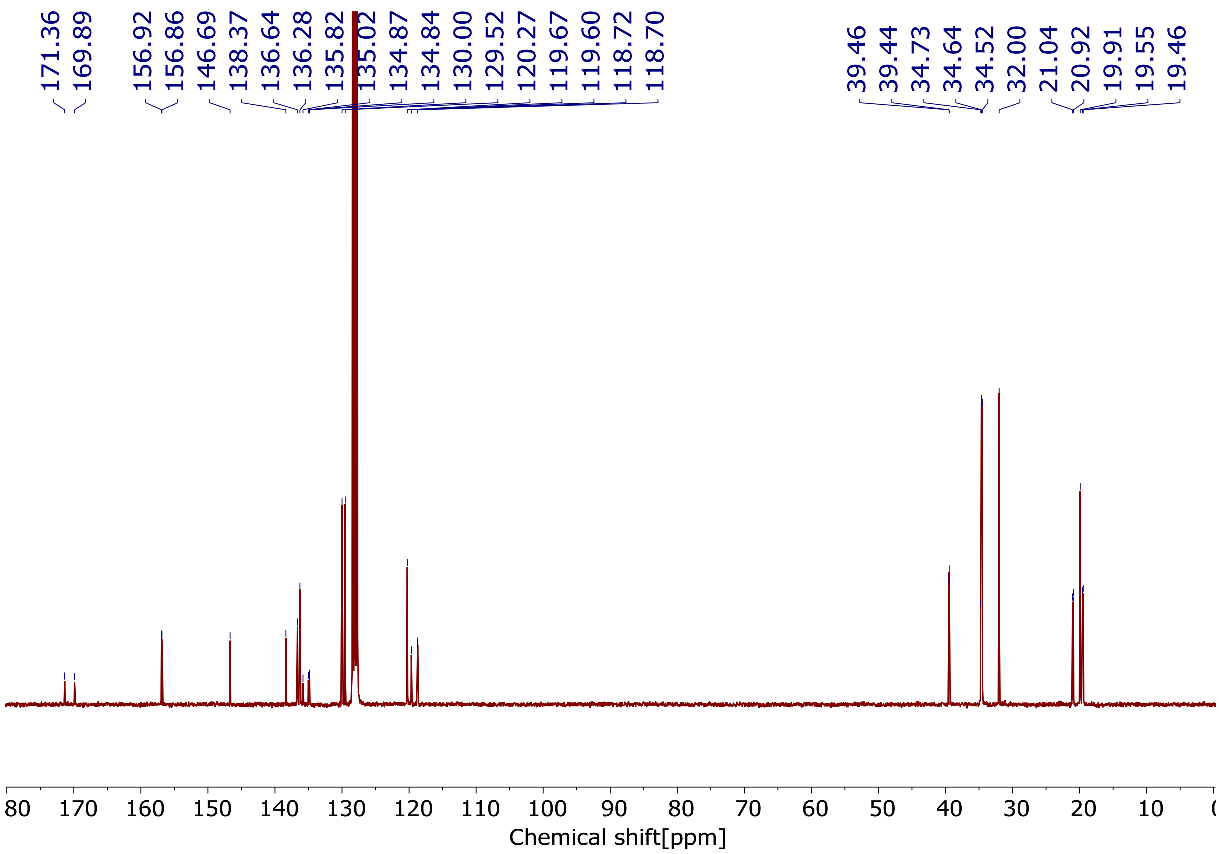
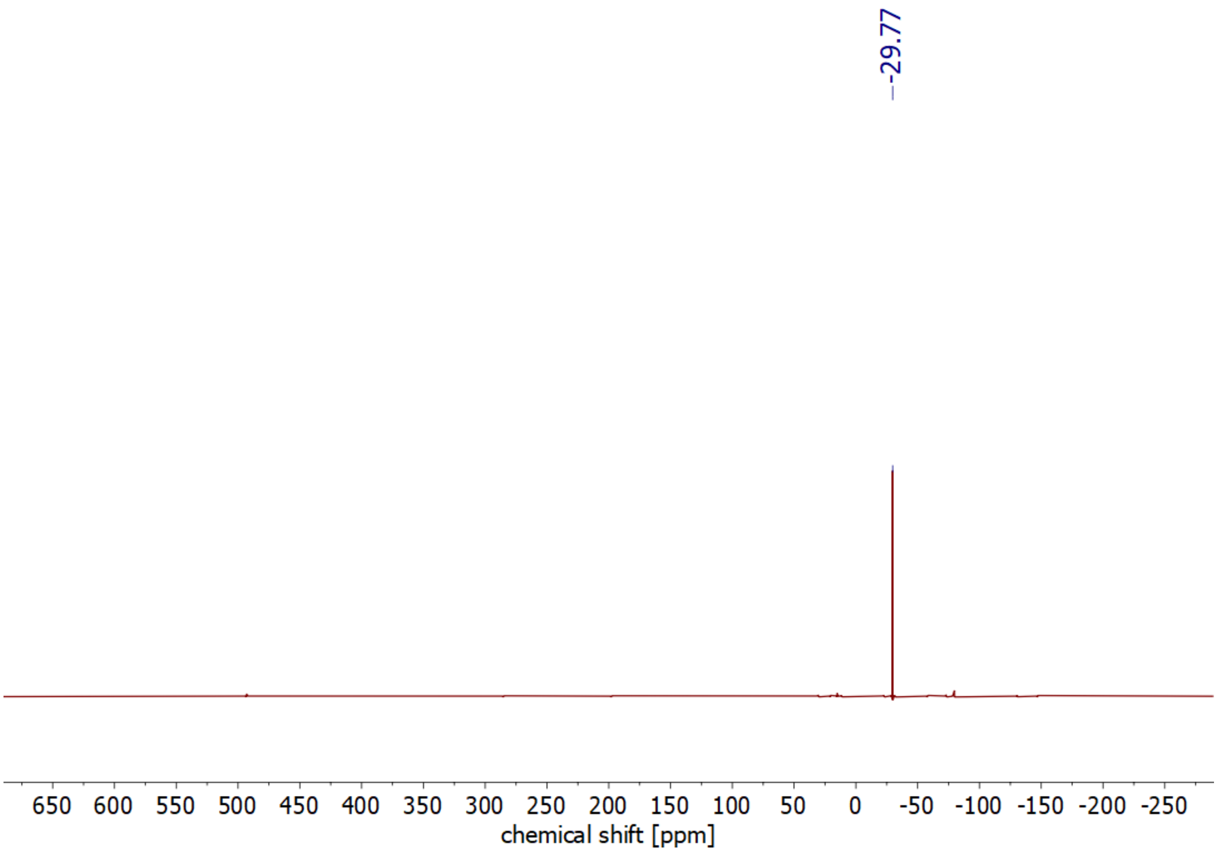
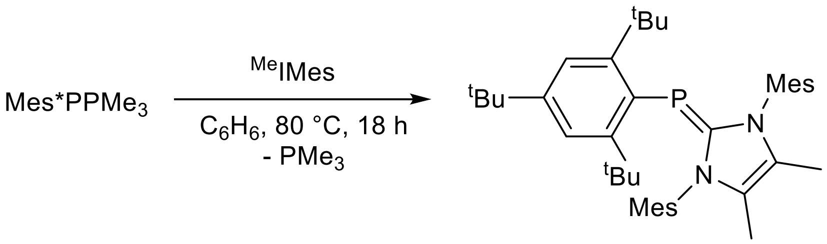


Figure S27: $^{31}P\{^{1}H\}$ NMR spectrum of Mes*PIMes (**7**) in C_6D_6.



3.4 Synthesis of Mes*P^{Me}IMes (8)



Mes*PPMe$_3$ (0.100 g, 0.284 mmol) and ^{Me}IMes (0.094 g, 0.284 mmol) were combined in a round bottomed flask, dissolved in benzene (5 mL) and stirred under exclusion of light for 18 h at 80 °C. This mixture was then dried and extracted with *n*-hexane. The resulting solution was filtered using a canula fitted with a glass microfiber filter. The volume of the filtrate was reduced to ca. 1 mL and placed in the freezer at −30 °C. This resulted in the deposition of Mes*P^{Me}IMes (**8**) as yellow crystalline solid.

Yield: 0.090 g, 0.147 mmol (52 %).

Mp. 191 (dec.) °C. **CHN** calc. (found) in %: for $C_{41}H_{57}N_2P$: C 80.88 (80.48); H 9.44 (9.33), N 4.60 (3.68). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.23 (s, 3H, (H_3CCNMes)$_2$C), 1.40 (s, 9H, *p*-C(CH_3)$_3$ of Mes*), 1.42 (s, 3H, (H_3CCNMes)$_2$C), 1.78 (d, J_{PH} = 1.2 Hz, 18H, *o*-C(CH_3)$_3$ Mes*), 2.04 (s, 6H, CH_3 NMes), 2.10 (d, 6H, J_{PH} = 4.8 Hz, CH_3 of Mes), 2.45 (s, 6H, CH_3 Mes), 6.51 (s, 2H, Ar-*H* of NMes), 6.86 (s, 2H, Ar-*H* NMes), 7.13 (d, 2H, J_{PH} = 2.0 Hz, Ar-*H*). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 9.1 (2C, (H_3*C*CNMes)$_2$C), 19.3 (d, 2C, J_{PC} = 5.5 Hz, *C*H$_3$ NMes), 20.0 (2C, *C*H$_3$ NMes), 21.1 (d, 2C, J_{PC} = 9.5 Hz, CH$_3$ NMes), 32.1 (3C, *p*-C(CH$_3$)$_3$), 34.5 (d, 6C, J_{PC} = 9.7 Hz, *o*-C(CH$_3$)$_3$), 34.7 (1C, *p*-*C*(CH$_3$)$_3$), 39.5 (d, 2C, J_{PC} = 1.4 Hz, *o*-*C*(CH$_3$)$_3$), 120.3 (2C, Ar*C*H), 121.0 (d, 1C, J_{PC} = 1.0 Hz, (MeCNMes)*C*), 121.8 (d, 2C, J_{CP} = 5.6 Hz, (Me*C*NMes)C), 129.6 (2C, Ar*C*H), 130.1 (2C, Ar*C*H), 133.2 (1C, ArC_{quat}), 133.3 (ArC_{quat}), 135.0 (1C, ArC_{quat}), 136.2 (d, 1C, $^1J_{PC}$ = 62.3 Hz, PC_{ipso}), 136.5 (1C, ArC_{quat}), 136.8−136.9 (m, 4C, ArC_{quat}), 137.0 (1C, ArC_{quat}), 138.4 (1C, ArC_{quat}), 146.4 (1C, ArC_{quat}), 156.7 (d, 2C, $^2J_{PC}$ = 5.0 Hz, ArC_{quat}), 170.6 (d, 1C, $^1J_{PC}$ = 110.8 Hz, PC_{NHC}). **^{31}P {^{1}H}** (121.55 MHz, C_6D_6): δ [ppm] = -33.18. **IR** (ATR, 32 scans, cm^{-1}): ν = 2947 (m), 2916 (m), 2862 (m), 1673 (w), 1609 (w), 1588 (w), 1477 (m), 1386 (m), 1352 (s), 1307 (s), 1278 (s), 1233 (m), 1199 (m), 1121 (w), 1032 (m), 968 (w), 924 (w), 901 (w), 871 (m), 852 (m), 797 (w), 747 (m), 659 (w), 636 (w), 594 (w), 565 (m), 514 (w), 498 (w), 462 (w), 437 (w). **MS** (ESI-TOF): expected: m/z = 609.4338; found: m/z = 609.4345.

X-Ray quality crystals of **8** were obtained from saturated *n*-hexane solutions at −30 °C.

Figure S28: ^{1}H NMR spectrum of Mes*P^{Me}IMes (**8**) in C_6D_6.

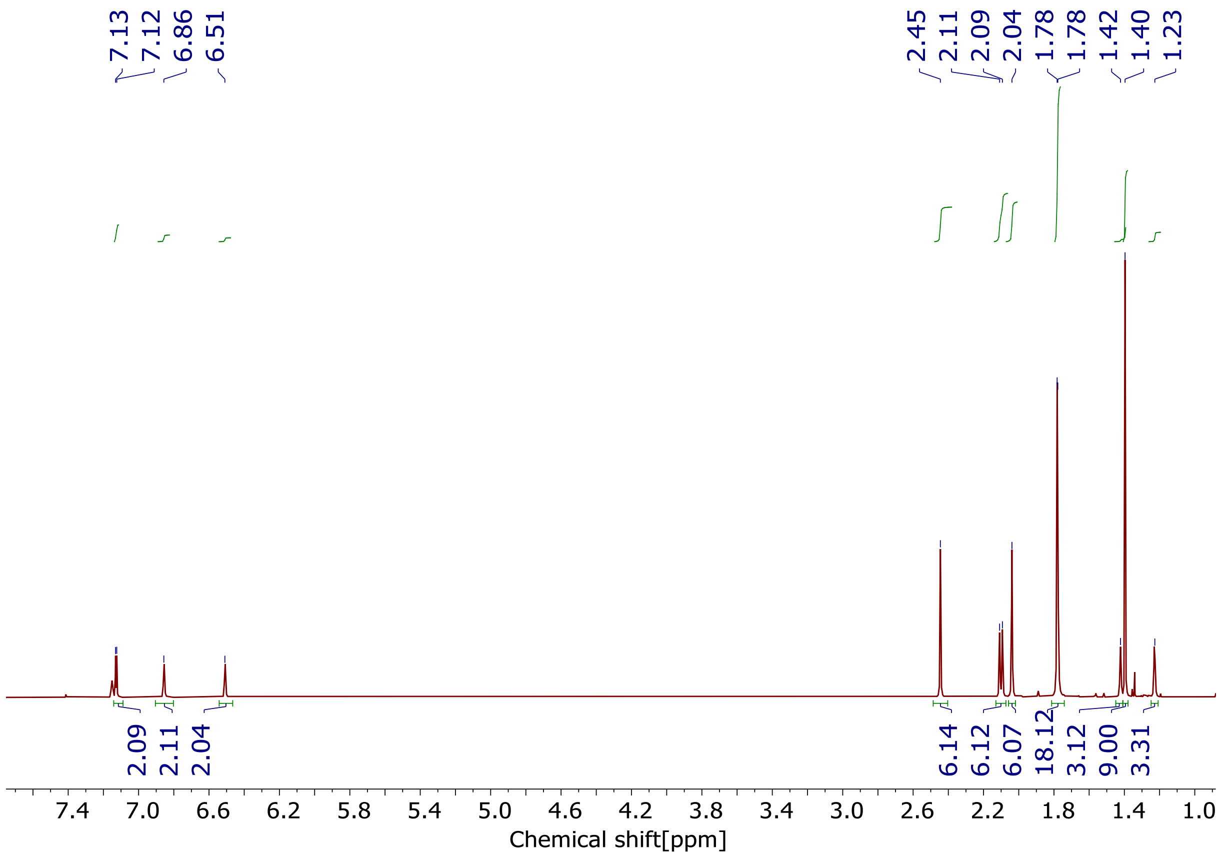


Figure S29: ^{13}C NMR spectrum of Mes*P^{Me}IMes (**8**) in C_6D_6.

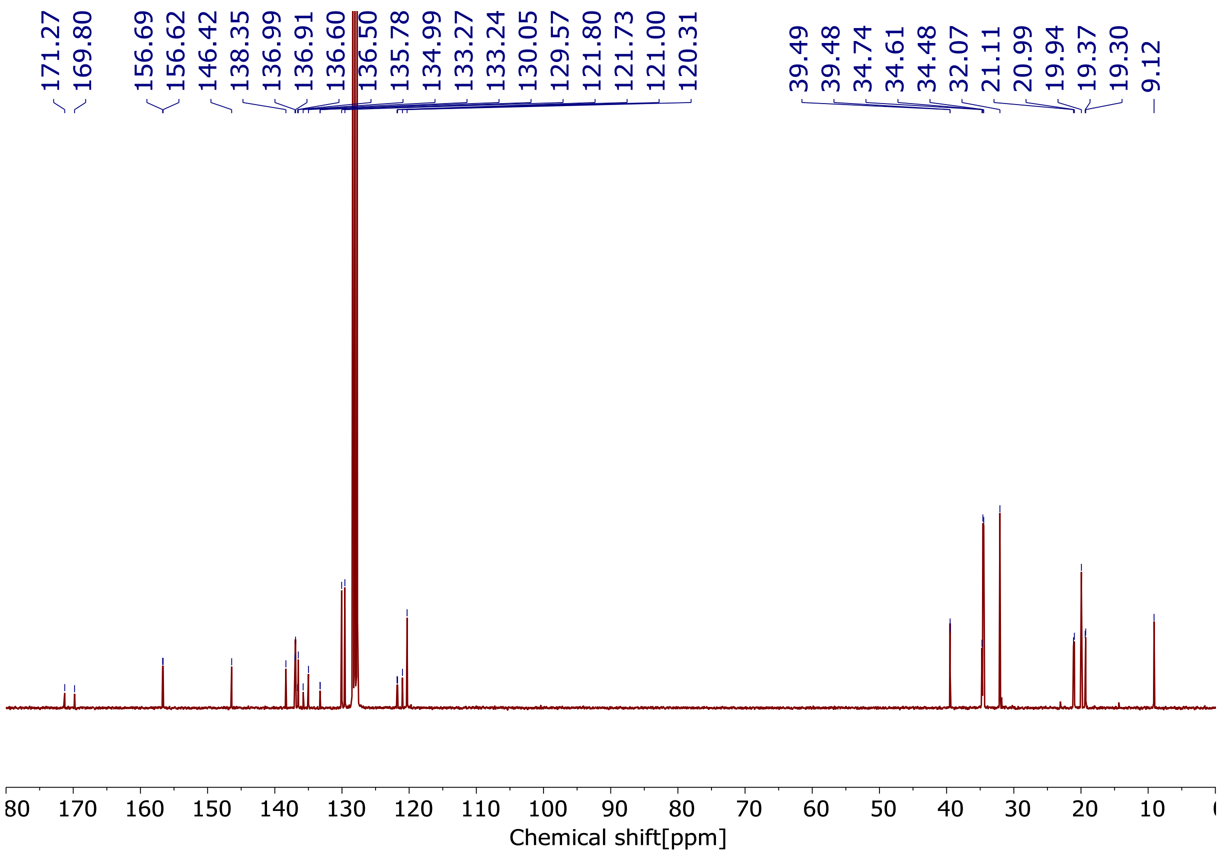
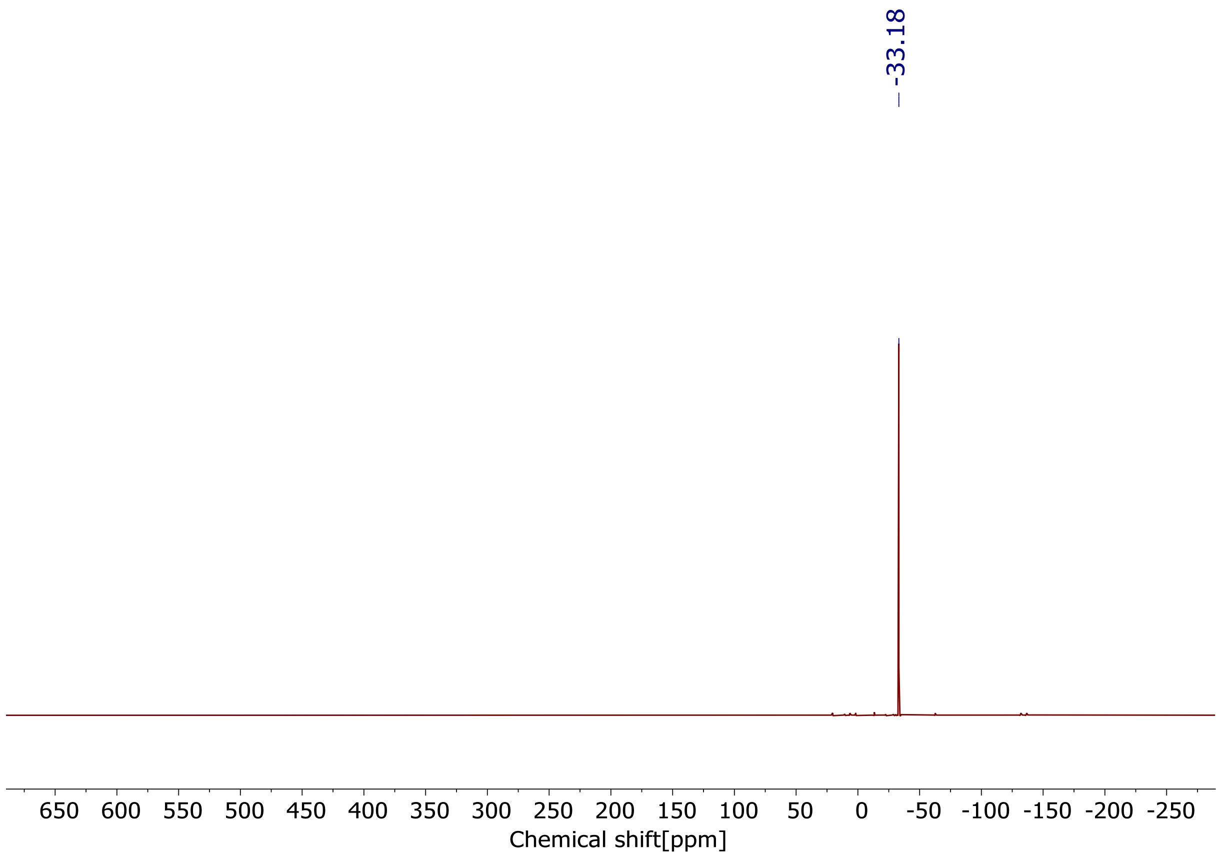
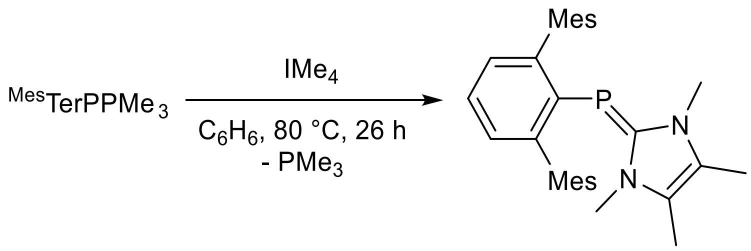


Figure S30: $^{31}P\{^1H\}$ NMR spectrum of Mes*P^{Me}IMes (**8**) in C_6D_6.



3.5 Synthesis of ^{Mes}TerPIMe$_4$ (9)



In a 25 ml Schlenk flask, ^{Mes}TerPPMe$_3$ (0.100 g, 0.237 mmol) and IMe$_4$ (0.029 g, 0.237 mmol) were dissolved in benzene (5 mL). The red reaction mixture was heated at 80 °C for 26 h. During the course of the reaction, the color of the reaction mixture changed from red to yellow. Subsequently, the solvent was removed *in vacuo* and the resulting solid was extracted using *n*-hexane and filtered using a pipette fitted with glass filter paper. The obtained yellow solution was further concentrated to incipient crystallization and placed in the freezer at −30 °C over a period of 24 h to afford ^{Mes}TerPIMe$_4$ (**9**) as a yellow solid. Yield: 0.060 g, 0.128 mmol (54 %).

Mp. 180 (dec.) °C. **CHN** calc. (found) in %: for $C_{31}H_{37}N_2P$: C 79.45 (79.47); H 7.96 (7.89), N 5.98 (6.03). **^{1}H NMR** (300 MHz, C_6D_6): δ [ppm] = 1.23 (s, 6H, (H_3CNCH$_3$)$_2$C), 2.16 (6H, *p*-CH_3 of Mes), 2.40 (12H, *o*-CH_3 of Mes), 2.83 (s, 6H, (H$_3$CNCH_3)$_2$C), 6.78 (s, 4H, Ar-*H* of Mes), 6.98–7.09 (m, 3H Ar-H, Mes$_2$C$_6$$H_3$). **^{13}C NMR** (75 MHz, C_6D_6): δ [ppm] = 8.5 (2C, (H$_3$*C*CNCH$_3$)$_2$C) 21.2 (4C, J_{CP} = 6.4 Hz, *o*-*C*H$_3$ Mes), 21.2 (2C, *p*-*C*H$_3$ Mes), 33.8 (2C, J_{CP} = 8.6 Hz, (H$_3$CCN*C*H$_3$)$_2$C), 122.2 (m, 2C, (H$_3$C*C*NCH$_3$)$_2$C), 128.2 (4C, *m*-Ar-CH of Mes), 128.7, 134.4, 135.9, 142.5, 144.4, 144.5, 150.7 (d, J_{PC} = 56.6 Hz, *ipso*-C Ter), 167.7 (d, J_{CP} = 97.7 Hz, (H$_3$CCNCH$_3$)$_2$*C*). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −76.9. **IR** (ATR, 32 scans, cm^{-1}): ν = 2916 (s), 2849 (m), 1723 (w), 1639 (w), 1650 (w), 1610 (w), 1568 (w), 1444 (s), 1368 (s), 1259 (w), 1231 (w), 1195 (w), 1177 (w), 1125 (w), 1095 (m), 1030 (s), 846 (s), 796 (s), 737 (s), 717 (m), 699 (w), 672 (w), 654 (w), 589 (m), 573 (w), 558 (w), 548 (w), 509 (w), 498 (w), 476 (w), 417 (w). **MS** (ESI-TOF): expected: m/z = 469.2773; found: m/z = 469.2778.

Figure S31: ^{1}H NMR spectrum of ^{Mes}TerPIMe$_4$ (**9**) in C_6D_6.

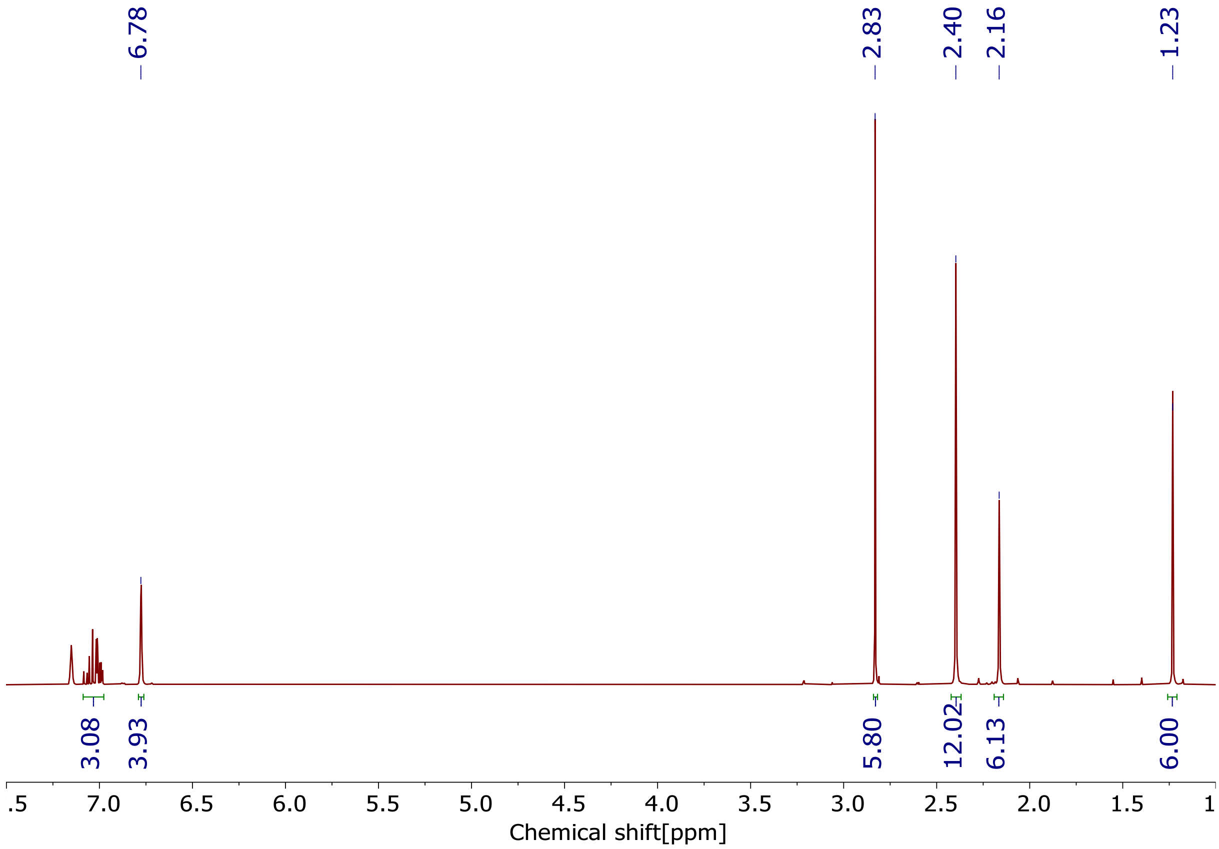


Figure S32: ^{13}C NMR spectrum of ^{Mes}TerPIMe$_4$ (**9**) in C_6D_6.

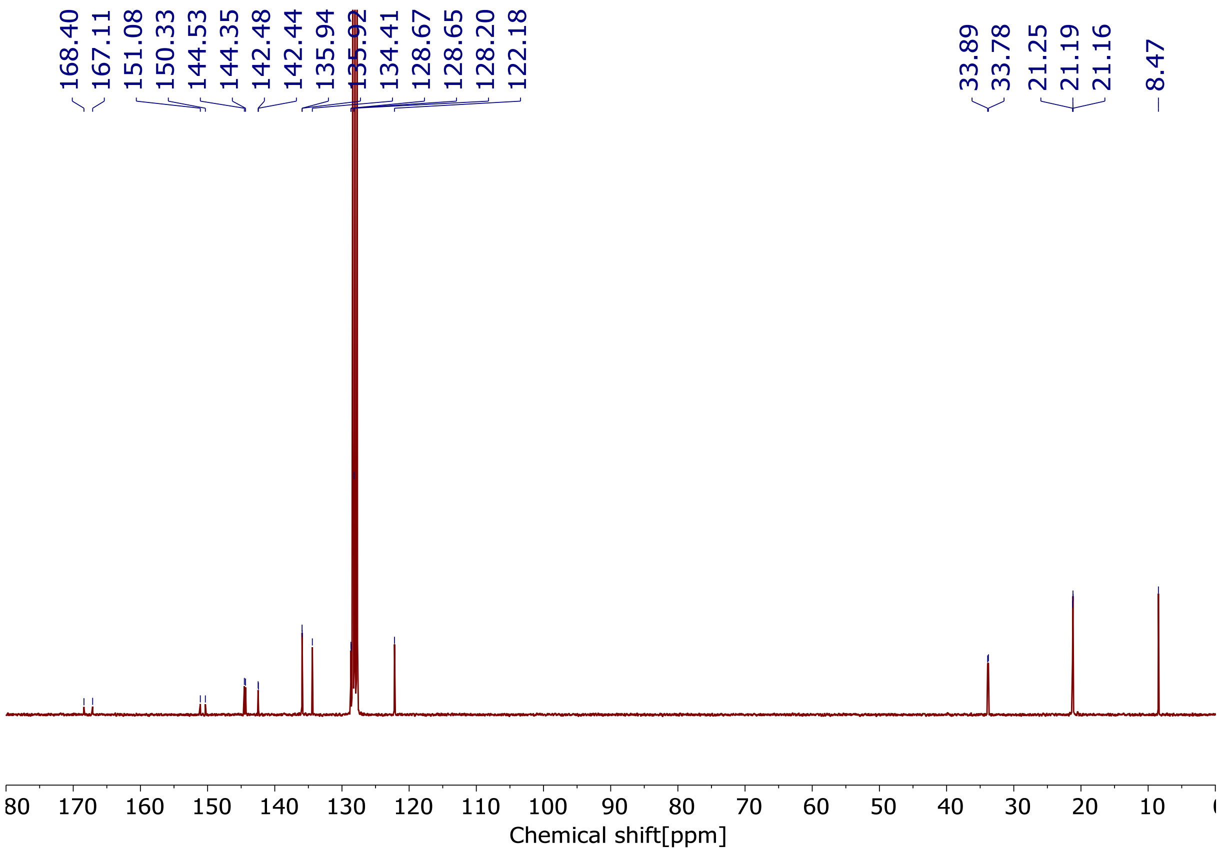
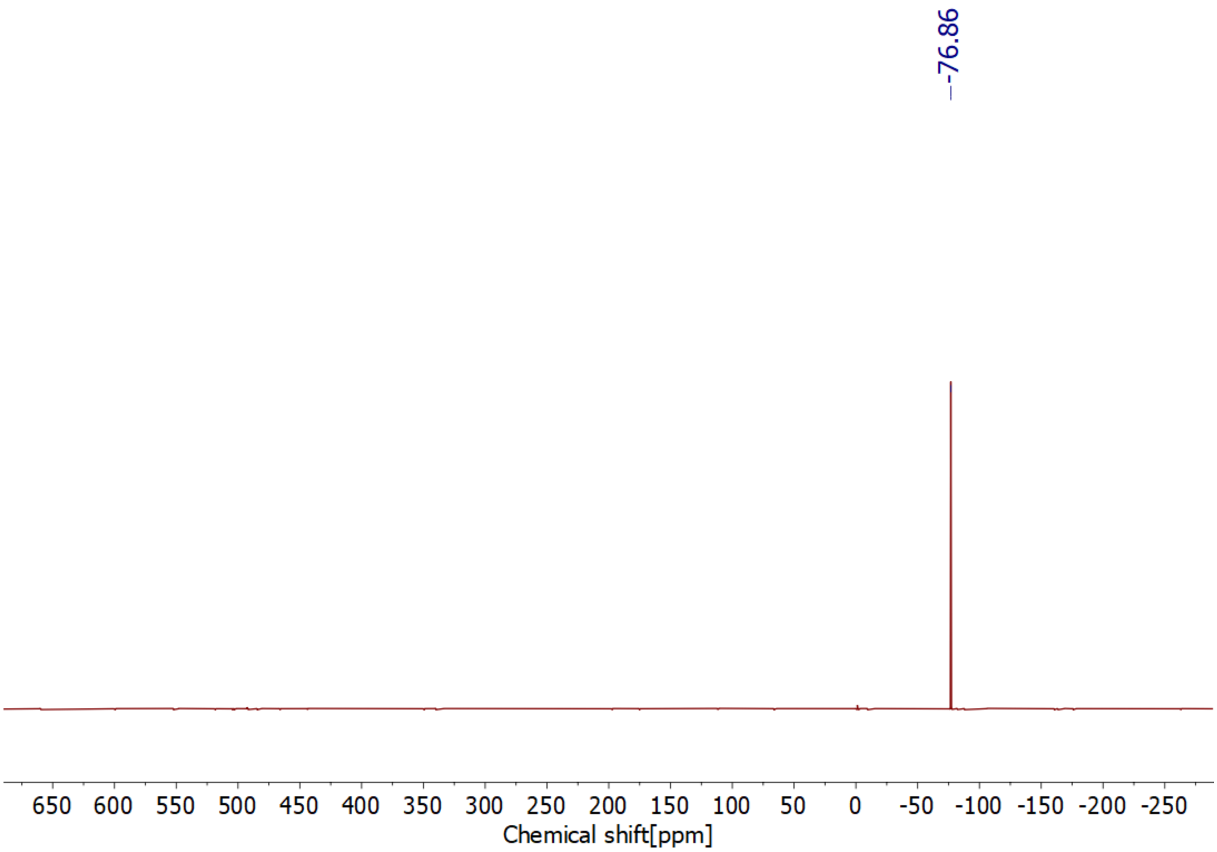
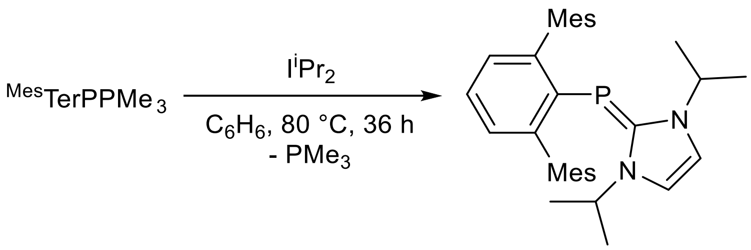


Figure S33: $^{31}P\{^{1}H\}$ NMR spectrum of $^{Mes}TerPIMe_4$ (**9**) in C_6D_6.



3.6 Synthesis of $^{Mes}TerPI^{i}Pr_2$ (10)



$^{Mes}TerPPMe_3$ (0.100 g, 0.237 mmol) and $I^{i}Pr_2$ (0.039 g, 0.237 mmol) were dissolved in benzene (3 mL) and stirred for 36 h at 80 °C. The solvent was then evaporated *in vacuo*, and the residue was extracted with small amounts of *n*-hexane and filtered. The volume of the filtrate was reduced to incipient crystallisation and standing at −30 °C for 24 h afforded $^{Mes}TerPI^{i}Pr_2$ (**10**) as an orange crystalline solid. Yield: 0.066 g, 0.132 mmol (56 %).

Mp. 176 (dec.) °C. **CHN** calc. (found) in %: for $C_{33}H_{41}N_2P$: C 79.80 (78.27); H 8.32 (8.26), N 5.64 (5.68). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 0.81 (d, 12H, $^3J_{HH}$ = 6.7 Hz, (HCN(HC*Me*$_2$))$_2$C), 2.22 (s, 6H, *p*-C*H*$_3$ of Mes), 2.36 (s, 12H, *o*-C*H*$_3$ of Mes), 4.43 (hept-d, 2H, $^3J_{HH}$ = 6.7 Hz, J_{PH} = 2.3 Hz, (HCN(*H*CMe$_2$))$_2$C), 5.94 (s, 2H, (HCN^{i}Pr)$_2$C), 6.84 (s, 4Hz, *m*-Ar*H* of Mes), 7.03–7.13 (m, 3H, *m,p*-Ar*H* of 2,6-Mes$_2$C$_6$*H*$_3$). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 21.2 (2C, *p*-CH$_3$ of Mes), 21.6 (d, 4C, J_{CP} = 6.3 Hz, *o*-CH$_3$ Mes), 21.8 (d, 4C, J_{CP} = 1.9 Hz, (HCN(HC*Me*$_2$))$_2$C), 49.9 (d, 2C, J_{PC} = 7.6 Hz, (HCN(CMe$_2$))$_2$C), 114.2 (d, 2C, J_{CP} = 3.2 Hz, (HCN^{i}Pr)$_2$C), 124.0 (1C, ArCH, p-C$_6$H$_3$), 128.2 (4C, *m*-ArCH Mes), 129.1 (2C, Ar-CH, m-C$_6$H$_3$), 134.9 (2C, Ar*C*$_{quat}$), 136.1 (4C, Ar*C*$_{quat}$), 142.4 (2C, Ar*C*$_{quat}$), 147.1 (d, J_{PC} = 11.6 Hz, *o*-C$_{quat}$ Ter), 147.6 (d, 1C, J_{PC} = 54.9 Hz, *ipso*-C Ter), 168.6 (d, 1C, J_{CP} = 104.6 Hz, (HCN^{i}Pr)$_2$C). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −79.8. **IR** (ATR, 32 scans, cm^{-1}): ν = 3129 (w), 2953 (m), 2915 (m), 2849 (w), 1665 (w), 1636 (w), 1609 (w), 1568 (w), 1553 (w), 1525 (w), 1445 (m), 1419 (m), 1404 (m), 1384 (m), 1362 (s), 1325 (w), 1300 (m), 1281 (m), 1261 (m), 1203 (s), 1169 (m), 1121 (m), 1081 (w), 1029 (m), 989 (w), 934 (w), 882 (w), 852 (m), 843 (s), 795 (m), 777 (w), 737 (s), 707 (s), 680 (s), 654 (w), 626 (w), 589 (m), 573 (m), 549 (w), 517 (w), 500 (w), 476 (w), 438 (w). **MS** (ESI-TOF): expected: m/z = 497.3086; found: m/z = 497.3083.

X-ray quality crystals of **10** were obtained from a saturated *n*-hexane solution at −30 °C.

Figure S34: ^{1}H NMR spectrum of ^{Mes}TerPI^{i}Pr$_2$ (**10**) in C_6D_6.

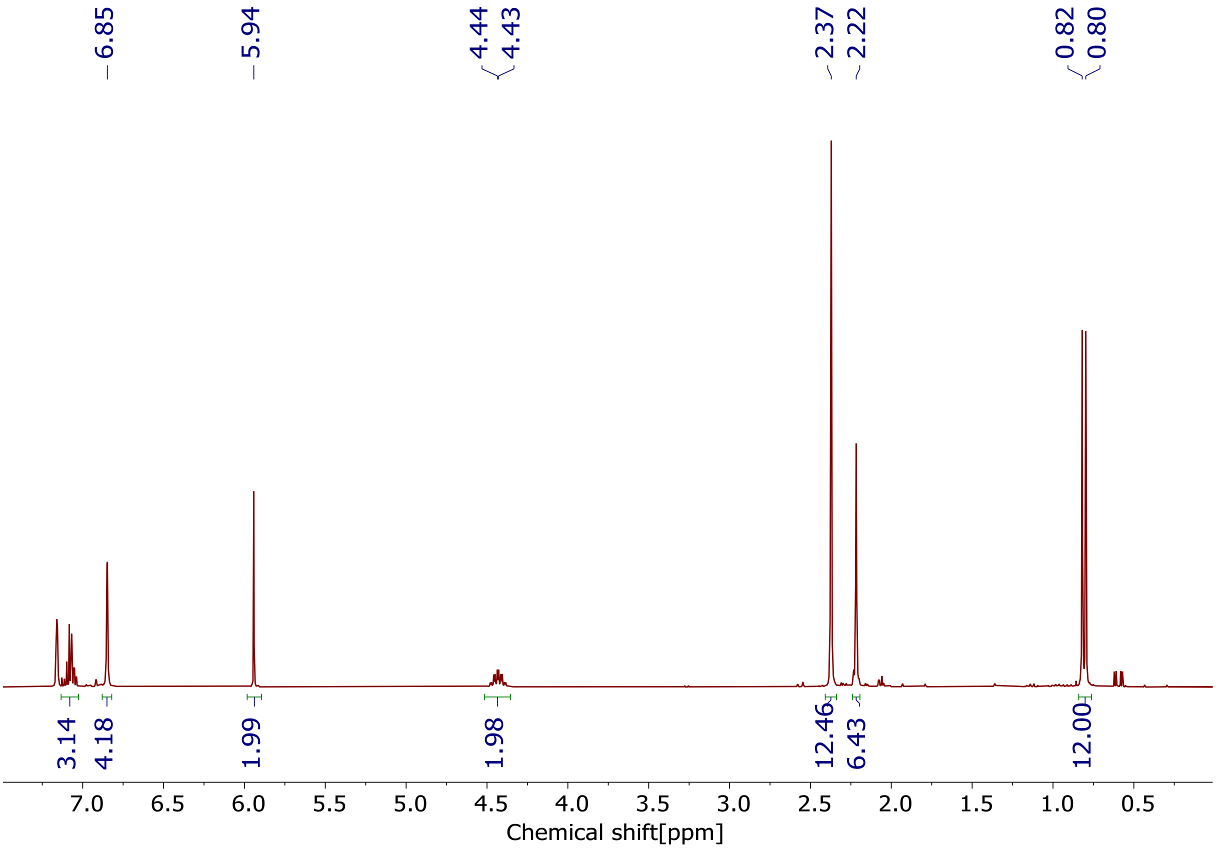


Figure S35: ^{13}C NMR spectrum of ^{Mes}TerPI^{i}Pr$_2$ (**10**) in C_6D_6..

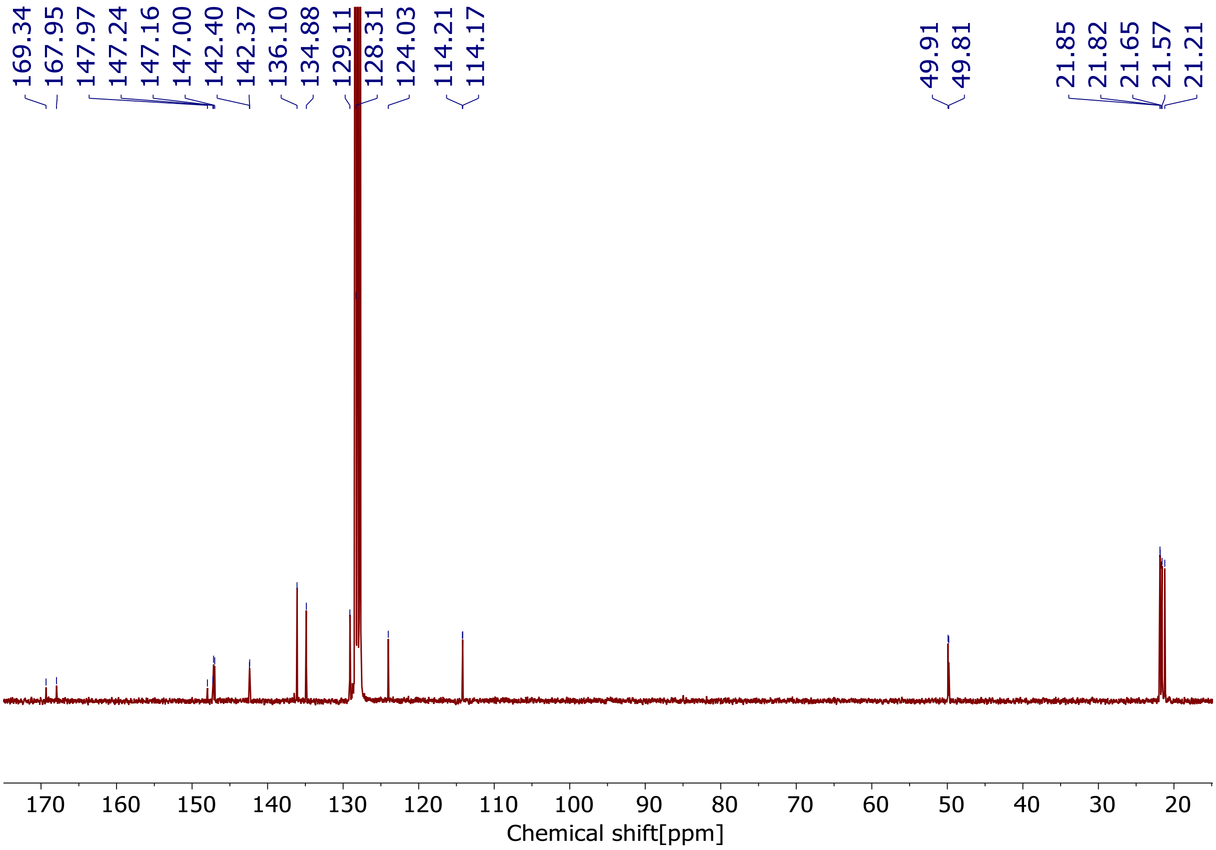
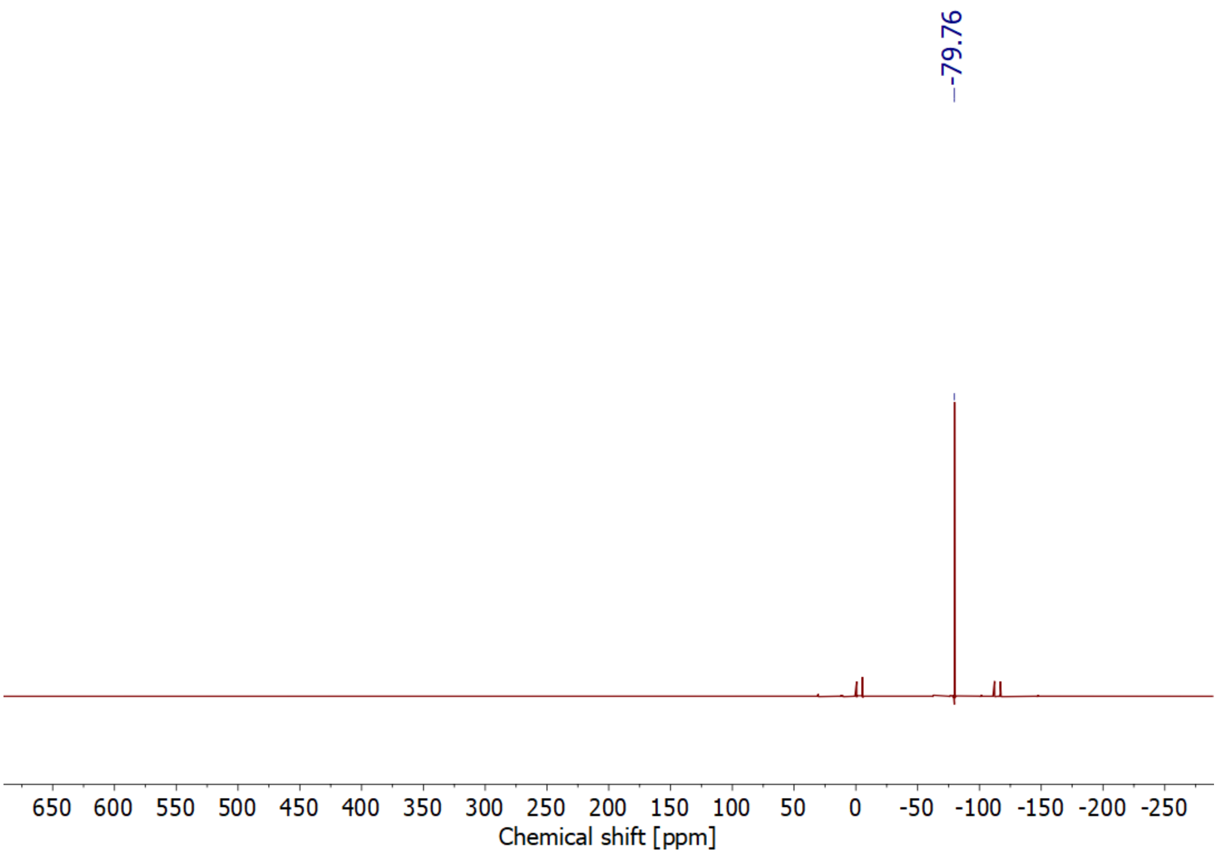
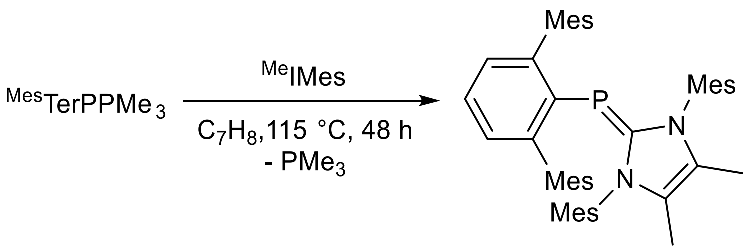


Figure S36: $^{31}P\{^1H\}$ NMR spectrum of $^{Mes}TerPI^iPr_2$ (**10**) in C_6D_6 (taken from reaction mixture, minimal amounts of **2** appear as set of doublets).



3.7 Synthesis of $^{Mes}TerP^{Me}IMes$ (11)



$^{Mes}TerPPMe_3$ (0.060 g, 0.143 mmol) and $^{Me}IMes$ (0.052 g, 0.143 mmol) were combined in a 10 mL schlenk flask, dissolved in toluene (3 mL) under the exclusion of light (wrap flask with tin foil) and stirred for 48 h at 115 °C. After that, the solvent was evaporated under reduced pressure and the residue was extracted using *n*-hexane and filtered inside the glove box using a pipette, fitted with a glass microfiber filter. Then the volume of the filtrate was reduced to ca. 1 mL and standing at −30 °C afforded $^{Mes}TerP^{Me}IMes$ (**11**) as a red amorphous solid. Yield: 0.050 g, 0.074 mmol (52 %).

Mp. 172 (dec.) °C. **CHN** calc. (found) in %: for $C_{47}H_{53}N_2P$: C 83.39 (83.49); H 7.89 (7.98), N 4.14 (3.19). **^{1}H NMR** (400 MHz, C_6D_6) δ [ppm] = 1.19 (s, 6H, (H_3C-CNMes)$_2$C), 1.91 (s, 12H, *o*-CH_3 of Mes), 2.11 (s, 6H, *p*-CH_3 of NMes), 2.14 (s, 12H, *o*-CH_3 of ^{Mes}Ter), 2.37 (s, 6H, *p*-CH_3 of ^{Mes}Ter), 6.80 (s, 4H, *m*-ArH of ^{Mes}Ter), 6.81 – 6.89 (m, 3H, *m*,*p*-ArH $Mes_2C_6H_3$), 6.96 (s, 4H, *m*-ArH of NMes). **^{13}C NMR** (101 MHz, C_6D_6) δ [ppm] = 8.9 (2C, (H_3C-CNMes)$_2$C), 18.9 (d, 4C, J_{PC} = 4.1 Hz, o-CH_3 of NMes), 21.2 (2C, *p*-CH_3 of Mes), 21.33 (2C, *p*-CH_3 of NMes), 23.0 (d, 2C, J_{CP} = o-CH_3 of Mes), 120.7 (d, J_{CP} = 3.0 Hz, (H_3C-CNMes)$_2$C), 126.0 (1C, p-ArCH C_6H_3), 128.2 (4C, m-ArCH NMes), 129.46 (4C, m-ArCH N*Mes*), 129.54 (2C, m-ArCH C_6H_3), 133.9 (2C, ArC_{quat}), 134.9 (2C, ArC_{quat}), 136.9 (4C, ArC_{quat}), 137.5 (d, 4C, J_{CP} = 3.2 Hz, ArC_{quat}), 138.0 (2C, ArC_{quat}), 139.3 (d, J_{PC} = 73.4 Hz, *ipso*-C of Ter), 143.0 (2C, ArC_{quat}), 149.5 (d, J_{PC} = 11.6 Hz, *o*-C of Ter), 163.2 (d, 1C, J_{CP} = 129.6 Hz, (H_3CCNMes)$_2$C). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −45.07. **IR** (ATR, 32 scans, cm^{-1}): ν = 2946 (w), 2914 (m), 2853 (w), 2730 (w), 1671 (w), 1608 (w), 1563 (w), 1482 (m), 1434 (m), 1391 (m), 1368 (s), 1310 (s), 1280 (s), 1210 (w), 1187 (m), 1079 (w), 1031 (m), 1012 (m), 968 (w), 934 (w), 846 (s), 802 (m), 768 (w), 749 (m), 738 (m), 712 (w), 653 (w), 591 (w), 566 (m), 497 (w), 464 (w), 428 (w). **MS** (ESI-TOF): expected: m/z = 677.4025; found: m/z = 677.4037.

Figure S37: ^{1}H NMR spectrum of ^{Mes}TerP^{Me}IMes (**11**) in C_6D_6.

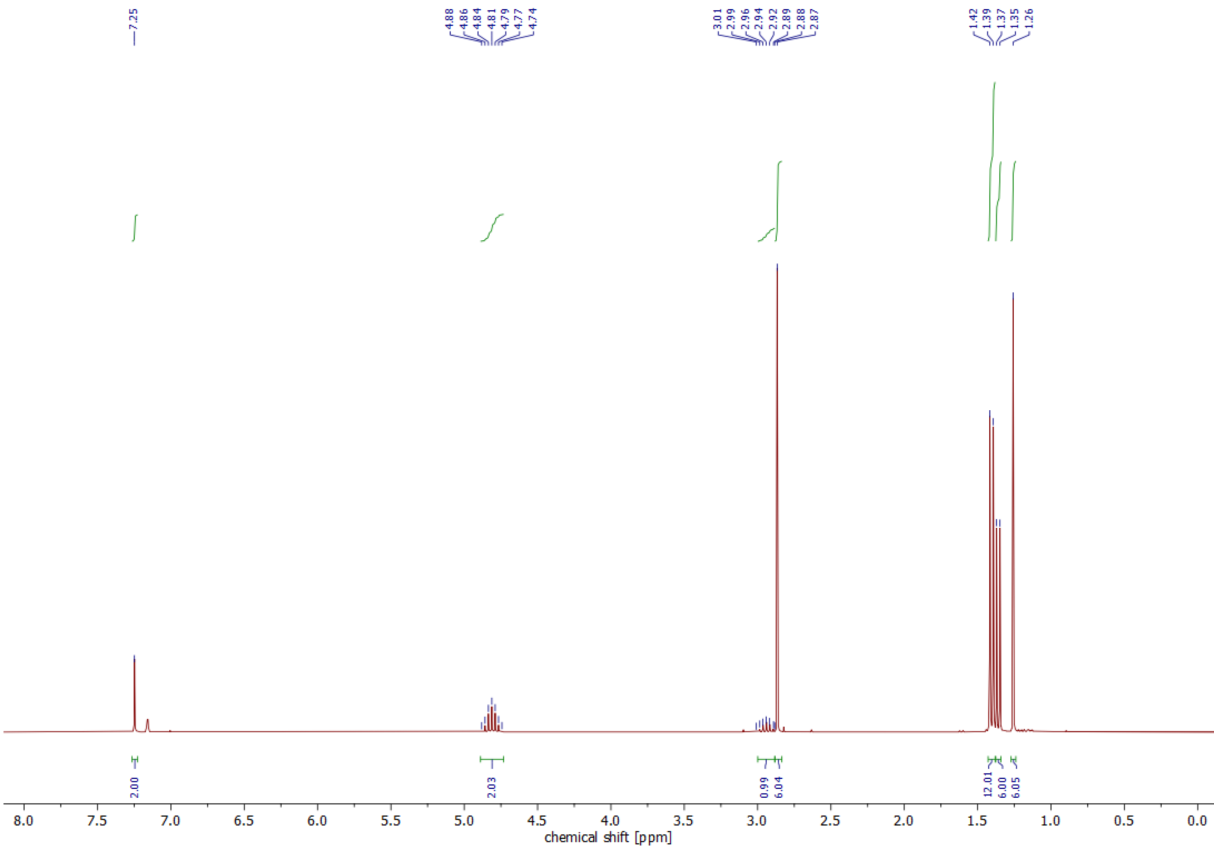


Figure S38: ^{13}C NMR spectrum of ^{Mes}TerP^{Me}IMes (**11**) in C_6D_6.

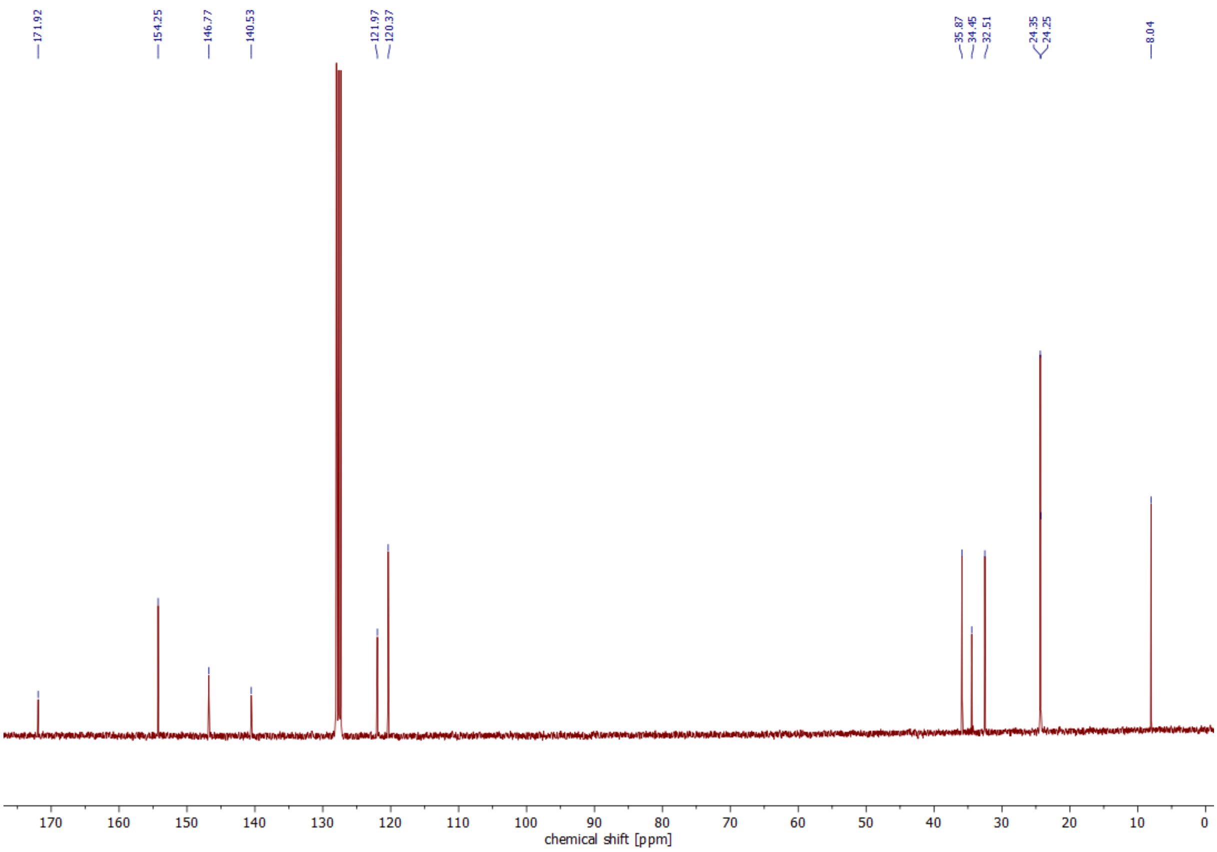
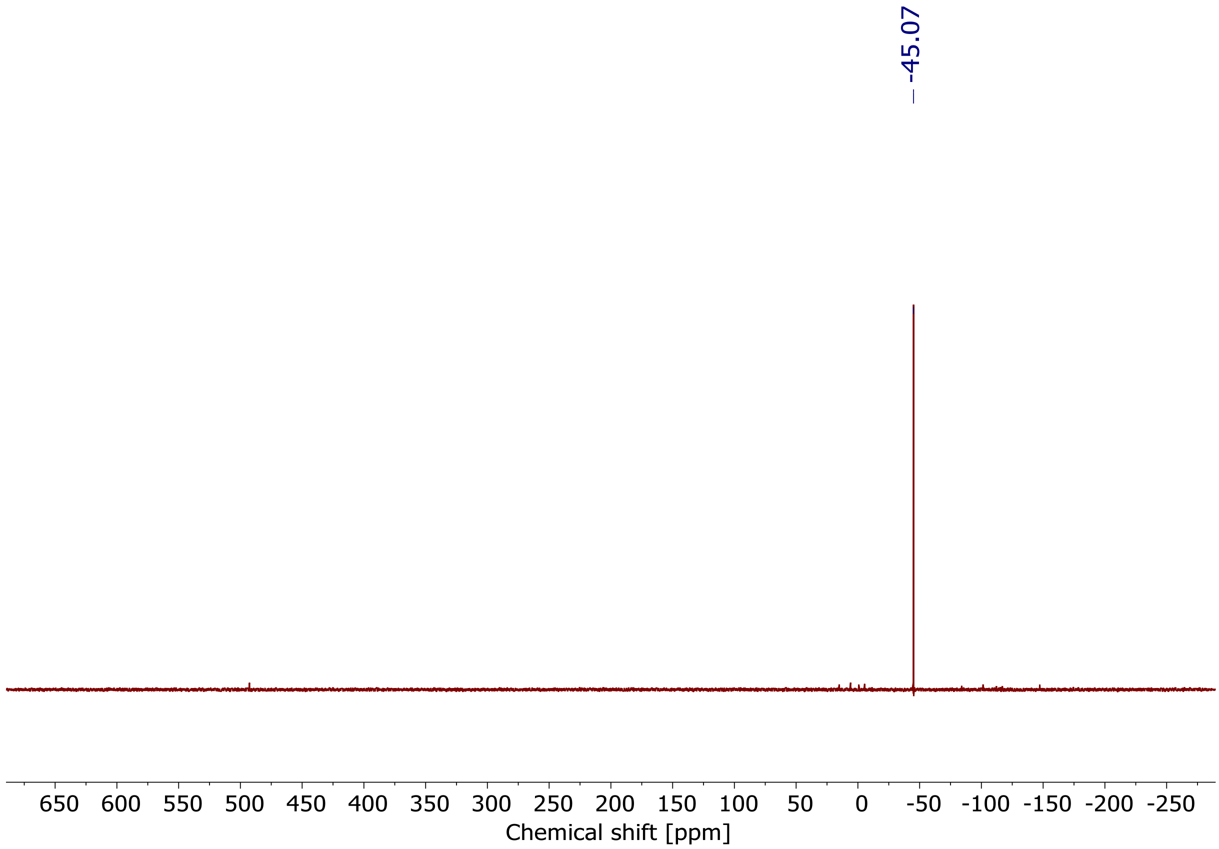
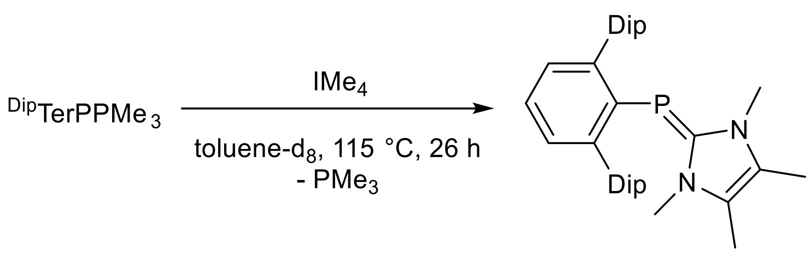


Figure S39: $^{31}P\{^{1}H\}$ NMR spectrum of $^{Mes}TerP^{Me}IMes$ (**11**) in C_6D_6.



3.8 Synthesis of $^{Dip}TerPIMe_4$ (12)



$^{Dip}TerPPMe_3$ (0.075 g, 0.147 mmol) and IMe_4 (0.020 mg, 0.147 mmol) were dissolved in toluene-d_8 (1 mL) under the exclusion of light and stirred for at 115 °C for 26 h. Afterwards, the solution was dried and the remaining solid was extracted using *n*-hexane (5 mL). It was then filtered, and the volume of the filtrate was reduced to incipient crystallization and this concentrated solution was placed in the freezer at −30

°C for 24 h. This resulted in the deposition of ^{Dip}TerPIMe$_4$ (**12**) as yellow crystalline solid. Yield: 0.030 g, 0.054 mmol (37%).

Mp. 219 (dec.) °C. **CHN** calc. (found) in %: for $C_{37}H_{49}N_2P$: C 80.39 (80.55); H 8.94 (8.69), N 5.07 (4.46). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.18 (s, 6H, (H_3CCNMe)$_2$C), 1.22 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.45 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 2.94 (s, 6H, MeCNCH_3)$_2$C), 3.20 (hept, 4H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 7.04 – 7.16 (m, 6H, ArH), 7.21 (d, 2H, $^3J_{HH}$ = 2.0 Hz, ArH), 7.24 (t, 1H, $^3J_{HH}$ = 2.1 Hz, Ar-H). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 8.7 (2C, H_3CCNMe)$_2$C), 23.8 (d, 4C, J_{CP} = 2.5 Hz, CH(CH$_3$)$_2$), 26.7 (s, 4C, CH(CH$_3$)$_2$), 30.9 (d, 4C, J_{PC} = 2.5 Hz, CH(CH$_3$)$_2$), 33.5 (2C, J_{PC} = 9.0 Hz, MeCNCH$_3$)$_2$C), 121.7 (1C, ArCH), 122.1 (d, 2C, J_{CP} = 3.2 Hz, (MeCNCH$_3$)$_2$C), 122.7 (4C, *m*-ArCH$_{Dipp}$), 127.0 (2C, ArCH), 129.50 (2C, ArCH), 142.52 (d, J_{CP} = 3.3 Hz, ArC_{quat}), 144.37 (2C, J_{PC} = 13.3 Hz, *o*-ArC_{Ter}), 146.70 (4C, *o*-ArC_{Dip}), 150.1 (1C, $^1J_{PC}$ = 56.6 Hz, ipso-C_{Ter}), 166.1 (d, 1C, $^1J_{PC}$ = 101.0 Hz, P=C_{IMe4}). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −63.15. **IR** (ATR, 32 scans, cm^{-1}): ν = 3044 (w), 3028 (w), 2961 (s), 2923 (m), 2864 (m), 1649 (w), 1569 (w), 1444 (m), 1424 (m), 1359 (s), 1322 (w), 1248 (w), 1226 (w), 1174 (w), 1159 (w), 1093 (m), 1055 (w), 1038 (m), 1001 (w), 954 (w), 933 (w), 856 (w), 802 (m), 783 (m), 757 (s), 744 (s), 698 (w), 670 (w), 655 (w), 632 (w), 606 (w), 587 (w), 562 (w), 549 (w), 472 (m), 423 (w). **MS** (ESI-TOF): expected: m/z = 553.3712; found: m/z = 553.3711.

X-Ray quality crystals of **12** were grown from a saturated *n*-hexane solution at −30 °C.

Figure S40: ^{1}H NMR spectrum of $^{Dip}TerPIMe_4$ (**12**) in C_6D_6.

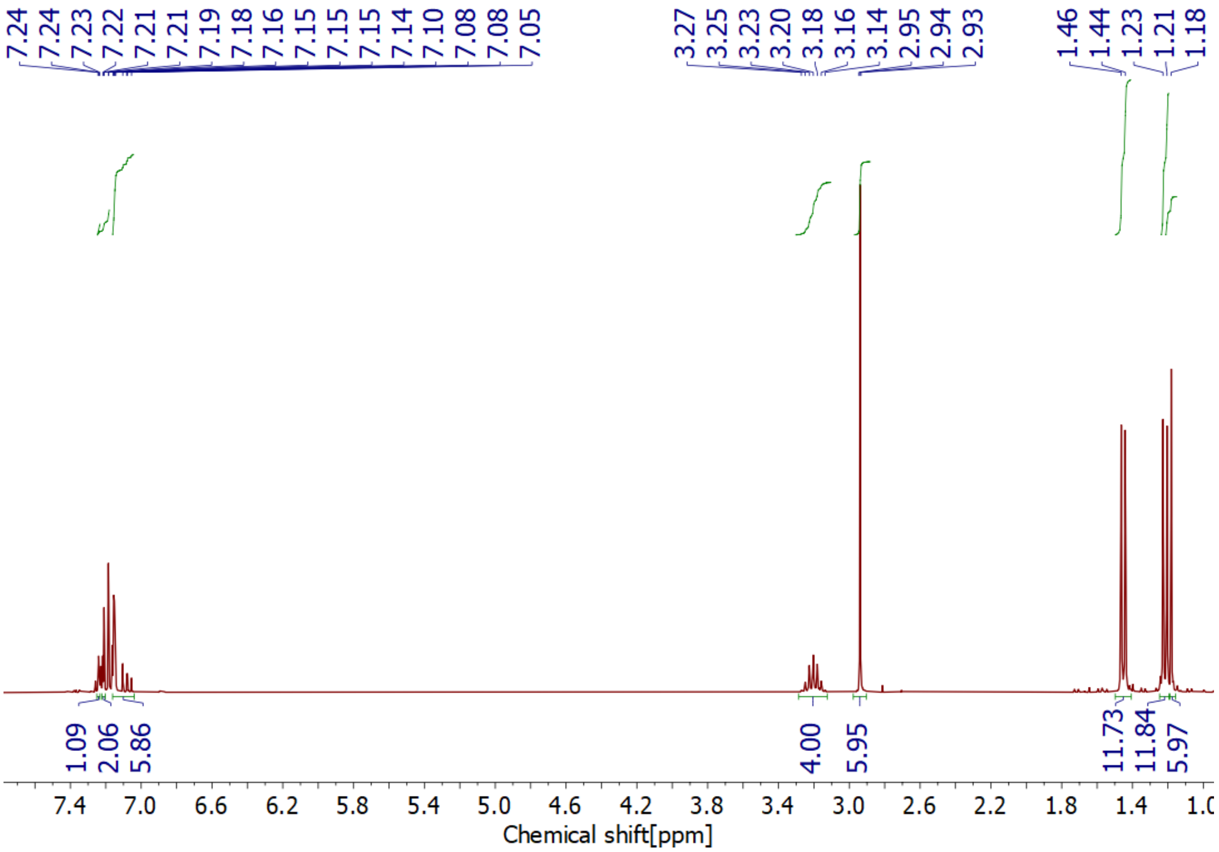


Figure S41: ^{13}C NMR spectrum of $^{Dip}TerPIMe_4$ (**12**) in C_6D_6.

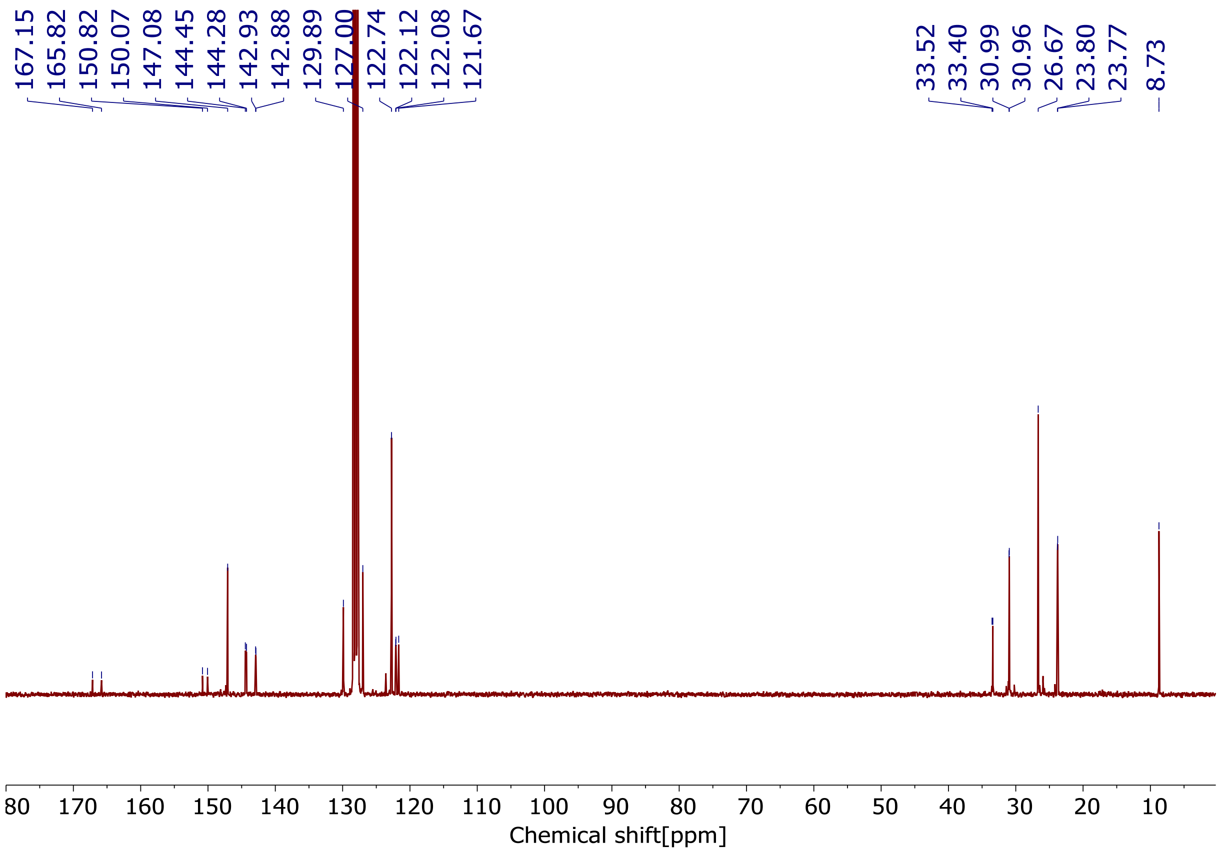
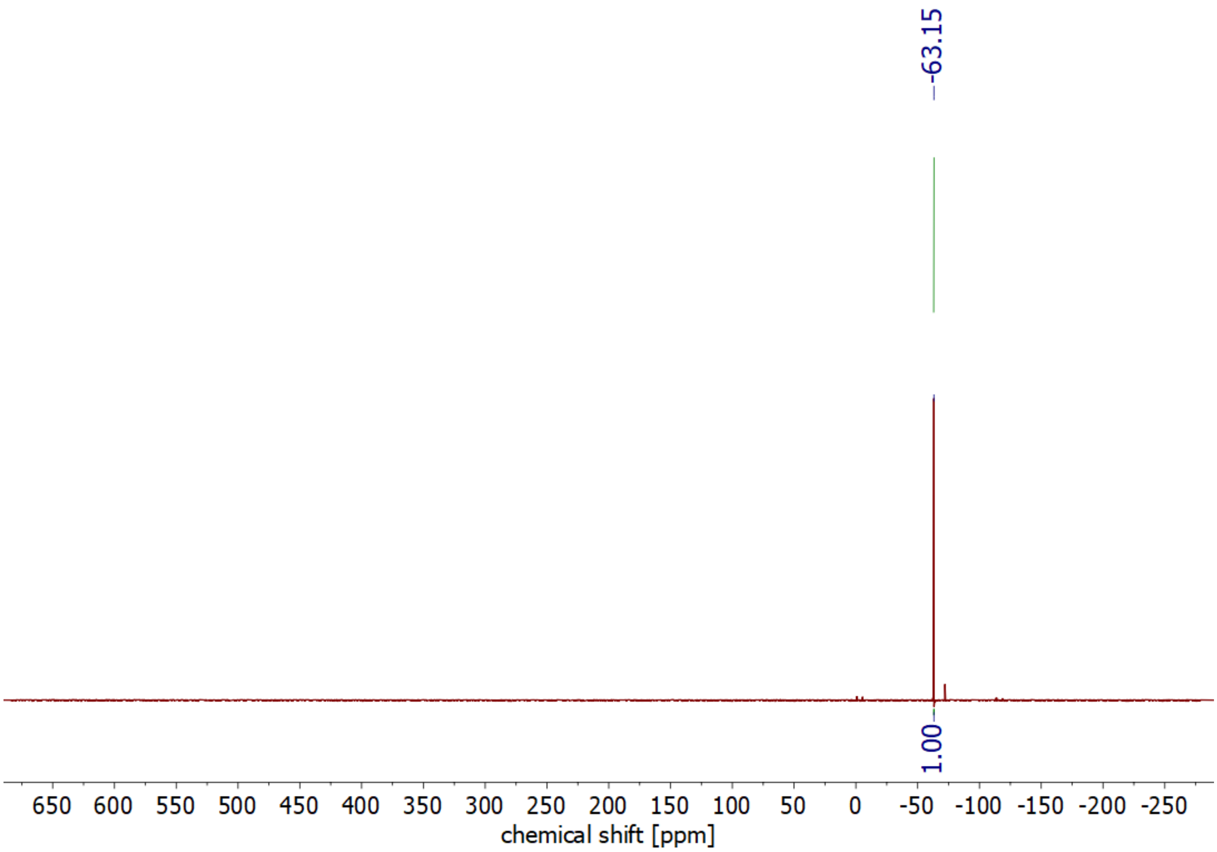
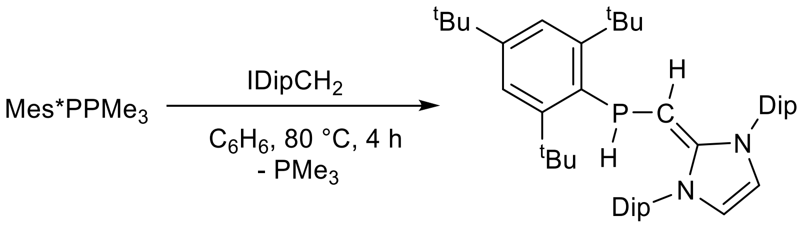


Figure S42: $^{31}P\{^{1}H\}$ NMR spectrum of $^{Dip}TerPIMe_4$ (**12**) in C_6D_6.



3.9 Synthesis of Mes*PHCHIDip (13)



In a 25 mL Schlenk flask, Mes^*PPMe_3 (0.100 g, 0.284 mmol) and $IDipCH_2$ (0.114 g, 0.284 mmol) were dissolved in benzene (5 mL) under the exclusion of light. The reaction completes upon heating the reaction mixture at 80 °C for 4 h. Subsequently, the solvent was evaporated under reduced pressure and the resulting solid was extracted with *n*-hexane (5 mL). It was then filtered using a filter canula and the obtained solution was concentrated to incipient crystallization and kept at −30 °C for 24 h. This resulted in the deposition of Mes*PHCHIDip (**13**) as deep yellow, crystalline solid. Yield: 0.120 g, 0.177 mmol (62.3%).

Mp. 205 (dec.) °C. **CHN** calc. (found) in %: for $C_{46}H_{67}N_2P$: C 81.37 (81.59); H 9.95 (10.04), N 4.13 (3.57). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.06 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.07 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.14 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.19 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.21 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.23 (s, 9H, *p*-C(CH_3)$_3$), 1.28 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.57 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.63 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.66 (s, 18H, *o*-C(CH_3)$_3$), 2.17 (d, 1H, $^2J_{PH}$ = 3.0 Hz, C*H*IDip), 3.12 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.21 (hept, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.51 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.67 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 5.20 (d, $^1J_{PH}$ = 216.2 Hz, $^3J_{HH}$ = 1.0 Hz, P*H*), 5.81 (dd, $^3J_{HH}$ = 2.5 Hz, J_{PH} = 1.0 Hz, (*H*CNDip)$_2$CCH), 5.94 (dd, $^3J_{HH}$ = 2.5 Hz, J_{PH} = 0.8 Hz, (*H*CNDip)$_2$CCH), 6.86–6.96 (m, 1H, Ar*H*), 6.92–7.05 (m, 2H, Ar*H*), 7.18–7.29 (m, 2H, Ar*H*), 7.26–7.37 (m, 1H, Ar*H*), 7.41 (d, 2H, $^4J_{PH}$ = 2.1 Hz, *m*-Ar*H*). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 23.0 (s, 2C, CH(*C*H$_3$)$_2$), 23.6 (s, 2C, CH(*C*H$_3$)$_2$), 23.7 (s, 1C, *C*H(CH$_3$)$_2$), 23.9 (s, 1C, *C*H(CH$_3$)$_2$), 24.9 (s, 2C, CH(*C*H$_3$)$_2$), 25.3 (s, 2C, CH(*C*H$_3$)$_2$), 25.8 (s, 2C, CH(*C*H$_3$)$_2$), 26.2 (s, 2C, CH(*C*H$_3$)$_2$), 28.3 (s, 1C, *C*H(CH$_3$)$_2$), 28.4 (s, 1C, *C*H(CH$_3$)$_2$), 28.6 (s, 1C, *C*H(CH$_3$)$_2$), 28.9 (s, 1C, *C*H(CH$_3$)$_2$), 31.5 (s, 3C, p-C(*C*H$_3$)$_3$), 34.3 (d, 6C, J_{PC} = 7.6 Hz, o-C(*C*H$_3$)$_3$), 34.9 (s, 1C, *C*(CH$_3$)$_3$), 38.9 (s, 1C, *C*(CH$_3$)$_3$), 52.5 (d, 1C, $^1J_{PC}$ = 6.9 Hz, PCHIDip), 115.7 (s, 1C, (HCNDip)$_2$C) 117.1 (s, 1C, (H*C*NDip)$_2$C), 122.1 (d, 2C, J_{PC} = 3.9 Hz, m-ArCH$_{Mes*}$), 123.8 (s, 1C, ArC*H*), 124.1 (s, 1C, ArCH), 124.2 (s, 1C, Ar*C*H), 124.5 (1C, Ar*C*H), 129.5 (d, 1C, Ar*C*H), 129.5 (1C, Ar*C*H), 129.6 (1C, Ar*C*H), 134.0 (1C, Ar*C*$_{quat}$) (136.6 (d, 1C, J_{PC} = 3.4 Hz, *p*-Ar*C*$_{Mes*}$), 137.5 (d, 1C, J_{PC} = 23.5 Hz, N$_2$CCP), 137.7 (1C, Ar*C*$_{quat}$), 147.1 (1C, Ar*C*$_{quat}$), 148.27 (1C, Ar*C*$_{quat}$), 148.31 (1C, Ar*C*$_{quat}$), 148.6 (1C, Ar*C*$_{quat}$), 149.6 (1C, J_{PC} = 41.5 Hz, ipso-C$_{Mes*}$), 149.7 (1C, Ar*C*$_{quat}$), 149.8 (1C, Ar*C*$_{quat}$), 154.6 (2C, J_{PC} = 9.1 Hz, o-Ar*C*$_{Mes*}$). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −80.65. **IR** (ATR, 32 scans, cm^{-1}): ν = 2958 (s), 2905 (m), 2867 (m), 2348 (w), 1607 (m), 1593 (m), 1577 (m), 1553 (s), 1465 (s), 1409 (s), 1393 (m), 1383 (m), 1361 (s), 1329 (m), 1298 (w), 1257 (m), 1234 (m), 1210 (m), 1178 (m), 1117 (m), 1075 (m), 1062 (w), 1047 (w), 959 (w), 929 (m), 877 (m), 851 (m), 824 (w), 800 (m), 780 (w), 756 (s), 731 (w), 709 (w), 652 (s), 614 (m), 577 (w), 542 (w), 524 (w), 459 (w), 423 (w).. **MS** (ESI-TOF): expected: m/z = 679.5120; found: m/z = 679.5109.

X-ray quality crystals of **13** were obtained from a saturated *n*-hexane solution at −30 °C.

Figure S43: ^{1}H NMR spectrum of Mes*PHCHIDip (**13**) in C_6D_6.

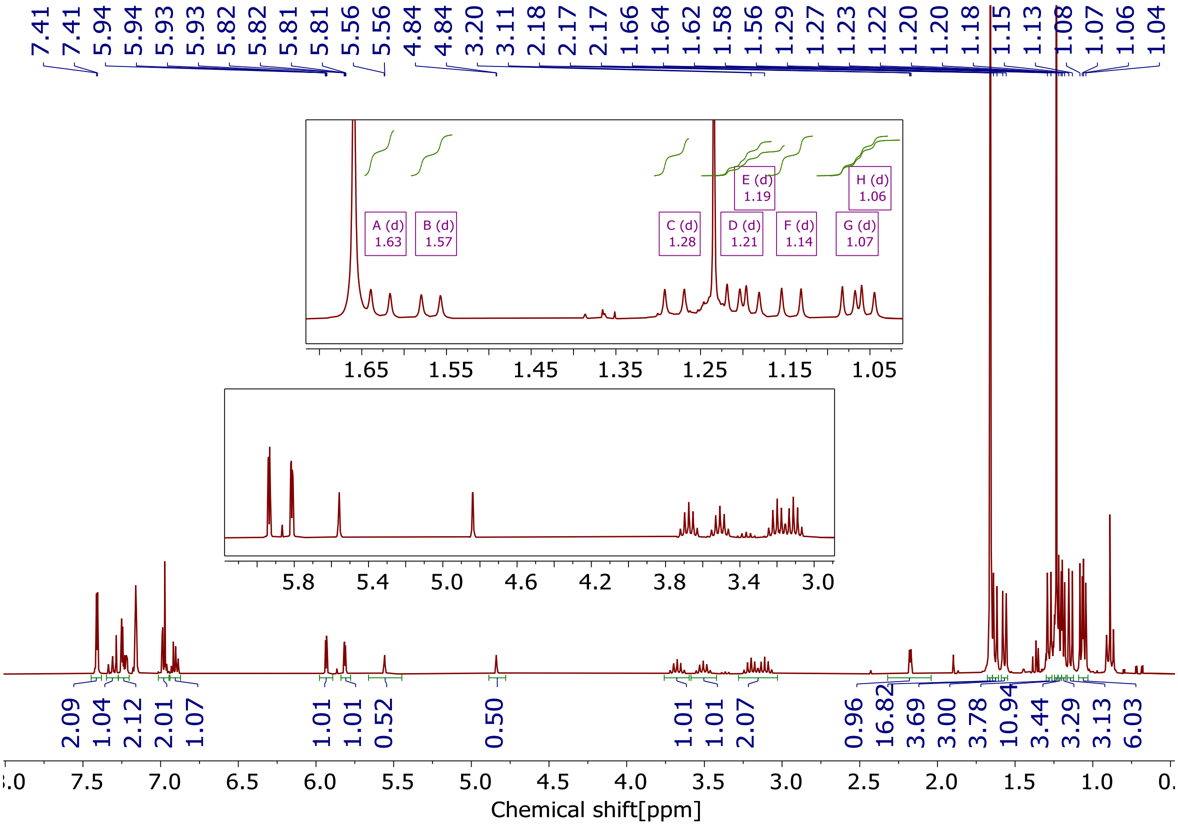


Figure S44: ^{13}C NMR spectrum of Mes*PHCHIDip (**13**) in C_6D_6.

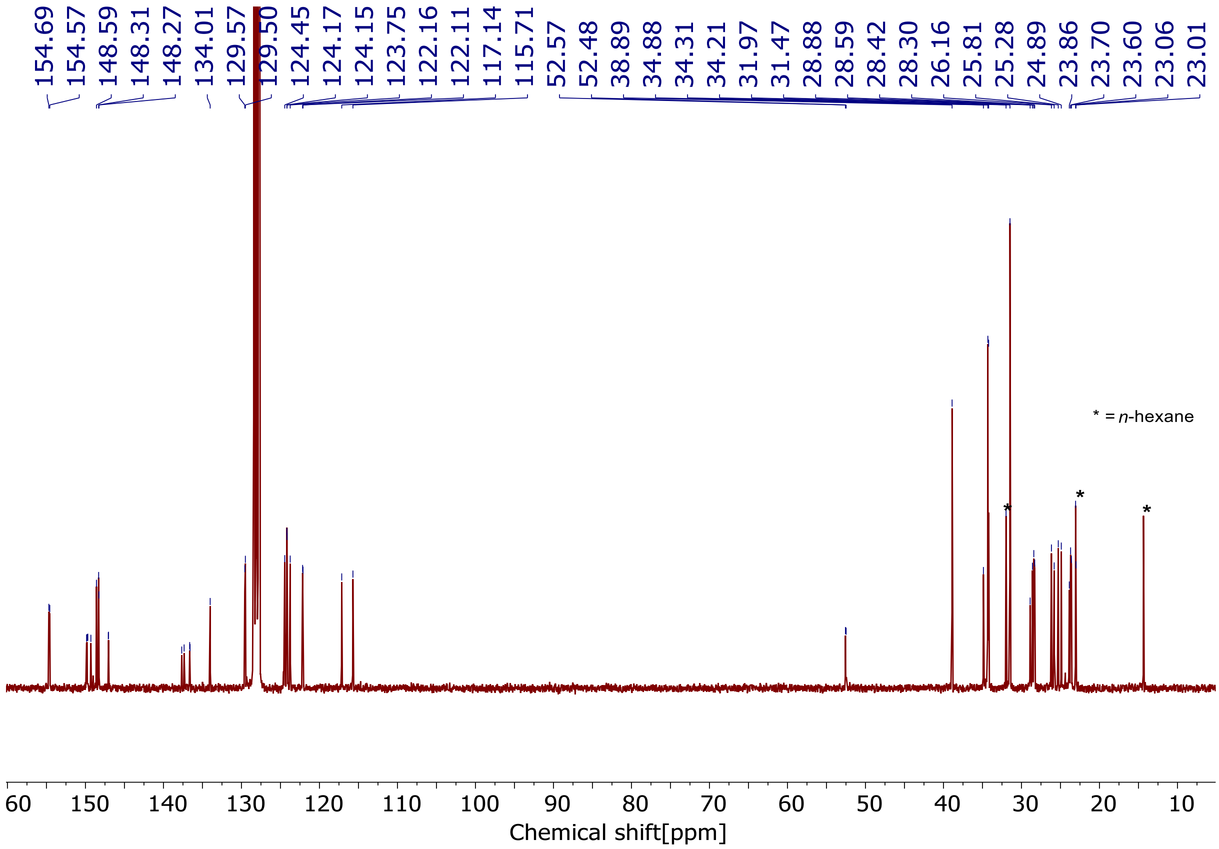
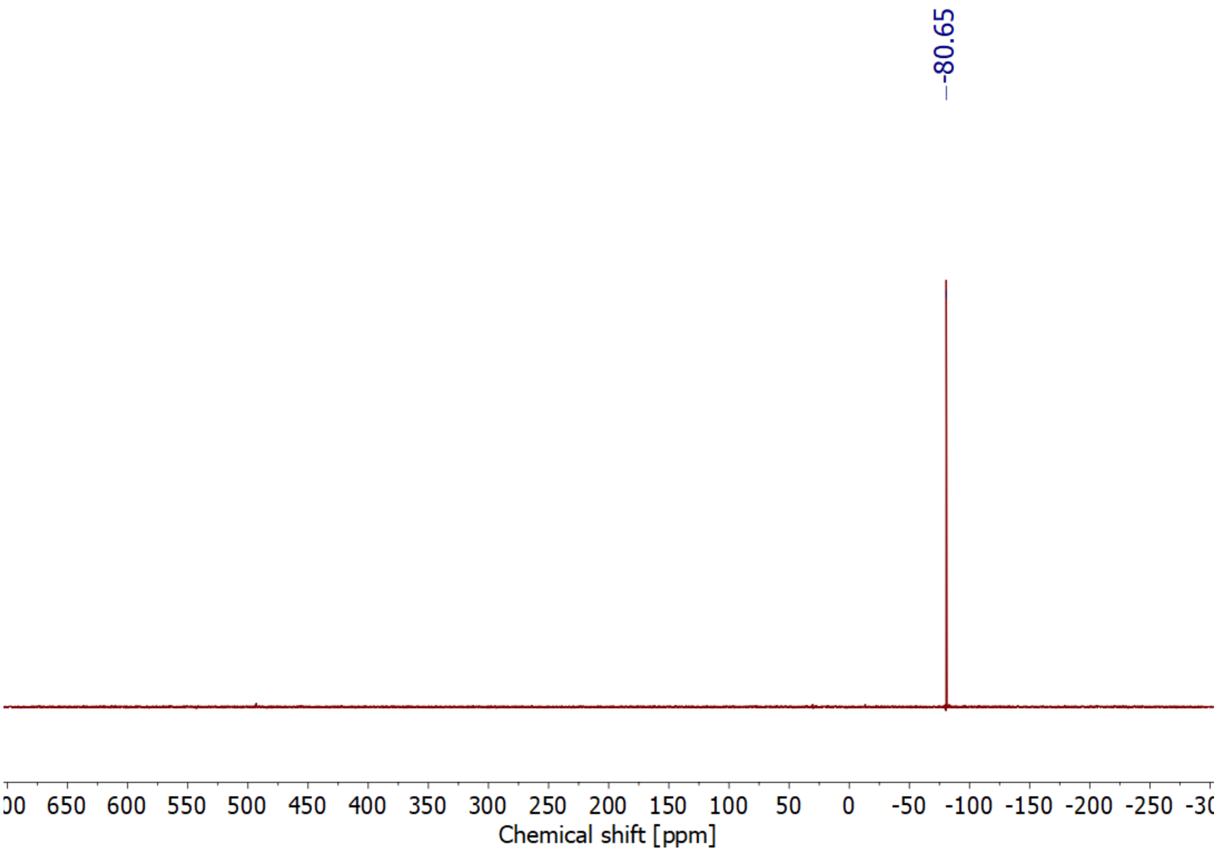
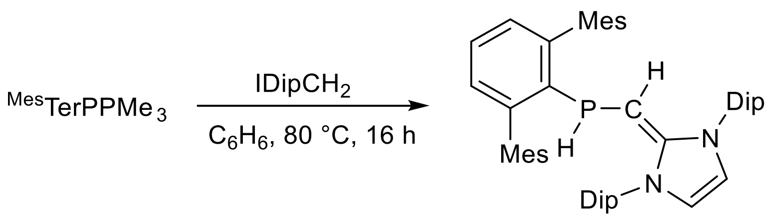


Figure S45: $^{31}P\{^1H\}$ NMR spectrum of Mes*PHCHIDip (**13**) in C_6D_6.



3.10 Synthesis of ^{Mes}TerPHCHIDip (14)



In a 10 ml Schlenk flask, ^{Mes}TerPPMe$_3$ (0.100 g, 0.24 mmol) and IDipCH$_2$ (0.096 g, 0.24 mmol) were dissolved in benzene (5 mL) and stirred at 80 °C over a period of 16 h. Afterwards the solvent was removed *in vacuo* and the resulting yellow solid was extracted using *n*-hexane (5 mL). The solvent was pumped off again to obtain ^{Mes}TerPHCHIDip (**14**) as a yellowish amorphous solid. Yield: 0.110 g, 0.147 mmol (62%).

Mp. 190 °C. **CHN** calc. (found) in %: for $C_{52}H_{63}N_2P$: C 83.60 (81.41); H 8.50 (8.78), N 3.75 (3.20). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.00 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.07

d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.08 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.10−1.17 (overlapping doublets, 15H, CH(CH_3)$_2$), 1.89 (s, 6H, CH_3), 1.95 (s, 6H, CH_3), 2.30 (d, 1H, $^2J_{PH}$ = 2.4 Hz, PC*H*IDip), 2.32 (s, 6H, CH_3), 2.89–3.15 (overlapping heptetts, 4H, C*H*(CH$_3$)$_2$), 4.15 (dd, 1H, $^1J_{PH}$ = 210.5 Hz, $^3J_{HH}$ = 2.2 Hz, P*H*), 5.73 (dd, 1H, $^3J_{HH}$ = 2.5 Hz, J_{PH} = 0.7 Hz, (*H*CNDip)$_2$C), 5.74 (dd, 1H, $^3J_{HH}$ = 2.5 Hz, J_{PH} = 0.8 Hz, (*H*CNDip)$_2$C), 6.75–6.83 (m, 6H, Ar*H*), 6.93 – 7.06 (m, 3H, Ar*H*), 7.08–7.17 (m, 3H, Ar*H*, overlapping with C_6D_5H), 7.22–7.28 (m, 1H, Ar*H*). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 21.2 (s, 2C, *C*H$_3$ Ter), 21.3 (d, 2C, J_{PC} = 6.3 Hz, *C*H$_3$ Ter), 21.3 (s, 2C, *C*H$_3$ Ter), 22.5 (1C, CH(*C*H$_3$)$_2$), 22.8 (d, 1C, J_{PC} = 5.2 Hz, CH(*C*H$_3$)$_2$), 23.5 (1C, CH(*C*H$_3$)$_2$), 23.7 (1C, CH(*C*H$_3$)$_2$), 24.4 (1C, CH(*C*H$_3$)$_2$), 24.6 (1C, CH(*C*H$_3$)$_2$), 25.0 (2C, CH(*C*H$_3$)$_2$), 28.5 (1C, *C*H(CH$_3$)$_2$), 28.6 (1C, *C*H(CH$_3$)$_2$), 28.8 (1C, *C*H(CH$_3$)$_2$), 29.3 (d, 1c, J_{PC} = 2.5 Hz, *C*H(CH$_3$)$_2$), 44.0 (d, 1C, $^1J_{PC}$ = 10.7 Hz, PCHIDip), 115.6 (1C, (H*C*NDip)$_2$C), 116.4 (1C, (H*C*NDip)$_2$C), 123.3 (1C, Ar*C*H), 123.8 (1C, Ar*C*H), 124.4 (1C, Ar*C*H), 124.7 (1C, Ar*C*H), 128.5 (2C, Ar*C*H) 128.7 (2C, Ar*C*H), 129.1– 129.4 (m, 5C, Ar*C*H), 135.1 (2C, ArC_{quat}), 135.3 (2C, ArC_{quat}), 135.5 (2C, ArC_{quat}), 135.8 (1C, ArC_{quat}), 136.0 (2C, ArC_{quat}), 137.9 (d, 1C, J_{PC} = 12.7 Hz, N_2CCP), 141.0 (d, 2C, J_{PC} = 1.9 Hz, o-ArC_{Ter}), 147.10 (1C, ArC_{quat}), 147.2 (1C, ArC_{quat}), 147.6 (1C, ArC_{quat}), 147.6 (1C, ArC_{quat}), 148.6 (1C, ArC_{quat}), 148.9 (1C, ArC_{quat}), 149.3 (d, 1C, J_{PC} = 31.1 Hz, PC_{ipso}), 149.5 (1C, ArC_{quat}). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −81.09. **IR** (ATR, 32 scans, cm^{-1}): ν = 3130 (w), 2961 (m), 2921 (m), 2865 (m), 2298 (w), 2263 (w), 1608 (m), 1581 (m), 1552 (s), 1459 (s), 1443 (s), 1407 (m), 1381 (m), 1360 (m), 1328 (w), 1297 (w), 1256 (w), 1228 (w), 1208 (w), 1179 (w), 1118 (w), 1101 (w), 1073 (w), 1059 (w), 1031 (w), 927 (m), 852 (s), 804 (m), 797 (m), 776 (w), 758 (s), 744 (m), 663 (m), 655 (m), 642 (w), 608 (w), 591 (w), 573 (w), 546 (w), 522 (w), 496 (w), 476 (w), 444 (m). **MS** (ESI-TOF): expected: m/z = 747.4809; found: m/z = 747.4801.

X-ray quality crystals of **14** were obtained from a saturated solution of *n*-hexane at −30 °C.

Figure S46: ^{1}H NMR spectrum of ^{Mes}TerPHCHIDip (**14**) in C_6D_6.

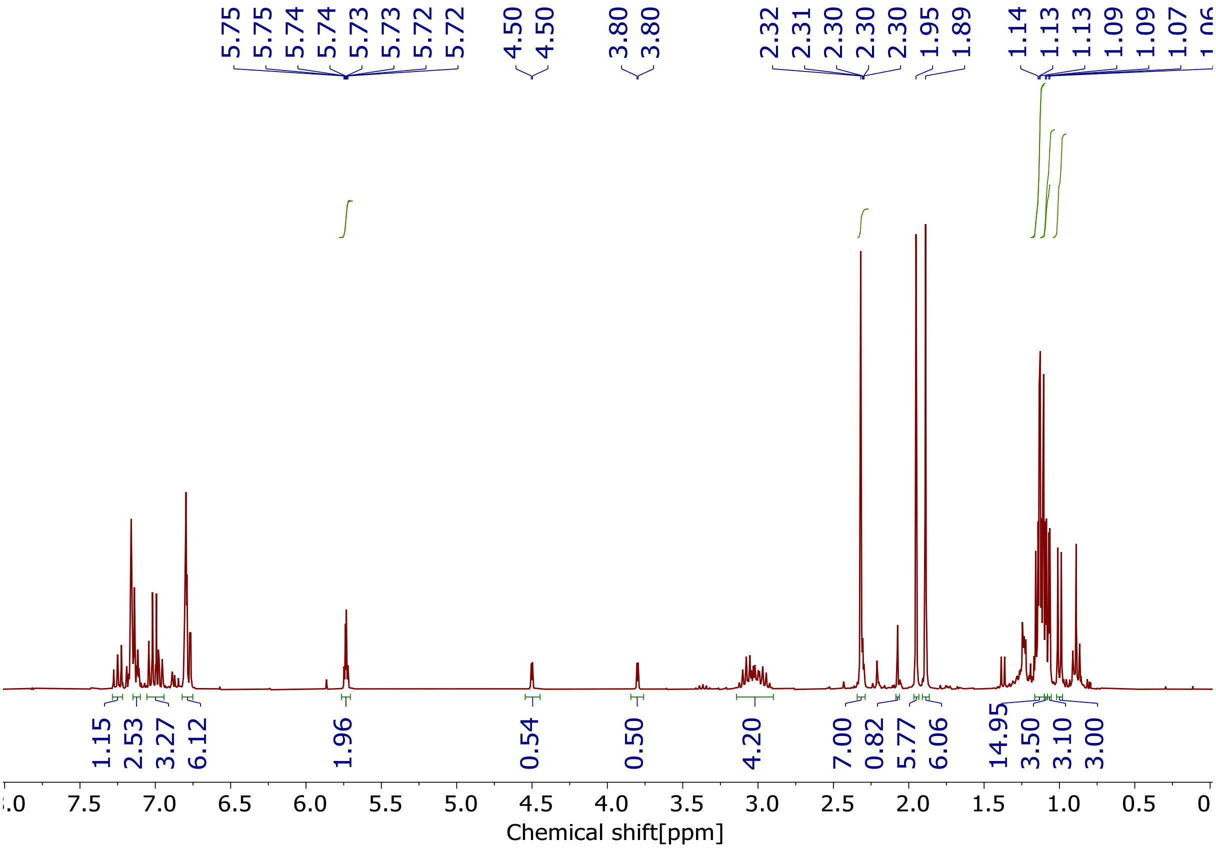


Figure S47: ^{13}C NMR spectrum of ^{Mes}TerPHCHIDip (**14**) in C_6D_6.

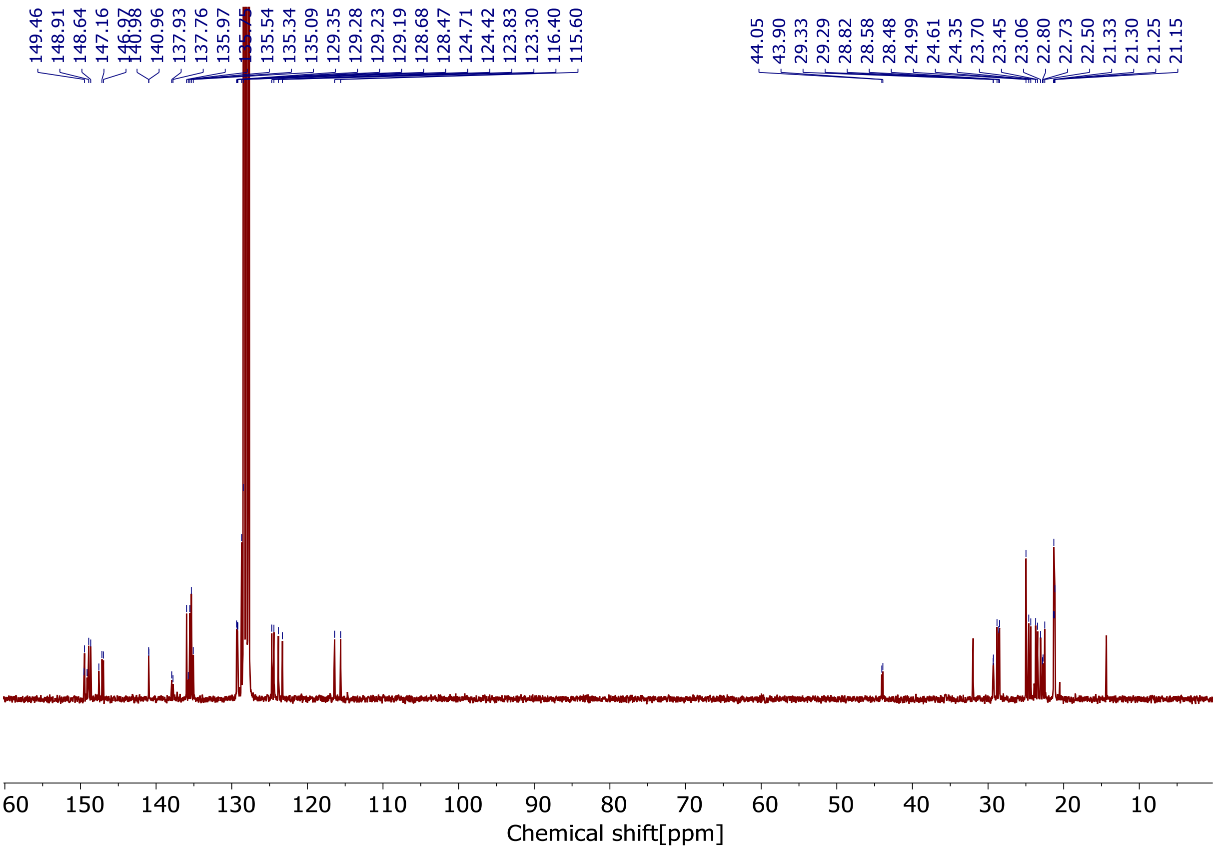
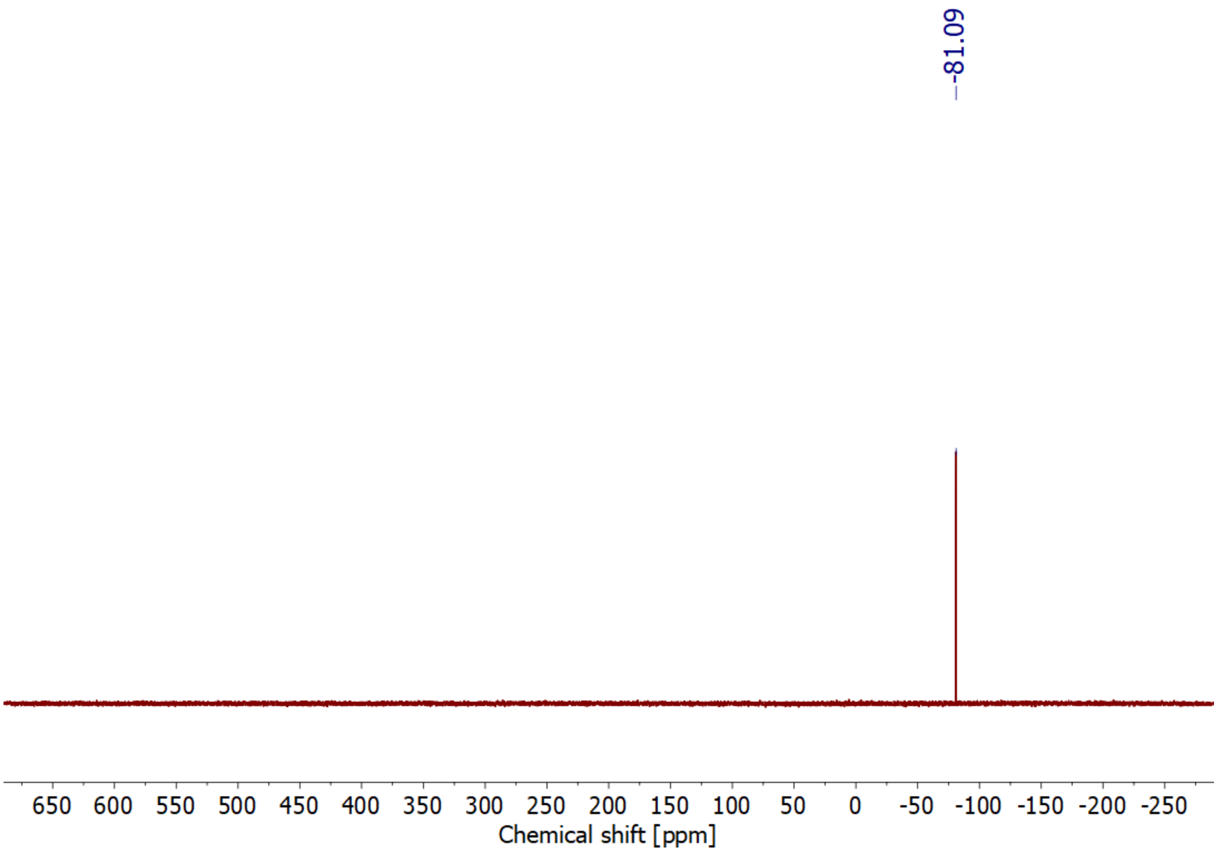
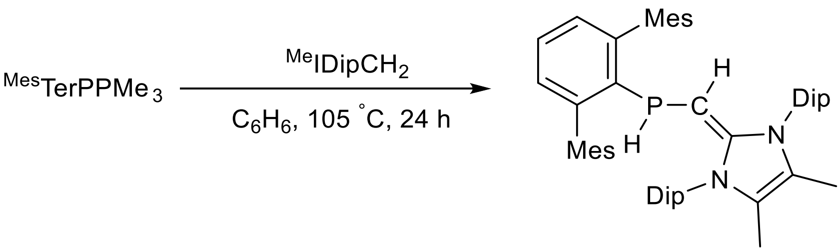


Figure S48: $^{31}P\{^{1}H\}$ NMR spectrum of ^{Mes}TerPHCHIDip (**14**) in C_6D_6.



3.11 Synthesis of ^{Mes}TerPHCH^{Me}IDip (15)



In a 25ml Schlenk flask, ^{Mes}TerPPMe$_3$ (0.080 g, 0.190 mmol) and ^{Me}IDipCH$_2$ (0.086 g, 0.190 mmol) were dissolved in benzene (5 mL). The yellow reaction mixture was heated at 105 °C for 24 h. During the reaction, the color of the reaction mixture changed from yellow to red. Subsequently, the solvent was removed *in vacuo* and the resulting solid was extracted using *n*-hexane (2 mL) and filtered inside the glove box. The obtained solution was then evaporated to afford ^{Mes}TerPHCH^{Me}IDip (**15**) as a reddish amorphous solid. Yield: 0.055 g, 0.071 mmol (37%)

Mp. 215 °C (dec.). **CHN** calc. (found) in %: for $C_{54}H_{67}N_2P$: C 83.68 (83.41); H 8.71 (8.60), N 3.61 (2.71). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.00 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.02−1.16 (overlapping doublets, 21H, CH(CH_3)$_2$), 1.43 (d, 3H, J_{PH} = 1.1 Hz, (H_3CCNDip)$_2$C), 1.45 (d, 3H, J_{PH} = 1.1 Hz, (H_3CCNDip)$_2$C), 1.88 (s, 6H, CH_3), 1.97 (s, 6H, CH_3), 2.17 (t, 1H, $^3J_{HH}$ = 2.3 Hz, PC*H*IDip), 2.32 (s, 6H, CH_3), 2.86 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 2.90–3.08 (overlapping heptetts, 3H, C*H*(CH$_3$)$_2$), 4.11 (dd, 1H, $^1J_{PH}$ = 211.8 Hz, $^3J_{HH}$ = 2.4 Hz, P*H*), 6.74–6.82 (m, 6H, Ar*H*), 6.94–7.07 (m, 3H, Ar*H*), 7.11–7.31 (m, 4H, Ar*H*, overlapping with C_6D_5H). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 9.4 (1C, (H$_3$*C*CNDip)$_2$C), 9.8 (1C, (H$_3$*C*CNDip)$_2$C), 21.1−21.5 (overlapping signals, 6C, *C*H$_3$ Mes), 23.4 (s, 1C, CH(*C*H$_3$)$_2$), 23.5 (d, 1C, J_{PC} = 7.6 Hz, CH(*C*H$_3$)$_2$), 23.7 (s, 1C, CH(*C*H$_3$)$_2$), 23.9 (s, 1C, CH(*C*H$_3$)$_2$), 24.1 (s, 1C, CH(*C*H$_3$)$_2$), 24.4 (s, 1C, CH(*C*H$_3$)$_2$), 24.8 (s, 1C, CH(*C*H$_3$)$_2$), 25.1 (s, 1C, CH(*C*H$_3$)$_2$), 28.5 (s, 2C, *C*H(CH$_3$)$_2$), 28.7 (s, 1C, *C*H(CH$_3$)$_2$), 29.1 (d, 1C, J_{PC} = 2.4 Hz, *C*H(CH$_3$)$_2$), 42.7 (d, 1C, $^1J_{PC}$ = 10.3 Hz, PCH^{Me}IDip), 117.0 (s, 2C, (H$_3$CCNDip)$_2$C), 123.3 (1C, ArCH), 123.8 (1C, ArCH), 124.4 (1C, ArCH), 124.6 (1C, ArCH), 128.6 (2C, ArCH), 128.7 (2C, ArCH), 129.2 (1C, ArCH), 129.4 (4C, ArCH), 133.7 (1C, ArC_{quat}), 134.0 (1C, ArC_{quat}), 135.2 (2C, ArC_{quat}), 135.6 (2C, ArC_{quat}), 136.1 (2C, ArC_{quat}), 138.2 (d, 1C, J_{PC} = 14.3 Hz, N$_2$*C*CP), 141.2 (d, 2C, J_{PC} = 1.6 Hz, o-ArC_{Ter}), 147.0 (1C, ArC_{quat}), 147.2 (1C, ArC_{quat}), 148.2 (1C, ArC_{quat}), 149.0 (1C, ArC_{quat}), 149.3 (1C, ArC_{quat}), 149.9 (d, 1C, J_{PC} = 31.1 Hz, PC_{ipso}), 150.1 (1C, ArC_{quat}). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −79.03. **IR** (ATR, 32 scans, cm^{-1}): ν = 3030 (w), 2956 (m), 2920 (m), 2665 (m), 2314 (w), 2225 (w), 1687 (w), 1610 (w), 1590 (w), 1560 (s), 1546 (s), 1456 (s), 1443 (s), 1381 (s), 1361 (s), 1321 (m), 1253 (m), 1230 (m), 1178 (w), 1092 (w), 1058 (w), 1030 (w), 954 (w), 936 (m), 903 (m), 847 (s), 802 (s), 777 (s), 759 (m), 737 (s), 721 (m), 686 (w), 672 (w), 630 (w), 611 (w), 500 (m), 575 (w), 542 (m), 496 (w), 445 (m). **MS** (ESI-TOF): expected: m/z = 775.5120; found: m/z = 775.5123.

X-ray quality crystals of **15** were obtained from a saturated solution of *n*-hexane at −30 °C.

Figure S49: ^{1}H NMR spectrum of ^{Mes}TerPHCH^{Me}IDip (**15**) in C_6D_6.

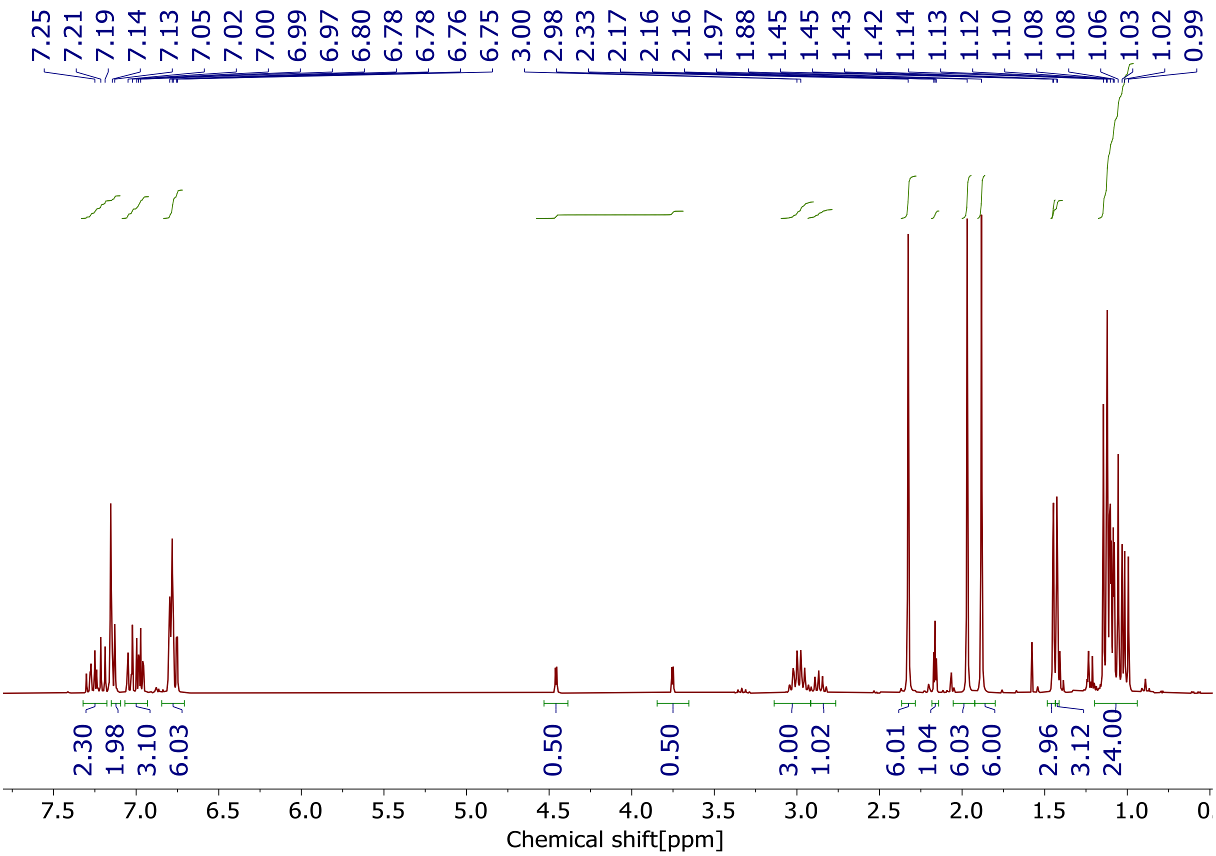


Figure S50: ^{13}C NMR spectrum of ^{Mes}TerPHCH^{Me}IDip (**15**) in C_6D_6.

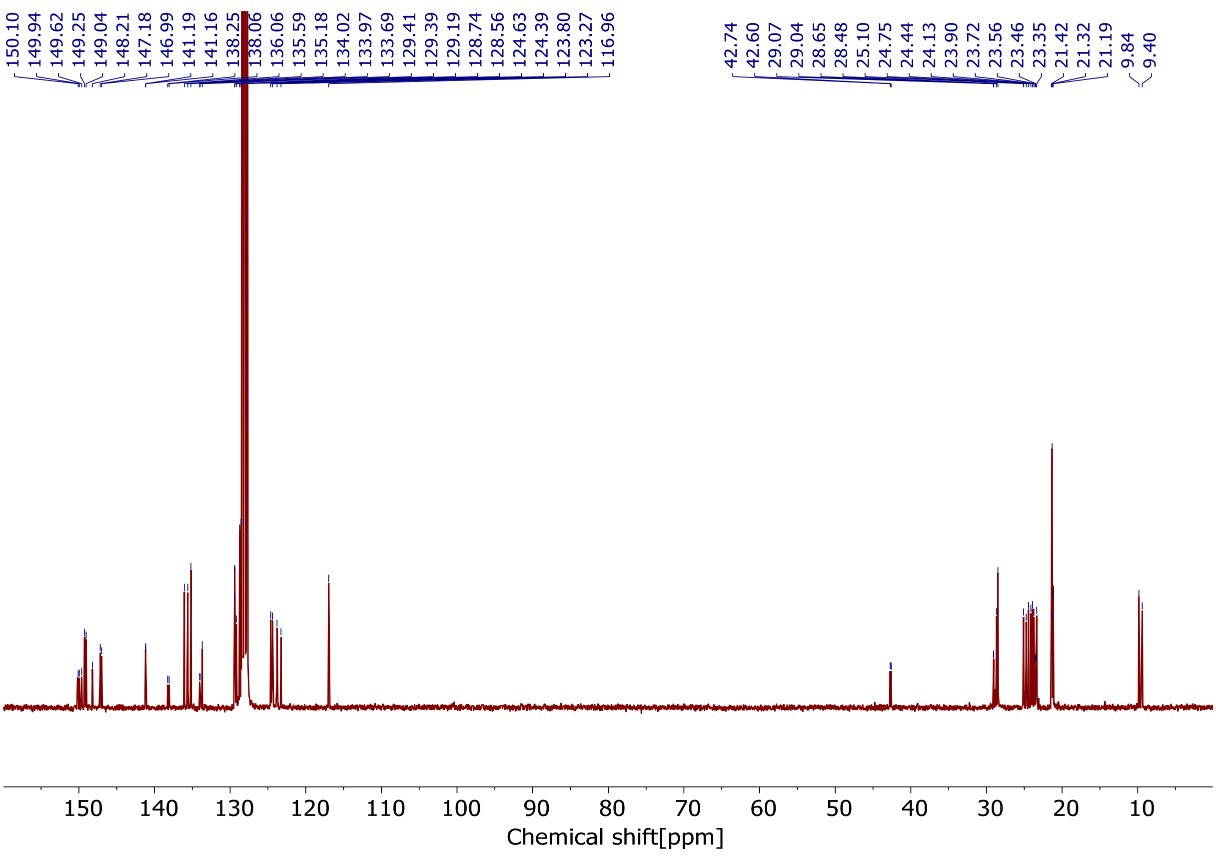
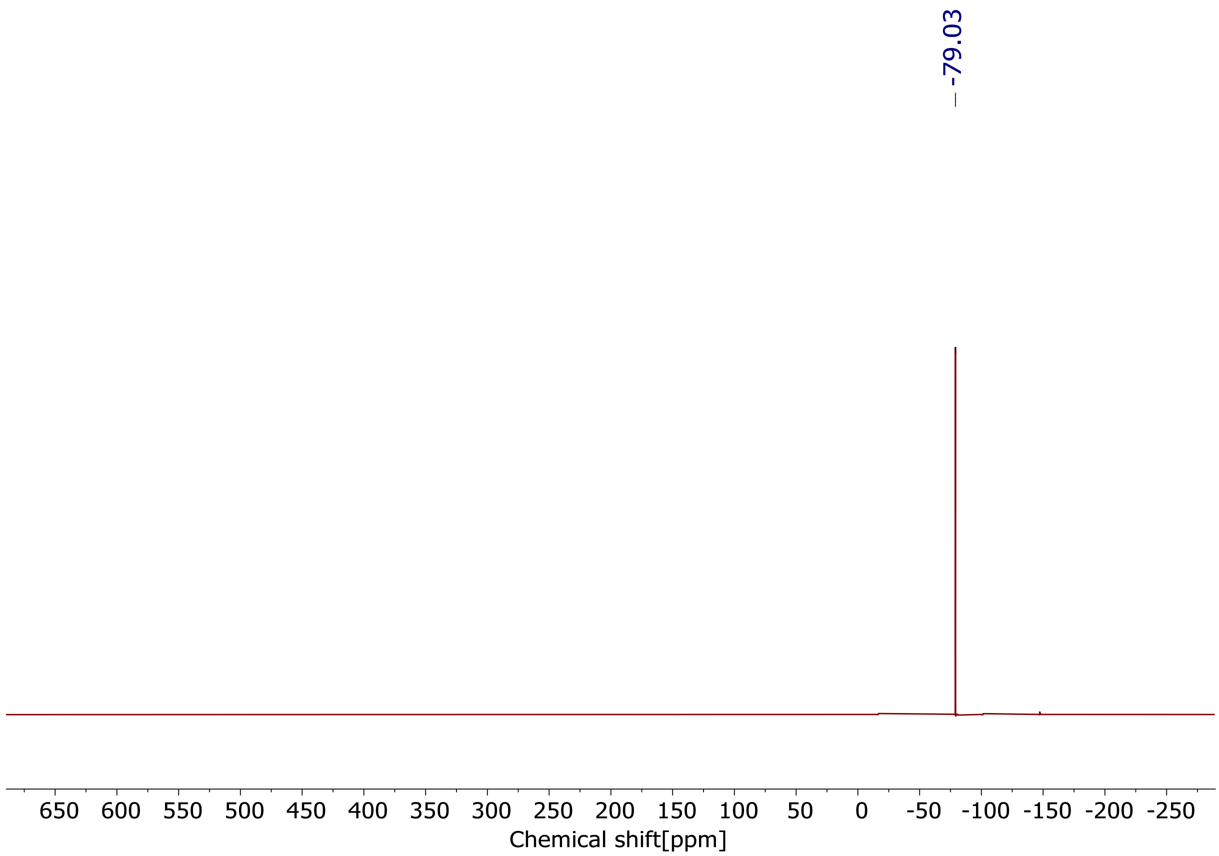
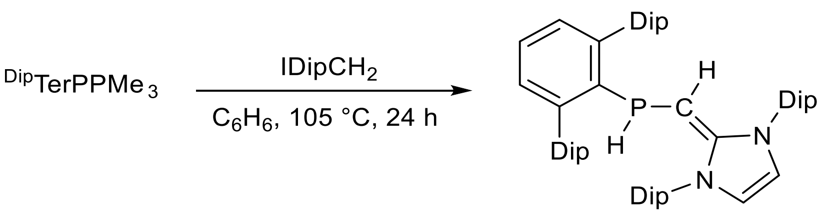


Figure S51: $^{31}P\{^1H\}$ NMR spectrum of ^{Mes}TerPHCH^{Me}IDip (**15**) in C_6D_6.



3.12 Synthesis of ^{Dip}TerPHCHIDip (16)



^{Dip}TerPPMe$_3$ (0.096 g, 0.190 mmol) and IDipCH$_2$ (0.085 g, 0.190 mmol) were dissolved in benzene (5 mL) under exclusion of light and stirred for 24 h at 105 °C. Afterwards, the volatiles were evaporated and the remaining solid was extracted using *n*-hexane (5 mL). It was then filtered, and the volume of the filtrate was reduced to incipient crystallization and placed in the freezer at −30 °C for 24 h. This resulted in the deposition of ^{Dip}TerPHCHIDip (**16**) as yellow crystalline solid. Yield: 0.088 g, 0.105 mmol (56%).

Mp. 194 °C (dec.). **CHN** calc. (found) in %: for $C_{58}H_{75}N_2P$: C 83.81 (83.65); H 9.10 (8.67), N 3.37 (3.04). **^{1}H NMR** (300 MHz, C_6D_6) δ 0.83 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 0.90 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 0.95 – 1.20 (m, 42H, overlapping CH(CH_3)$_2$), 2.51–2.56 (m, 1H, C*H*IDip), 2.68 (hept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 2.72 (hept, 2H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 2.96 (hept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.12 (hept, 1H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 3.13 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 4.29 (dd, 1H, $^1J_{PH}$ = 211.4 Hz, $^3J_{HH}$ = 1.7 Hz, P*H*), 5.57 (dd, 1H, $^3J_{HH}$ = 2.5 Hz, J_{PH} = 1.0 Hz, (*H*CNDip)$_2$C), 5.67 (dd, 1H, $^3J_{HH}$ = 2.5 Hz, J_{PH} = 0.7 Hz, (*H*CNDip)$_2$C), 6.91–6.96 (m, 4H, Ar*H*), 6.97–6.99 (m, 1H, Ar*H*), 7.05–7.10 (m, 2H, Ar*H*), 7.12–7.14 (m, 2H, Ar*H*), 7.14–7.16 (m, 4H, Ar*H*), 7.23–7.31 (m, 2H, Ar*H*). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] = 22.8–23.1 (m, 3C, CH(*C*H$_3$)$_2$), 23.2–23.4 (m, 3C, CH(*C*H$_3$)$_2$), 24.1 (1C, CH(*C*H$_3$)$_2$), 24.3 (1C, CH(*C*H$_3$)$_2$), 24.6 (1C, CH(*C*H$_3$)$_2$), 24.7 (1C, CH(*C*H$_3$)$_2$), 25.2 (1C, CH(*C*H$_3$)$_2$), 25.7 (2C, CH(*C*H$_3$)$_2$), 25.8 (2C, CH(*C*H$_3$)$_2$), 26.0 (1C, CH(*C*H$_3$)$_2$)28.4 (s, 2C, *C*H(CH$_3$)$_2$), 28.6 (s, 1C, *C*H(CH$_3$)$_2$), 28.9 (s, 1C, *C*H(CH$_3$)$_2$), 31.0 (d, 2C, J_{PC} = 3.0 Hz, *C*H(CH$_3$)$_2$), 31.1 (s, 2C, *C*H(CH$_3$)$_2$), 43.8 (d, J_{CP} = 14.3 Hz, *C*HIDip), 116.43 (s, 1C, (HCNDip)$_2$C), 116.92 (s, 1C, (HCNDip)$_2$C), 123.1 (s, 2C, Ar*C*H), 123.2 (s, 2C, Ar*C*H), 123.3 (s, 1C, Ar*C*H), 123.7 (s, 1C, Ar*C*H), 125.2 (d, 2C, J_{CP} = 4.8 Hz, ArCH), 126.8 (s, 1C, Ar*C*H), 129.2 (s, 1C, Ar*C*H), 129.6 (s, 1C, Ar*C*H), 130.6 (d, 2C, J_{CP} = 2.6 Hz, Ar*C*H), 135.4 (1C, ArC$_{quat}$), 136.2 (d, 1C, J_{CP} = 4.3 Hz, ArC$_{quat}$), 138.6 (d, 1C, J_{CP} = 2.6 Hz, N$_2$CCP), 141.3 (d, 2C, J_{PC} = 2.0 Hz, o-ArC$_{quat}$ ^{Dip}Ter), 146.2 (1C, Ar*C*$_{quat}$), 146.4 (1C, Ar*C*$_{quat}$), 146.4 (1C, Ar*C*$_{quat}$), 146.6 (1C, ArC$_{quat}$), 146.9 (d, 1C, J_{PC} = 2.3 Hz, Ar*C*$_{quat}$), 148.77 (1C, Ar*C*$_{quat}$), 148.84 (1C, ArC$_{quat}$), 149.8 (d, 1C, J_{PC} = 6.4 Hz, Ar*C*$_{quat}$), 150.4 (1C, ArC$_{quat}$), 150.2 (1C, Ar*C*$_{quat}$), 150.2 (d, 1C, J_{PC} = 27.8 Hz, PC$_{ipso}$). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −78.47. **IR** (ATR, 32 scans, cm^{-1}): ν = 3060 (w), 2960 (m), 2925 (w), 2865 (w), 2279 (w), 1609 (w), 1577 (w), 1548 (m), 1458 (m), 1399 (w), 1382 (m), 1360 (m), 1322 (m), 1306 (m), 1227 (s), 1197 (s), 1177 (s), 1150 (s), 1120 (s), 1069 (m), 1057 (m), 982 (m), 932 (m), 848 (w), 803 (m), 793 (s), 751 (w), 712 (m), 685 (w), 659 (m), 640 (m), 607 (w), 576 (w), 554 (w), 540 (w), 508 (m), 466 (w), 441 (m), 420 (m). **MS** (ESI-TOF): expected: m/z = 831.5746; found: m/z = 831.5737.

Figure S52: ^{1}H NMR spectrum of ^{Dip}TerPHCHIDip (**16**) in C_6D_6.

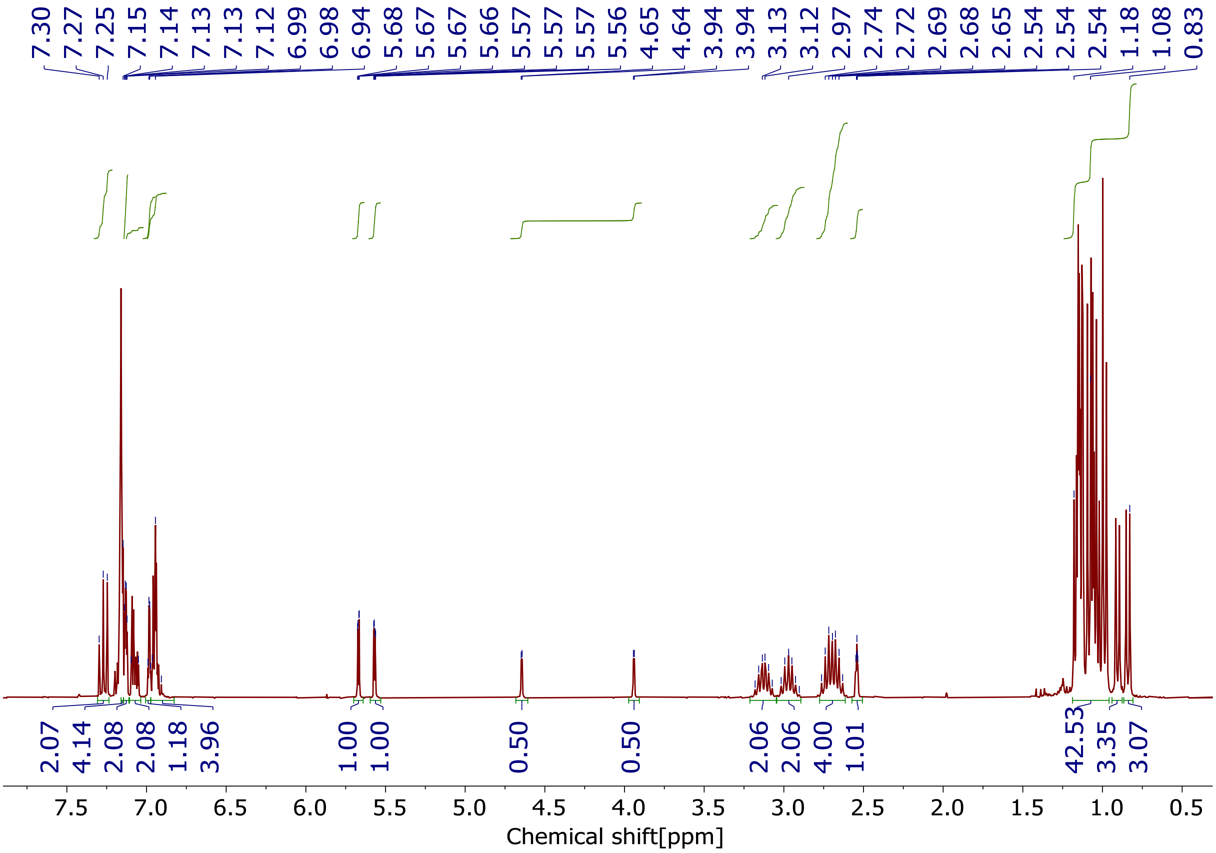


Figure S53: ^{13}C NMR spectrum of ^{Dip}TerPHCHIDip (**16**) in C_6D_6.

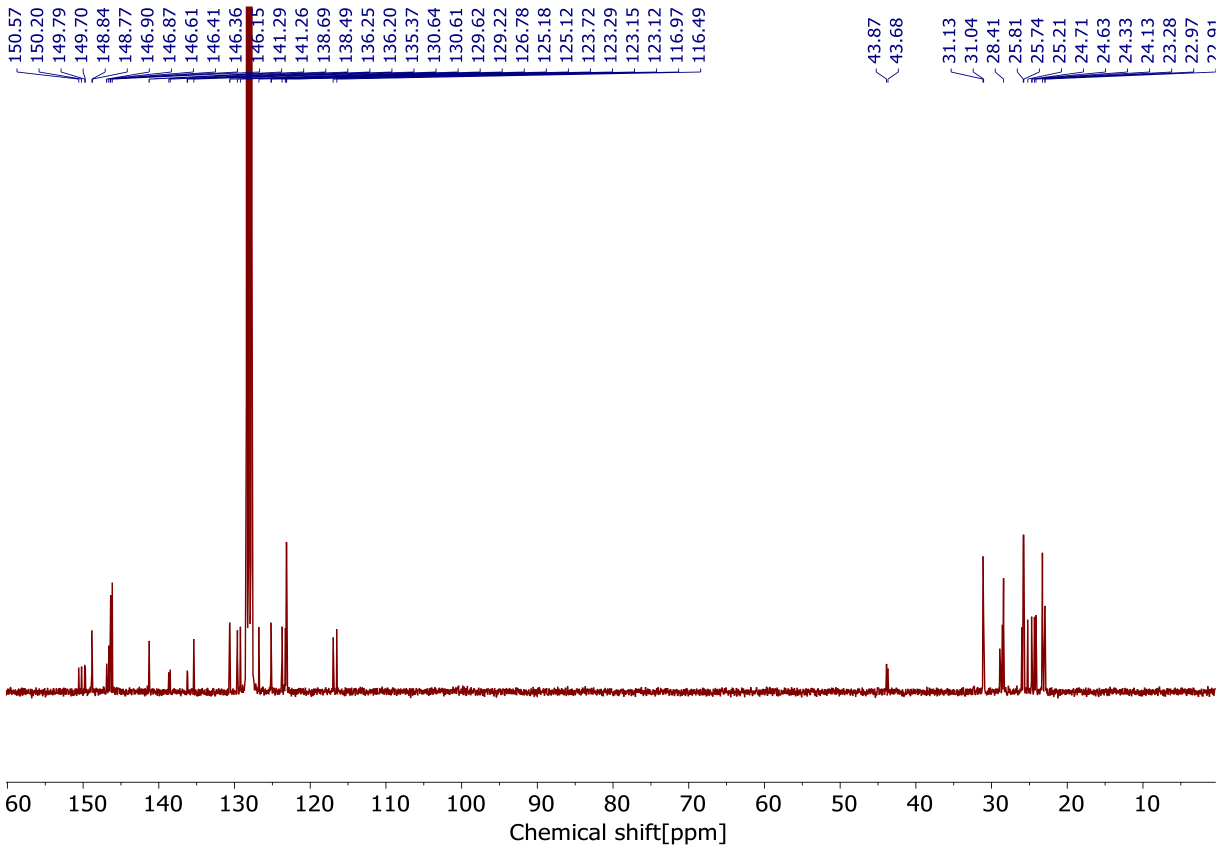
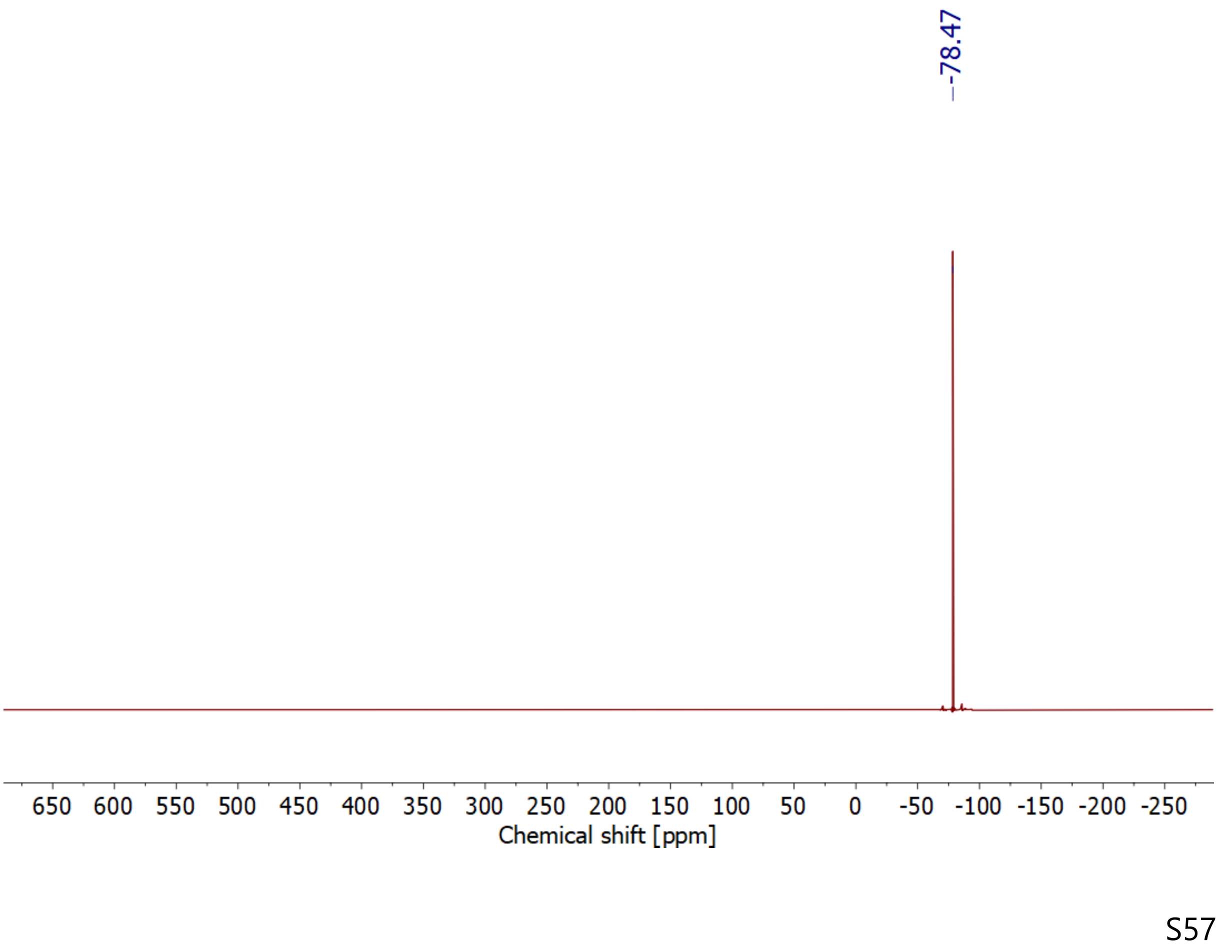
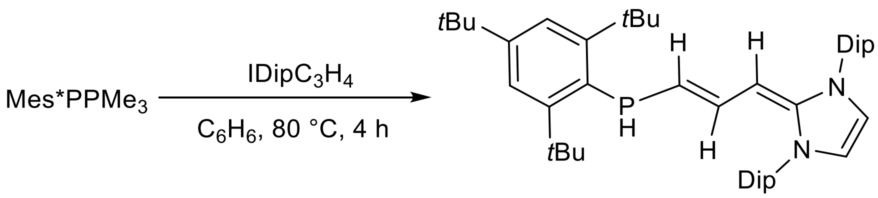


Figure S54: $^{31}P\{^{1}H\}$ NMR spectrum of ^{Dip}TerPHCHIDip (**16**) in C_6D_6.



3.13 Synthesis of $Mes^*PHC_3H_3IDip$ (17)



In a round-bottomed flask Mes^*PPMe_3 (0.100 g, 0.283 mmol) and $IDipC_3H_4$ (121.74 g, 0.283 mmol) were suspended in benzene (5 mL) and stirred for 4 h at 80 °C. Later, the solvent was evaporated under vacuo and the remaining solid was extracted using *n*-hexane. It was then filtered using a filter canula and the obtained solution was concentrated and placed in the freezer at −30 °C for crystallization for 24 h. This resulted in the deposition of X-ray quality crystals of $Mes^*PHC_3H_3IDip$ (0.127 g, 0.180 mmol, 63%).

Mp. 148 °C (dec.). **CHN** calc. (found) in %: for $C_{48}H_{69}N_2P$: C 81.77 (81.85); H 9.86 (9.86), N 3.97 (3.31). **^{1}H NMR** (300 MHz, C_6D_6) δ [ppm] = 1.08–1.23 (m, 18H, CH(C*H*$_3$)$_2$), 1.29 (s, 9H, p-C(C*H*$_3$)$_3$), 1.39 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.39 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.58 (s, 18H, o-C(C*H*$_3$)$_3$), 3.03 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.06 (heptett, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.18 (hept, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.23 (heptett, 1H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 4.04 (1H, ^3J(H3-H4) = 12.0 Hz, H4) 4.66 (1H, ^3J(H1-H2) = 3.6 Hz, ^3J(H3-H2) = 15.5 Hz, H2), 5.67 (1H, $^1J_{PH}$ = 225 Hz, ^3J(H2-H1) = 3.6 Hz, ^5J(H3-H1) = 1.8 Hz, H1) 5.75–5.80 (m, 2H, (*H*CNDip)$_2$C), 6.01 (1H, ^5J(H1-H3) = 1.8 Hz, ^5J(H2-H3) = 15.5 Hz, ^3J(H4-H3) = 12.0 Hz, $^5J_{PH}$ = 15.5), 7.02–7.10 (m, 4H, Ar*H*), 7.17–7.23 (m, 3H, Ar*H*), 7.32 (1H, Ar*H*), 7.50 (d, 2H, J_{PH} = 2.0 Hz, Ar*H* Mes*). **^{13}C NMR** (75 MHz, C_6D_6) δ 23.72 (1C, CH(*C*H$_3$)$_2$), 23.71 (1C, CH(*C*H$_3$)$_2$), 23.73 (1C, CH(*C*H$_3$)$_2$), 23.9 (1C, CH(*C*H$_3$)$_2$), 24.1–24.3 (m, 3C, CH(*C*H$_3$)$_2$), 24.5 (1C, CH(*C*H$_3$)$_2$), 28.80 (1C, *C*H(CH$_3$)$_2$), 28.84 (1C, *C*H(CH$_3$)$_2$), 29.0 (2C, *C*H(CH$_3$)$_2$), 31.6 (3C, p-C(*C*H$_3$)$_3$), 34.1 (d, 6C, J_{PC} = 7.5 Hz, o-C(*C*H$_3$)$_3$), 34.56 (1C, p-*C*(CH$_3$)$_3$), 38.9 (2C, o-*C*(CH$_3$)$_3$), 73.7 (d, 1C, J_{PC} = 19.9 Hz, *C***H4**), 105.7 (d, 1C, J_{PC} = 4.5 Hz, *C***H2**), 115.6 (1C, (H*C*NDip)$_2$C), 117.2 (1C, (H*C*NDip)$_2$C), 122.3 (d, 2C, J_{PC} = 3.4 Hz, ArCH Mes*), 124.7 (2C, Ar*C*H), 124.8 (1C, Ar*C*H), 124.9 (1C, Ar*C*H), 129.9 (1C, ArCH), 130.2 (1C, ArCH), 133.6 (1C, Ar*C*$_{quat}$), 135.14 (1C, ArC$_{quat}$), 135.7 (d, 1C, $^{1}J_{PC}$ = 26.7 Hz, PC$_{ipso}$), 135.8 (1C, Ar*C*$_{quat}$), 138.9 (d, 1C, J_{PC} = 44 Hz, C**H3**), 146.3 (1C, Ar*C*$_{quat}$), 147.5 (1C, Ar-Cquat), 147.9 (1C, Ar-Cquat), 148.1 (1C, Ar-Cquat), 148.40 (1C, ArC$_{quat}$), 148.42 (1C, ArC$_{quat}$), 155.0 d, 2C, $^{2}J_{PC}$ = 7.8 Hz, Ar*C*$_{quat}$. **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −66.70 (*E*-configured, major), −82.3 (*Z*-configured, minor). **IR** (ATR, 32 scans, cm^{-1}): ν = 2959 (m), 2867 (m), 2355 (w), 1612 (m), 1596 (s), 1559 (s), 1457 (s), 1424 (m), 1391 (w), 1383 (w), 1359 (m), 1323 (m), 1296 (m), 1275 (w), 1256 (w), 1234 (m), 1210 (m), 1180 (m), 1149 (m), 1120 (w), 1081 (w), 1059 (w), 988 (w), 972 (w), 955 (w), 932 (m), 909 (m), 875 (m), 845 (w), 802 (m), 766 (m), 741 (m), 712 (m), 690 (m), 664 (m), 648 (m), 610 (w), 595 (w), 555 (w), 518 (w), 493 (w), 448 (w). **MS** (ESI-TOF): expected: m/z = 704.5192; found: m/z = 704.5152.

Figure S55: ^{1}H NMR spectrum of Mes*PHC$_3$H$_3$IDip (**17**) in C_6D_6.

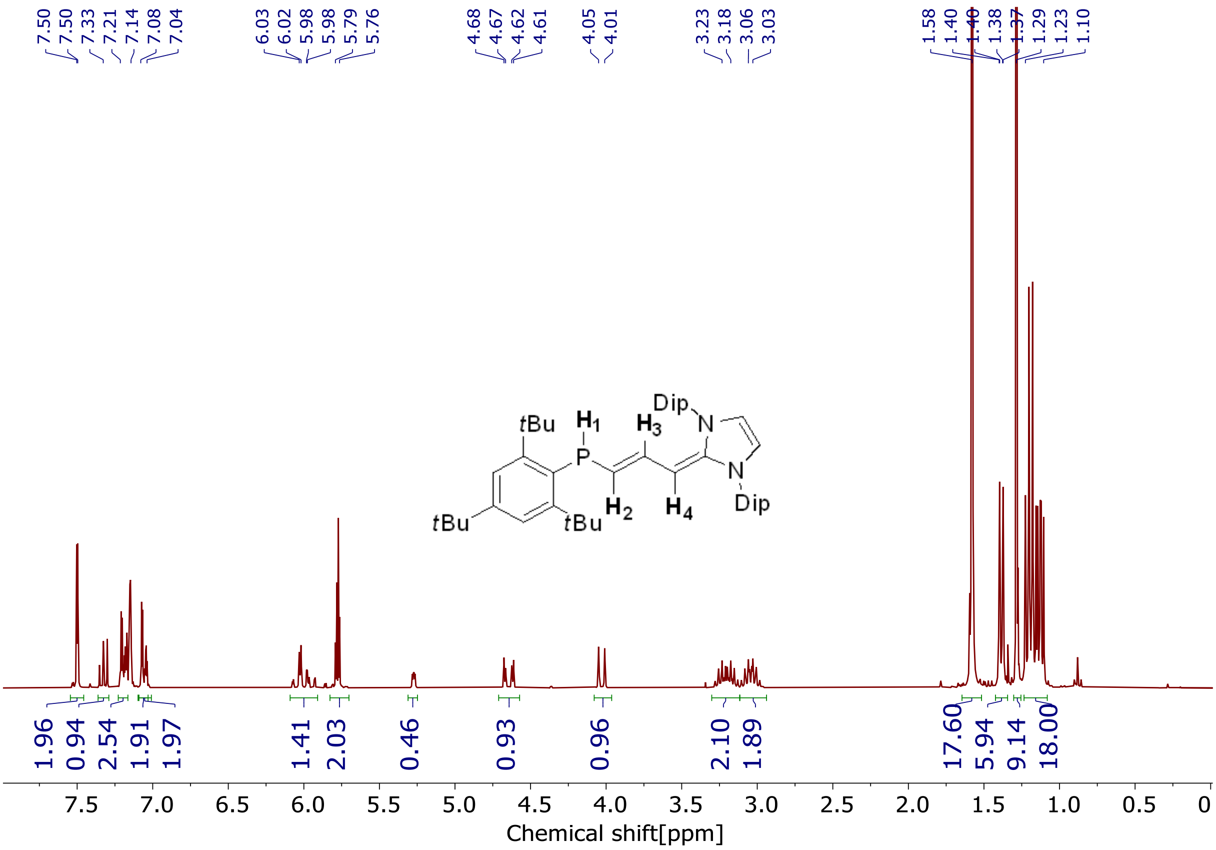


Figure S56: ^{13}C NMR spectrum of Mes*PHC$_3$H$_3$IDip (**17**) in C_6D_6.

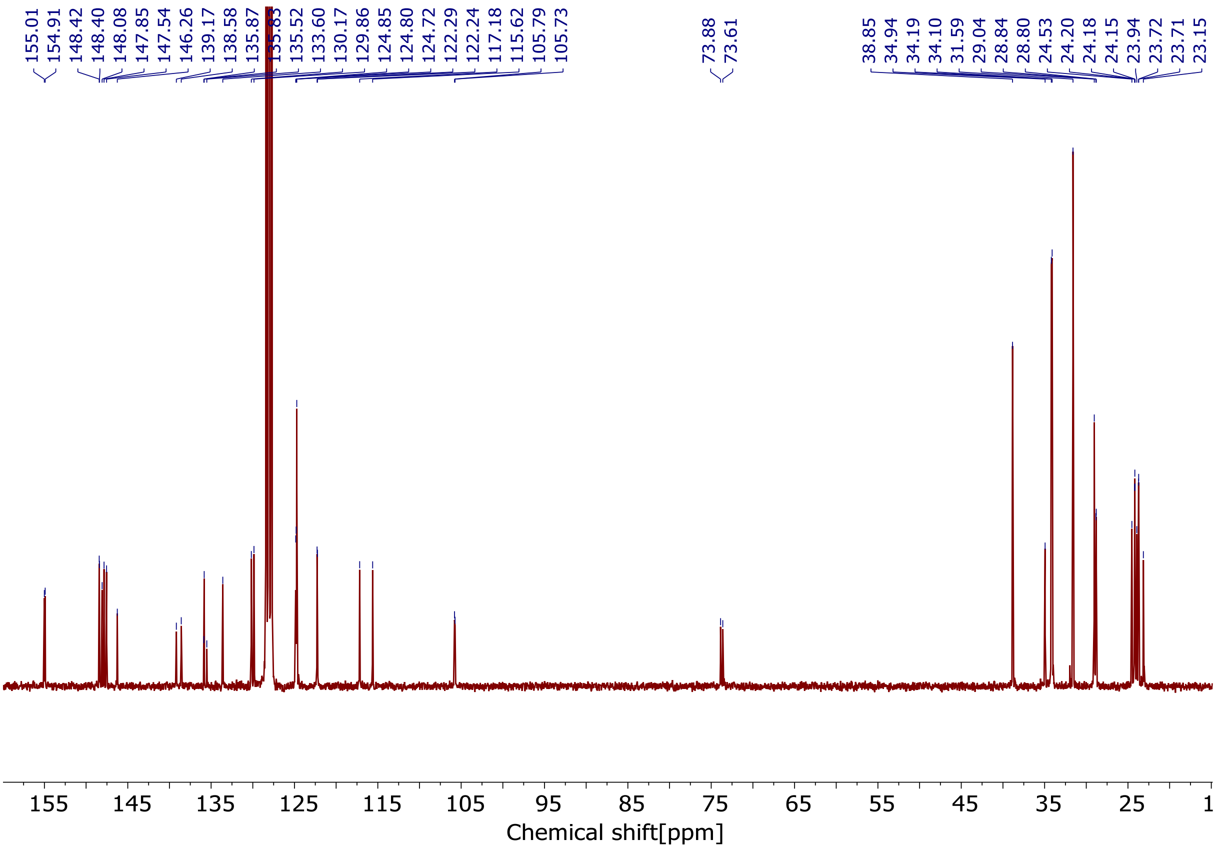
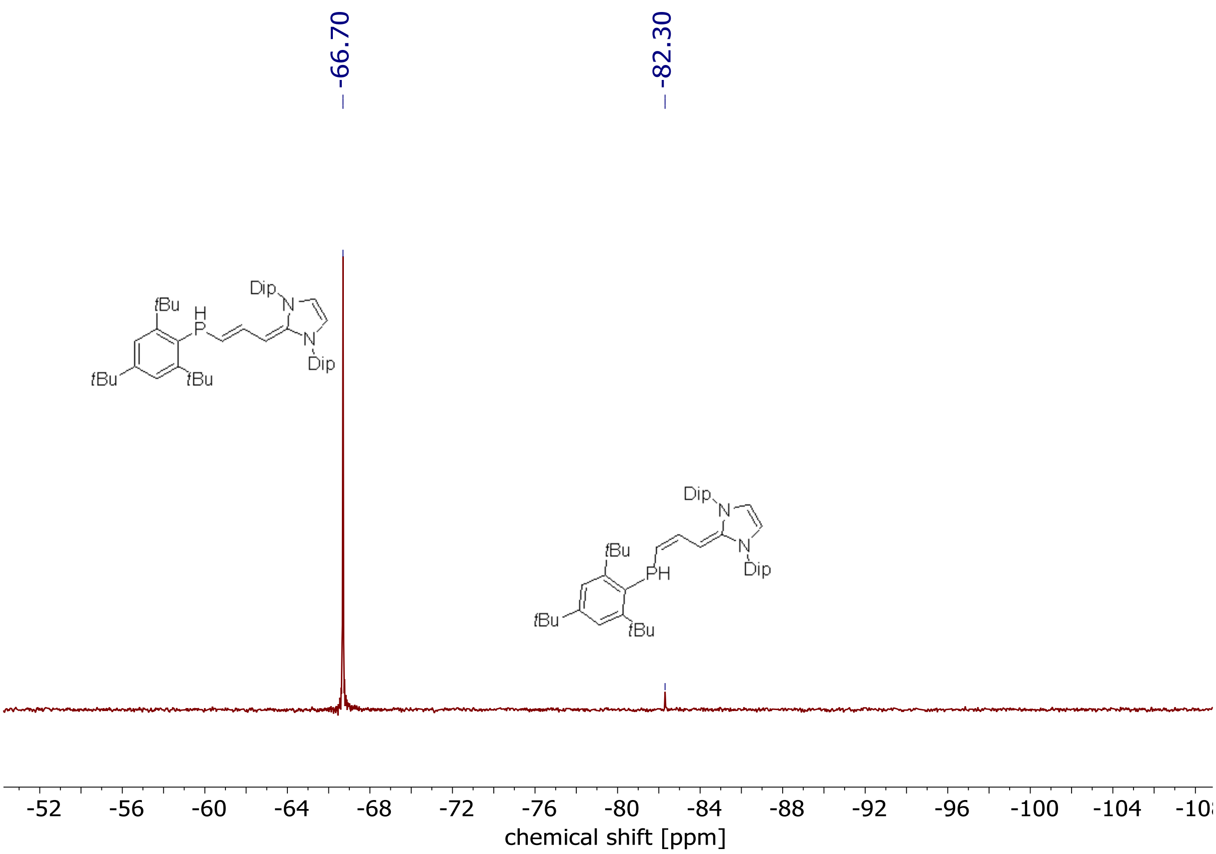
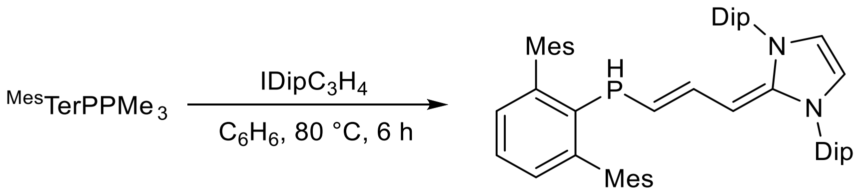


Figure S57: ^{31}P{^{1}H} NMR spectrum of Mes*PHC$_3$H$_3$IDip (**17**) in C_6D_6.



3.14 Synthesis of ^{Mes}TerPHC$_3$H$_3$IDip (18)



^{Mes}TerPPMe$_3$ (0.080 g, 0.190 mmol) and IDipC$_3$H$_4$ (0.081 g, 0.190 mmol) were combined in a 10 mL schlenk flask, dissolved in benzene (3 mL) under the exclusion of light (wrap flask with tin foil) and stirred for 6 h at 80 °C. After that, the solvent was evaporated under reduced pressure and the residue was extracted using *n*-hexane. The resulting solution was filtered inside the glove box using a pipette, fitted with a glass microfiber filter, and the volume of the filtrate was reduced to ca. 1 mL and placed in the freezer at −30 °C. This resulted in the deposition of X-ray quality crystals of ^{Mes}TerPHC$_3$H$_3$IDip (**18**).

Yield: 0.050 g, 0.064 mmol (34 %).

Mp. 194 °C (dec.). **CHN** calc. (found) in %: for C$_{54}$H$_{65}$N$_2$P: C 83.90 (83.72); H 8.47 (8.33), N 3.62 (2.90). **^{1}H NMR** (300 MHz, C$_6$D$_6$) δ [ppm] = 1.07 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.09–1.17 (m, 15H, CH(C*H*$_3$)$_2$), 1.23 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.30 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 2.05 (s, 6H, C*H*$_3$ Mes), 2.10 (s, 6H, C*H*$_3$ Mes), 2.24 (s, 6H, C*H*$_3$ Mes), 2.90–3.15 (m, 4H, C*H*(CH$_3$)$_2$), 3.83 (1H, ^3J(H1-H2) = 8.1 Hz, ^3J(H3-H2) = 15.1 Hz, ^2J(P-H2) = 22.4 Hz, **H2**), 4.04 (1H, ^3J(H3-H4) = 11.6 Hz, **H4**) 4.29 (1H, ^1J(P-H1) = 227.8 Hz, ^3J(H2-H1) = 8.1 Hz, ^5J(H3-H1) = 0.8 Hz, **H1**), 5.44 (1H, ^3J(H2-H3) = 15.1 Hz, ^3J(H4-H3) = 11.6 Hz, ^5J(H1-H3) = 0.8 Hz, ^4J(P-H3) = 13.2 Hz, **H3**), 5.71 (dd, $^3J_{HH}$ = 2.4 Hz, J_{PH} = 0.7 Hz, (*H*CNDip)$_2$C), 5.76 (dd, $^3J_{HH}$ = 2.4 Hz, (*H*CNDip)$_2$C), 6.79 (s, 2H, Ar*H*), 6.84 (s, 2H, Ar*H*), 6.86-6.901 (m, 2H, Ar*H*), 6.98–7.15 (m overlapping with C$_6$D$_6$, 5H, Ar*H*), 7.21–7.30 (m, 2H, Ar*H*). **^{13}C NMR** (75 MHz, C$_6$D$_6$) δ [ppm] = 21.1 (d, 2C, J_{PC} = 2.1 Hz, CH$_3$ Mes), 21.2 (d, 2C, J_{PC} = 3.7 Hz, CH$_3$ Mes), 21.4 (2C, CH$_3$), 23.1, 23.3, 23.8, 24.02, 24.06, 24.18, 24.21 24.3 (8C, CH(*C*H$_3$)$_2$), 28.76, 28.79, 28.88, 28.91 (4C, *C*H(CH$_3$)$_2$), 73.5 (d, J_{PC} = 13.9 Hz, C**H4**), 99.7 (d, J_{PC} = 5.2 Hz, C**H2**), 115.5 (1C, (HCNDip)$_2$C), 116.9 (1C, (HCNDip)$_2$C), 124.57, 124.61, 124.65 (4C, ArCH), 127.6 (2C, ArCH), 128.4 (2C, ArCH), 129.8 (1C, ArCH), 129.9 (1C, ArCH), 133.6 (1C, ArC_{quat}), 135.5 (2C, ArC_{quat}), 135.9 (2C, ArC_{quat}), 136.5 (2C, ArC_{quat}), 138.3 (d, 1C, J_{PC} = 22.1 Hz, *C***H3**), 138.8 (1C, ArC_{quat}), 138.53 (1C, ArC_{quat}), 140.5 (2C, J_{PC} = 2.0 Hz, ArC_{quat}), 144.41 (1C, Ar-Cquat), 144.9 (d, 1C, J_{PC} = 11.9 Hz, ArC_{quat}), 145.6 (1C, ArC_{quat}), 147.4 (1C, ArC_{quat}), 147.6 (1C, ArC_{quat}), 148.4 (1C, ArC_{quat}), 148.6 (1C, ArC_{quat}). **^{31}P{^{1}H} NMR** (121.55 MHz, C_6D_6): δ [ppm] = −58.38. **IR** (ATR, 32 scans, cm^{-1}): ν = 3130 (w), 2961 (m), 2923 (w), 2868 (w), 2308 (w), 1605 (s), 1558 (s), 1458 (s), 1423 (m), 1383 (w), 1361 (m), 1324 (s), 1296 (m), 1255 (w), 1215 (w), 1180 (w), 1160 (m), 1112 (w), 1080 (w), 1060 (w), 1031 (w), 989 (w), 962 (m), 934 (m), 849 (m), 799 (s), 767 (m), 757 (m), 741 (m), 727 (m), 694 (m), 683 (m), 660 (m), 590 (w), 573 (w), 547 (w), 507 (w), 494 (w), 448 (w). **MS** (ESI-TOF): expected: m/z = 773.4963; found: m/z = 773.4948.

Figure S58: ^{1}H NMR spectrum of ^{Mes}TerPHC$_3$H$_3$IDip (**18**) in C_6D_6.

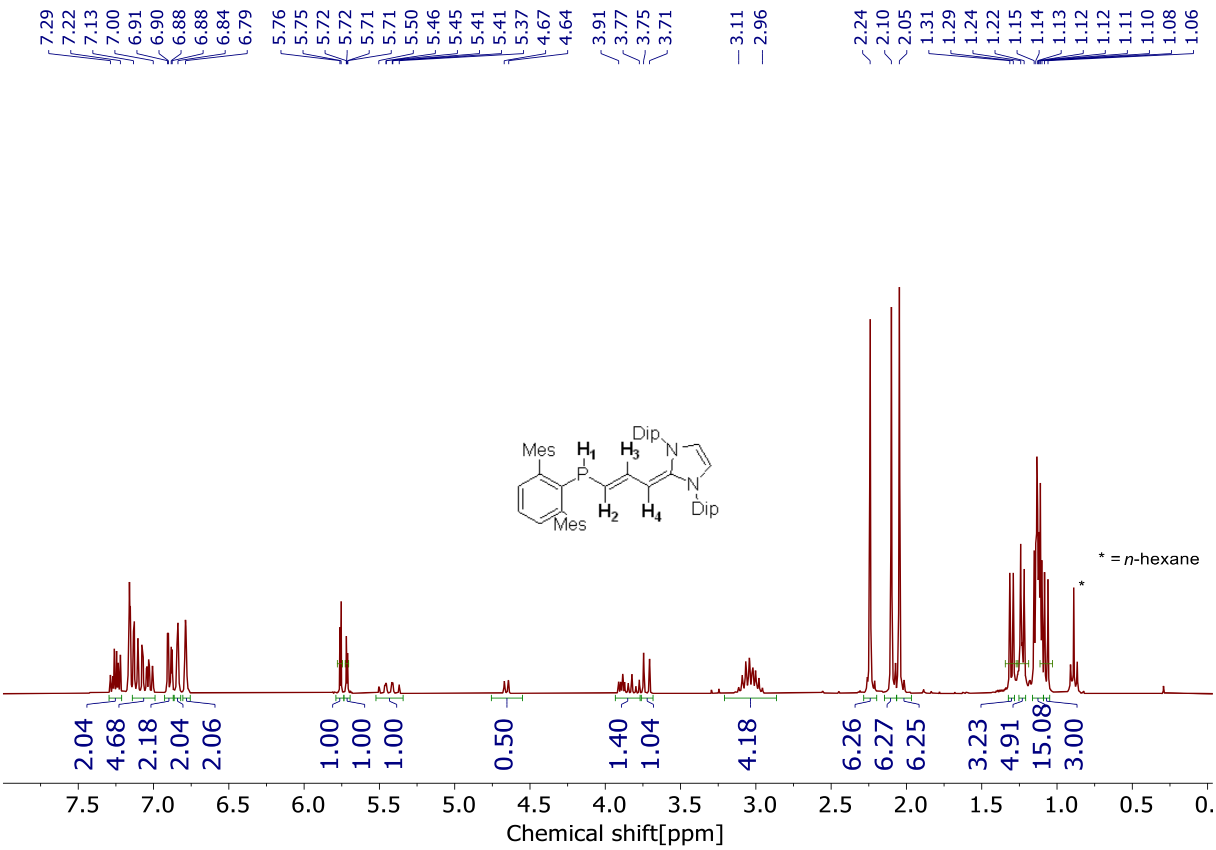


Figure S59: ^{13}C NMR spectrum of ^{Mes}TerPHC$_3$H$_3$IDip (**18**) in C$_6$D$_6$.

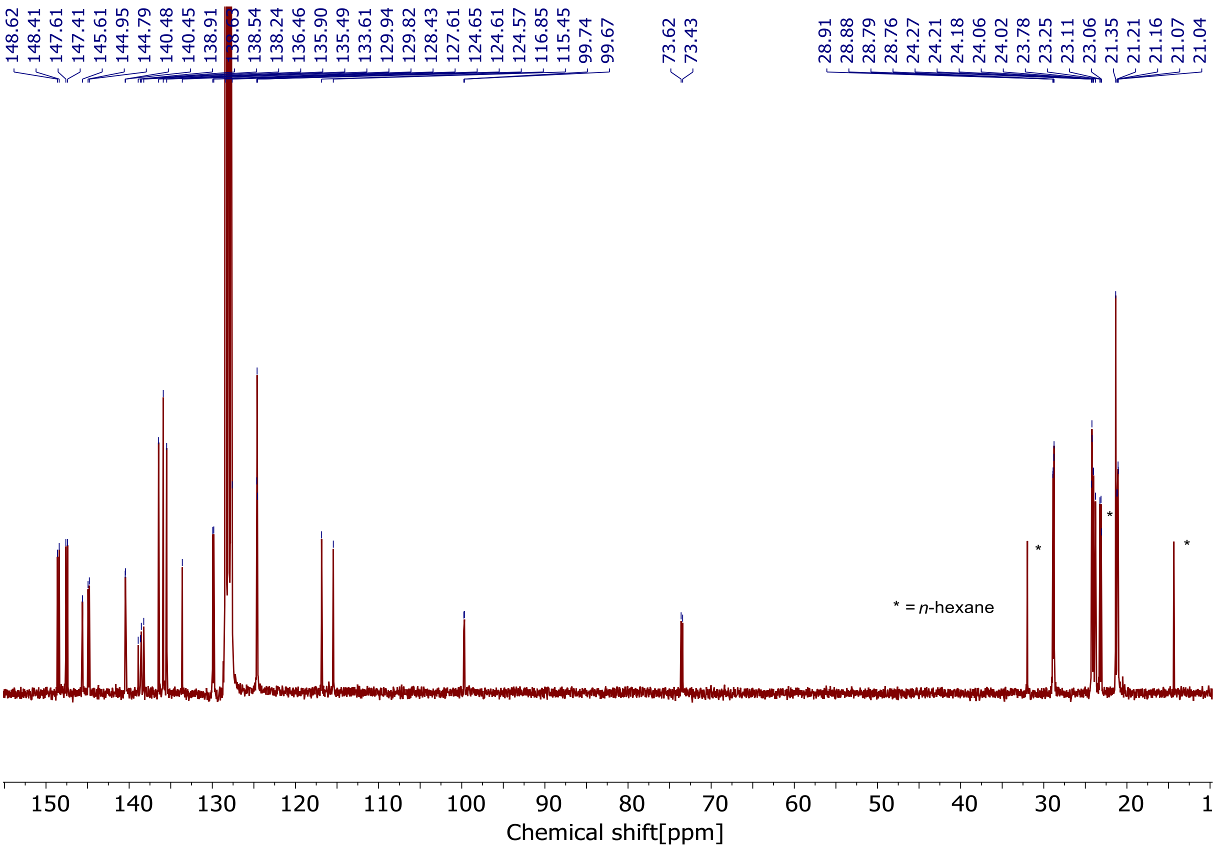
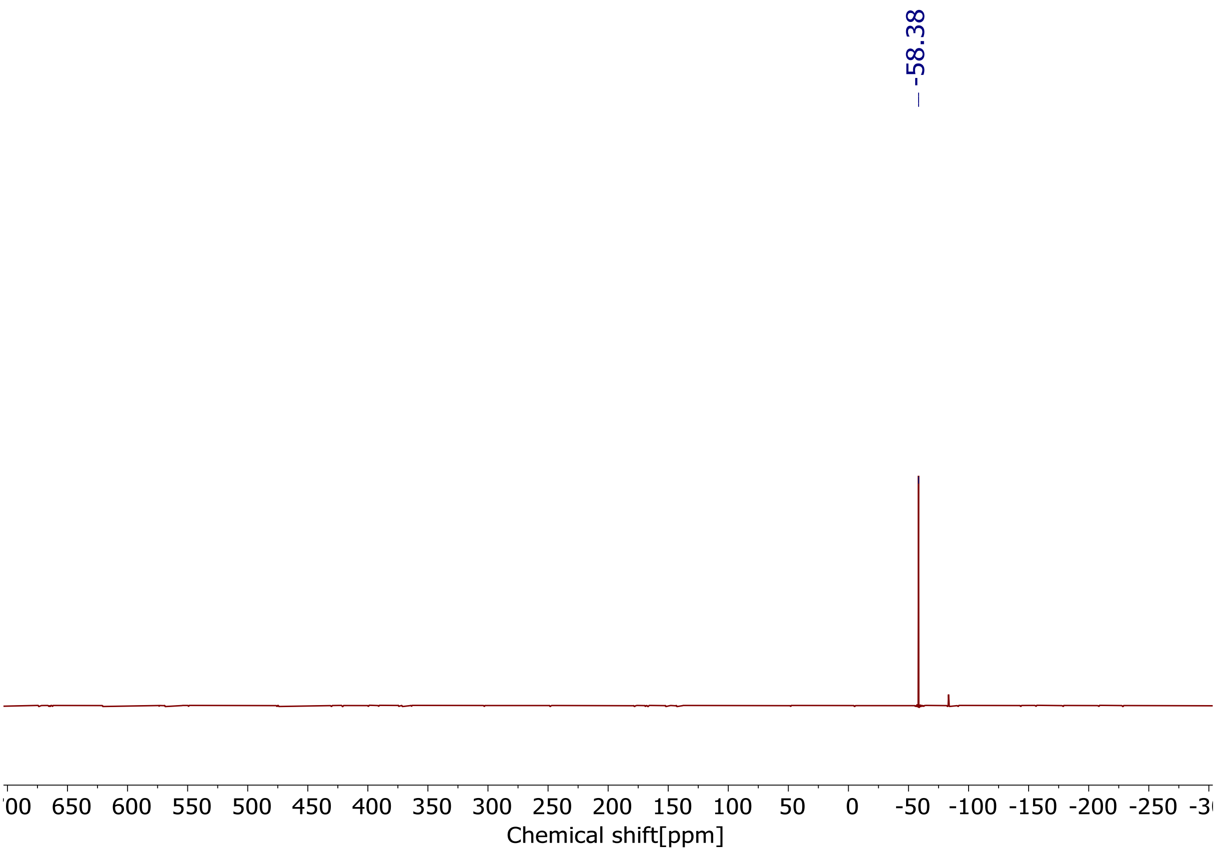
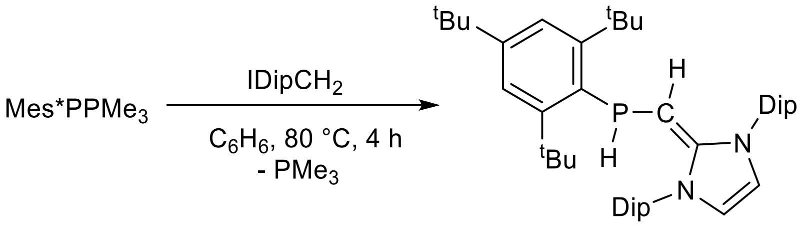


Figure S60: ^{31}P{^{1}H} NMR spectrum of ^{Mes}TerPHC$_3$H$_3$IDip (**18**) in C$_6$D$_6$.

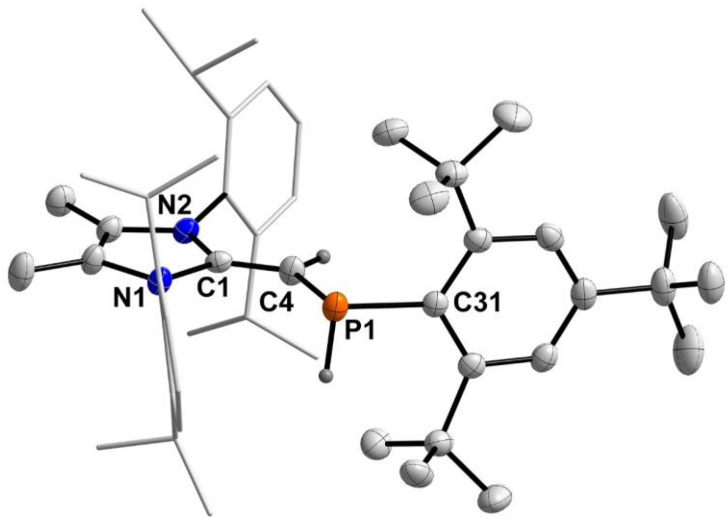


3.15 Attempted Synthesis of Mes*PHCH^{Me}IDip (19)



In a 25 mL Schlenk flask, Mes*PPMe$_3$ (0.100 g, 0.284 mmol) and ^{Me}IDipCH$_2$ (0.123 g, 0.284 mmol) were dissolved in benzene (5 mL) under the exclusion of light. The reaction was heated at 80 °C for 24 h. A ^{31}P NMR experiment indicated that the reaction did not go to completion. Subsequently, the solvent was evaporated under reduced pressure and the resulting solid was extracted with *n*-hexane (5 mL). It was then filtered using a filter canula and the obtained solution was concentrated to incipient crystallization and kept at −30 °C for 24 h. This resulted in the deposition minimal amounts of X-Ray quality crystals of Mes*PHCH^{Me}IDip (**19**) as yellow, crystalline solid.

Figure S61: POV-ray depiction of the molecular structure of **19**. ORTEPs drawn at 50% probability, all H-atoms (except H1 and H4) are omitted for clarity. Selected bond lengths (Å) and angles (°) of **19**: P1-C4 1.8117(15), P1-C31 1.8738(15), C1-C4 1.366(2); C1-C4-P1 126.47(11), C4-P1-C31 103.86(6).



4 Structure elucidation

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 150(2) K during measurement. The data were collected on a Bruker Kappa APEX II Duo diffractometer using Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å), or on a STOE-IPDS II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by iterative methods (SHELXT)[11] and refined by full matrix least squares procedures (SHELXL).[12] Semi-empirical absorption corrections were applied (SADABS).[13] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

The unit cell in **6** contains four disordered THF molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[14]

8 crystallizes with two molecules of **8** in the asymmetric unit as well as one n-hexane solvent molecule. One of the ^{t}Bu groups (C52-C55) was found to be disordered and was split in two parts and the occupancy of each part was allowed to refine freely. The *n*-hexane molecule was found to be disordered and was split in two parts and the occupancy of each part was allowed to refine freely.

The unit cell in **12** contains two heavily disordered *n*-pentane molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

The unit cell in **13** contains four disordered *n*-hexane molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

The unit cell in **14** contains one disordered *n*-pentane molecule. This has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

The unit cell in **16** contains four disordered *n*-pentane molecules. These have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. One of isopropyl groups (C14–C16) of the Dip moiety was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely.

The unit cell in **18** contains one disordered *n*-hexane molecule. This has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. One of the o-mesityl groups in the terphenyl moiety was found to be disordered and was split in two parts. The occupancy of each part was allowed to refine freely.

Table S2: Crystallographic details for **6**, **8** and **10**.

Compound	**6**	**8**	**10**
Chem. Formula	$C_{25}H_{41}N_2P$, C_4H_8O	2 ($C_{41}H_{57}N_2P$), C_6H_{14}	$C_{33}H_{41}N_2P$
Wavelength	0,71073	1,54078	0,71073
X-Ray Source	MoK/a	CuK/a	MoK/a
Formula weight [g/mol]	472.67	1303.88	496.65
Colour	yellow	yellow	yellow
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
a [Å]	15.0307(9)	9.8045(4)	8.342(2)
b [Å]	9.7034(6)	17.1656(8)	10.832(3)
c [Å]	20.4134(12)	24.3050(11)	16.967(4)
α [°]	90	86.6392(22)	80.3487(38)
β [°]	104.0204(24)	87.4849(22)	76.2360(36)
γ [°]	90	84.6245(21)	73.6442(37)
V [Å^3]	2888.6(3)	4062.5(3)	1417.3(6)
Z	4	2	2
$\rho_{calcd.}$ [g/cm^3]	1.087	1.066	1.164
μ [mm^{-1}]	0.117	0.810	0.121
T [K]	150(2)	150(2)	150(2)
Measured reflections	59656	71311	19377
Independent reflections	8430	14362	6496
Reflections with $I > 2\sigma(I)$	6370	11989	4010
R_{int}	0.0412	0.0427	0.0643
F(000)	1040	1428	536
$R_1(R[F^2>2\sigma(F^2)])$	0.0405	0.0502	0.0559
w$R_2(F^2)$	0.1136	0.1454	0.1467
GooF	1.005	1.025	1.005
No. of Parameters	266	924	335
CCDC #	2046859	2046860	2046861

Table S3: Crystallographic details for **12**, **13** and **14**.

Compound	**12**	**13**	**14**
Chem. Formula	$C_{37}H_{49}N_2P$, C_5H_{12}	$C_{46}H_{67}N_2P$, C_6H_{14}	$C_{52}H_{63}N_2P$, C_5H_{12}
Wavelength	0,71073	1,54178	1,54178
X-Ray Source	MoK/a	CuK/a	CuK/a
Formula weight [g/mol]	624.89	751.09	819.16
Colour	yellow	yellow	colourless
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1	$P2_1/n$	*P*-1
a [Å]	11.1141(8)	14.9777(3)	10.6116(3)
b [Å]	13.0309(9)	17.4497(3)	10.1511(3)
c [Å]	14.5537(10)	19.3800(4)	22.9820(6)
α [°]	107.3420(10)	90	83.9073(11)
β [°]	102.5540(10)	106.6127(10)	80.6522(11)
γ [°]	96.1670(10)	90	67.6900(10)
V [Å^3]	1930.0(2)	4853.66(16)	2390.61(12)
Z	2	4	2
$\rho_{calcd.}$ [g/cm^3]	1.075	1.047	1.138
μ [mm^{-1}]	0.101	0.738	0.786
T [K]	150(2)	150(2)	150(2)
Measured reflections	66599	33300	26537
Independent reflections	11264	8557	8411
Reflections with $I > 2\sigma(I)$	8675	7106	7420
R_{int}	0.0325	0.0394	0.0288
F(000)	684	1688	892
$R_1(R[F^2>2\sigma(F^2)])$	0.0425	0.1363	0.0407
$wR_2(F^2)$	0.1213	0.1458	0.1168
GooF	1.036	1.036	1.041
No. of Parameters	373	467	518
CCDC #	2046862	2046863	2046864

Table S4: Crystallographic details for **16**, **17** and **18**.

Compound	**16**	**17**	**18**
Chem. Formula	$C_{58}H_{75}N_2P$, C_5H_{12}	$C_{48}H_{69}N_2P$	$C_{54}H_{65}N_2P$, 0.5 (C_6H_{14})
Wavelength	1,54178	1,54178	0,71073
X-Ray Source	CuK/a	CuK/a	MoK/a
Formula weight [g/mol]	903.31	705.02	816.13
Colour	yellow	yellow	yellow
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a [Å]	13.3114(4)	10.4692(4)	9.0953(9)
b [Å]	18.0342(5)	18.3677(7)	12.8174(12)
c [Å]	24.3084(7)	23.4081(9)	22.854(2)
α [°]	90	90	86.172(3)
β [°]	104.2346(19)	100.562(2)	87.117(3)
γ [°]	90	90	69.713(3)
V [Å^3]	5656.3(3)	4425.0(3)	2492.4(4)
Z	4	4	2
$\rho_{calcd.}$ [g/cm^3]	1.061	1.058	1.087
μ [mm^{-1}]	0.703	0.776	0.092
T [K]	150(2)	150(2)	150(2)
Measured reflections	48976	36806	102569
Independent reflections	9620	7781	14514
Reflections with $I > 2\sigma(I)$	7565	7065	10677
R_{int}	0.0538	0.0322	0.0387
F(000)	1976	1544	886
$R_1(R[F^2>2\sigma(F^2)])$	0.0521	0.0496	0.0473
w$R_2(F^2)$	0.1579	0.1369	0.1346
GooF	1.026	1.046	1.027
No. of Parameters	595	509	605
CCDC #	2046865	2046866	2046867

Table S5: Crystallographic details for **19**, **4** and **5**.

Compound	**19**	**4**	**5**
Chem. Formula	$C_{48}H_{71}N_2P$	$C_{33}H_{46}P_2$	$C_{27}H_{46}N_2P$
	0,71073	1,54178	0,71073
	MoK/a	CuK/a	MoK/a
Formula weight [g/mol]	707.03	504.64	429.63
Colour	yellow	yellow	yellow
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	*P*-1	*P*-1
a [Å]	10.4250(10)	9.921(2)	13.5971(10)
b [Å]	13.7255(13)	18.279(4)	11.6792(8)
c [Å]	16.5992(16)	17.314(4)	33.827(2)
α [°]	77.9987(25)	90	90
β [°]	74.6150(25)	101.82(3)	99.900(3)
γ [°]	71.7355(25)	90	90
V [Å^3]	2154.4(4)	3073.4(11)	5291.8(6)
Z	2	4	8
$\rho_{calcd.}$ [g/cm^3]	1.09	1.091	1.079
μ [mm^{-1}]	0.097	1.400	0.119
T [K]	150(2)	150(2)	123(2)
Measured reflections	87182	58227	87460
Independent reflections	11466	5799	15135
Reflections with $I > 2\sigma(I)$	8784	4923	9990
R_{int}	0.0417	0.0425	0.0417
F(000)	776	1096	1896
$R_1(R[F^2>2\sigma(F^2)])$	0.0530	0.0423	0.0753
$wR_2(F^2)$	0.1482	0.1157	0.1986
GooF	1.013	1.007	1.053
No. of Parameters	518	327	567
CCDC #	2046868	2046869	Not deposited

Figure S62: Numbering scheme of Mes*PIMe$_4$ (**6**).

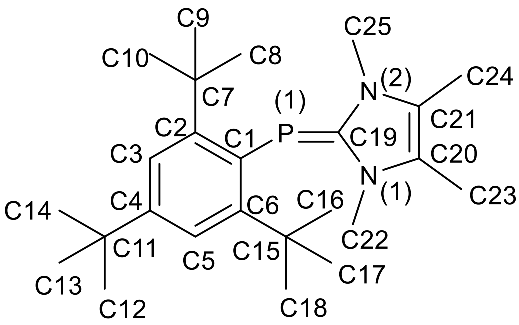


Table S6: Selected bond lengths (Å) and angles (°) for Mes*PIMe$_4$ (**6**).

P1–C19	1.7709(12)	**P1–C1**	1.8653(11)
N1–C19	1.3723(14)	**N1–C20**	1.3964(15)
N1–C22	1.4539(15)	**N2–C19**	1.3704(14)
N2–C21	1.4069(15)	**N2–C25**	1.4527(14)
C19–P1–C1	102.58(5)	**C19–N1–C20**	111.05(9)
C19–N1–C22	123.19(10)	**C20–N1–C22**	125.72(10)
C19–N2–C21	110.42(9)	**C19–N2–C25**	125.29(10)
C21–N2–C25	123.85(9)	**N2–C19–N1**	104.52(9)
N2–C19–P1	135.38(8)	**N1–C19–P1**	120.09(8)
C19–P1–C1–C2	73.25(10)	**C1–C2–C3–C4**	-3.87(17)
P1–C1–C2–C3	-167.75(8)	**C25–N2–C19–P1**	6.00(18)

Figure S63: Numbering scheme of Mes*P^{Me}IMes (**8**).

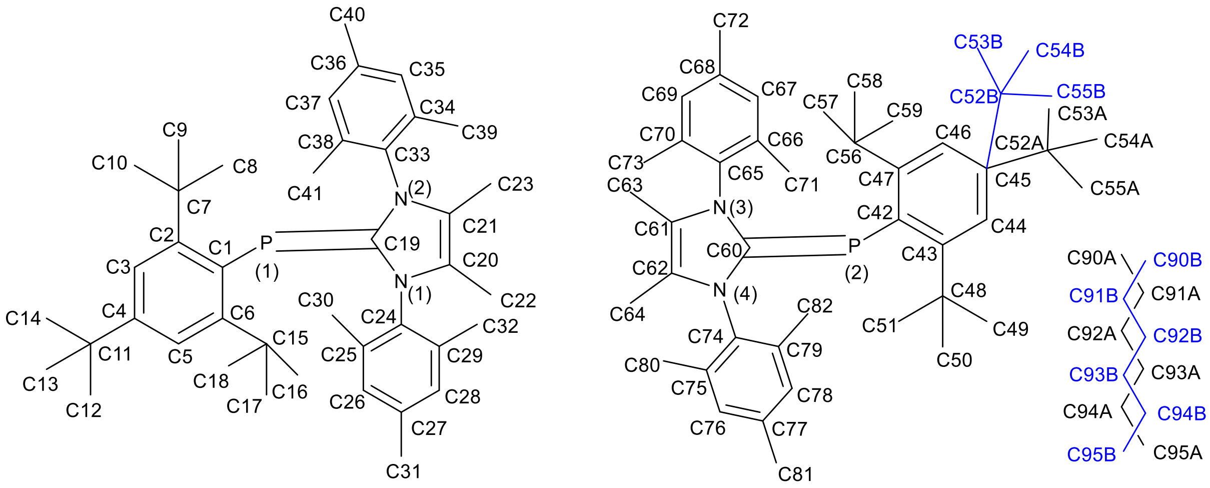


Table S7: Selected bond lengths (Å) and angles (°) for Mes*P^{Me}IMes (**8**).

P1–C19	1.7630(19)	**P1–C1**	1.8683(18)
N1–C19	1.383(2)	**N1–C20**	1.416(3)
N1–C24	1.446(2)	**N2–C19**	1.392(2)
N2–C21	1.403(3)	**N2–C33**	1.438(2)
C19–P1–C1	106.38(8)	**C19–N1–C20**	110.06(15)
C19–N1–C24	126.53(16)	**C20–N1–C24**	119.44(15)
C19–N2–C21	110.86(15)	**C19–N2–C33**	125.87(16)
C21–N2–C33	123.23(15)	**N2–C19–N1**	103.92(16)
N2–C19–P1	136.38(14)	**N1–C19–P1**	119.61(13)
C19–P1–C1–C6	-79.01(16)	**C1–C2–C3–C4**	-5.5(3)
P1–C1–C2–C3	-165.93(14)	**C25–N2–C19–P1**	-7.5(2)
P2–C60	1.7594(19)	**P2–C42**	1.8639(18)
N3–C60	1.391(2)	**N3–C61**	1.422(2)
N3–C65	1.444(2)	**N4–C60**	1.383(2)
N4–C62	1.405(3)	**N4–C74**	1.438(2)
C60–P2–C42	105.22(8)	**C60–N3–C61**	109.36(15)
C60–N3–C65	125.84(14)	**C61–N3–C65**	118.84(15)
C60–N4–C62	110.66(16)	**C60–N4–C74**	124.06(15)
C62–N4–C74	125.09(16)	**N3–C60–N4**	104.43(15)
N4–C60–P2	117.84(13)	**N3–C60–P2**	137.68(14)
C60–P2–C42–C43	-83.20(16)	**C42–C43–C44–C45**	4.3(3)
P2–C42–C43–C44	169.40(13)	**C74–N4–C60–P2**	-2.2(2)

Figure S64: Numbering scheme of $^{Mes}TerPI^{i}Pr_2$ (**10**).

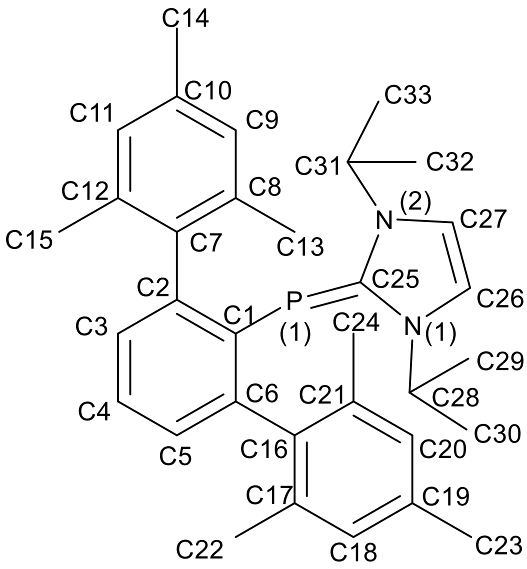


Table S8: Selected bond lengths (Å) and angles (°) for of $^{Mes}TerPI^{i}Pr_2$ (**10**).

P1–C25	1.786(2)	**P1–C1**	1.833(2)
N1–C25	1.354(3)	**N1–C26**	1.391(3)
N1–C28	1.468(3)	**N2–C25**	1.372(3)
N2–C27	1.381(3)	**N2–C31**	1.488(3)
C19–P1–C1	102.90(10)	**C25–N1–C26**	110.36(19)
C25–N1–C28	124.35(19)	**C26–N1–C28**	125.16(18)
C25–N2–C27	109.42(19)	**C25–N2–C31**	123.66(19)
C27–N2–C31	124.32(19)	**N2–C25–N1**	105.26(18)
N2–C25–P1	122.85(17)	**N1–C25–P1**	131.07(17)
C25–P1–C1–C6	-145.75(16)	**C1–C2–C5–C6**	-4.4(3)
C5–C6–C1–P1	-176.37(16)	**C31–N2–C25–P1**	7.6(3)

Figure S65: Numbering scheme of ^{Dip}TerPIMe$_4$ (**12**).

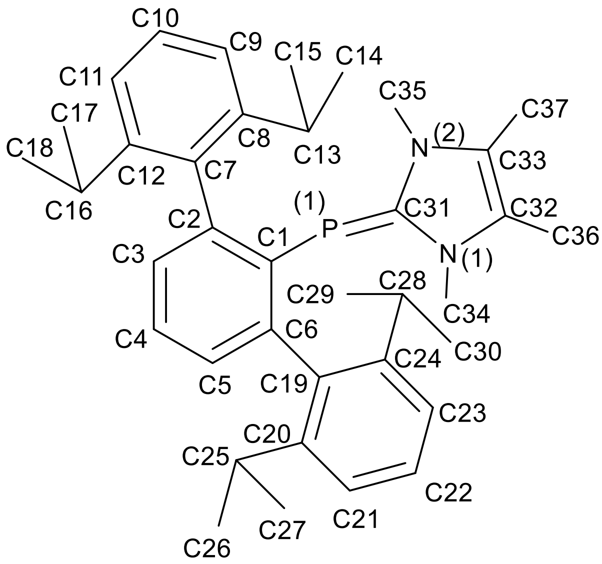


Table S9: Selected bond lengths (Å) and angles (°) for ^{Dip}TerPIMe$_4$ (**12**).

P1–C31	1.8074(11)	**P1–C1**	1.8280(10)
N1–C31	1.3585(15)	**N1–C32**	1.3958(14)
N1–C34	1.4520(16)	**N2–C31**	1.3576(14)
N2–C33	1.3891(14)	**N2–C35**	1.4523(16)
C31–P1–C1	104.21(5)	**C31–N1–C32**	110.82(10)
C31–N1–C34	124.14(10)	**C32–N1–C34**	124.74(10)
C31–N2–C33	111.01(10)	**C31–N2–C35**	125.24(10)
C33–N2–C35	123.74(10)	**N2–C31–N1**	104.71(9)
N2–C31–P1	125.47(9)	**N1–C31–P1**	128.21(8)
C31–P1–C1–C2	147.01(7)	**C1–C2–C3–C4**	-1.19(15)
P1–C1–C2–C3	175.44(8)	**C34–N1–C31–P1**	8.07(16)

Figure S66: Numbering scheme of Mes*PHCHIDip (**13**).

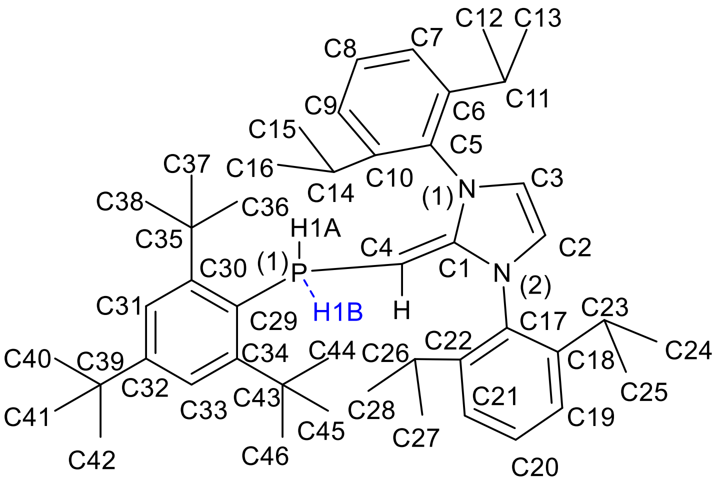


Table S10: Selected bond lengths (Å) and angles (°) for Mes*PHCHIDip (**13**).

P1–C4	1.8013(18)	**P1–C29**	1.8679(17)
P1–H1A	1.28(3)	**C1–C4**	1.360(2)
N1–C1	1.392(2)	**N1–C2**	1.402(2)
N1–C5	1.434(2)	**N2–C1**	1.392(2)
N2–C3	1.400(2)	**N2–C17**	1.435(2)
C4–P1–C29	105.12(8)	**C4–P1–H1A**	106.6(14)
C29–P1–H1A	101.2(14)	**C1–N1–C2**	109.73(14)
C1–N1–C5	125.56(14)	**C2–N1–C5**	124.71(14)
C1–N2–C3	110.14(14)	**C1–N2–C17**	124.78(14)
C3–N2–C17	124.71(14)	**C4–C1–N2**	126.03(15)
C4–C1–N1	129.97(16)	**N2–C1–N1**	104.01(14)
C1–C4–P1	126.51(14)	**C3 N2 C1 C4**	-178.28(16)
N1–C1–C4–P1	4.0(3)	**C29–P1–C4–C1**	176.76(16)

Figure S67: Numbering scheme of MesTerPHCHIDip (**14**).

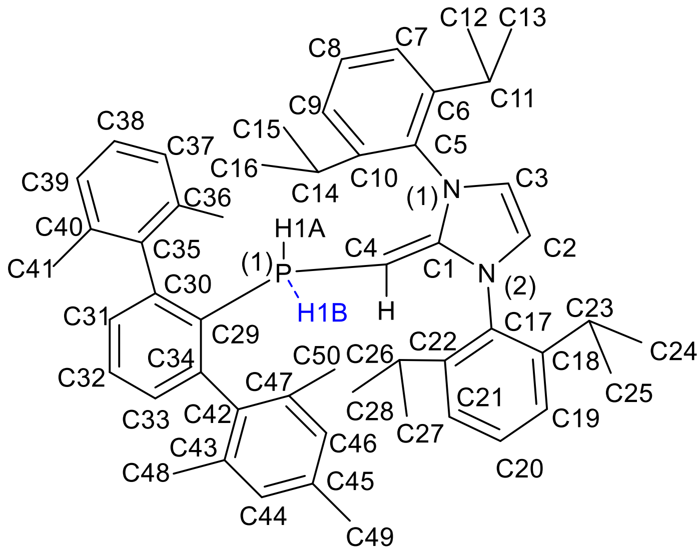


Table S11: Selected bond lengths (Å) and angles (°) for MesTerPHCHIDip (**14**).

P1−C4	1.8540(13)	**P1−C29**	1.8540(13)
P1−H1A	1.25(3)	**C1−C4**	1.3580(18)
N1−C1	1.3987(17)	**N1−C2**	1.3991(18)
N1−C5	1.4277(18)	**N2−C1**	1.3912(17)
N2−C3	1.4011(17)	**N2−C17**	1.4312(18)
C4−P1−C29	100.59(6)	**C4−P1−H1A**	108.3(13)
C29−P1−H1A	98.2(13)	**C1−N1−C2**	109.77(11)
C1−N1−C5	123.59(11)	**C2−N1−C5**	124.18(11)
C1−N2−C3	109.68(11)	**C1−N2−C17**	126.56(11)
C3−N2−C17	123.32(11)	**C4−C1−N2**	130.66(12)
C4−C1−N1	125.19(12)	**N2−C1−N1**	104.13(11)
C1−C4−P1	126.93(10)	**C3−N2−C1−C4**	-178.46(13)
N1−C1−C4−P1	-177.00(10)	**C29−P1−C4−C1**	164.34(12)

Figure S68: Numbering scheme of ^{Dip}TerPHCHIDip (**16**).

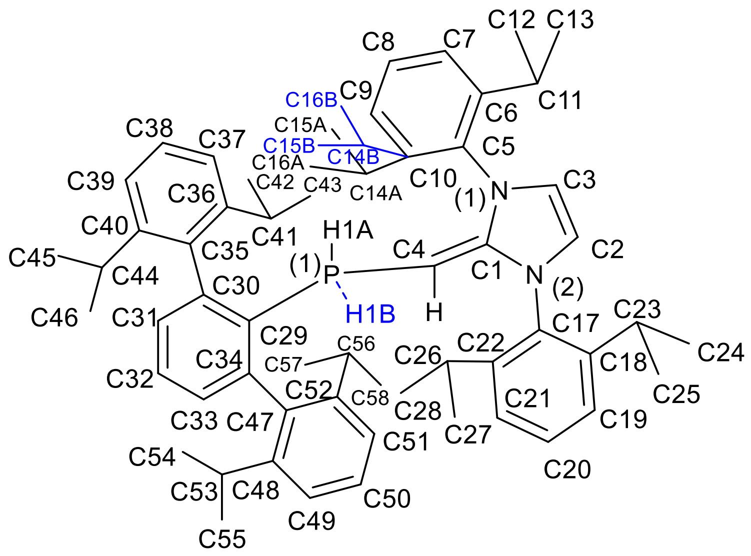


Table S12: Selected bond lengths (Å) and angles (°) for ^{Dip}TerPHCHIDip (**16**).

P1–C4	1.7976(18)	**P1–C29**	1.8493(17)
P1–H1A	1.27(3)	**C1–C4**	1.361(3)
N1–C1	1.386(3)	**N1–C2**	1.393(3)
N1–C5	1.438(3)	**N2–C1**	1.399(3)
N2–C3	1.386(3)	**N2–C17**	1.441(3)
C4–P1–C29	103.52(8)	**C4–P1–H1A**	107.0(12)
C29–P1–H1A	103.3(12)	**C1–N1–C2**	109.95(17)
C1–N1–C5	128.31(15)	**C2–N1–C5**	121.07(17)
C1–N2–C3	109.63(17)	**C1–N2–C17**	127.72(16)
C3–N2–C17	121.12(17)	**C4–C1–N2**	127.07(17)
C4–C1–N1	129.10(17)	**N2–C1–N1**	103.81(16)
C1–C4–P1	124.00(14)	**C3–N2–C1–C4**	177.9(2)
N1–C1–C4–P1	6.0(3)	**C29–P1–C4–C1**	-172.28(16)

Figure S69: Numbering scheme of Mes*PHC_3H_3IDip (**17**).

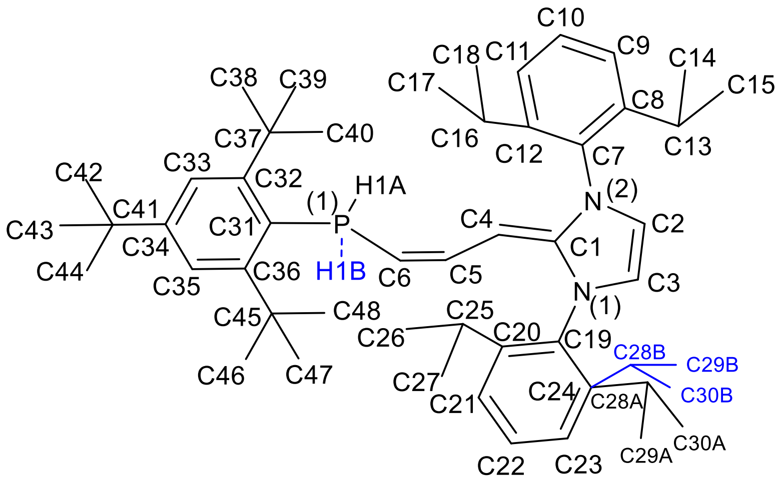


Table S13: Selected bond lengths (Å) and angles (°) for Mes*PHC_3H_3IDip (**17**).

P1–C6	1.8157(18)	**P1–C31**	1.8623(16)
C6–C5	1.355(2)	**C5–C4**	1.422(2)
P1–H1A	1.30(3)	**C1–C4**	1.376(2)
N1–C1	1.386(2)	**N1–C3**	1.396(2)
N1–C19	1.432(2)	**N2–C1**	1.388(2)
N2–C2	1.400(2)	**N2–C7**	1.433(2)
C6–P1–C31	97.74(8)	**C6–P1–H1A**	104.6(13)
C31–P1–H1A	105.5(13)	**C1–N1–C3**	110.04(13)
C1–N1–C19	126.56(13)	**C3–N1–C19**	122.85(13)
C1–N2–C2	110.12(13)	**C1–N2–C7**	126.22(13)
C2–N2–C7	123.20(13)	**C4–C1–N2**	131.08(15)
C4–C1–N1	124.84(15)	**N2–C1–N1**	104.08(13)
C5–C6–P1	125.03(13)	**C4–C5–C6**	127.50(16)
C5–C4–C1	127.72(16)	**C3–N1–C1–C4**	-178.69(15)
N1–C1–C4–C5	176.42(16)	**C1–C4–C5–C6**	-178.81(17)
C4–C5–C6–P1	-1.7(3)	**C31–P1–C6–C5**	-151.86(16)

Figure S70: Numbering scheme of ^{Mes}TerPHC$_3$H$_3$IDip (**18**).

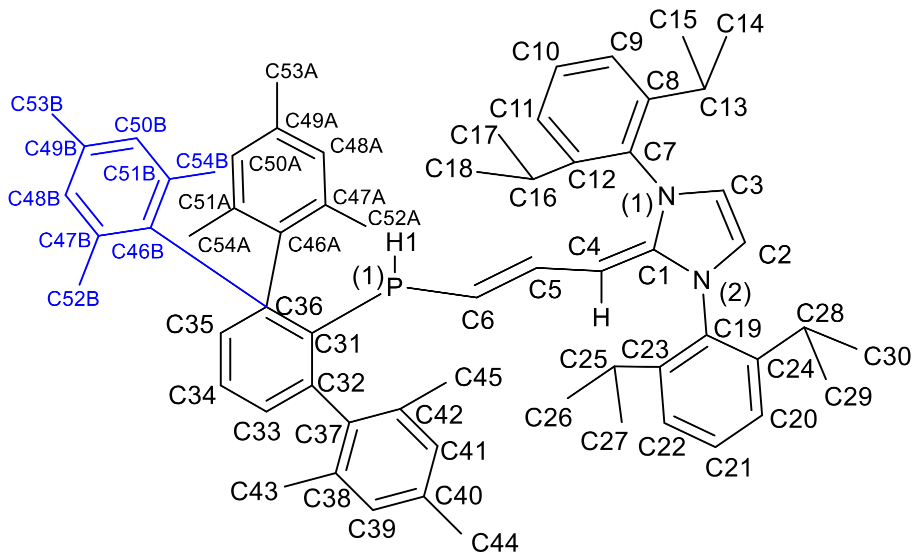


Table S14: Selected bond lengths (Å) and angles (°) for ^{Mes}TerPHC$_3$H$_3$IDip (**18**).

P1–C6	1.7876(12)	**P1–C31**	1.8523(12)
C6–C5	1.3483(16)	**C5–C4**	1.4309(15)
P1–H1	1.215(19)	**C1–C4**	1.3734(16)
N1–C1	1.3893(14)	**N1–C2**	1.3964(14)
N1–C7	1.4340(14)	**N2–C1**	1.3812(14)
N2–C3	1.3963(15)	**N2–C19**	1.4342(15)
C6–P1–C31	108.27(5)	**C6–P1–H1**	96.4(9)
C31–P1–H1	98.1(9)	**C1–N1–C2**	110.13(9)
C1–N1–C7	124.05(9)	**C2–N1–C7**	125.49(9)
C1–N2–C3	110.12(9)	**C1–N2–C19**	125.39(10)
C3–N2–C19	124.41(10)	**C4–C1–N2**	131.20(10)
C4–C1–N1	124.45(10)	**N2–C1–N1**	104.32(9)
C5–C6–P1	123.74(9)	**C4–C5–C6**	123.78(11)
C5–C4–C1	128.19(10)	**C3–N2–C1–C4**	179.35(12)
N1–C1–C4–C5	-179.68(11)	**C1–C4–C5–C6**	-170.82(11)
C4–C5–C6–P1	175.64(9)	**C31–P1–C6–C5**	103.08(11)

Figure S71: Numbering scheme of Mes*PHCHIDip (**19**).

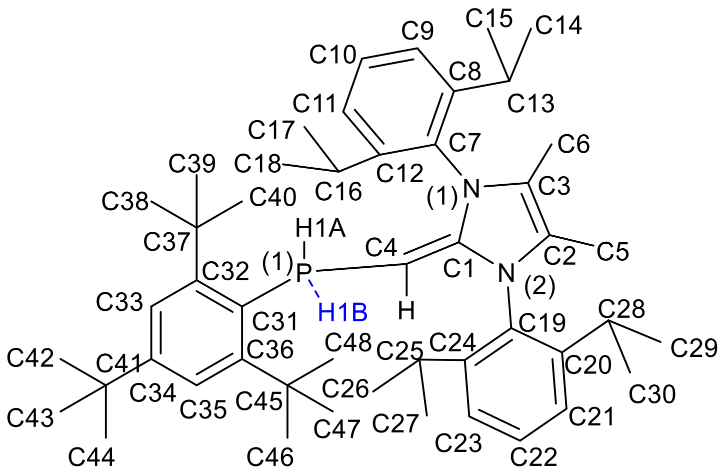


Table S15: Selected bond lengths (Å) and angles (°) for Mes*PHCH^{Me}IDip (**19**).

P1–C4	1.8117(15)	**P1–C31**	1.8738(15)
P1–H1A	1.28(3)	**C1–C4**	1.366(2)
N1–C1	1.3913(17)	**N1–C2**	1.4134(19)
N1–C7	1.4354(17)	**N2–C1**	1.3981(17)
N2–C3	1.4088(19)	**N2–C19**	1.4324(17)
C4–P1–C31	103.86(6)	**C4–P1–H1A**	107.1(12)
C31–P1–H1A	99.1(12)	**C1–N1–C2**	110.65(11)
C1–N1–C7	125.43(12)	**C2–N1–C7**	123.91(12)
C1–N2–C3	110.49(11)	**C1–N2–C19**	124.03(12)
C3–N2–C19	124.60(11)	**C4–C1–N2**	126.03(12)
C4–C1–N1	130.34(12)	**N2–C1–N1**	103.62(12)
C1–C4–P1	126.47(11)	**C3–N2–C1–C4**	-179.08(15)
N1–C1–C4–P1	-4.3(2)	**C31–P1–C4–C1**	176.76(11)

Figure S72: Numbering scheme of $^{Dip}TerPPMe_3$ (**4**).

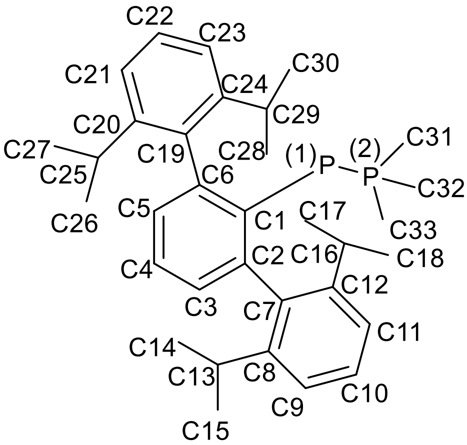


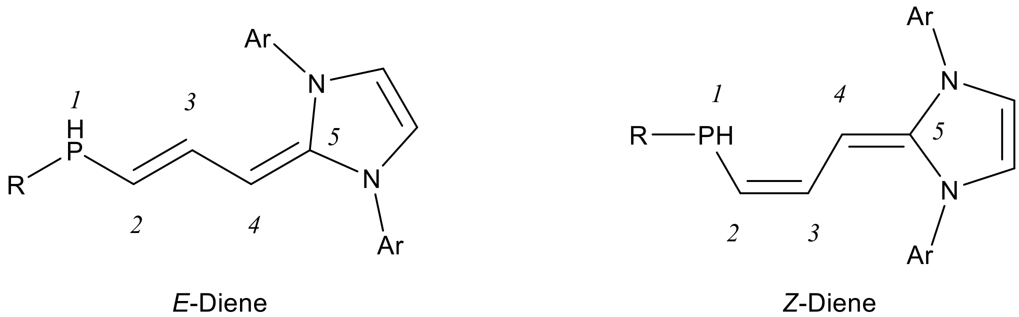
Table S16: Selected bond lengths (Å) and angles (°) for $^{Dip}TerPPMe_3$ (**4**).

P1–C1	1.8481(14)	**P1–P2**	2.0955(7)
C1–P1–P2	108.47(5)		

5 Additional spectroscopic details

5.1 Investigation on the *E/Z*-configuration of 17 and 18 in solution

1. Problem: double bonds, *E/Z* configuration



(Fig. NMR)

17: R = 2,4,6-tBu$_3$C$_6$H$_2$, Ar = 2,6-iPrC$_6$H$_3$, Dip

18: R = 2,6-Mes$_2$-C$_6$H$_3$, Ar = 2,6--iPrC$_6$H$_3$, Dip

2. Results

18 is a single compound. For **17** depending on the crystallization conditions a mixture of two components (presumably isomers) can be obtained. For this study a mixture containing two isomers in a 3/2 ratio, designated as "major" and "minor" hereafter, was used.

Spectra can be analyzed by standard methods. Results for the diene part are as follows:

18:

Position (Fig. NMR)	**signal ^{1}H**	***J*(H,H)**	***J*(H,P)**	**signal $^{13}C/^{31}P$**	***J*(C,P)**
1	4.29	1-2: 8.1, 1-3: 0.8	227.8	–58.4	
2	3.83	2-1: 8.1, 2-3: 15.1	22.4	99.6_5	5.2
3	5.44	3-1: 0.8, 3-2: 15.1, 3-4: 11.6	13.2	138.33	22.1
4	4.04	4-3: 11.6		73.47	13.9
5				145.55	small

17, major form:

Position (Fig. NMR)	**signal ^{1}H**	***J*(H,H)**	***J*(H,P)**	**signal $^{13}C/^{31}P$**	***J*(C,P)**
1	5.67	1-2: 3.6, 1-3: 1.8	225	–66.7	
2	4.66	2-1: 3.6, 2-3: 15.5	small	105.70	4.5
3	6.02	3-1: 1.8, 3-2: 15.5, 3-4: 12.0	15.5	138.81	44.3
4	4.04	4-3: 12.0	small	73.68	19.9
5				149.19	small

17, minor form:

Position (Fig. NMR)	**signal ^{1}H**	***J*(H,H)**	***J*(H,P)**	**signal $^{13}C/^{31}P$**	***J*(C,P)**
1	5.46	1-2: 3.7, 1-3: 2.6	221	–82.3	
2	4.10	2-1: 3.7, 2-3: 11.2	3.1	105.61	9.5
3	5.74	3-1: 2.6, 3-2: 11.2, 3-4: 12.5	21.0	131.31	17.1
4	4.40	4-3: 12.5	≈2	71.18	22.7
5				146.32	2.6.re

Assignment of these series is primarily based on scalar coupling constants. The chemical shifts are not so characteristic as for common butadienes (central positions at higher frequencies) due to the very specific electronic situation of **17** and **18**.

3. Interpretation

The criteria for the discrimination of *E*/*Z* isomers may be the following, among others:

1. the homonuclear coupling constant ^{3}J(2-H,3-H), from the well-known *Karplus* relation
2. the heteronuclear coupling constant ^{3}J(P,3-H), there is a similar *Karplus* relation established, and was described for styryl,[15] and propenyl phosphanes,[16] as ^{3}J(P,H-*trans*) > ^{3}J(P,H-*cis*)
3. the phosphorus chemical shift, δ(*E* isomer) > δ(*Z* isomer), according to the refs. given above
4. spatial correlation via dipolar couplings, in particular homonuclear NOE, between 1-H and 3-H as well as 2-H and 4-H for the *E* isomer or between 1-H and 4-H (2-H and 3-H) for the *Z* isomer

5. maybe heteronuclear NOE between phosphorus and 3-H for the *E* isomer or between phosphorus and 4-H for the *Z* isomer

For criteria 1 to 3, a comparison of both forms is mandatory, for 4 and 5 it is at least helpful. Therefore, it is a fortunate situation to presumably have both isomers of **17** and compare their data.

The *coupling constants*, both ^3J(H,H) and ^3J(P,H), let conclude that **17**(major) is the *E* isomer and **17**(minor) is the *Z* isomer:

$^3J(\mathrm{H,H})_{major}$ = 15.5 Hz > $^3J(\mathrm{H,H})_{minor}$ = 11.2 Hz

$^3J(\mathrm{P,H})_{major}$ = 15.5 Hz < $^3J(\mathrm{P,H})_{minor}$ = 21.0 Hz.

Schmidbaur reported an α-substituted *Z*-styrylphosphane (by X-ray) with a remarkably small $^3J(\mathrm{P,H})_{trans}$ of 9.6 Hz but there is neither a full analysis of the spectra nor a comparison to the other conformer.[17]

The heteronuclear coupling constant ^3J(P,C) follows the reverse pattern (*cis* > *trans*) $^3J(\mathrm{P,C})_{minor}$ = 22.7 Hz > $^3J(\mathrm{P,C})_{major}$ = 19.9 Hz as also observed for RCH=CH_2PPh_2, R = methyl or styryl,[15] but this is not a general rule.

The *phosphorus shift* (criterion 3) matches the expectation, δ(*E*) > δ(*Z*):

$\delta(^{31}\mathrm{P})_{major}$ = –66.7 ppm > $\delta(^{31}\mathrm{P})_{minor}$ = –82.3 ppm.

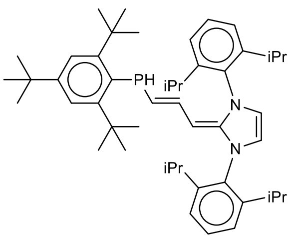
When comparing the H,H and P,H coupling constants and the chemical shift patterns (diene system) of **18**, and **17**, the former clearly better resemble those of **17**(major) than those of **17**(minor). So it is reasonable to assume that **18** has *E* configuration.

Evaluation of the *homonuclear NOE* reveals for both E forms, **18** and **17**(major) the expected strong correlation signals between 2-H and 4-H, for **18** also between 1-H and 3-H. For **17**(minor), a strong correlation 2-H/3-H is seen accordingly together with 1-H/4-H, as expected.

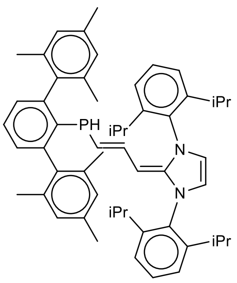
There are additional, albeit weak cross peaks not compatible with the postulated configuration, namely 2-H/3-H and 3-H/4-H for the *E* isomers. the latter may be explained by some a participation of an *s-cis* configuration, even if ^{3}J(3-H,4-H) of ca. 12 Hz are more characteristic for a preferred *s-trans* arrangement. Additional confirmation of the stereochemistry by heteronuclear NOE (criterion 5) failed, for only contacts to the nearest neighbours of phosphorus (1-H, 2-H, *ortho*-*t*Bu) were detected.

4. Result

It can be concluded that the major isomer of **17** and **18** are *E*-configured 1,3-dienes:

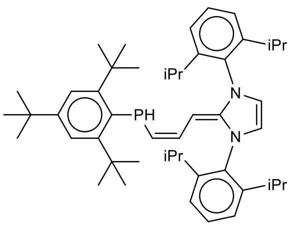


17(major)



18

17 contains a minor isomer, most likely the *Z*-configured diene:



17(minor)

6 Computational details

6.1 General remarks

Computations were carried out using Gaussian09,[18] and NBO 6.0.[19]

Structure optimizations employed the DFT exchange-correlation functional B3LYP[[20]] in conjunction with Grimme's dispersion correction D3,[21] the 6-311G(d,p) basis set and the SMD[22] universal solvation model to simulate a benzene solution dipole (notation B3LYP-D3/6-311G(d,p)/smd(benzene)). All structures were fully optimized and confirmed as minima or transition states (one imaginary frequency) by frequency analyses using Guassian09. Natural Bond Orbitals (NBOs) were evaluated at the optimized geometries using the electron density matrix at the B3LYP-D3/6-311G(d,p) level of theory. Partial charges were determined by Natural Population analysis using the NBO program.

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

6.2 Mechanism of NHC-Phosphinidene formation

The calculated transition states follow a S_N2-like mechanism. The NHC donates electrons into the corresponding σ*(P-P) orbital to form a T-shaped structure. The calculated structures were confirmed as transition states via an internal reaction coordinate (IRC) scan. In Figure S73 the Laplacian of the electron density of the Me_3P-P-C_{NHC} plain is depicted. The existence of the bond critical points between the phosphinidene and NHC further supports the simultaneously bonded fragments. The

Laplacian of the electron density was calculated with *Multiwfn – A Multifunctional Wavefunction Analyzer version 3.6*.[23]

Figure S73. Contour map of electron density Laplacian of the transition state of Mes*PPMe$_3$ and I^{i}Pr$_2$ (point group C_1, B3LYP-D3/6-311G(d,p) cpcm (benzene)). Bond critical points (3,-1) are shown in blue and bond paths in brown.

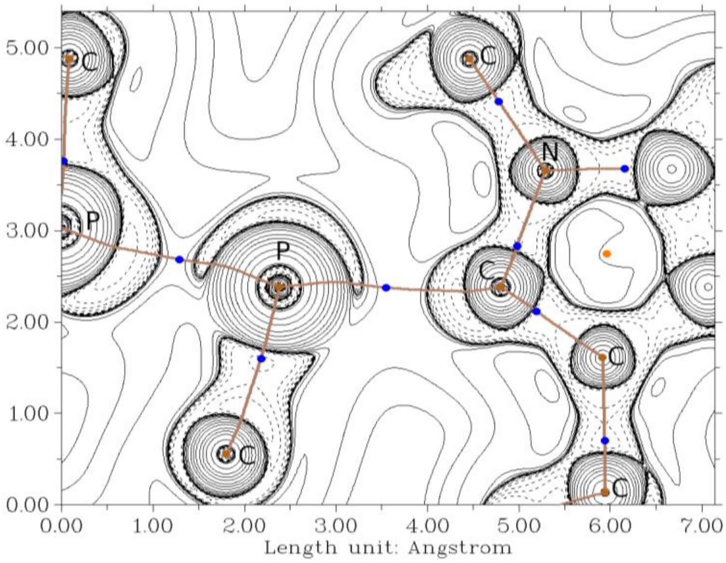


Table S17.: Calculated point groups, number of imaginary frequencies and values for E_{tot}, U_{298}, H_{298} and $G°_{298}$ (p° = 1 atm) of **5**-**8**, corresponding intermediate products and transition states. Energies in [a.u.]. All calculations were carried out on the B3LYP-D3/6-311G(d,p)/smd(benzene) level of theory.

Compound	PG	NIMAG	E_{tot}	U_{298}	H_{298}	$G°_{298}$
Mes*PPMe$_3$	C_1	0	-1506.15495	-1505.582776	-1505.597448	-1505.682713
IMe$_4$	C_{2v}	0	-383.548532	-383.356688	-383.373228	-383.418166
TS1	C_1	1	-1889.70692	-1888.935178	-1888.95576	-1889.06907
Mes*PIMe$_4$ (**6**)	C_1	0	-1428.57498	-1427.929815	-1427.94895	-1428.0446
PMe$_3$	C_{3v}	0	-461.169273	-461.050291	-461.051639	-461.087477
Mes*PPMe$_3$	C1	0	-1506.15495	-1505.582776	-1505.597448	-1505.682713
I^{i}Pr$_2$	C_{2v}	0	-462.203713	-461.952602	-461.970665	-462.020986
TS1	C_1	1	-1968.35289	-1967.527422	-1967.54966	-1967.66648
Mes*PI^{i}Pr$_2$ (**5**)	C_1	0	-1507.22989	-1506.525692	-1506.54575	-1506.64537
PMe$_3$	C_{3v}	0	-461.169273	-461.050291	-461.051639	-461.087477

Mes*PPMe3	*C*1	0	-1506.15495	-1505.582776	-1505.597448	-1505.682713
IMes	*C*2v	0	-924.443088	-924.024188	-924.050482	-924.130614
TS1	*C*1	1	-2430.60180	-2429.603932	-2429.63286	-2429.77484
Mes*PIMes (**7**)	*C*1	0	-1969.47013	-1968.597729	-1968.62462	-1968.74752
PMe3	*C*3v	0	-461.169273	-461.050291	-461.051639	-461.087477
Mes*PPMe3	*C*1	0	-1506.15495	-1505.582776	-1505.597448	-1505.682713
MeIMes	*C*2v	0	-1003.11243	-1002.63482	-1002.66109	-1002.74731
TS1	*C*1	1	-2509.27226	-2508.215495	-2508.24372	-2508.3915
Mes*PMeIMes (**8**)	*C*1	0	-2048.14176	-2047.210440	-2047.23672	-2047.365
PMe3	*C*3v	0	-461.169273	-461.050291	-461.051639	-461.087477

Table S18.: Calculated point groups, number of imaginary frequencies and values for E_{tot}, U_{298}, H_{298} and $G°_{298}$ (p° = 1 atm) of **9**-**11**, corresponding intermediate products and transition states. Energies in [a.u]. All calculations were carried out on the B3LYP-D3/6-311G(d,p)/smd(benzene) level of theory.

Compound	PG	NIMAG	E_{tot}	U_{298}	H_{298}	$G°_{298}$
MesTerPPMe3	*C*1	0	-1732.46695	-1731.903059	-1731.92505	-1732.02405
IMe4	*C*2v	0	-383.548532	-383.356688	-383.373228	-383.418166
TS1	*C*1	1	-2116.00756	-2115.249380	-2115.27584	-2115.39703
MesTerPPIMe4 (**9**)	*C*1	0	-1654.88918	-1654.251674	-1654.27856	-1654.38302
PMe3	*C*3v	0	-461.169273	-461.050291	-461.051639	-461.087477
MesTerPPMe3	*C*1	0	-1732.46695	-1731.903059	-1731.92505	-1732.02405
IiPr2	*C*2v	0	-462.203713	-461.952602	-461.970665	-462.020986
TS1	*C*1	1	-2194.66759	-2193.850056	-2193.87621	-2194.00150
MesTerPPIiPr2 (**10**)	*C*1	0	-1733.54179	-1732.844963	-1732.87207	-1732.97998
PMe3	*C*3v	0	-461.169273	-461.050291	-461.051639	-461.087477
MesTerPPMe3	*C*1	0	-1732.46695	-1731.903059	-1731.92505	-1732.02405
MeIMes	*C*2v	0	-1003.11243	-1002.63482	-1002.66109	-1002.74731
TS1	*C*1	1	-2735.57133	-2734.527120	-2734.55941	-2734.71461
MesTerPMeIMes (**11**)	*C*1	0	-2274.44433	-2273.520940	-2273.55345	-2273.69228
PMe3	*C*3v	0	-461.169273	-461.050291	-461.051639	-461.087477

Table S19.: Calculated point groups, number of imaginary frequencies and values for E_{tot}, U_{298}, H_{298} and $G°_{298}$ (p° = 1 atm) of **12**, corresponding intermediate products and transition states. Energies in [a.u.]. All calculations were carried out on the B3LYP-D3/6-311G(d,p)//smd(benzene) level of theory.

Compound	PG	NIMAG	E_{tot}	U_{298}	H_{298}	$G°_{298}$
^{Dip}TerPPMe$_3$	C_1	0	-1968.42617	-1967.682133	-1967.70581	-1967.81526
IMe$_4$	C_{2v}	0	-383.5485328	-383.356688	-383.373228	-383.418166
TS1	C_1	1	-2351.95983	-2351.021730	-2351.04891	-2351.17997
^{Dip}TerPPIMe$_4$ (**12**)	C_1	0	-1890.84425	-1890.027064	-1890.05601	-1890.17407
PMe$_3$	C_{3v}	0	-461.169273	-461.050291	-461.051639	-461.087477

Table S20.: Calculated point groups, number of imaginary frequencies and values for E_{tot}, U_{298}, H_{298} and $G°_{298}$ (p° = 1 atm) of **13**, corresponding intermediate products and transition states. Energies in [a.u.]. All calculations were carried out on the B3LYP-D3/6-311G(d,p)//smd(benzene) level of theory.

Compound	PG	NIMAG	E_{tot}	U_{298}	H_{298}	$G°_{298}$
Mes*PPMe$_3$	C_1	0	-1506.15495	-1505.582776	-1505.597448	-1505.682713
ICH$_2$Dip$_2$	C_1	0	-1199.74537	-1199.117996	-1199.14027	-1199.23801
TS1	C_1	1	-2705.87586	-2704.672355	-2704.70324	-2704.85805
Int1	C_1	0	-2244.75412	-2243.674592	-2243.67811	-2243.81713
TS2	C_1	1	-2244.68806	-2243.612386	-2243.64338	-2243.78354
Mes*P(H)C(H)I Dip (**13**)	C_1	0	-2244.72221	-2243.640947	-2243.70327	-2243.8455
PMe$_3$	C_{3v}	0	-461.169273	-461.050291	-461.051639	-461.087477

Table S21.: Calculated point groups, number of imaginary frequencies and values for E_{tot}, U_{298}, H_{298} and $G°_{298}$ (p° = 1 atm) of compounds used for the evaluation of electronic properties. Energies in [a.u.]. All calculations were carried out on the B3LYP-D3/6-311G(d,p)/smd(benzene) level of theory.

Compound	PG	NIMAG	E_{tot}	U_{298}	H_{298}	$G°_{298}$
PH$_3$	C3V	0	-343.173096	-343.146348	-343.145172	-343.169033
PPh$_3$	C3	0	-1036.52262	-1036.23389	-1036.2518	-1036.31377
^{Mes}TerPHC$_3$H$_3$I Dip	C1	0	-2548.5002	-2547.39329	-2547.43172	-2547.58949
Mes*PHC$_3$H$_3$I Dip	C1	0	-2322.17754	-2321.06248	-2321.09675	-2321.24669
PhPHC$_3$H$_3$IMe$_2$ *trans*	C1	0	-802.956561	-802.717669	-802.731632	-802.788707
PhPHC$_3$H$_3$IMe$_2$ *cis*	C1	0	-802.954091	-802.714872	-802.728925	-802.785885

6.3 Calculated ^{31}P-NMR shifts

The ^{31}P NMR chemical shifts were derived by the GIAO method.[24] To evaluate the best method three different strategies and reference molecules were tested. The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase, to the calculated absolute shift of PPh_3 in benzene.

Method 1: calc1

Chemical shifts were calculated using B3LYP-D3/6-311G(d,p). The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[25] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm)[26] as a secondary standard:

$$\delta_{calc,X} = (\sigma_{ref,1} - \sigma r_{ef,2}) - (\sigma_{calc,X} - \sigma_{calc,PH3}) = \sigma_{calc,PH3} - \sigma_{calc,X} - 266.1 \text{ ppm}$$

At the B3LYP-D3/6-311G(d,p) level of theory, $\sigma_{calc,PH3}$ amounts to 562.10 ppm.

Method 2: calc2

Chemical shifts were calculated with PBE0-D3/def2-TZVP. The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm), using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:

$$\delta_{calc,X} = (\sigma_{ref,1} - \sigma r_{ef,2}) - (\sigma_{calc,X} - \sigma_{calc,PH3}) = \sigma_{calc,PH3} - \sigma_{calc,X} - 266.1 \text{ ppm}$$

At the PBE0-D3/def2-TZVP level of theory, $\sigma_{calc,PH3}$ amounts to 565.69 ppm.

Method 3: calc3

Chemical shifts were calculated with PBE0-D3/def2-TZVP. The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental shift of PPh_3 in benzene ($\delta_{ref,1}$ = -4.7 ppm):

$$\delta_{calc,X} = \sigma_{ref,1} - \sigma_{calc,X} + \delta_{ref,1} = (296.05 \text{ ppm} - \sigma_{calc,X}) - 4.7 \text{ ppm.}$$

At the PBE0-D3/def2-TZVP level of theory, σ_{ref1} amounts to 296.05 ppm.

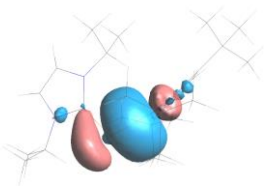
Table S22.: Calculated ^{31}P-NMR shifts calc1: B3LYP-D3/6-311G(d,p) reference PH_3, calc2: PBE0-D3/def2-tzvp reference PH_3, calc3: PBE0/def2-tzvp reference PPh_3.

Compound	**δ_{exp} [ppm]**	**δ_{calc1} [ppm]**	**δ_{calc2} [ppm]**	**δ_{calc3} [ppm]**
Mes*PPMe$_3$	4.1, −133.4	−8.0, −101.0	−8.0, −123.4	−2.6, −131.7
^{Mes}TerPPMe$_3$	−3.0, −114.9	−9.4, −86.1	5.7, −108.1	−2.5, −116.3
^{Dip}TerPPMe$_3$	3.1, −116.5	−8.4, −99.1	7.0, −118.2	−1.2, −126.5
Mes*PIMe$_4$	−47.47	−27.74	−34.74	−42.98
Mes*PI^{i}Pr$_2$	−50.67	−42.14	−49.77	−58.01
Mes*PIMes	−29.77	−11.00	−19.48	−27.72
Mes*PI^{Me}Mes	−33.18	−20.64	−29.57	−37.81
^{Mes}TerPIMe$_4$	−76.86	−65.05	−71.55	−79.79
^{Mes}TerPI^{i}Pr$_2$	−79.76	−65.13	−71.97	−80.21
^{Mes}TerPI^{Me}Mes	−41.93	−37.49	−46.47	−54.71
^{Dip}TerPIMe$_4$	−63.47	−50.68	−58.90	−67.13
Mes*PHCHIDip	−80.65	−84.57	−83.49	−91.73

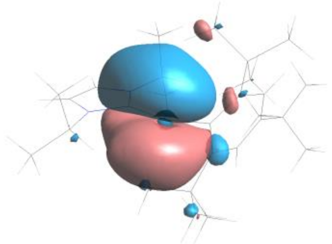
6.4 Inspection of Kohn-Sham Orbitals and NBO analysis

An NBO analysis were performed for the NHC-phosphinidene adduct **5** as a representation for this compound class. The NLMOs (Figure S74), which include delocalization effects on the strictly localized NBOs, clearly indicate an *s*-type LP at the P atom, two polarized P-C σ bonds and an inversely polarized π(P-C) bond, which is largely localized in a *p* atomic orbital at the P atom (66 % P, 31 % C). In the Kohn-Sham orbitals the HOMO indicates π-density located at the P-atom and the HOMO-1 resembles the s-type lone pair on phosphorus (Figure S75).

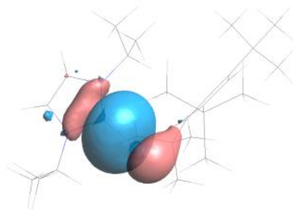
Figure S74. Selected NLMOs of Mes*PI^{i}Pr$_2$ (point group C_1, B3LYP-D3/6-311G(d,p)).



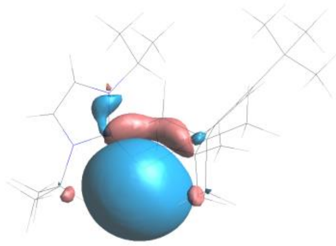
σ (P-C_{Aryl})
−14.2 eV
35 % P
63 % C_{Aryl}



π (P-C_{NHC})
−6.4 eV
66 % P
31 % C_{NHC}

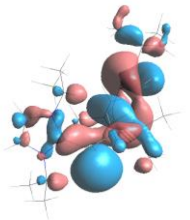


σ (P-C_{NHC})
−16.2 eV
32 % P
66 % C_{NHC}

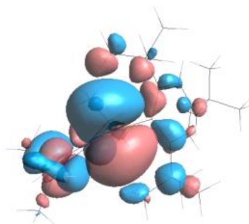


LP P
-12.1 eV
97 % P

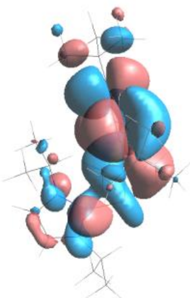
Figure S75. Relevant Kohn-Sham orbitals of Mes*PI^{i}Pr$_2$ (point group C_1, B3LYP-D3/6-311G(d,p)).



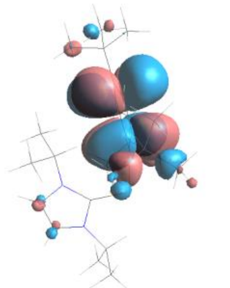
HOMO−1
−5.7 eV
a



HOMO
−4.0 eV
a



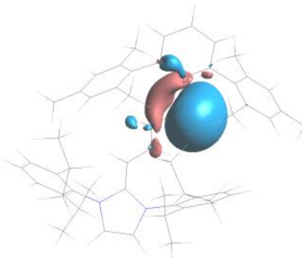
LUMO
−0.4 eV
a



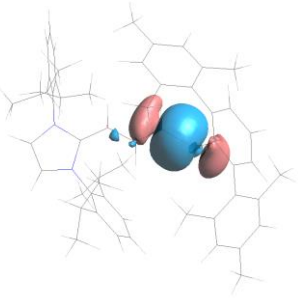
LUMO+1
0.1 eV
a

To gain further insights into the bonding in dienediamines **17** and **18** an NBO analysis were performed on the RPHC$_3$H$_3$IDip$_2$ (R = Mes*, ^{Mes}Ter) systems (Figure S76-S77). The NLMOs show a σ-type lone pair located at the phosphorous atom, a typical P-H bond and P-C_{Aryl} bond. Thus the NLMOs confirm a trivalent phosphane. The C_γ-C_β π-bond exhibits only small contributions (approx. 1%) from the P-atom.

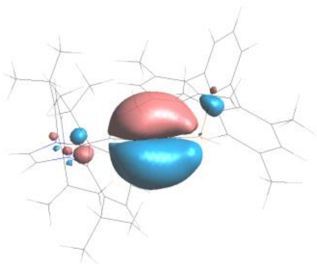
Figure S76. Selected NLMOs of ^{Mes}TerPHC$_3$H$_3$IDip (point group C_1, B3LYP-D3/6-311G(d,p)).



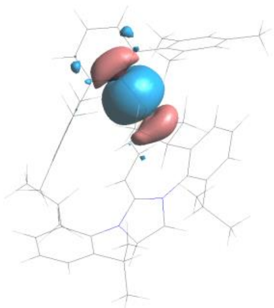
LP P
−10.3 eV
97 % P



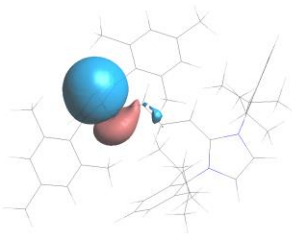
σ (P-C$_\gamma$)
−15.0 eV
39 % P
60 % C



π (C$_\gamma$-C$_\beta$)
−7.0 eV
42 % C$_\beta$
53 % C$_\alpha$
1 % P

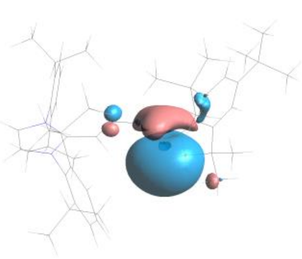


σ (P-C$_{Aryl}$)
-14.1 eV
36 % P
62 % C$_{Aryl}$

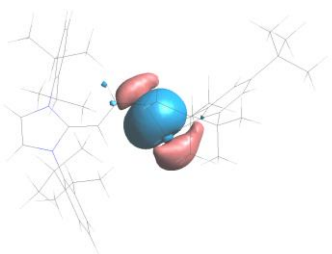


σ (P-H)
-12.0 eV
47 % P
52 % H

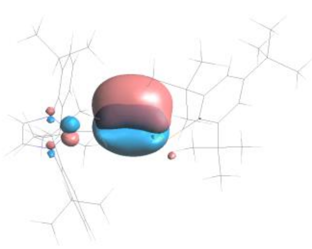
Figure S77. Selected NLMOs of Mes*PHC$_3$H$_3$IDip (point group C_1, B3LYP-D3/6-311G(d,p)).



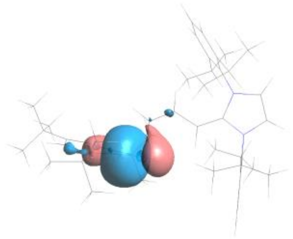
LP P
−10.5 eV
96 % P



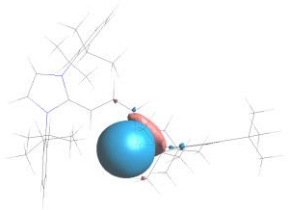
σ (P-C$_\gamma$)
−14.8 eV
39 % P
59 % C



π (C_{γ}-C_{β})
−7.0 eV
44 % C_{β}
53 % C_{α}
0.5 % P



σ (P-C_{Aryl})
-14.3 eV
37 % P
61 % C_{Aryl}



σ (P-H)
-12.6 eV
47 % P
51 % H

An NRT-analysis was performed on the truncated model compound $MeP(H)C_3H_3IMe_2$, were the aryl-rings were changed for methyl-groups. To elucidate the effect of P-substitution in γ-position in **17** and **18** an NRT analysis was performed for $IMe_2C_3H_4$. The 1,3-butadiene resonances dominate the Lewis picture.

Scheme S1. Natural resonance theory (NRT) performed on model compounds to investigate the allyl character in corresponding phosphanes **17** and **18**. NPA-charges are given in red.

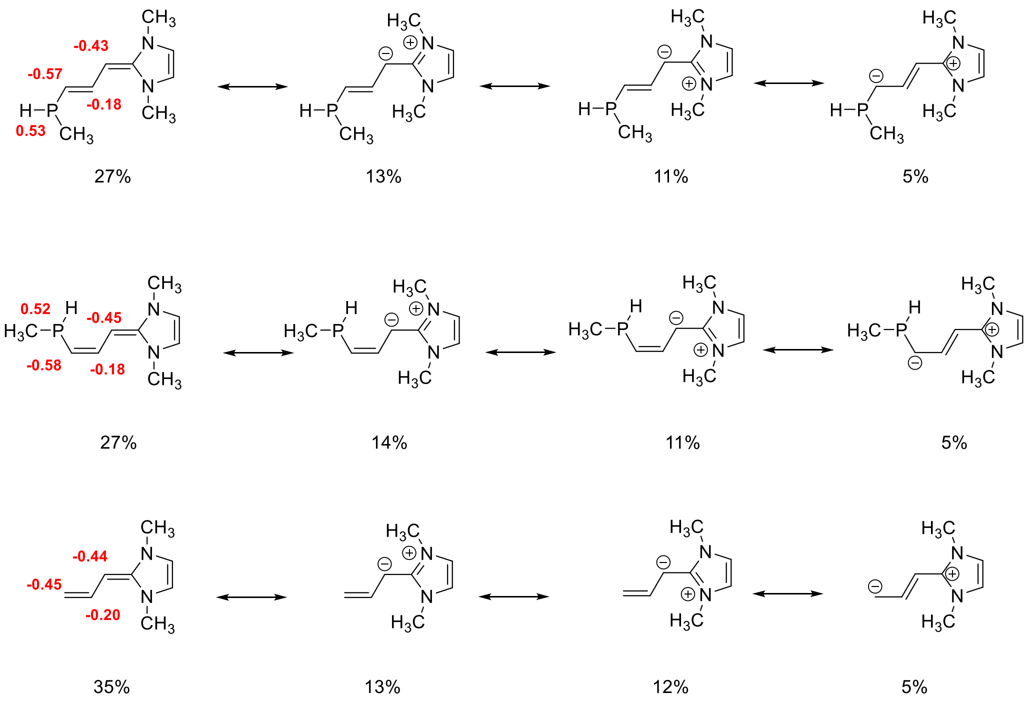


Figure S78. Relevant Kohn-Sham orbitals of TerP_Allyl (point group C_1, B3LYP-D3/6-311G(d,p)).

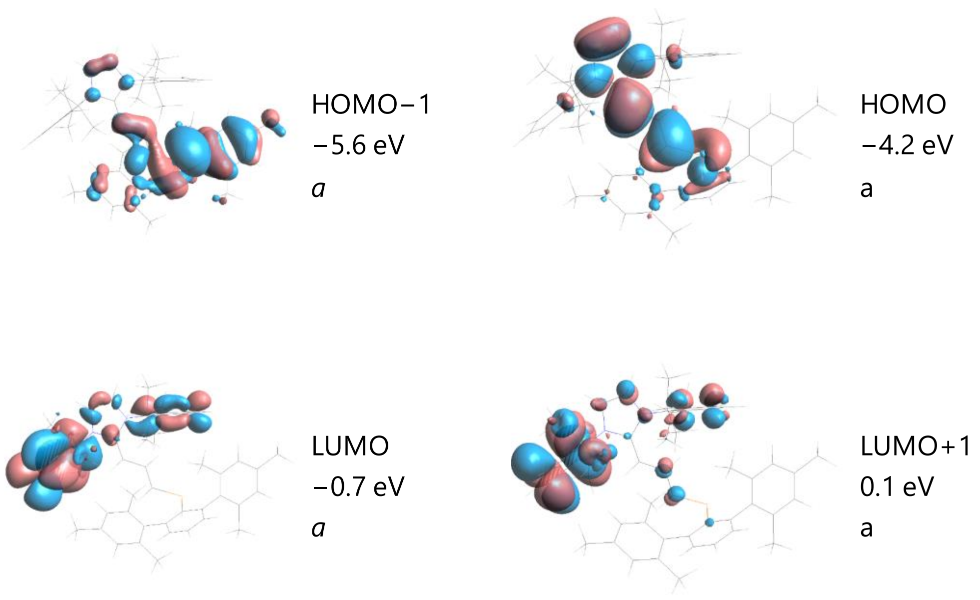
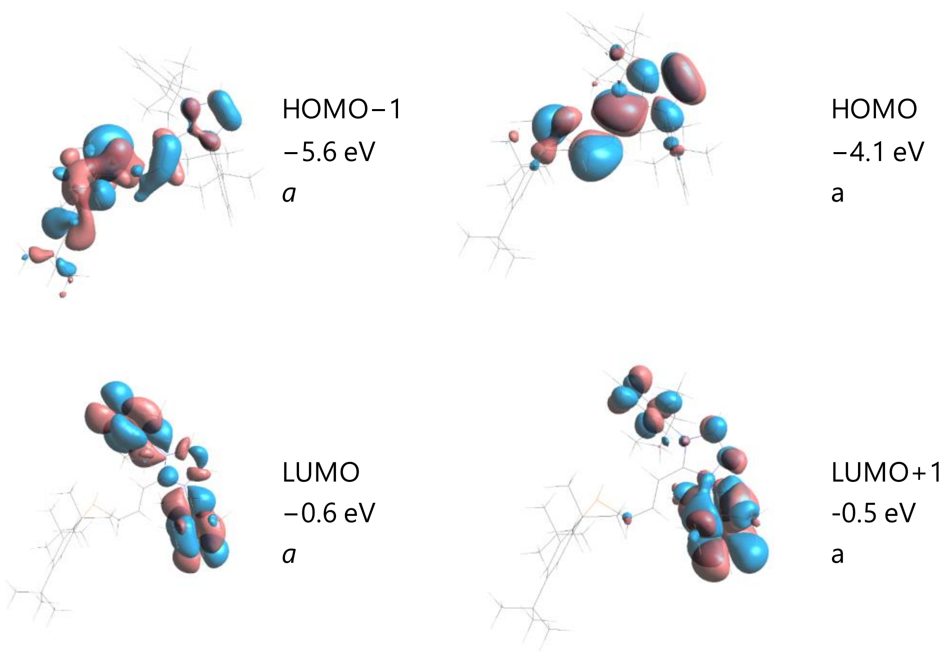


Figure S79. Relevant Kohn-Sham orbitals of Mes*P_Allyl (B3LYP-D3/6-311G(d,p)).



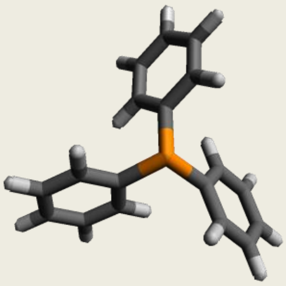
6.5 Optimized structures (.xyz-files)

6.5.1 PH_3 (NMR standard)

```
4
PH3, C3V, B3LYP-D3/6-311G(d,p)
P          0.00000         0.00000         0.12799
H          0.00000         1.19918        -0.63996
H         -1.03852        -0.59959        -0.63996
H          1.03852        -0.59959        -0.63996
```

6.5.2 PPh_3 (NMR standard)

```
34
PPh3, C3, B3LYP-D3/6-311G(d,p)
P          0.00000         0.00000         1.27066
C         -0.37220         1.61402         0.44152
C          0.21175         2.76274         0.99358
C         -1.19025         1.74997        -0.68645
C          0.00000         4.01381         0.42164
H          0.83735         2.67511         1.87617
C         -1.41213         3.00529        -1.25082
H         -1.65562         0.87524        -1.12470
C         -0.81576         4.13848        -0.70219
H          0.46330         4.89176         0.85813
H         -2.05075         3.09574        -2.12281
H         -0.98916         5.11343        -1.14382
C         -1.21168        -1.12934         0.44152
C         -0.92040        -1.90577        -0.68645
C         -2.49848        -1.19799         0.99358
C         -1.89659        -2.72558        -1.25082
H          0.06983        -1.87143        -1.12470
C         -3.47606        -2.00691         0.42164
H         -2.73539        -0.61240         1.87617
C         -3.17614        -2.77571        -0.70219
H         -1.65561        -3.32387        -2.12281
H         -4.46804        -2.04465         0.85813
H         -3.93378        -3.41335        -1.14382
C          1.58388        -0.48468         0.44152
C          2.28673        -1.56475         0.99358
C          2.11064         0.15580        -0.68645
C          3.47606        -2.00691         0.42164
H          1.89805        -2.06272         1.87617
C          3.30872        -0.27970        -1.25082
H          1.58579         0.99619        -1.12470
C          3.99191        -1.36277        -0.70219
H          4.00474        -2.84711         0.85813
H          3.70636         0.22813        -2.12281
H          4.92294        -1.70008        -1.14382
```

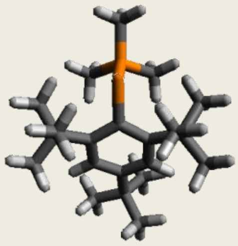


6.5.3 PMe3

```
13
PMe3, C3V, B3LYP-D3/6-311G(d,p)
P          0.00000         0.00000         0.60915
C          0.00000         1.63491        -0.28206
H         -0.88254         2.20993         0.00828
H          0.88254         2.20993         0.00828
H          0.00000         1.51256        -1.36998
C          1.41587        -0.81745        -0.28206
H          2.35513        -0.34067         0.00828
H          1.47259        -1.86927         0.00828
H          1.30992        -0.75628        -1.36998
C         -1.41587        -0.81745        -0.28206
H         -1.47259        -1.86927         0.00828
H         -2.35513        -0.34067         0.00828
H         -1.30992        -0.75628        -1.36998
```

6.5.4 Mes*PPMe3

```
61
Mes*PPMe3, C1, B3LYP-D3/6-311G(d,p)
C          0.21923         1.24328        -0.65687
C         -0.48406         0.00893        -0.74992
C          1.50598         1.23086        -0.09790
C          0.26960        -1.20258        -0.67171
C          2.15485         0.05601         0.26956
C          1.54851        -1.14266        -0.11314
H          2.01372         2.16970         0.05003
H          2.10193        -2.05966         0.02474
P         -2.37979        -0.03232        -0.69533
C         -4.18654        -0.09670         1.94107
C         -1.65768        -1.45935         2.33921
C         -1.72051         1.37671         2.35978
H         -4.69869         0.78660         1.55820
H         -4.65930        -0.98794         1.52714
H         -4.26119        -0.11768         3.03017
H         -0.60687        -1.52719         2.05450
H         -1.73649        -1.30101         3.41761
H         -2.15764        -2.38618         2.06375
H         -1.78598         1.19820         3.43589
H         -0.67541         1.49726         2.07090
H         -2.26349         2.28401         2.10103
P         -2.42692        -0.05097         1.43437
C         -0.19578        -2.55179        -1.30408
C         -1.18423        -3.35351        -0.43137
C         -0.83594        -2.27159        -2.68442
C          1.01470        -3.47968        -1.56837
H         -0.74228        -3.58466         0.54170
H         -2.11150        -2.80283        -0.28396
H         -1.42135        -4.30260        -0.92361
H         -0.14321        -1.71900        -3.32488
H         -1.08158        -3.21670        -3.17894
H         -1.75615        -1.69587        -2.59273
H          0.67555        -4.34915        -2.13732
H          1.79278        -2.97911        -2.15034
H          1.46189        -3.85813        -0.64546
C          3.51831         0.03587         0.97702
```



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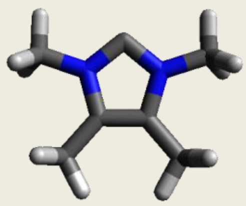
C          3.39743        -0.78403         2.28195
C          4.57378        -0.61818         0.05665
C          4.00909         1.44794         1.34362
H          2.65809        -0.33613         2.95222
H          3.09048        -1.81350         2.08415
H          4.35824        -0.81497         2.80516
H          4.66799        -0.05897        -0.87804
H          5.55199        -0.63438         0.54765
H          4.30836        -1.64731        -0.19481
H          4.96185         1.38148         1.87589
H          4.17075         2.06462         0.45555
H          3.29798         1.96449         1.99435
C         -0.30064         2.58344        -1.26550
C         -0.93364         2.30199        -2.64907
C         -1.31780         3.33053        -0.37727
C          0.87075         3.56373        -1.51754
H         -0.22164         1.78777        -3.30027
H         -1.83049         1.68940        -2.56564
H         -1.21716         3.24507        -3.12698
H         -0.88211         3.56596         0.59763
H         -1.59654         4.27597        -0.85454
H         -2.22041         2.73899        -0.23477
H          0.49454         4.42702        -2.07237
H          1.30473         3.94578        -0.58987
H          1.66693         3.10480        -2.10931
```

6.5.5 IMe_4

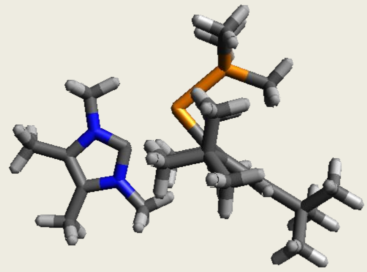
```
21
IMe4, C2V, B3LYP-D3/6-311G(d,p)
C         -1.66180         1.75982        -0.00003
C         -2.43727        -1.16707         0.00004
C         -0.68007         0.63740        -0.00002
C          0.68007         0.63740        -0.00002
C          0.00000        -1.57036         0.00009
C          1.66180         1.75982        -0.00017
C          2.43727        -1.16707         0.00009
H         -2.31013         1.73163         0.88249
H         -2.96943        -0.81452         0.88852
H         -1.14615         2.72132        -0.00092
H         -2.41666        -2.25472         0.00069
H         -2.31121         1.73059        -0.88172
H         -2.96909        -0.81561        -0.88909
H          2.31061         1.73129         0.88199
H          1.14614         2.72133        -0.00038
H          2.96923        -0.81497         0.88888
H          2.31072         1.73093        -0.88222
H          2.41667        -2.25472         0.00020
H          2.96930        -0.81515        -0.88873
N         -1.05938        -0.70979         0.00005
N          1.05939        -0.70978         0.00001
```



6.5.6 Mes^*PPMe_3 – IMe_4 TS

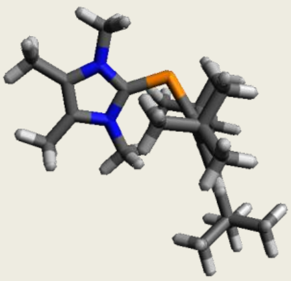
```
82
Mes*PPMe3-IMe4 TS
C          4.34929         1.66635        -0.04313
```

C	-1.05402	-0.30282	1.25062
C	-0.46578	0.12638	0.01310
C	-2.28461	-0.97899	1.21577
C	-1.06337	-0.33864	-1.21317
C	2.74358	-0.22690	0.00225
C	-2.94635	-1.30196	0.04219
C	-2.28854	-1.00937	-1.14722
C	4.96917	-0.77244	-0.01031
C	4.26878	-1.93700	0.01486
C	1.83241	-2.54359	0.04694
H	3.42039	2.23122	-0.04260
H	-2.75345	-1.24805	2.14462
H	-2.77029	-1.30911	-2.06272
H	0.88996	-2.00494	0.04681
N	4.01552	0.25017	-0.01724
N	2.91736	-1.57554	0.02221
P	0.90927	1.45605	-0.01242
C	-0.69810	4.34574	-1.45774
C	-2.59583	2.70470	-0.01481
C	-0.68585	4.39335	1.35445
H	-1.32523	5.22719	-1.29695
H	0.34251	4.65983	-1.56529
H	-1.00100	3.85287	-2.37927
H	-2.79608	2.11625	0.88112
H	-3.24756	3.58250	-0.03779
H	-2.80000	2.06682	-0.87541
H	-1.32005	5.26565	1.17277
H	-0.97382	3.92972	2.29578
H	0.35413	4.71682	1.43765
P	-0.81337	3.17149	-0.03093
C	-0.48012	-0.17238	-2.66317
C	-0.57947	1.28315	-3.16312
C	0.98860	-0.63433	-2.74744
C	-1.24195	-1.03522	-3.70211
H	-1.60236	1.65908	-3.06011
H	0.10037	1.91924	-2.60297
H	-0.31059	1.33245	-4.22424
H	1.07128	-1.69935	-2.51546
H	1.36114	-0.48557	-3.76640
H	1.62080	-0.07463	-2.06500
H	-0.71984	-0.96176	-4.65945
H	-1.27010	-2.09200	-3.42248
H	-2.26571	-0.69104	-3.87223
C	-4.32570	-1.97922	0.01092
C	-5.31400	-1.08174	-0.76866
C	-4.21301	-3.35015	-0.69379
C	-4.89996	-2.21005	1.41998
H	-5.40978	-0.10517	-0.28595
H	-4.98311	-0.91543	-1.79624
H	-6.30511	-1.54515	-0.80603
H	-3.51456	-4.00056	-0.15999
H	-5.18839	-3.84620	-0.72516
H	-3.85579	-3.24787	-1.72095
H	-5.88553	-2.67785	1.34493
H	-4.26349	-2.87192	2.01335
H	-5.01891	-1.27005	1.96584
C	-0.46358	-0.09209	2.69257
C	1.00701	-0.54738	2.78347
C	-0.56385	1.37779	3.14760
C	-1.21710	-0.92490	3.76166



```
H           1.09110        -1.61938        2.58708
H           1.63410        -0.00956        2.07915
H           1.38498        -0.36350        3.79469
H          -1.58830         1.74805        3.03969
H          -0.28760         1.46141        4.20472
H           0.11085         1.99653        2.56239
H          -0.68956        -0.82076        4.71317
H          -2.24106        -0.57939        3.92728
H          -1.24334        -1.98976        3.51444
H           4.92062         1.90774       -0.94303
H           4.93889         1.93596        0.83674
H           1.87839        -3.19104       -0.83205
H           1.89388        -3.16309        0.94494
C           4.72394        -3.35602        0.03337
H           4.37286        -3.88105        0.92780
H           4.35533        -3.90994       -0.83624
H           5.81336        -3.40867        0.02338
C           6.43595        -0.50869       -0.02933
H           6.73557         0.04730       -0.92392
H           6.75353         0.07588        0.84048
H           6.99249        -1.44661       -0.01984
```

6.5.7 Mes*IMe$_4$

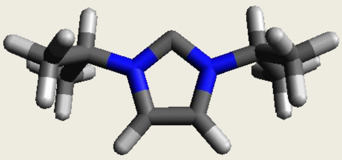


```
69
Mes*PIMe4, C1, B3LYP-D3/6-311G(d,p)
C           4.38859         0.40048       -1.44385
C          -1.21971         1.36785       -0.46151
C          -0.41543         0.28086       -0.92110
C          -2.42170         1.08110        0.20041
C          -0.96734        -1.04201       -0.89057
C           2.31545         0.18226       -0.09034
C          -2.89181        -0.21091        0.39213
C          -2.16793        -1.24020       -0.20383
C           4.27898        -0.20431        1.02132
C           3.27104        -0.37497        1.90960
C           0.75557        -0.18130        1.86634
H           4.00038        -0.25079       -2.23322
H          -3.00487         1.89562        0.59182
H          -2.56500        -2.23878       -0.12250
H           0.18456         0.71429        1.63719
N           3.69279         0.13419       -0.20086
N           2.06536        -0.12805        1.23042
P           1.34380         0.57966       -1.51974
C          -0.35457        -2.29602       -1.59646
C          -0.08635        -1.99071       -3.08920
C           0.93410        -2.79690       -0.90274
C          -1.33164        -3.49841       -1.58773
H          -1.01263        -1.68789       -3.58602
H           0.64964        -1.19930       -3.21705
H           0.29086        -2.88873       -3.58947
H           0.74742        -3.00019        0.15668
H           1.26268        -3.73199       -1.36816
H           1.74413        -2.07719       -0.97901
H          -0.89126        -4.30931       -2.17315
H          -1.50718        -3.89003       -0.58197
H          -2.29528        -3.25097       -2.04029
C          -4.17333        -0.53063        1.17792
```

```
C          -5.19869          -1.20981          0.24168
C          -3.82931          -1.48828          2.34164
C          -4.82853           0.72890          1.77286
H          -5.45252          -0.55186         -0.59375
H          -4.81104          -2.14260         -0.17357
H          -6.11846          -1.44226          0.78775
H          -3.10393          -1.02760          3.01832
H          -4.72842          -1.72994          2.91706
H          -3.40149          -2.42600          1.98014
H          -5.72372           0.44857          2.33468
H          -4.15463           1.24941          2.45898
H          -5.13488           1.43245          0.99419
C          -0.86198           2.87935         -0.63137
C           0.32009           3.29202          0.27763
C          -0.55481           3.19901         -2.11370
C          -2.04179           3.80406         -0.24486
H           0.07393           3.11012          1.32920
H           1.22895           2.74706          0.03224
H           0.51984           4.36268          0.16342
H          -1.40712           2.92780         -2.74347
H          -0.37178           4.27205         -2.23198
H           0.32512           2.67011         -2.47447
H          -1.76004           4.83764         -0.46093
H          -2.94481           3.58069         -0.81927
H          -2.28434           3.75515          0.82003
C           5.75344          -0.33136          1.19426
H           6.17380          -1.11095          0.54977
H           6.27172           0.60510          0.96224
H           5.99122          -0.59301          2.22509
C           3.32082          -0.75320          3.35058
H           2.92651           0.03674          3.99893
H           2.74776          -1.66416          3.55193
H           4.35146          -0.93994          3.65232
H           4.23343           1.43749         -1.75778
H           5.45334           0.21941         -1.31326
H           0.89061          -0.24302          2.94367
H           0.18312          -1.04489          1.52804
```

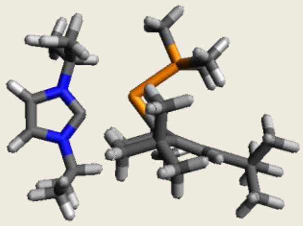
6.5.8 IPr$_2$

```
27
IPr2, C2V, B3LYP-D3/6-311G(d,p)
C          -0.00000           0.00053         -0.93885
C           2.45432           0.00034         -0.55100
C           0.67698          -0.00068          1.25537
C          -0.67698          -0.00097          1.25537
C          -2.45432           0.00019         -0.55100
H           2.36232           0.00101         -1.63844
H          -2.36232           0.00033         -1.63844
N           1.06367           0.00007         -0.08127
N          -1.06367          -0.00015         -0.08127
C           3.18204           1.27271         -0.10716
H           3.27477           1.31595          0.98223
H           4.18920           1.30063         -0.53086
H           2.63908           2.15956         -0.44044
C           3.18199          -1.27262         -0.10874
H           4.18914          -1.30007         -0.53248
H           3.27472          -1.31720          0.98060
```



```
H           2.63897         -2.15903         -0.44311
C          -3.18174          1.27295         -0.10775
H          -4.18892          1.30088         -0.53138
H          -3.27434          1.31673          0.98163
H          -2.63859          2.15950         -0.44152
C          -3.18229         -1.27239         -0.10815
H          -4.18941         -1.29981         -0.53196
H          -2.63946         -2.15910         -0.44203
H          -3.27514         -1.31642          0.98120
H          -1.37305         -0.00159          2.07711
H           1.37304         -0.00110          2.07711
```

6.5.9 Mes^*PPMe_3 – IPr_2 TS



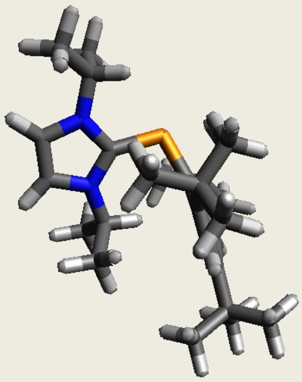
```
88
Mes*PPMe3 – IPr2 TS, B3LYP-D3/6-311G(d,p)
C           3.95281          1.86361          0.14622
C          -1.31852         -0.55764          1.24874
C          -0.62420         -0.27509          0.03249
C          -2.70968         -0.73777          1.20629
C          -1.32291         -0.49510         -1.20095
C           2.87736         -0.40797          0.06068
C          -3.43937         -0.71464          0.02478
C          -2.70948         -0.66285         -1.16123
C           5.15139         -0.34975         -0.08993
C           4.77871         -1.64650         -0.16646
C           2.60508         -2.90889         -0.05593
H           2.97757          2.09035          0.57835
H          -3.23958         -0.87394          2.13372
H          -3.25163         -0.73967         -2.09142
H           1.56698         -2.58003         -0.03031
N           3.98696          0.38982          0.06028
N           3.39240         -1.66507         -0.07201
P           0.86817          0.92506          0.04236
C           0.34747          4.26702          0.08207
C          -1.89111          3.22747         -1.37187
C          -1.90080          3.13308          1.45891
H          -0.21956          5.20122          0.09729
H           0.97520          4.21177          0.97354
H           0.99527          4.25205         -0.79673
H          -2.61846          2.42385         -1.49909
H          -2.41664          4.16864         -1.18388
H          -1.31063          3.31577         -2.28961
H          -2.43931          4.07568          1.32240
H          -2.61536          2.31182          1.53812
H          -1.32378          3.17663          2.38179
P          -0.76534          2.79446          0.03579
H           5.37166         -2.53761         -0.27451
H           6.13007          0.09462         -0.12446
C          -0.65445         -0.60292         -2.60938
C          -0.39968          0.76823         -3.26951
C           0.66778         -1.38104         -2.50973
C          -1.54392         -1.41038         -3.58962
H          -1.33949          1.30756         -3.40975
H           0.27236          1.36894         -2.65847
H           0.05251          0.62415         -4.25726
H           0.48173         -2.37839         -2.10406
H           1.10959         -1.49732         -3.50512
```

```
H           1.38637        -0.86931        -1.87523
H          -0.97355        -1.60686        -4.50165
H          -1.84529        -2.37240        -3.16629
H          -2.44382        -0.86922        -3.89149
C          -4.97377        -0.78129        -0.01960
C          -5.50868         0.48780        -0.72242
C          -5.42258        -2.03192        -0.80895
C          -5.60105        -0.85026         1.38415
H          -5.20830         1.38640        -0.17581
H          -5.12685         0.57353        -1.74224
H          -6.60211         0.46784        -0.77270
H          -5.04766        -2.94217        -0.33323
H          -6.51519        -2.08909        -0.84632
H          -5.05330        -2.01593        -1.83671
H          -6.69102        -0.87653         1.29970
H          -5.28814        -1.74871         1.92277
H          -5.33520         0.02118         1.98884
C          -0.64882        -0.70835         2.65168
C           0.67380        -1.48263         2.52606
C          -0.39423         0.64705         3.34504
C          -1.53433        -1.54116         3.61354
H           0.48803        -2.47007         2.09532
H           1.38874        -0.95503         1.90051
H           1.12090        -1.62403         3.51597
H          -1.33612         1.17753         3.50572
H           0.06607         0.47990         4.32536
H           0.27023         1.26666         2.74439
H          -0.96092        -1.75784         4.51907
H          -2.43520        -1.01008         3.93018
H          -1.83342        -2.49420         3.16855
C           5.03576         2.38834         1.08982
H           6.04213         2.24563         0.68546
H           4.89414         3.46131         1.23898
H           4.97849         1.89559         2.06288
C           4.03369         2.47646        -1.25299
H           3.22004         2.09438        -1.87159
H           3.94452         3.56471        -1.19356
H           4.98919         2.23770        -1.73089
C           2.91902        -3.72291         1.20393
H           2.25019        -4.58478         1.26785
H           3.94721        -4.09592         1.18032
H           2.79197        -3.11949         2.10204
C           2.85647        -3.72778        -1.32605
H           2.16126        -4.56971        -1.36729
H           2.71785        -3.12146        -2.22040
H           3.87166        -4.13506        -1.33795
```

6.5.10 Mes*PIPr$_2$

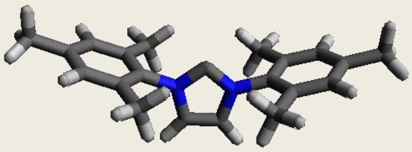
```
75
Mes*PIPr2, C1, B3LYP-D3/6-311G(d,p)
C           4.48921        -0.03203        -0.56358
C          -1.27204         1.35784        -0.69590
C          -0.32950         0.30745        -0.91578
C          -2.55918         1.02453        -0.25303
C          -0.80706        -1.04627        -0.93060
C           2.17451         0.08811         0.43491
C          -2.97314        -0.28575        -0.05012
```

C	-2.09303	-1.29203	-0.44297
C	3.84180	-0.59692	1.82821
C	2.69421	-0.61440	2.53240
C	0.31306	0.08900	2.20048
H	3.89323	-0.18669	-1.46956
H	-3.25449	1.81756	-0.04136
H	-2.44152	-2.31069	-0.37851
H	-0.26506	0.42440	1.34822
N	3.53073	-0.18801	0.53946
N	1.66803	-0.19476	1.68947
P	1.50229	0.68962	-1.10311
H	2.51400	-0.88641	3.55652
H	4.84136	-0.85529	2.12553
C	-0.04440	-2.26710	-1.54728
C	0.43715	-1.90672	-2.97273
C	1.14558	-2.76301	-0.69441
C	-0.97776	-3.49144	-1.71776
H	-0.41128	-1.61748	-3.59931
H	1.15342	-1.08684	-2.95888
H	0.91958	-2.77590	-3.43173
H	0.83741	-2.95901	0.33596
H	1.52885	-3.70018	-1.11150
H	1.95993	-2.04616	-0.67609
H	-0.43496	-4.27104	-2.25818
H	-1.28569	-3.92242	-0.76088
H	-1.87301	-3.25017	-2.29638
C	-4.36144	-0.65070	0.50070
C	-5.15550	-1.42278	-0.57807
C	-4.20179	-1.54245	1.75249
C	-5.17842	0.59016	0.90277
H	-5.27642	-0.81344	-1.47765
H	-4.64962	-2.34686	-0.86617
H	-6.15042	-1.68626	-0.20521
H	-3.67360	-1.00404	2.54408
H	-5.18255	-1.83754	2.13867
H	-3.63977	-2.45301	1.53439
H	-6.14282	0.27920	1.31358
H	-4.66478	1.17980	1.66719
H	-5.37800	1.23905	0.04611
C	-0.96781	2.87361	-0.90083
C	-0.06058	3.41931	0.22594
C	-0.33038	3.11474	-2.28931
C	-2.25528	3.73278	-0.87858
H	-0.55417	3.30695	1.19587
H	0.89439	2.89657	0.25510
H	0.13265	4.48560	0.06764
H	-0.98654	2.73648	-3.07840
H	-0.18619	4.18786	-2.45052
H	0.64098	2.63345	-2.38760
H	-1.98994	4.76650	-1.11436
H	-2.98440	3.39930	-1.62203
H	-2.73732	3.74354	0.10228
C	5.05804	1.39020	-0.58601
H	5.64303	1.58291	0.31872
H	5.71004	1.52403	-1.45309
H	4.25212	2.12368	-0.64623
C	5.58234	-1.09976	-0.50721
H	5.15180	-2.10069	-0.43241
H	6.17917	-1.04949	-1.42033
H	6.26292	-0.94621	0.33526



```
C          0.35927       1.21979       3.23314
H         -0.65835       1.49877       3.51716
H          0.89162       0.91635       4.13918
H          0.85368       2.09951       2.81851
C         -0.33470      -1.18165       2.75376
H         -1.34733      -0.95723       3.09357
H         -0.40181      -1.94614       1.98010
H          0.22522      -1.58443       3.60302
```

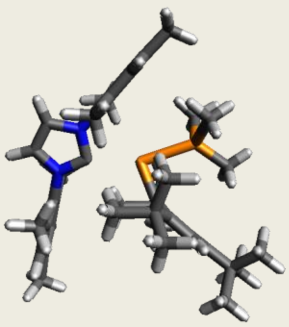
6.5.11 IMes$_2$



```
47
IMes2, C2V, B3YLP-D3/6-311G(d,p)
C          0.00000       0.00560      -0.28592
C         -0.67588       0.11906       1.91843
C          0.67588       0.11906       1.91843
N         -1.06083       0.05064       0.57819
C         -2.43077       0.01592       0.15089
C         -3.10477       1.22189      -0.07124
C         -3.05625      -1.22367      -0.02155
C         -4.44295       1.16398      -0.46277
C         -4.39533      -1.23458      -0.41477
C         -5.10419      -0.05303      -0.63856
H         -4.97964       2.09138      -0.63850
H         -4.89441      -2.18903      -0.55179
C         -2.28796      -2.50339       0.19086
H         -1.43614      -2.55153      -0.49276
C         -2.38658       2.53813       0.08665
H         -1.52506       2.58307      -0.58505
N          1.06083       0.05067       0.57819
C          2.43077       0.01597       0.15089
C          3.05637      -1.22361      -0.02122
C          3.10466       1.22194      -0.07155
C          4.39545      -1.23449      -0.41445
C          4.44284       1.16405      -0.46308
C          5.10420      -0.05294      -0.63855
H          4.89462      -2.18894      -0.55122
H          4.97944       2.09147      -0.63905
C          2.28820      -2.50334       0.19154
H          1.43618      -2.55160      -0.49182
H          2.92268      -3.37502       0.02359
H          1.88295      -2.56245       1.20584
C          6.54189      -0.08967      -1.09854
H          6.59978      -0.07980      -2.19240
H          7.10041       0.77578      -0.73381
H          7.04987      -0.99251      -0.75162
C          2.38633       2.53815       0.08597
H          1.52505       2.58297      -0.58605
H          2.00106       2.66525       1.10179
H          3.04861       3.37609      -0.13721
C         -6.54189      -0.08974      -1.09855
H         -7.04955      -0.99316      -0.75266
H         -7.10070       0.77509      -0.73278
H         -6.59982      -0.07860      -2.19239
H         -1.88241      -2.56258       1.20503
H         -2.92245      -3.37508       0.02301
H         -2.00169       2.66516       1.10263
H         -3.04883       3.37604      -0.13668
```

```
H          -1.38727         0.15850          2.72586
H           1.38726         0.15852          2.72586
```

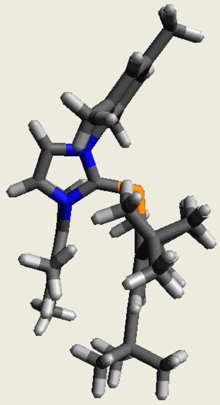
6.5.12 Mes*PPMe$_3$ – IMes$_2$ TS



```
108
Mes*PPMe3 – IMes2 TS, C1, B3LYP-D3/6-311G(d,p)
C           2.01887         1.11484          0.23302
C          -2.19127         0.07392         -1.00852
C          -1.30641        -0.22932          0.07102
C          -3.54718        -0.27071         -0.90222
C          -1.89737        -0.64045          1.31157
C          -4.09454        -0.84946          0.23336
C          -3.25594        -0.96601          1.33907
C           4.26735         1.45528          0.54099
C           3.67480         2.66635          0.59043
H          -4.18970        -0.09987         -1.74881
H          -3.68404        -1.33981          2.25611
N           3.25556         0.52660          0.32569
P           0.54759        -0.63305         -0.27535
C           0.61246        -3.41023         -2.57117
C           0.41654        -4.32339          0.10527
C          -1.97185        -3.53206         -1.28443
H           0.47549        -4.46367         -2.83360
H           0.22610        -2.78270         -3.37492
H           1.67812        -3.20360         -2.45510
H          -0.14932        -4.34556          1.03653
H           0.35297        -5.30252         -0.37962
H           1.45759        -4.09870          0.34417
H          -2.02540        -4.58106         -1.59211
H          -2.54361        -3.38484         -0.36679
H          -2.41891        -2.90005         -2.05235
P          -0.23336        -2.97934         -0.98553
H           4.07832         3.65326          0.73844
H           5.29739         1.15906          0.63958
C          -1.14560        -0.72951          2.67496
C          -0.30399        -2.01759          2.79598
C          -0.26426         0.51768          2.85594
C          -2.12407        -0.72861          3.87668
H          -0.94593        -2.89741          2.68761
H           0.46865        -2.04746          2.03064
H           0.16742        -2.06678          3.78430
H          -0.88170         1.41918          2.83203
H           0.25360         0.48270          3.82089
H           0.47594         0.59720          2.06489
H          -1.54389        -0.63864          4.79934
H          -2.82060         0.11314          3.83498
H          -2.70122        -1.65345          3.95492
C          -5.55714        -1.31207          0.32250
C          -5.59581        -2.81301          0.69083
C          -6.29233        -0.49944          1.41250
C          -6.31218        -1.12946         -1.00607
H          -5.08913        -3.41021         -0.07235
H          -5.10708        -3.00723          1.64834
H          -6.63068        -3.16206          0.76613
H          -6.27274         0.56771          1.17537
```

H	-7.33781	-0.81611	1.48714
H	-5.83068	-0.63182	2.39363
H	-7.33852	-1.49240	-0.90148
H	-6.36154	-0.07849	-1.30308
H	-5.84008	-1.69203	-1.81632
C	-1.77478	0.79819	-2.32379
C	-0.86872	1.98834	-1.97906
C	-1.05651	-0.14404	-3.31488
C	-2.99388	1.38795	-3.07500
H	-1.38397	2.69283	-1.32175
H	0.03137	1.65032	-1.47478
H	-0.57730	2.52120	-2.88965
H	-1.67795	-1.01779	-3.53731
H	-0.86716	0.38092	-4.25825
H	-0.10778	-0.47824	-2.89866
H	-2.62940	2.00956	-3.89775
H	-3.63404	0.61992	-3.51720
H	-3.60664	2.01886	-2.42530
C	3.54535	-0.87683	0.17517
C	3.62468	-1.67602	1.32090
C	3.80320	-1.37954	-1.10463
C	3.94358	-3.02325	1.15674
C	4.12248	-2.73389	-1.21927
C	4.18706	-3.57183	-0.10498
H	3.99368	-3.66107	2.03380
H	4.31918	-3.14360	-2.20529
C	3.67731	-0.49889	-2.32110
H	2.62931	-0.21239	-2.45375
C	3.33494	-1.09373	2.67813
H	2.32967	-0.66978	2.69632
N	2.31121	2.44632	0.40149
C	1.39102	3.54093	0.25042
C	1.25151	4.10722	-1.02601
C	0.73330	4.06382	1.36647
C	0.35907	5.16453	-1.17898
C	-0.16471	5.11579	1.16017
C	-0.37699	5.66599	-0.10197
H	0.22372	5.59866	-2.16462
H	-0.70107	5.51769	2.01436
C	2.06136	3.59566	-2.19115
H	1.99150	2.51045	-2.28028
H	1.71848	4.04000	-3.12641
H	3.12078	3.84144	-2.06639
C	-1.39055	6.76425	-0.31139
H	-2.34276	6.34743	-0.65658
H	-1.58626	7.31164	0.61323
H	-1.05434	7.47907	-1.06666
C	1.03404	3.59328	2.76704
H	1.45567	2.59141	2.78405
H	1.75789	4.26902	3.23620
H	0.13459	3.59585	3.38482
C	4.46905	-5.04607	-0.26111
H	5.04705	-5.25072	-1.16504
H	5.02230	-5.44076	0.59440
H	3.53267	-5.61087	-0.33391
H	4.25900	0.42114	-2.21648
H	4.01555	-1.01983	-3.21840
H	4.03275	-0.28810	2.92581
H	3.40233	-1.85648	3.45512

6.5.13 Mes*PIMes$_2$



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95
Mes*PIMes2, C1, B3LYP-D3/6-311G(g,d)
C          -1.63055          0.02992          1.62262
C          -0.61106          0.71442          0.89166
C          -2.96637          0.28484          1.29734
C          -0.98705          1.86798          0.13016
C           1.45349         -0.58301         -0.59547
C          -3.35149          1.25160          0.37494
C          -2.34605          2.06698         -0.13373
C           2.69997         -1.40074         -2.33855
C           1.40784         -1.58873         -2.65299
H          -3.73620         -0.28271          1.79090
H          -2.64115          2.90254         -0.74594
N           2.74473         -0.78551         -1.08893
N           0.63088         -1.10342         -1.59198
P           1.18624          0.17146          0.98236
H           0.94574         -2.04004         -3.51316
H           3.60277         -1.62401         -2.87904
C          -0.01805          3.04104         -0.24781
C           0.62008          3.56054          1.06507
C           1.10360          2.69170         -1.24710
C          -0.77684          4.23798         -0.86791
H          -0.15627          3.85999          1.77454
H           1.24161          2.79751          1.53363
H           1.25040          4.43172          0.85766
H           0.70450          2.28003         -2.17760
H           1.66006          3.59980         -1.50165
H           1.79896          1.97873         -0.82018
H          -0.06554          5.04836         -1.04621
H          -1.22924          3.98546         -1.83145
H          -1.55512          4.62708         -0.20724
C          -4.82981          1.54998          0.07127
C          -5.27002          2.75040          0.94119
C          -5.03650          1.91168         -1.41508
C          -5.73810          0.34731          0.39080
H          -5.14137          2.52395          2.00289
H          -4.67236          3.63682          0.71357
H          -6.32362          2.99180          0.76468
H          -4.72640          1.09052         -2.06426
H          -6.09411          2.11468         -1.60777
H          -4.47630          2.80183         -1.70741
H          -6.76635          0.56690          0.08977
H          -5.40759         -0.54569         -0.14332
H          -5.75615          0.11823          1.45880
C          -1.36093         -0.85361          2.88345
C          -0.69300         -2.20729          2.57809
C          -0.47995         -0.04525          3.86811
C          -2.66661         -1.17954          3.64616
H          -1.32356         -2.80362          1.91729
H           0.27622         -2.06749          2.10722
H          -0.54607         -2.76524          3.50924
H          -0.94690          0.91563          4.10131
H          -0.35702         -0.60301          4.80223
H           0.51426          0.14693          3.46477
H          -2.41203         -1.72160          4.56080
H          -3.21170         -0.27767          3.93615
H          -3.33595         -1.82147          3.06678
```
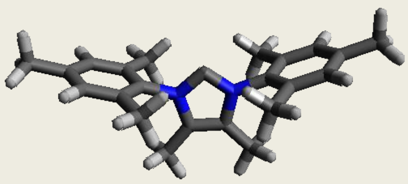

```
C          3.96532      -0.35584      -0.47048
C          4.46977      -1.08190       0.62391
C          4.65200       0.74757      -0.99463
C          5.65126      -0.64390       1.21557
C          5.83497       1.14578      -0.36458
C          6.34252       0.47552       0.74436
H          6.04590      -1.19308       2.06490
H          6.36716       2.00731      -0.75657
C         -0.71741      -1.58282      -1.42783
C         -0.90292      -2.81782      -0.78699
C         -1.77836      -0.90538      -2.03454
C         -2.20081      -3.30911      -0.67066
C         -3.06047      -1.44487      -1.90320
C         -3.29536      -2.62855      -1.20833
H         -2.35905      -4.25500      -0.16144
H         -3.89337      -0.92776      -2.36575
C          7.59804       0.94667       1.43645
H          7.35259       1.47509       2.36366
H          8.24443       0.10609       1.70280
H          8.17153       1.63043       0.80716
C          3.76091      -2.30568       1.14252
H          2.85427      -2.02090       1.68500
H          3.45640      -2.96421       0.32534
H          4.40548      -2.86972       1.81851
C          4.19028       1.49681      -2.22192
H          3.17143       1.24774      -2.50738
H          4.23725       2.57464      -2.05169
H          4.84233       1.26988      -3.07215
C         -1.54277       0.32041      -2.87528
H         -2.45286       0.91299      -2.96840
H         -0.77134       0.95063      -2.44197
H         -1.21632       0.03742      -3.88260
C          0.27497      -3.62752      -0.30819
H         -0.05372      -4.47727       0.29112
H          0.84427      -4.01048      -1.16151
H          0.95912      -3.02991       0.29228
C         -4.69255      -3.16903      -1.03026
H         -5.05854      -2.96576      -0.01826
H         -5.39329      -2.71239      -1.73232
H         -4.72199      -4.25221      -1.17540
```

6.5.14 $IMes_2Me_2$



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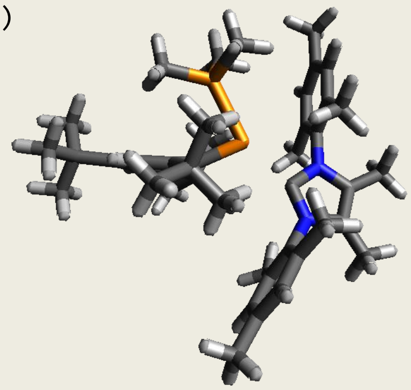
53
IMes2Me2, C2V, B3LYP-D3/6-311G(d,p)
C          0.00000      -0.00019      -0.57805
C          0.67848      -0.00097       1.64141
C         -0.67848      -0.00100       1.64141
N          1.05788      -0.00054       0.28749
C          2.42524      -0.00010      -0.14244
C          3.07848      -1.22232      -0.33468
C          3.07794       1.22254      -0.33364
C          4.41963      -1.19931      -0.71974
C          4.41913       1.20045      -0.71873
C          5.10580       0.00081      -0.91547
H          4.93911      -2.14048      -0.87279
H          4.93817       2.14198      -0.87098
C          2.33158       2.51890      -0.14673
```

```
H          1.47710         2.56474        -0.82717
C          2.33265        -2.51915        -0.14889
H          1.47827        -2.56481        -0.82946
N         -1.05788        -0.00054         0.28749
C         -2.42524        -0.00012        -0.14244
C         -3.07795         1.22253        -0.33367
C         -3.07847        -1.22234        -0.33465
C         -4.41913         1.20042        -0.71876
C         -4.41964        -1.19934        -0.71971
C         -5.10580         0.00076        -0.91547
H         -4.93818         2.14194        -0.87103
H         -4.93910        -2.14052        -0.87274
C         -2.33158         2.51889        -0.14679
H         -1.47706         2.56468        -0.82717
H         -2.97866         3.37699        -0.33559
H         -1.92991         2.60714         0.86717
C         -6.54648         0.00126        -1.36764
H         -6.61026         0.00188        -2.46123
H         -7.07836        -0.88339        -1.00940
H         -7.07806         0.88569        -1.00841
C         -2.33264        -2.51916        -0.14883
H         -1.47829        -2.56486        -0.82943
H         -1.93078        -2.60831         0.86497
H         -2.98014        -3.37684        -0.33810
C          6.54648         0.00119        -1.36764
H          7.07731         0.88716        -1.01111
H          7.07911        -0.88192        -1.00670
H          6.61026        -0.00152        -2.46122
H          1.92982         2.60710         0.86720
H          2.97867         3.37701        -0.33543
H          1.93082        -2.60834         0.86492
H          2.98014        -3.37683        -0.33822
C          1.67037        -0.00123         2.75364
H          2.32129        -0.88013         2.70989
H          2.32099         0.87793         2.71055
H          1.16350        -0.00168         3.71969
C         -1.67037        -0.00131         2.75363
H         -2.32101         0.87783         2.71056
H         -2.32126        -0.88022         2.70987
H         -1.16350        -0.00176         3.71969
```

6.5.15 Mes*$PPMe_3$ - $IMes_2Me_2$ TS

```
114
Mes*PPMe3 – IMes2Me2 TS, C1, B3LYP-D3/6-311G(d,p)
C         -2.02676         0.44835        -0.16785
C          2.37056         0.68081         0.94377
C          1.56556         0.10235        -0.08425
C          3.76403         0.72098         0.78384
C          2.19917        -0.17115        -1.34141
C          4.40676         0.27937        -0.36309
C          3.59219        -0.10413        -1.42603
C         -4.29389         0.12479        -0.44289
C         -4.07392         1.46030        -0.50504
H          4.36533         1.09419         1.59531
H          4.07272        -0.37275        -2.35411
N         -3.03977        -0.46940        -0.24301
P         -0.08983        -0.78781         0.36075
```



C	0.65578	-3.38755	2.70851
C	1.09619	-4.27719	0.05149
C	3.16309	-2.80666	1.39490
H	1.08840	-4.35103	2.99455
H	0.85183	-2.65483	3.49194
H	-0.42504	-3.49490	2.59941
H	1.64868	-4.16167	-0.88101
H	1.43333	-5.18547	0.56057
H	0.03526	-4.36355	-0.18974
H	3.50702	-3.78405	1.74750
H	3.66570	-2.55237	0.46029
H	3.42186	-2.03931	2.12484
P	1.33714	-2.77541	1.10373
C	1.44710	-0.50911	-2.66466
C	0.97077	-1.97668	-2.70747
C	0.26346	0.45988	-2.83432
C	2.34001	-0.29863	-3.91238
H	1.82871	-2.65131	-2.62551
H	0.28055	-2.18099	-1.89100
H	0.47301	-2.18371	-3.66179
H	0.62635	1.49043	-2.86655
H	-0.26679	0.25631	-3.77151
H	-0.43999	0.37901	-2.01030
H	1.72139	-0.41072	-4.80730
H	2.78210	0.70123	-3.93395
H	3.14394	-1.03519	-3.98973
C	5.93549	0.24314	-0.51289
C	6.38152	-1.19750	-0.85304
C	6.36721	1.19366	-1.65260
C	6.66134	0.67444	0.77400
H	6.09916	-1.88810	-0.05351
H	5.92472	-1.55318	-1.77936
H	7.46847	-1.24261	-0.97523
H	6.05894	2.21981	-1.43484
H	7.45553	1.17930	-1.77239
H	5.92052	0.90650	-2.60703
H	7.74332	0.61065	0.62755
H	6.42403	1.70633	1.04597
H	6.40000	0.02937	1.61738
C	1.81632	1.31965	2.25266
C	0.59982	2.19062	1.90980
C	1.42651	0.26289	3.30980
C	2.84746	2.26044	2.92227
H	0.87192	2.98438	1.20956
H	-0.18136	1.59069	1.45345
H	0.19613	2.65689	2.81419
H	2.27514	-0.39055	3.53706
H	1.12856	0.75826	4.24117
H	0.59680	-0.34310	2.94988
H	2.35237	2.79768	3.73610
H	3.69066	1.72236	3.36358
H	3.23809	3.00234	2.22050
C	-2.89982	-1.89372	-0.09356
C	-2.75727	-2.68350	-1.23955
C	-2.98992	-2.45123	1.18657
C	-2.66481	-4.06491	-1.07612
C	-2.89818	-3.83932	1.30225
C	-2.72406	-4.66030	0.18642
H	-2.53568	-4.68983	-1.95438
H	-2.95692	-4.28807	2.28926

```
C          -3.11816       -1.56828        2.40115
H          -2.20613       -0.97390        2.51461
C          -2.67754       -2.04230       -2.59854
H          -1.87076       -1.30955       -2.62110
N          -2.68963        1.63464       -0.33415
C          -2.11605        2.94052       -0.16450
C          -2.13395        3.49722        1.12431
C          -1.64106        3.65348       -1.26717
C          -1.59227        4.76686        1.29908
C          -1.08782        4.91811       -1.03957
C          -1.04309        5.48384        0.23211
H          -1.57997        5.20052        2.29411
H          -0.69233        5.47360       -1.88457
C          -2.72382        2.73351        2.28301
H          -2.26814        1.74586        2.37597
H          -2.57360        3.27184        3.21980
H          -3.79890        2.57775        2.14861
C          -0.39661        6.82730        0.46591
H          -0.34589        7.41483       -0.45336
H          -0.94376        7.40856        1.21258
H           0.62685        6.70216        0.83530
C          -1.78200        3.13642       -2.67649
H          -1.93032        2.05973       -2.70672
H          -2.64321        3.60958       -3.16200
H          -0.89965        3.37547       -3.27263
C          -2.55957       -6.15207        0.34359
H          -2.94127       -6.69127       -0.52657
H          -1.50066       -6.41273        0.45188
H          -3.08043       -6.52203        1.22972
H          -3.95451       -0.86940        2.30765
H          -3.26610       -2.16235        3.30456
H          -3.60264       -1.51227       -2.84651
H          -2.49131       -2.78597       -3.37451
C          -5.54700       -0.67566       -0.54170
H          -5.50586       -1.38881       -1.36997
H          -5.71794       -1.25572        0.36993
H          -6.40497       -0.02085       -0.69711
C          -5.00047        2.60705       -0.72043
H          -4.95514        3.32207        0.10612
H          -4.74747        3.15570       -1.63269
H          -6.02837        2.25387       -0.81036
```

6.5.16 Mes*PIMes$_2$Me$_2$

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101
Mes*PIMes2Me2, C1, B3LYP-D3/6-311G(d,p)
C           1.75708       -0.69883        1.58297
C           0.81685       -1.16351        0.60970
C           3.11579       -0.70247        1.25103
C           1.31732       -1.93848       -0.48651
C          -1.38444        0.47508       -0.29968
C           3.60873       -1.25673        0.07520
C           2.69547       -1.93474       -0.72441
C          -2.78734        1.83315       -1.52307
C          -1.52443        2.22323       -1.79255
H           3.81846       -0.27407        1.94456
H           3.08013       -2.48883       -1.56483
N          -2.70792        0.76472       -0.61495
```
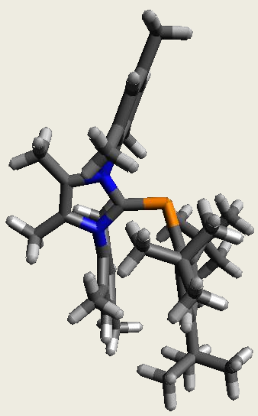
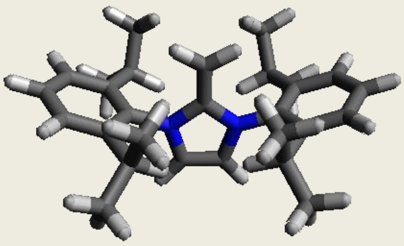



N	-0.65132	1.39748	-1.04006
P	-1.03040	-0.84483	0.81973
C	0.46033	-2.90183	-1.37204
C	-0.40134	-3.81910	-0.46890
C	-0.42780	-2.15886	-2.39144
C	1.34304	-3.86428	-2.20454
H	0.23379	-4.35207	0.24432
H	-1.15029	-3.26047	0.08965
H	-0.91952	-4.56119	-1.08528
H	0.18554	-1.68623	-3.16083
H	-1.09287	-2.87054	-2.89194
H	-1.03691	-1.39712	-1.91713
H	0.69002	-4.55844	-2.74008
H	1.94047	-3.34433	-2.95812
H	2.01285	-4.45623	-1.57560
C	5.10894	-1.28036	-0.25990
C	5.67801	-2.66399	0.12983
C	5.34099	-1.05170	-1.76958
C	5.88541	-0.19139	0.50403
H	5.53869	-2.85095	1.19792
H	5.17243	-3.46311	-0.41828
H	6.74893	-2.71980	-0.09289
H	4.91933	-0.09628	-2.08876
H	6.41308	-1.04239	-1.98801
H	4.89163	-1.83716	-2.38037
H	6.93045	-0.18377	0.18176
H	5.46119	0.79677	0.31503
H	5.88059	-0.36403	1.58269
C	1.39232	-0.34279	3.06060
C	0.59875	0.96730	3.21566
C	0.58870	-1.52141	3.66375
C	2.65147	-0.18738	3.94552
H	1.17967	1.81008	2.83852
H	-0.34157	0.91797	2.67362
H	0.37932	1.14590	4.27389
H	1.15060	-2.45495	3.57098
H	0.39981	-1.33875	4.72669
H	-0.37569	-1.65070	3.17332
H	2.33342	-0.02217	4.97828
H	3.28150	-1.08054	3.93244
H	3.26013	0.67353	3.65496
C	-3.85851	0.09281	-0.08252
C	-4.38097	0.51833	1.15044
C	-4.47394	-0.92483	-0.82161
C	-5.52285	-0.11219	1.63851
C	-5.62022	-1.52439	-0.29325
C	-6.15419	-1.13996	0.93405
H	-5.93308	0.20927	2.59090
H	-6.10387	-2.31389	-0.86051
C	0.66960	1.87541	-0.71809
C	0.79113	2.80830	0.32859
C	1.76326	1.55124	-1.52379
C	2.05273	3.31205	0.62656
C	3.01148	2.09046	-1.19145
C	3.18262	2.94888	-0.11180
H	2.15506	4.02033	1.44335
H	3.86553	1.83828	-1.81054
C	-7.37019	-1.82797	1.50484
H	-7.07461	-2.59892	2.22442
H	-8.01743	-1.12188	2.03130

```
H           -7.95981         -2.31413          0.72454
C           -3.71466          1.61553          1.93779
H           -2.77280          1.25386          2.36016
H           -3.48071          2.47812          1.30942
H           -4.35113          1.95007          2.75866
C           -3.92248         -1.40730         -2.13810
H           -3.33068         -0.64689         -2.64752
H           -3.26784         -2.26629         -1.97445
H           -4.72951         -1.72283         -2.80335
C            1.63269          0.70406         -2.76034
H            2.19222         -0.22558         -2.64729
H            0.59530          0.44897         -2.96138
H            2.03614          1.23735         -3.62648
C           -0.42621          3.31501          1.05693
H           -0.14276          3.91667          1.92126
H           -1.03791          3.93634          0.39426
H           -1.05727          2.49916          1.40105
C            4.54065          3.49167          0.25800
H            4.90950          3.01942          1.17448
H            5.27563          3.30740         -0.52806
H            4.50106          4.56903          0.44146
C           -4.10132          2.32290         -2.02409
H           -3.96208          3.18093         -2.68178
H           -4.63585          1.54658         -2.57980
H           -4.74819          2.62535         -1.19520
C           -0.99527          3.29862         -2.67597
H           -0.42016          4.03727         -2.10922
H           -0.32781          2.89157         -3.44169
H           -1.81468          3.81413         -3.17755
```

6.5.17 ICH_2Dip_2



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68
ICH2Dip2, C1, B3LYP-D3/6-311G(d,p)
C           -0.67256          0.01287          1.96693
C            0.67168          0.02299          1.96851
N           -1.09986          0.03927          0.63158
N            1.10175          0.05586          0.63404
H            1.37770          0.01671          2.77980
H           -1.38040         -0.00241          2.77650
C            0.00168          0.05957         -0.22637
C            0.00222          0.07527         -1.58204
H           -0.93009          0.07328         -2.12420
H            0.93492          0.08474         -2.12339
C           -2.45117         -0.00265          0.17943
C           -3.13467          1.20787         -0.03150
C           -3.04232         -1.25176         -0.07984
C           -4.44981          1.14246         -0.49863
C           -4.36056         -1.26707         -0.54295
C           -5.05828         -0.08235         -0.74965
H           -5.00087          2.05924         -0.67532
H           -4.84225         -2.21563         -0.75194
H           -6.07971         -0.11339         -1.11311
C            2.45381          0.01990          0.18334
C            3.06870         -1.22788         -0.02471
C            3.11323          1.23323         -0.07989
C            4.38291         -1.23659         -0.49910
C            4.42655          1.17400         -0.55321
```

```
C          5.05590      -0.04814      -0.76050
H          4.88160      -2.18292      -0.67475
H          4.95901       2.09358      -0.76870
H          6.07477      -0.07494      -1.13139
C          2.32279      -2.53382       0.21345
C          3.10046      -3.48676       1.13620
C          1.97077      -3.20899      -1.12473
H          1.38226      -2.29448       0.71308
H          3.34475      -3.00533       2.08684
H          2.50285      -4.37792       1.34842
H          4.03633      -3.81963       0.67863
H          1.36428      -2.54330      -1.74203
H          2.87658      -3.47055      -1.68036
H          1.40226      -4.12763      -0.95083
C          2.41970       2.57398       0.11411
C          2.18516       3.27414      -1.23625
C          3.18945       3.47911       1.09063
H          1.43934       2.37770       0.55160
H          1.59443       2.63908      -1.89929
H          1.64203       4.21249      -1.08904
H          3.13326       3.50720      -1.73067
H          3.33247       2.98688       2.05625
H          4.17633       3.74437       0.70059
H          2.63920       4.40924       1.25972
C         -2.27356      -2.55249       0.10506
C         -2.03451      -3.24762      -1.24680
C         -2.97094      -3.49002       1.10516
H         -1.29411      -2.30451       0.51724
H         -1.49458      -2.58548      -1.92651
H         -1.43776      -4.15393      -1.10785
H         -2.97965      -3.53451      -1.71765
H         -3.11072      -3.00089       2.07281
H         -3.95443      -3.80327       0.74323
H         -2.37188      -4.39174       1.26172
C         -2.45945       2.55210       0.20078
C         -3.26197       3.44326       1.16307
C         -2.19211       3.26617      -1.13669
H         -1.49055       2.35860       0.66457
H         -3.43874       2.93751       2.11602
H         -2.71662       4.36980       1.36438
H         -4.23428       3.71738       0.74380
H         -1.57643       2.64273      -1.78818
H         -3.12904       3.49200      -1.65528
H         -1.66402       4.20932      -0.96661
```

6.5.18 Mes*PPMe$_3$ + ICH$_2$Dip$_2$ TS1

```
129
Mes*PPMe3 + ICH2Dip2 TS1, C1, B3LYP-D3/6-311G(d,p)
C          1.45117       0.13118       0.94860
C         -1.86589      -1.29824      -2.10200
C         -2.54051      -0.46526      -0.95857
C         -1.98289      -0.14014       0.33096
C         -2.34383       1.31486       2.56870
C         -3.85534      -0.08838      -1.25051
C         -2.76220       0.72510       1.17720
C          2.17421       0.33079      -0.23314
C         -4.65589       0.64710      -0.38763
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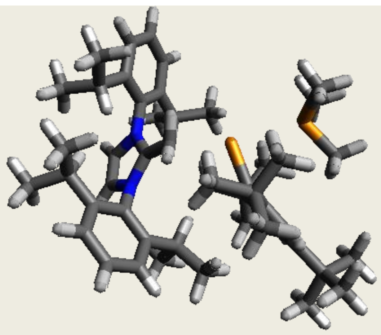
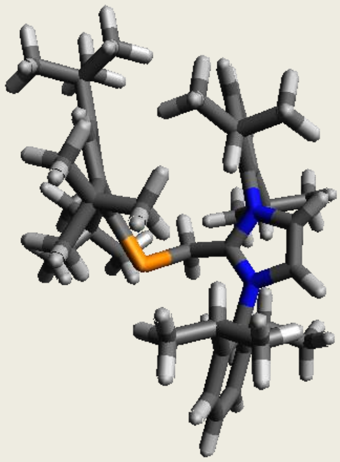


C	-4.06866	1.06638	0.79426
C	3.01734	1.27284	-2.11463
C	3.56608	0.04899	-1.99985
H	-4.28812	-0.39124	-2.19009
H	-4.66003	1.66798	1.46004
N	2.15463	1.46380	-1.02909
N	3.05868	-0.54068	-0.83617
P	-0.53924	-1.18007	1.03950
C	-2.63026	-3.47268	3.62672
C	-4.37899	-2.57908	1.54350
C	-2.66021	-4.82751	1.14500
H	-1.65429	-3.87038	3.91432
H	-2.80044	-2.55637	4.19250
H	-3.40445	-4.20241	3.88495
H	-4.55342	-2.44914	0.47433
H	-5.08901	-3.30833	1.94667
H	-4.53971	-1.60908	2.01492
H	-3.43477	-5.42923	1.63133
H	-2.84811	-4.80701	0.07104
H	-1.68796	-5.29764	1.31016
C	-6.10325	0.98255	-0.77698
H	4.25872	-0.47634	-2.63226
H	3.15507	2.03849	-2.85650
H	1.14105	1.05705	1.40658
H	1.88979	-0.58708	1.62825
C	3.56880	-1.77380	-0.27625
C	3.27989	-2.98971	-0.91796
C	4.40692	-1.72014	0.85958
C	3.82149	-4.16294	-0.38170
C	4.89973	-2.92325	1.36641
C	4.61042	-4.13714	0.75582
H	3.60996	-5.10961	-0.86366
H	5.53596	-2.91131	2.24143
H	5.00965	-5.05894	1.16406
C	1.75667	2.78545	-0.57454
C	0.47897	3.29118	-0.88541
C	2.69811	3.54739	0.14354
C	0.16305	4.57825	-0.44300
C	2.33105	4.83218	0.55566
C	1.07548	5.34361	0.27113
H	-0.81435	4.98700	-0.65801
H	3.04149	5.43544	1.10817
H	0.80493	6.33943	0.60429
C	-6.10333	1.80896	-2.08330
H	-5.64284	1.25980	-2.90753
H	-7.12728	2.06092	-2.37743
H	-5.54540	2.73983	-1.94923
C	-6.83048	1.79879	0.30634
H	-7.85610	2.00400	-0.01296
H	-6.87965	1.25685	1.25473
H	-6.34026	2.75938	0.48564
C	-6.88901	-0.32986	-0.99875
H	-7.92410	-0.11364	-1.28198
H	-6.44437	-0.93608	-1.79112
H	-6.90149	-0.93082	-0.08543
C	-0.36135	-1.03201	-2.28359
H	0.02309	-1.70589	-3.05320
H	-0.17800	-0.01663	-2.62943
H	0.17942	-1.20319	-1.35632
C	-2.49043	-0.99015	-3.49035

H	-2.52347	0.08417	-3.69117
H	-1.87116	-1.45541	-4.26171
H	-3.49737	-1.39480	-3.61363
C	-2.09343	-2.79903	-1.82620
H	-1.55089	-3.10185	-0.93330
H	-3.15874	-3.00189	-1.68050
H	-1.74634	-3.40212	-2.67183
C	-0.87682	1.77552	2.61916
H	-0.62347	2.40182	1.75926
H	-0.70314	2.36102	3.52747
H	-0.22576	0.90931	2.64220
C	-2.56780	0.26194	3.67520
H	-1.91004	-0.59027	3.50871
H	-2.34391	0.69281	4.65770
H	-3.60767	-0.07900	3.68573
C	-3.18283	2.56566	2.94418
H	-3.15568	3.32410	2.15627
H	-4.22672	2.33714	3.16919
H	-2.76042	3.00874	3.84938
C	-0.51982	2.49735	-1.70821
C	-0.15432	2.56203	-3.20485
C	-1.97470	2.93919	-1.51510
H	-0.45476	1.46256	-1.37240
H	-0.88338	2.00349	-3.79772
H	-0.15853	3.59981	-3.55186
H	-2.25526	2.95516	-0.46175
H	-2.16190	3.92672	-1.94842
H	-2.63695	2.22911	-2.01010
C	4.09444	3.04844	0.48491
C	4.32815	3.05158	2.00537
C	5.17453	3.86489	-0.24684
H	4.19267	2.02135	0.13939
H	3.58114	2.44196	2.51830
H	5.31772	2.65285	2.23963
H	4.27632	4.06303	2.41548
H	5.02138	3.83835	-1.32856
H	5.16469	4.91198	0.06793
H	6.16712	3.45795	-0.03372
C	4.87155	-0.40461	1.46795
C	6.14461	0.06843	0.73858
C	5.09629	-0.47119	2.98537
H	4.09403	0.33829	1.30652
H	5.96332	0.19906	-0.33113
H	6.49353	1.02302	1.14100
H	6.94771	-0.66436	0.85791
H	4.21847	-0.87288	3.49709
H	5.95850	-1.08979	3.24835
H	5.28657	0.53067	3.37579
C	2.43138	-3.08485	-2.17316
C	1.24564	-4.04057	-1.97079
C	3.28262	-3.49803	-3.38765
H	2.02218	-2.09841	-2.37819
H	0.64137	-3.72524	-1.11884
H	0.60812	-4.04653	-2.85794
H	1.58219	-5.06685	-1.79961
H	4.11703	-2.80910	-3.54744
H	3.70236	-4.49938	-3.25564
H	2.67052	-3.50671	-4.29398
H	0.83053	2.13892	-3.40762
P	-2.61998	-3.09186	1.81071

6.5.19 Mes*P-ICH$_2$Dip$_2$ Int1



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116
Mes*P-ICH2Dip2 Int1, C1, B3LYP-D3/6-311G(d,p)
C           1.48280       -0.48114        3.51475
C           2.00883       -0.58769        2.04128
C           1.38973       -1.39744        1.03102
C           1.84609       -3.23056       -0.79676
C           3.28010       -0.05711        1.78043
C           2.25477       -1.99336        0.05719
C          -1.51861        0.56834       -0.45940
C           4.05375       -0.44745        0.69280
C           3.55236       -1.49636       -0.08210
C          -3.02147        0.69432       -2.13036
C          -1.94836        1.42440       -2.49866
H           3.70029        0.64799        2.47828
H           4.19885       -1.92247       -0.83514
N          -2.75822        0.17565       -0.86776
N          -1.01926        1.35193       -1.46019
P          -0.47215       -1.58017        0.94319
C           5.45446        0.12320        0.41868
H          -1.75609        1.99904       -3.38473
H          -3.94697        0.48949       -2.63628
C          -0.92012        0.30873        0.85047
H          -1.60940        0.61532        1.63934
H          -0.00877        0.89411        0.94419
C          -3.69264       -0.62493       -0.10881
C          -4.44583        0.00067        0.89879
C          -3.83626       -1.98431       -0.43626
C          -5.36179       -0.78578        1.60156
C          -4.77345       -2.71997        0.29293
C          -5.52253       -2.13225        1.30409
H          -5.95932       -0.33602        2.38520
H          -4.91031       -3.77079        0.07212
H          -6.23687       -2.72714        1.86216
C           0.15460        2.19152       -1.36741
C           0.10870        3.30790       -0.51028
C           1.27509        1.89594       -2.16371
C           1.25507        4.09922       -0.41473
C           2.38505        2.73689       -2.04398
C           2.38642        3.81264       -1.16672
H           1.25445        4.95869        0.24459
H           3.26492        2.54223       -2.64202
H           3.26870        4.43638       -1.07861
C           1.21224       -4.29508        0.12958
H           0.29553       -3.93782        0.59796
H           0.96729       -5.19593       -0.44301
H           1.91064       -4.57092        0.92469
C           0.87060       -2.87411       -1.94156
H           1.35999       -2.22948       -2.67222
H           0.55511       -3.78643       -2.45979
H          -0.00747       -2.36532       -1.54833
C           3.07011       -3.90963       -1.45248
H           3.54033       -3.27866       -2.21138
H           3.82748       -4.18644       -0.71394
H           2.74125       -4.82410       -1.95440
C           0.16435        0.28876        3.73225
H           0.22107        1.29734        3.31488
H          -0.67108       -0.24665        3.28584
```

H	-0.02894	0.38562	4.80601
C	2.52320	0.18953	4.44277
H	2.15547	0.14897	5.47160
H	3.48940	-0.31963	4.41864
H	2.67971	1.24399	4.19510
C	1.29494	-1.93000	4.02961
H	0.98704	-1.91890	5.08094
H	0.52968	-2.44799	3.45093
H	2.23179	-2.48817	3.95037
C	5.75513	1.36492	1.27857
H	5.00506	2.14556	1.12274
H	5.78345	1.12607	2.34455
H	6.73307	1.77396	1.00849
C	5.57646	0.54050	-1.06319
H	5.41888	-0.30282	-1.73832
H	4.83493	1.30515	-1.30518
H	6.57267	0.94758	-1.26491
C	6.51550	-0.95664	0.73069
H	7.52502	-0.57341	0.54601
H	6.45074	-1.26693	1.77701
H	6.37205	-1.84480	0.11060
C	1.28448	0.76129	-3.17929
C	2.63029	0.02495	-3.23511
C	0.93025	1.29513	-4.58295
H	0.52526	0.03438	-2.88033
H	2.91943	-0.33684	-2.25010
H	2.55664	-0.83027	-3.91113
H	3.42826	0.66671	-3.61695
H	-0.02987	1.81391	-4.60619
H	1.69253	2.00232	-4.92293
H	0.88627	0.47207	-5.30148
C	-1.15073	3.72469	0.23778
C	-1.76126	4.98312	-0.40694
C	-0.91217	3.92883	1.74150
H	-1.88859	2.93034	0.13803
H	-1.97227	4.82099	-1.46712
H	-2.69764	5.24965	0.09179
H	-1.08003	5.83465	-0.32659
H	-0.48692	3.03427	2.19760
H	-0.23405	4.76428	1.93355
H	-1.85730	4.14920	2.24468
C	-3.05256	-2.64137	-1.56314
C	-3.91456	-2.73862	-2.83703
C	-2.51032	-4.02409	-1.17314
H	-2.18689	-2.01208	-1.77499
H	-4.27518	-1.76056	-3.16529
H	-3.33449	-3.17580	-3.65456
H	-4.78910	-3.37300	-2.66450
H	-1.94080	-3.96015	-0.24659
H	-3.31361	-4.75635	-1.05105
H	-1.84504	-4.39341	-1.95677
C	-4.34041	1.48841	1.20373
C	-4.11241	1.76934	2.69819
C	-5.58023	2.23615	0.67963
H	-3.47985	1.88694	0.66734
H	-3.24177	1.23063	3.07798
H	-3.94855	2.83831	2.85879
H	-4.97691	1.47533	3.29874
H	-5.71265	2.07680	-0.39372
H	-6.48690	1.89006	1.18365

```
H          -5.48313        3.31144        0.85619
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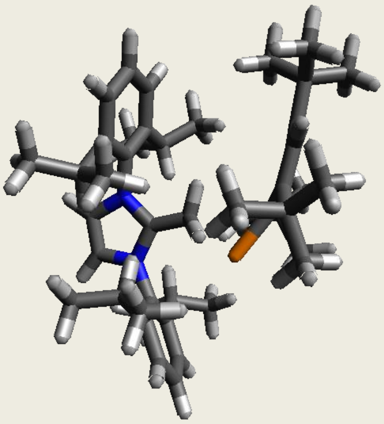
6.5.20 Mes*P-H-ICHDip$_2$ TS2



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116
Mes*P-H-ICHDip2 TS2, C1, B3LYP/6-311G(d,p)
C           1.74792       -1.59030        3.28840
C           2.19494       -1.48623        1.79842
C           1.41521       -1.89039        0.68407
C           1.43202       -2.83382       -1.77864
C           3.48129       -0.97554        1.56037
C           2.06526       -2.06985       -0.57829
C          -1.42296        0.76910       -0.47386
C           4.05444       -0.93356        0.29763
C           3.35379       -1.56215       -0.73515
C          -3.40795        1.55315       -1.27397
C          -2.48661        2.50480       -1.50864
H           4.04302       -0.58954        2.39457
H           3.83757       -1.64342       -1.69684
N          -2.77253        0.47717       -0.63390
N          -1.25854        2.04187       -1.02880
P          -0.46972       -1.82531        0.73384
C           5.42079       -0.28882        0.01754
H          -2.57453        3.47078       -1.97321
H          -4.45936        1.51972       -1.49465
C          -0.42475        0.02726        0.11631
H          -0.56712       -0.37039        1.37383
H           0.57189        0.44300        0.05267
C          -3.48037       -0.63067       -0.05438
C          -3.75253       -0.62143        1.32847
C          -3.90832       -1.67042       -0.89668
C          -4.49294       -1.68490        1.84817
C          -4.66803       -2.69655       -0.33155
C          -4.95777       -2.70496        1.02661
H          -4.71091       -1.71878        2.90765
H          -5.01523       -3.51088       -0.95593
H          -5.53748       -3.51730        1.45096
C          -0.08300        2.83608       -0.82986
C           0.01160        3.62260        0.33114
C           0.95390        2.76548       -1.77723
C           1.17499        4.37518        0.51523
C           2.09720        3.53462       -1.54831
C           2.20626        4.33270       -0.41403
H           1.27574        4.99310        1.40007
H           2.91500        3.50611       -2.25690
H           3.10394        4.91945       -0.25283
C           0.77822       -4.14721       -1.29007
H          -0.05960       -3.95972       -0.61881
H           0.40032       -4.71630       -2.14533
H           1.50941       -4.76634       -0.76318
C           0.40027       -1.96775       -2.53471
H           0.87630       -1.06358       -2.91458
H          -0.00036       -2.52470       -3.38740
H          -0.42919       -1.67524       -1.89557
C           2.50286       -3.24950       -2.81448
H           2.93911       -2.39250       -3.33392
H           3.31109       -3.82523       -2.35557
H           2.03406       -3.87801       -3.57649
```

C	0.99112	-0.32528	3.74759
H	1.58084	0.57257	3.54275
H	0.03059	-0.23097	3.24423
H	0.80032	-0.36831	4.82530
C	2.98159	-1.73974	4.21655
H	2.63883	-1.97578	5.22741
H	3.63843	-2.54779	3.88432
H	3.57266	-0.82404	4.28995
C	0.88690	-2.84904	3.53731
H	-0.06542	-2.80592	3.01181
H	1.41991	-3.74754	3.21407
H	0.67514	-2.94457	4.60709
C	6.00186	0.41484	1.25711
H	5.33405	1.19962	1.62316
H	6.18642	-0.28781	2.07401
H	6.95767	0.88091	1.00201
C	5.26275	0.76777	-1.09993
H	4.91852	0.31889	-2.03387
H	4.53690	1.53238	-0.80952
H	6.22113	1.25779	-1.29899
C	6.42252	-1.37314	-0.43925
H	7.39943	-0.92717	-0.65234
H	6.55341	-2.12973	0.33915
H	6.08040	-1.88035	-1.34422
C	0.80800	1.90817	-3.02516
C	2.12812	1.26554	-3.47239
C	0.17873	2.72892	-4.16679
H	0.11640	1.09895	-2.78080
H	2.58455	0.69944	-2.65803
H	1.94591	0.58133	-4.30525
H	2.84989	2.01054	-3.81877
H	-0.79231	3.13506	-3.87400
H	0.82630	3.56664	-4.44329
H	0.03142	2.10436	-5.05272
C	-1.09280	3.65588	1.37769
C	-1.68657	5.06638	1.53145
C	-0.59480	3.10482	2.72405
H	-1.89978	3.00552	1.04072
H	-2.06986	5.43861	0.57778
H	-2.51220	5.05375	2.24868
H	-0.93933	5.77815	1.89383
H	-0.19841	2.09557	2.60614
H	0.19586	3.73266	3.14448
H	-1.41455	3.06985	3.44717
C	-3.53846	-1.71090	-2.37189
C	-4.73183	-1.31183	-3.25861
C	-2.98619	-3.08655	-2.78261
H	-2.74275	-0.97985	-2.53155
H	-5.09147	-0.30820	-3.01899
H	-4.44816	-1.32620	-4.31508
H	-5.56510	-2.00773	-3.12167
H	-2.18652	-3.40226	-2.11117
H	-3.76601	-3.85319	-2.77159
H	-2.58415	-3.04141	-3.79841
C	-3.29227	0.52250	2.22457
C	-2.99965	0.08711	3.66782
C	-4.31113	1.67798	2.19999
H	-2.35540	0.90763	1.81984
H	-2.33496	-0.77877	3.69177
H	-2.51402	0.90373	4.20778

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H          -3.91465       -0.16323        4.21239
H          -4.46115        2.05765        1.18733
H          -5.27871        1.34539        2.58714
H          -3.96203        2.50747        2.82271
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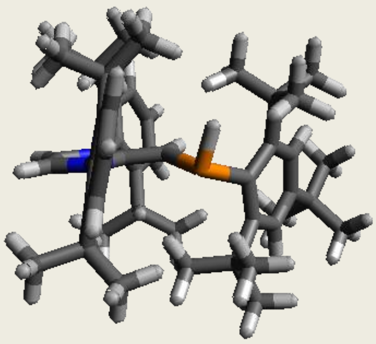
6.5.21 Mes*P(H)C(H)IDip$_2$



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116
Mes*P(H)C(H)IDip2, C1, B3LYP-D3/6-311G(d,p)
C           1.86159       -0.08864        3.34299
C           2.38568       -0.55697        1.94942
C           1.66295       -1.37733        1.03206
C           1.79572       -3.07953       -1.00042
C           3.69219       -0.17690        1.61405
C           2.36237       -1.95738       -0.07302
C          -1.51680        0.48512       -0.59724
C           4.33481       -0.59633        0.45731
C           3.66390       -1.52438       -0.33378
C          -3.53167        0.66111       -1.66682
C          -2.78728        1.70812       -2.05892
H           4.22537        0.47811        2.27973
H           4.18390       -1.91896       -1.19155
N          -2.77097       -0.10336       -0.76312
N          -1.54515        1.61414       -1.42192
P          -0.21748       -1.48671        0.98540
C           5.74060       -0.12016        0.05745
H          -3.00333        2.51223       -2.73966
H          -4.52975        0.36629       -1.93472
C          -0.46755        0.12191        0.19431
H          -0.51160       -1.18863        2.33659
H           0.36294        0.81554        0.21062
C          -3.34786       -1.11028        0.08393
C          -3.70365       -0.77515        1.40765
C          -3.58649       -2.38708       -0.45206
C          -4.31164       -1.76273        2.18467
C          -4.22608       -3.32891        0.35763
C          -4.58154       -3.02343        1.66399
H          -4.58936       -1.54316        3.20769
H          -4.43004       -4.31864       -0.03281
H          -5.06590       -3.77090        2.28271
C          -0.54998        2.64209       -1.38290
C          -0.75759        3.75582       -0.55244
C           0.62235        2.48130       -2.14501
C           0.22339        4.75273       -0.53954
C           1.57689        3.49824       -2.09123
C           1.37585        4.62798       -1.30302
H           0.08642        5.62691        0.08680
H           2.48969        3.40883       -2.66606
H           2.12881        5.40816       -1.27739
C           1.21647       -4.24022       -0.15516
H           0.36443       -3.93083        0.44599
H           0.88625       -5.04953       -0.81391
H           1.98463       -4.63909        0.51338
C           0.74358       -2.53286       -1.99213
H           1.17926       -1.73704       -2.59856
H           0.41605       -3.33230       -2.66327
H          -0.13497       -2.13389       -1.49193
C           2.90396       -3.72030       -1.87186
```

H	3.30977	-3.02711	-2.61306
H	3.72873	-4.10811	-1.26842
H	2.47293	-4.55982	-2.42308
C	0.77540	1.00822	3.22943
H	1.18448	1.88123	2.71297
H	-0.10806	0.69351	2.68361
H	0.46191	1.32498	4.22945
C	2.98347	0.54116	4.20756
H	2.57718	0.76155	5.19830
H	3.83086	-0.13579	4.34166
H	3.35110	1.48417	3.79562
C	1.37831	-1.31302	4.16110
H	0.99046	-0.98585	5.13112
H	0.59871	-1.88748	3.66855
H	2.21797	-1.98980	4.34314
C	6.32770	0.89003	1.05926
H	5.70222	1.78276	1.14540
H	6.44268	0.45382	2.05523
H	7.31764	1.20909	0.72195
C	5.66875	0.56493	-1.32635
H	5.28844	-0.11275	-2.09383
H	5.00699	1.43446	-1.29235
H	6.66272	0.90199	-1.63721
C	6.69649	-1.33242	-0.01953
H	7.70478	-1.00709	-0.29461
H	6.75229	-1.84119	0.94661
H	6.36671	-2.06129	-0.76299
C	0.81214	1.24704	-3.01577
C	2.28006	0.82586	-3.15859
C	0.15710	1.45817	-4.39370
H	0.29230	0.42405	-2.52225
H	2.74016	0.66327	-2.18238
H	2.34448	-0.11006	-3.71986
H	2.87217	1.56636	-3.70397
H	-0.90583	1.68999	-4.29409
H	0.63740	2.28302	-4.92911
H	0.25015	0.55513	-5.00425
C	-1.98290	3.88177	0.34256
C	-2.81875	5.12475	-0.00497
C	-1.58053	3.87241	1.82766
H	-2.61604	3.01102	0.17425
H	-3.13095	5.10969	-1.05247
H	-3.71718	5.16490	0.61758
H	-2.25415	6.04641	0.16270
H	-1.02664	2.96511	2.07427
H	-0.95117	4.73185	2.07555
H	-2.46974	3.91540	2.46314
C	-3.15486	-2.75816	-1.86255
C	-4.35406	-2.77100	-2.82831
C	-2.41455	-4.10565	-1.89838
H	-2.45763	-1.99009	-2.20416
H	-4.85427	-1.80033	-2.86214
H	-4.02850	-3.01865	-3.84294
H	-5.09192	-3.51673	-2.51729
H	-1.60785	-4.12726	-1.16512
H	-3.08858	-4.94155	-1.69145
H	-1.98327	-4.27039	-2.88949
C	-3.47910	0.62498	1.96647
C	-3.16309	0.64032	3.46940
C	-4.68679	1.52849	1.65294

```
H          -2.60584        1.04404        1.46738
H          -2.34885       -0.04674        3.70995
H          -2.85591        1.64516        3.76977
H          -4.03164        0.36994        4.07669
H          -4.86555        1.59458        0.57769
H          -5.59298        1.13907        2.12655
H          -4.51448        2.54136        2.02888
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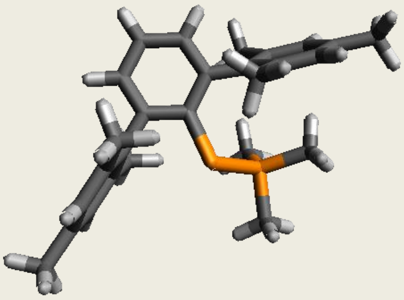
6.5.22 MesTerPPMe3



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63
MesTerPPMe3, C1, B3LYP-D3/6-311G(d,p)
C          -4.75424       -0.32481       -1.31344
C          -5.36475        0.48566       -0.35708
C          -2.86666       -1.76994       -2.15782
C          -3.50574       -0.90982       -1.09285
C          -4.69156        0.70849        0.84532
C           1.82031       -1.31305       -2.42000
C           4.06596       -0.59809       -1.55535
C           2.73866       -0.92915       -1.28820
C          -2.84438       -0.66942        0.12353
C           4.97174       -0.28136       -0.53962
C          -3.44379        0.14247        1.10205
C          -0.28788       -0.69002        0.10134
C           2.28466       -0.93786        0.05106
C          -2.72391        0.42542        2.39641
C           4.51773       -0.32665        0.77606
C          -1.52535       -1.32694        0.39954
C           0.90174       -1.41476        0.37061
C           3.19603       -0.66503        1.09004
C          -1.55860       -2.60678        0.95332
C           2.81304       -0.78380        2.55000
C           0.82888       -2.69349        0.94087
C          -0.38517       -3.29683        1.23414
H          -5.25942       -0.50401       -2.25826
H           4.40774       -0.59807       -2.58641
H          -5.14827        1.34236        1.60030
H           1.04042       -0.55677       -2.55379
H          -1.89932       -1.36085       -2.46358
H          -1.77170        0.92493        2.19149
H           5.20870       -0.10527        1.58473
H           1.74188       -0.66170        2.71126
H          -2.52359       -3.05458        1.16626
H           1.75528       -3.22382        1.13431
H          -0.41666       -4.29138        1.66454
P          -0.50396        0.93750       -0.77550
C           0.19104        3.93335       -0.39655
H          -0.77062        4.03202        0.10591
H           0.86205        4.73709       -0.08570
H           0.03068        3.99522       -1.47409
C           1.12800        2.36189        1.84322
H           1.82124        3.16003        2.12056
H           0.15320        2.54223        2.29657
H           1.51466        1.41025        2.19796
C           2.64381        2.48628       -0.62036
H           3.27087        1.67451       -0.26362
H           2.60838        2.45106       -1.70961
H           3.06328        3.44263       -0.29553
```

```
P            0.92641         2.30320         0.02171
C            6.39027         0.11593        -0.86799
H            6.79630        -0.49574        -1.67799
H            6.43767         1.16052        -1.19514
H            7.04730         0.01114        -0.00174
C           -6.73122         1.08051        -0.60075
H           -6.91931         1.22517        -1.66742
H           -7.51938         0.42429        -0.21465
H           -6.83987         2.04782        -0.10351
H           -2.67936        -2.78332        -1.79184
H           -3.50265        -1.83694        -3.04266
H           -3.31878         1.06595         3.05084
H           -2.48994        -0.49712         2.93526
H            3.35069        -0.05015         3.15649
H            3.07285        -1.77547         2.93471
H            1.31387        -2.25843        -2.20820
H            2.37329        -1.41718        -3.35554
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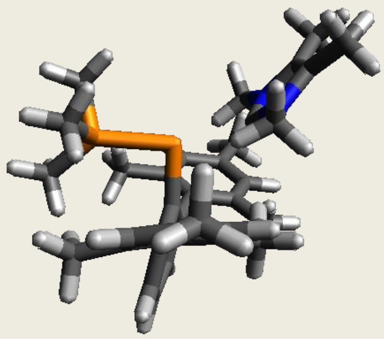
6.5.23 $^{Mes}TerPPMe_3$ – IMe_4 TS



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84
MesTerPPMe3 – IMe4 TS, C1, B3LYP-D3/6-311G(d,p)
C           -0.96449         1.97522         0.10675
C           -3.28759         1.37511         0.77959
C            1.62168        -1.37624        -1.13395
C            0.34143        -1.13140        -0.55811
C            1.81153        -2.42790        -2.03995
C           -0.74219        -1.87815        -1.08372
C            0.75287        -3.22417        -2.45197
C           -0.52229        -2.91536        -2.00160
C           -2.34838         3.69635         0.72091
C           -1.12027         4.23185         0.49072
C            1.14234         3.28850        -0.06162
H           -2.87605         0.37410         0.71478
H            2.80418        -2.59409        -2.44440
H           -1.37830        -3.47637        -2.36189
H            1.59004         2.31030         0.09548
N           -2.22432         2.32509         0.49002
N           -0.29481         3.16469         0.13072
P            0.10453         0.00030         0.95693
C            2.82325        -0.96603         3.06939
C            0.18688        -1.29808         4.00579
C            1.29453        -3.36194         2.34679
H            3.20444        -1.62586         3.85446
H            3.53523        -0.90663         2.25100
H            2.70206         0.04151         3.47292
H           -0.79404        -1.75865         3.88485
H            0.69819        -1.73873         4.86602
H            0.04012        -0.23027         4.17970
H            2.01489        -3.76067         3.06605
H            0.31242        -3.79000         2.54911
H            1.58440        -3.65712         1.33870
P            1.16366        -1.50998         2.45412
H            1.55364         3.98079         0.67511
H            1.38186         3.65216        -1.06297
H           -3.66028         1.53822         1.79376
H           -4.11050         1.47877         0.07186
C           -3.63307         4.33260         1.12896
```

```
H          -4.43420         4.11059         0.41669
H          -3.96628         3.98432         2.11238
H          -3.52345         5.41659         1.18157
C          -0.63999         5.64110         0.56977
H           0.09135         5.78017         1.37325
H          -0.16359         5.95631        -0.36394
H          -1.47409         6.31700         0.76304
H           0.91222        -4.04337        -3.14464
C          -2.19520        -1.60685        -0.81802
C          -2.90608        -2.28839         0.18416
C          -2.89290        -0.79624        -1.73587
C          -4.29112        -2.13117         0.27144
C          -4.28092        -0.68714        -1.63337
C          -4.99962        -1.34054        -0.63315
H          -4.83108        -2.65598         1.05462
H          -4.81259        -0.06663        -2.34954
C           2.80205        -0.46937        -0.95391
C           2.77789         0.77706        -1.61745
C           3.99047        -0.88611        -0.33005
C           3.87639         1.62848        -1.51635
C           5.06573         0.00406        -0.23431
C           5.02049         1.27637        -0.79691
H           3.84550         2.58787        -2.02558
H           5.96797        -0.31775         0.27871
C          -2.18022        -3.16661         1.16728
H          -1.53896        -2.54178         1.79351
C          -2.15403        -0.02638        -2.80345
H          -1.47130         0.68936        -2.33825
C           1.60466         1.15834        -2.48728
H           0.68591         1.25238        -1.90568
C           4.18051        -2.30203         0.16457
H           4.90582        -2.34664         0.98055
C          -6.49496        -1.16952        -0.51134
H          -6.95219        -0.95338        -1.48010
H          -6.96877        -2.06718        -0.10608
H          -6.74280        -0.33934         0.16033
C           6.16994         2.24323        -0.64612
H           6.29696         2.85493        -1.54342
H           5.99929         2.92710         0.19296
H           7.11108         1.72132        -0.45653
H          -2.87531        -3.71444         1.80714
H          -1.53216        -3.88481         0.65864
H          -2.84849         0.52220        -3.44332
H          -1.54933        -0.68418        -3.43264
H           1.79076         2.10331        -3.00231
H           1.42030         0.38816        -3.24155
H           4.56069        -2.93800        -0.64214
H           3.24948        -2.75074         0.50117
```

6.5.24 ^{Mes}TerPIMe$_4$

```
71
MesTerPIMe4, C1, B3LYP-D3/6-311G(d,p)
C           4.33261         2.38694        -1.45496
C           2.15950         0.74179        -2.72655
C           3.01384         2.13813        -0.81080
C          -5.01845        -0.31333        -1.52343
C          -5.64249         0.81154        -0.98643
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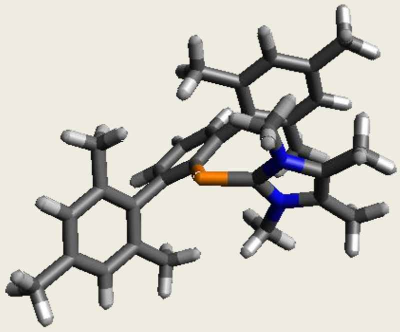

C	2.53423	2.50249	0.40870
C	0.94302	1.23192	-0.60174
C	3.16062	3.32847	1.47907
C	-3.24587	-2.09942	-1.55552
C	-3.88588	-0.87955	-0.93522
C	-5.10896	1.36507	0.17729
C	0.84269	-2.83688	-1.43920
C	3.22518	-2.10055	-1.17632
C	1.92052	-2.09699	-0.68798
C	-3.35229	-0.29569	0.22852
C	4.27053	-1.46088	-0.50539
C	-3.98116	0.82605	0.79636
C	0.28971	2.25134	1.56103
C	-0.83270	-0.66358	0.42784
C	1.63203	-1.41465	0.51702
C	-3.44432	1.44965	2.06137
C	3.98294	-0.85382	0.71203
C	-2.15527	-0.91291	0.88744
C	0.22348	-1.40622	1.03672
C	2.68946	-0.84382	1.24678
C	-2.38803	-1.78646	1.95123
C	2.48861	-0.25733	2.62454
C	-0.04744	-2.25414	2.11651
C	-1.34057	-2.44308	2.58839
H	4.21875	2.83688	-2.44581
H	2.01228	1.47653	-3.52200
H	4.93371	3.06357	-0.84771
H	1.38963	-0.02548	-2.80288
H	4.89364	1.45432	-1.57367
H	3.14373	0.28396	-2.81801
H	-5.42192	-0.76465	-2.42549
H	2.61698	4.26433	1.64528
H	4.18356	3.58590	1.20443
H	3.43414	-2.62278	-2.10625
H	-5.58225	2.23984	0.61435
H	0.13349	-2.13235	-1.88288
H	-3.06710	-2.87853	-0.81022
H	0.75532	2.87595	2.32016
H	3.19717	2.79273	2.43183
H	-0.55932	2.77265	1.11222
H	-0.07841	1.33749	2.02363
H	-2.39836	1.73286	1.93630
H	4.78427	-0.37904	1.27161
H	1.48154	0.12673	2.77065
H	-3.41119	-1.94803	2.27469
H	0.77650	-2.80003	2.56462
H	-1.53176	-3.11259	3.41941
P	-0.63163	0.46466	-1.03119
N	2.02972	1.36382	-1.41914
N	1.26075	1.94396	0.52290
H	2.64517	-1.02302	3.39205
H	3.20605	0.54338	2.81642
H	0.27099	-3.48479	-0.77024
H	1.27104	-3.45002	-2.23484
H	-3.87776	-2.51357	-2.34385
H	-2.27589	-1.85003	-1.99524
H	-3.48302	0.74920	2.90053
H	-4.01217	2.34154	2.33458
C	5.67025	-1.47071	-1.07299
H	6.08893	-2.48235	-1.07615

```
H          5.68501       -1.11675       -2.10905
H          6.34286       -0.83611       -0.49126
C         -6.88348        1.39014       -1.62323
H         -6.89130        1.22550       -2.70355
H         -7.78795        0.92563       -1.21441
H         -6.95905        2.46567       -1.44437
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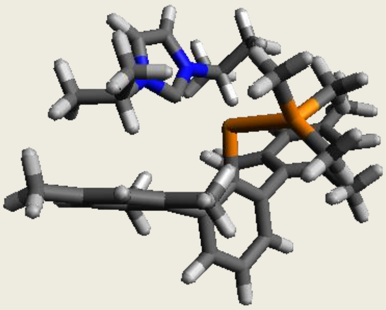
6.5.25 $^{Mes}TerPPMe_3$ – IPr_2 TS



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90
MesTerPPMe3 – IPr2 TS, C1, B3LYP-D3/6-311G(d,p)
C         -0.61398        2.14008       -0.09799
C         -3.03742        1.97048        0.52503
C          1.35354       -1.69560       -1.22162
C          0.12640       -1.24477       -0.66269
C          1.38671       -2.76835       -2.12028
C         -1.05682       -1.84292       -1.16214
C          0.21988       -3.39560       -2.53267
C         -0.99404       -2.90638       -2.07423
C         -1.57030        3.99538        0.82383
C         -0.26103        4.27530        0.62830
C          1.74503        2.98573       -0.17892
H         -2.86485        1.01360        0.04403
H          2.34617       -3.09095       -2.51083
H         -1.92386       -3.34574       -2.41988
H          1.85494        1.96158       -0.51759
N         -1.76841        2.69837        0.37381
N          0.30503        3.14105        0.06748
P          0.05827        0.00758        0.76015
C          2.61497       -0.79584        3.06309
C         -0.07754       -0.64962        3.92088
C          0.92785       -3.14707        3.00986
H          2.90251       -1.24030        4.02033
H          3.35046       -1.03850        2.29987
H          2.59155        0.29089        3.16020
H         -1.08519       -1.06558        3.87849
H          0.37347       -0.87611        4.89100
H         -0.15086        0.43231        3.79757
H          1.19831       -3.27228        4.06286
H         -0.06819       -3.55917        2.84396
H          1.63649       -3.69958        2.39488
P          0.92809       -1.34456        2.53632
H          0.25441       -4.23181       -3.22246
C         -2.45447       -1.39492       -0.85104
C         -3.17237       -1.92569        0.23431
C         -3.11104       -0.57063       -1.78551
C         -4.52273       -1.60636        0.38255
C         -4.47283       -0.30478       -1.62314
C         -5.19545       -0.80562       -0.54160
H         -5.06893       -2.01265        1.22940
H         -4.97471        0.32640       -2.35035
C          2.66523       -1.01039       -0.99731
C          2.93318        0.16288       -1.73393
C          3.68751       -1.59258       -0.23417
C          4.16640        0.79386       -1.58471
C          4.90703       -0.92060       -0.09359
C          5.15733        0.28705       -0.73902
H          4.36731        1.69670       -2.15410
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```
H            5.68261        -1.36407         0.52525
C           -2.48998        -2.82749         1.22736
H           -1.70223        -2.26727         1.73730
C           -2.34704         0.06334        -2.92379
H           -1.54845         0.69897        -2.52828
C            1.91630         0.69357        -2.71793
H            0.96846         0.93454        -2.22982
C            3.53044        -2.96519         0.37809
H            4.03882        -3.03882         1.34296
C           -6.65529        -0.46922        -0.35351
H           -6.78388         0.34201         0.37267
H           -7.11531        -0.14599        -1.29016
H           -7.21776        -1.32855         0.02118
C            6.45719         1.02866        -0.54101
H            6.78546         1.51294        -1.46467
H            6.34961         1.81309         0.21681
H            7.25419         0.35968        -0.20791
H           -3.19248        -3.21122         1.97031
H           -2.00961        -3.67522         0.73063
H           -3.00418         0.67780        -3.54284
H           -1.87211        -0.68517        -3.56273
H            2.28789         1.58902        -3.21919
H            1.69229        -0.05942        -3.47915
H            3.97101        -3.72414        -0.27751
H            2.48292        -3.23117         0.50708
C           -3.33656         1.71445         2.00386
H           -3.49358         2.64975         2.55072
H           -4.23900         1.10529         2.09290
H           -2.50794         1.16839         2.45784
C           -4.17048         2.70788        -0.18899
H           -5.08532         2.11646        -0.13530
H           -4.36957         3.68182         0.26875
H           -3.92588         2.86395        -1.24179
C            2.53710         3.11726         1.12334
H            3.58697         2.87986         0.93517
H            2.48106         4.12906         1.53634
H            2.15261         2.40915         1.85927
C            2.21916         3.95657        -1.26044
H            3.27494         3.78280        -1.47907
H            1.64599         3.82101        -2.17962
H            2.11008         4.99665        -0.93795
H            0.30035         5.17047         0.83259
H           -2.36003         4.60088         1.23301
```

6.5.26 $^{Mes}TerPIPr_2$

```
77
MesTerPIPr2, C1, B3LYP-D3/6-311G(d,p)
C            2.52938         2.84900         0.04242
C           -4.60881        -0.45096        -1.95097
C           -5.41370         0.41477        -1.20915
C            1.79955         2.88030         1.18057
C            0.83002         1.37745        -0.20273
C           -2.66052        -2.00699        -2.24820
C           -3.48496        -1.06568        -1.40153
C           -5.08359         0.63022         0.12611
C            1.51065        -2.77472        -1.68528
C            3.76066        -1.86356        -1.04082
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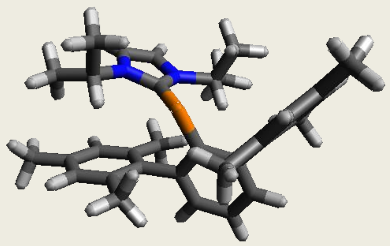

C	2.41065	-2.02214	-0.73804
C	-3.14163	-0.80187	-0.05946
C	4.64143	-1.20049	-0.18007
C	-3.97297	0.02250	0.71893
C	-0.61174	-1.01096	0.24319
C	1.90575	-1.48622	0.46934
C	-3.73262	0.23270	2.19737
C	4.13180	-0.69856	1.01163
C	-1.93150	-1.44277	0.54805
C	0.46900	-1.72358	0.83269
C	2.78255	-0.84565	1.35730
C	-2.14140	-2.50294	1.43539
C	2.32489	-0.34738	2.70737
C	0.21996	-2.75848	1.73972
C	-1.07701	-3.15243	2.04810
H	-4.86265	-0.65239	-2.98798
H	4.14164	-2.27857	-1.96995
H	-5.70836	1.28375	0.72854
H	0.76778	-2.09780	-2.11797
H	-2.37730	-2.90197	-1.68934
H	-2.67304	0.24630	2.44928
H	4.79672	-0.18886	1.70367
H	1.24419	-0.23072	2.74827
H	-3.16029	-2.81155	1.64414
H	1.06490	-3.27848	2.17912
H	-1.25415	-3.96872	2.73952
P	-0.34001	0.30424	-1.04533
N	1.94089	1.92168	-0.79921
N	0.75669	1.97958	1.03372
H	2.60380	-1.05602	3.49496
H	2.79221	0.61133	2.94560
H	0.96167	-3.56399	-1.16497
H	2.08500	-3.22828	-2.49563
H	-3.21421	-2.31547	-3.13747
H	-1.73350	-1.52907	-2.57970
H	-4.17940	-0.57969	2.78042
H	-4.18567	1.16651	2.53790
C	6.10327	-1.06544	-0.53349
H	6.61279	-2.03299	-0.47621
H	6.23379	-0.69273	-1.55403
H	6.61749	-0.37983	0.14396
C	-6.62681	1.06208	-1.83317
H	-6.39748	1.45947	-2.82588
H	-7.44076	0.33871	-1.95307
H	-7.00250	1.88374	-1.21919
C	2.42948	1.53580	-2.13665
C	3.95011	1.64997	-2.22261
C	1.72346	2.35468	-3.22051
H	2.13676	0.48645	-2.23434
H	4.42515	1.14080	-1.38458
H	4.28777	1.17676	-3.14688
H	4.28147	2.69258	-2.24857
H	0.64230	2.21693	-3.16911
H	1.94853	3.41965	-3.10745
H	2.06255	2.03434	-4.20919
C	-0.44609	1.94671	1.89649
C	-1.52789	2.85904	1.30780
C	-0.11709	2.32300	3.34055
H	-0.78935	0.91412	1.87361
H	-1.79825	2.53273	0.30306

```
H          -2.42232          2.82704          1.93247
H          -1.16706          3.89133          1.26974
H           0.71602          1.74225          3.73712
H           0.11642          3.38699          3.43812
H          -0.99476          2.12585          3.95939
H           3.42396          3.38265         -0.21990
H           1.94957          3.45015          2.07890
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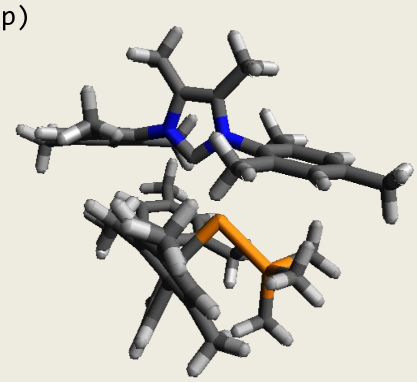
6.5.27 $^{Mes}TerPPMe_3$ – $IMes_2Me_2$ TS



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116
MesTerPPMe3 - IMes2Me2 TS, C1, B3LYP-D3/6-311G(d,p)
C          -0.24033          1.56107         -0.32558
C          -1.04057         -2.75007          0.48400
C           0.01923         -1.86560          0.79908
C          -1.21966         -3.93236          1.22008
C           0.73906         -2.11894          2.00303
C          -0.42640         -4.22567          2.31938
C           0.51545         -3.29236          2.73325
C           0.17779          3.64528         -1.22287
C          -1.05773          3.69418         -0.67216
H          -2.01798         -4.60734          0.92935
H           1.08266         -3.46130          3.64176
N           0.65573          2.34415         -1.00322
N          -1.28428          2.41968         -0.11979
P           0.69914         -0.61868         -0.47961
C           2.68822         -2.35997         -3.01444
C           4.07451         -1.67797         -0.67714
C           2.48469         -4.13784         -0.76499
H           3.63480         -2.84721         -3.26754
H           1.87145         -2.88391         -3.51098
H           2.71211         -1.32904         -3.37130
H           4.08785         -1.45062          0.38521
H           4.88206         -2.37256         -0.92784
H           4.22153         -0.73862         -1.21053
H           3.49730         -4.54444         -0.84013
H           2.09701         -4.29752          0.24173
H           1.83443         -4.67178         -1.45934
P           2.42171         -2.32877         -1.18212
H          -0.57073         -5.14684          2.87366
C           1.66719         -1.11703          2.62228
C           3.02965         -1.37924          2.85303
C           1.10346          0.06955          3.14090
C           3.82830         -0.39235          3.44286
C           1.92623          1.01395          3.75018
C           3.30323          0.82067          3.87689
H           4.88753         -0.59175          3.58065
H           1.48005          1.92510          4.13940
C          -2.13787         -2.48071         -0.51015
C          -3.34962         -1.97675          0.00856
C          -2.08554         -2.89850         -1.85053
C          -4.46981         -1.90422         -0.82053
C          -3.21767         -2.77034         -2.65817
C          -4.42375         -2.28164         -2.16069
H          -5.40391         -1.54115         -0.40459
H          -3.15904         -3.08553         -3.69618
C           3.65795         -2.72497          2.56622
H           3.18313         -3.24015          1.73562
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C	-0.38521	0.30047	3.09670
H	-0.70947	0.57835	2.09288
C	-3.45477	-1.51930	1.44444
H	-2.79503	-0.66780	1.62600
C	-0.82426	-3.48379	-2.42037
H	-0.98196	-3.87730	-3.42703
C	4.18595	1.89771	4.45735
H	4.43190	2.64901	3.69815
H	3.69136	2.42000	5.28097
H	5.12716	1.48836	4.83201
C	-5.63450	-2.13339	-3.04985
H	-5.66618	-1.13708	-3.50690
H	-5.62768	-2.86339	-3.86300
H	-6.56233	-2.26243	-2.48626
H	4.72427	-2.62661	2.34967
H	3.56493	-3.37966	3.43956
H	-0.66829	1.09510	3.78708
H	-0.93354	-0.60314	3.37052
H	-4.47295	-1.20831	1.67997
H	-3.16196	-2.30565	2.14359
H	-0.44225	-4.28890	-1.78742
H	-0.06203	-2.70283	-2.45373
C	-2.56173	2.08459	0.43801
C	-3.50071	1.46766	-0.40224
C	-2.88851	2.50915	1.73049
C	-4.78884	1.27765	0.09127
C	-4.18128	2.25418	2.19610
C	-5.14268	1.64608	1.39128
H	-5.52989	0.81619	-0.55128
H	-4.44292	2.55598	3.20580
C	1.91493	1.94476	-1.57882
C	1.93830	1.57561	-2.93013
C	3.08823	2.08806	-0.83002
C	3.17947	1.34412	-3.52553
C	4.30562	1.85424	-1.46947
C	4.37263	1.48107	-2.81366
H	3.21297	1.05066	-4.57049
H	5.22350	1.95101	-0.89762
C	-3.11297	1.03598	-1.79191
H	-2.66709	1.86283	-2.35306
H	-2.36659	0.23784	-1.74592
H	-3.97705	0.66369	-2.34106
C	-1.91351	3.27877	2.58731
H	-0.87908	3.06423	2.32267
H	-2.06973	4.35683	2.47279
H	-2.05713	3.04284	3.64336
C	-6.52452	1.34919	1.91920
H	-6.58310	0.31740	2.28402
H	-6.78887	2.00664	2.75036
H	-7.28215	1.46214	1.13967
C	5.70048	1.17690	-3.46293
H	5.66223	1.32585	-4.54444
H	6.49691	1.80700	-3.05967
H	5.98705	0.13402	-3.28475
C	3.01816	2.40464	0.63586
H	2.38587	3.27410	0.83676
H	2.57453	1.55568	1.16226
H	4.01028	2.59058	1.05026
C	0.65444	1.39003	-3.69762
H	0.06291	0.59356	-3.23720

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H          0.04016        2.29548       -3.68803
H          0.85496        1.12402       -4.73685
C          0.98215        4.68525       -1.92511
H          1.93535        4.85640       -1.41658
H          1.21743        4.38947       -2.95137
H          0.43644        5.62883       -1.95490
C         -2.07483        4.78361       -0.64115
H         -3.02900        4.43900       -1.04980
H         -2.26921        5.13941        0.37401
H         -1.73597        5.63199       -1.23696
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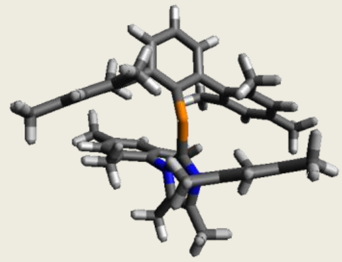
6.5.28 MesTerPIMes2Me2



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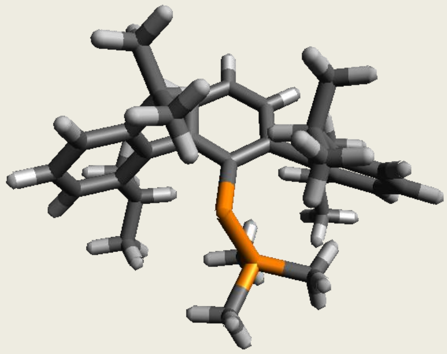
103
MesTerPIMes2Me2, C1, B3LYP-D3/6-311G(d,p)
C         -0.43974       -0.67629        0.93700
C          1.74899        0.35267       -2.43928
C          0.53395        0.61282       -1.75024
C          2.10669        1.11378       -3.55978
C         -0.24059        1.71869       -2.19092
C          1.31367        2.16026       -4.00509
C          0.16020        2.47329       -3.29822
C         -1.30170       -1.50801        2.90331
C         -0.23743       -0.74101        3.22525
H          3.03104        0.87333       -4.07443
H         -0.46238        3.30492       -3.61130
N         -1.44035       -1.45243        1.51127
N          0.27703       -0.21599        2.01757
P         -0.29687       -0.78868       -0.83047
H          1.59406        2.73041       -4.88396
C         -1.49375        2.18949       -1.51718
C         -2.76039        1.68966       -1.87386
C         -1.39460        3.28360       -0.63646
C         -3.89760        2.26280       -1.30101
C         -2.55563        3.81008       -0.06545
C         -3.81784        3.30960       -0.38340
H         -4.87315        1.87329       -1.57763
H         -2.47206        4.64577        0.62384
C          2.76062       -0.66311       -2.00057
C          3.89332       -0.19244       -1.30782
C          2.68350       -2.01651       -2.37475
C          4.88634       -1.09656       -0.92874
C          3.69245       -2.89119       -1.96326
C          4.79352       -2.45532       -1.22706
H          5.75396       -0.72834       -0.38856
H          3.62264       -3.93889       -2.24178
C         -2.90450        0.56296       -2.86434
H         -2.54832       -0.37112       -2.41974
C         -0.05711        3.93805       -0.37413
H          0.71419        3.20685       -0.12404
C          4.05962        1.27936       -1.00957
H          3.18897        1.68247       -0.48820
C          1.55537       -2.52431       -3.23826
H          1.77319       -3.52441       -3.61922
C         -5.05946        3.86397        0.27125
H         -5.27118        3.34269        1.21240
H         -4.94947        4.92564        0.50635
H         -5.93631        3.74788       -0.37053
```

C	5.84581	-3.42727	-0.75076
H	5.59835	-3.81488	0.24446
H	5.93171	-4.28577	-1.42144
H	6.82774	-2.95215	-0.68073
H	-3.94671	0.43356	-3.16335
H	-2.30469	0.74323	-3.76032
H	-0.12717	4.66427	0.43727
H	0.29272	4.46433	-1.26699
H	4.93963	1.45310	-0.38957
H	4.17469	1.85592	-1.93120
H	1.38405	-1.86044	-4.08979
H	0.62077	-2.56453	-2.67163
C	1.49695	0.53020	2.01650
C	2.70750	-0.16561	1.90433
C	1.44260	1.89275	2.33072
C	3.88666	0.55229	2.09660
C	2.65038	2.57655	2.48112
C	3.87825	1.92137	2.37112
H	4.83394	0.02997	2.01306
H	2.62956	3.63757	2.70952
C	-2.61978	-1.89399	0.82327
C	-2.66612	-3.17384	0.26378
C	-3.70770	-1.01379	0.76782
C	-3.83561	-3.55280	-0.39667
C	-4.85327	-1.43229	0.09287
C	-4.93122	-2.69335	-0.50268
H	-3.88771	-4.53934	-0.84690
H	-5.70081	-0.75716	0.02830
C	2.71272	-1.64307	1.61653
H	2.12057	-2.19029	2.35698
H	2.27070	-1.84166	0.63676
H	3.72818	-2.03721	1.61681
C	0.11715	2.56835	2.57680
H	-0.61094	2.32854	1.80142
H	-0.31476	2.24088	3.52784
H	0.23282	3.65141	2.62036
C	5.17316	2.68359	2.50434
H	5.51367	3.03571	1.52406
H	5.05948	3.56032	3.14599
H	5.96548	2.05631	2.91973
C	-6.16232	-3.10570	-1.27282
H	-6.31030	-4.18776	-1.24276
H	-7.06137	-2.62796	-0.87617
H	-6.07357	-2.81563	-2.32540
C	-3.61363	0.34475	1.40881
H	-3.38486	0.26818	2.47598
H	-2.81768	0.93127	0.94508
H	-4.54554	0.89737	1.29454
C	-1.47258	-4.09011	0.34833
H	-0.61378	-3.64209	-0.15967
H	-1.17557	-4.26699	1.38631
H	-1.68548	-5.05515	-0.11436
C	0.42334	-0.48501	4.53577
H	1.45425	-0.85171	4.53884
H	0.46420	0.58089	4.77435
H	-0.12139	-0.99047	5.33349
C	-2.24250	-2.29798	3.74513
H	-3.26873	-1.93232	3.64548
H	-2.24845	-3.35129	3.44985
H	-1.95808	-2.23755	4.79573

6.5.29 DipTerPPMe$_3$



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81
DipTerPPMe3, C1, B3LYP-D3/6-311G(d,p)
C          2.59666          3.23499         -1.22777
C         -1.37502          3.32544         -2.03652
C          4.69476          1.06396         -0.56890
C          5.30915         -0.17212         -0.71530
C          2.77505          2.54679          0.13683
C          3.42081          1.17168         -0.00212
C          4.64862         -1.32694         -0.30743
C          3.55656          3.43832          1.11690
C         -1.44399          2.80170         -0.59571
C         -3.80574          1.98673         -0.89996
C         -2.53207          1.75458         -0.37733
C          2.76389         -0.00265          0.41575
C         -4.87444          1.15050         -0.59861
C          3.37163         -1.26258          0.25088
C          2.76742         -3.66646         -0.33444
C         -1.62628          3.95226          0.41241
C          0.21133          0.10010          0.37500
C         -2.32332          0.61936          0.44549
C          2.65658         -2.53116          0.69489
C         -4.67782          0.06494          0.24160
C          1.43332          0.12242          1.09999
C         -0.97911          0.41819          1.08462
C         -3.41312         -0.22370          0.76958
C         -3.92650         -2.70547          1.08348
C          3.15639         -2.98774          2.07699
C          1.45071          0.36009          2.47521
C         -3.28095         -1.44061          1.68392
C         -0.91873          0.67204          2.46197
C          0.27554          0.62412          3.16690
C         -3.89156         -1.17180          3.07311
H          3.56053          3.45052         -1.69838
H          2.02014          2.60420         -1.90763
H         -1.26756          2.49690         -2.73964
H          2.06499          4.18409         -1.10715
H          5.21073          1.95913         -0.89834
H          6.30078         -0.23869         -1.14997
H         -0.50540          3.97822         -2.15102
H         -2.25947          3.90879         -2.30950
H          4.57110          3.63179          0.75588
H         -3.97311          2.85168         -1.53036
H          5.13579         -2.28747         -0.43048
H          2.45126         -3.32364         -1.32302
H          3.05519          4.40287          1.24263
H         -0.48178          2.34091         -0.38681
H          1.77752          2.40946          0.55747
H         -5.85881          1.35448         -1.00578
H          3.79067         -4.04207         -0.42027
H         -0.82134          4.68595          0.30440
H          3.63506          2.96377          2.09853
H         -2.57973          4.46571          0.25408
H          2.13913         -4.51243         -0.03732
H         -3.62346         -2.86709          0.04853
H          1.59696         -2.28416          0.79293
H         -5.51834         -0.57323          0.48816
H         -1.60912          3.57720          1.43896
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H           4.22442        -3.22366         2.04252
H          -5.01766        -2.64201         1.10001
H          -2.21622        -1.63869         1.82821
H           2.40440         0.36323         2.99125
H          -3.64321        -3.58745         1.66506
H           3.00818        -2.20345         2.82276
H           2.61977        -3.88182         2.41046
H          -1.83204         0.94664         2.97478
H          -4.95887        -0.94802         2.98551
H           0.29326         0.82429         4.23220
H          -3.41390        -0.32675         3.56970
H          -3.78143        -2.04936         3.71748
P           0.43017        -0.09901        -1.46957
C          -0.22357        -2.36865        -3.52620
H           0.75100        -2.80721        -3.31443
H          -0.89760        -3.12887        -3.92746
H          -0.09728        -1.57544        -4.26513
C          -0.96902        -3.06020        -0.80890
H          -1.70258        -3.80711        -1.11948
H           0.02419        -3.50535        -0.77489
H          -1.21898        -2.69215         0.18424
C          -2.66646        -1.34425        -2.47438
H          -3.22955        -0.92110        -1.64740
H          -2.65310        -0.61899        -3.28959
H          -3.14076        -2.26957        -2.81344
P          -0.91671        -1.65481        -1.98442
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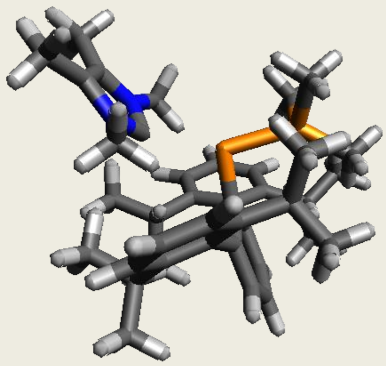
6.5.30 $^{Dip}TerPPMe_3$ – IMe_4 TS



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102
DipTerPPMe3 – IMe4 TS, C1, B3LYP-D3/6-311G(d,p)
C           1.48251         1.94653        -0.52323
C           3.72466         0.89269        -0.67222
C          -1.69661        -0.71465         1.07034
C          -0.43069        -0.85730         0.43153
C          -2.11913        -1.66129         2.01469
C           0.42948        -1.86516         0.94198
C          -1.31793        -2.72837         2.38921
C          -0.03089        -2.79860         1.87961
C           3.17487         3.24195        -1.37272
C           2.03151         3.97291        -1.44972
C          -0.39173         3.51723        -1.03054
H           3.13350        -0.00210        -0.51773
H          -3.07864        -1.52671         2.49501
H           0.65162        -3.56713         2.22490
H          -0.97891         2.70959        -0.60793
N           2.81130         2.01416        -0.81544
N           1.01694         3.16655        -0.92981
P           0.06054         0.13030        -1.12323
C          -2.67119         0.35371        -3.09245
C          -0.51738        -1.09826        -4.17021
C          -2.40853        -2.53453        -2.58453
H          -3.36087         0.00348        -3.86615
H          -3.21888         0.71700        -2.22504
H          -2.08702         1.18916        -3.48342
H           0.10708        -1.98942        -4.14270
H          -1.19546        -1.15165        -5.02672
H           0.13344        -0.22831        -4.27643
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H	-1.68915	-3.35482	-2.54356
H	-3.04062	-2.59418	-1.70055
H	-3.02763	-2.64094	-3.48032
P	-1.45200	-0.94121	-2.58756
H	-0.67229	3.62965	-2.08171
H	-0.59939	4.45318	-0.50754
H	4.31102	0.77176	-1.58480
H	4.40046	1.03460	0.17291
C	4.57636	3.57291	-1.75786
H	5.26295	3.45840	-0.91297
H	4.94036	2.92718	-2.56399
H	4.64323	4.60490	-2.10464
C	1.78378	5.35461	-1.95072
H	1.07537	5.36151	-2.78555
H	1.37039	5.99895	-1.16769
H	2.71263	5.80741	-2.29961
H	-1.67061	-3.45755	3.11007
C	1.90603	-1.95296	0.67583
C	2.43356	-2.70706	-0.39240
C	2.76557	-1.39311	1.64734
C	3.81767	-2.87276	-0.48138
C	4.14381	-1.60337	1.53326
C	4.67017	-2.33175	0.47653
H	4.24018	-3.44546	-1.29798
H	4.81138	-1.18382	2.27804
C	-2.57964	0.49413	0.91348
C	-2.13083	1.72982	1.46048
C	-3.89495	0.39627	0.39672
C	-2.94707	2.85494	1.33748
C	-4.66542	1.56010	0.27812
C	-4.19027	2.78503	0.71693
H	-2.61447	3.80518	1.73477
H	-5.66423	1.49917	-0.13857
C	1.50748	-3.38681	-1.39042
H	0.58805	-2.79752	-1.41140
C	2.23943	-0.57342	2.82328
H	1.16209	-0.46836	2.70601
C	-0.82984	1.82051	2.26653
H	-0.06443	1.26215	1.72686
C	-4.57574	-0.94239	0.09949
H	-3.80453	-1.71338	0.06349
H	5.74147	-2.48395	0.39809
H	-4.80018	3.67636	0.61564
C	-0.28024	3.24057	2.46172
H	-0.14413	3.76901	1.52017
H	-0.92624	3.84357	3.10747
H	0.69756	3.18060	2.94534
C	-1.01740	1.17974	3.65895
H	-1.78325	1.72061	4.22393
H	-1.31648	0.13477	3.59506
H	-0.08217	1.22704	4.22473
C	-5.36437	-1.00331	-1.22047
H	-5.79330	-2.00194	-1.34608
H	-6.19489	-0.29278	-1.22841
H	-4.74302	-0.79830	-2.08816
C	-5.53963	-1.29663	1.25426
H	-6.37723	-0.59316	1.27714
H	-5.94610	-2.30415	1.12272
H	-5.05181	-1.24956	2.22852
C	1.15519	-4.81163	-0.92389

```
H          2.05434      -5.43274      -0.86187
H          0.68256      -4.79868       0.05967
H          0.46241      -5.28748      -1.62603
C          2.06803      -3.40894      -2.81839
H          2.33474      -2.40232      -3.14816
H          2.95331      -4.04577      -2.90174
H          1.32259      -3.81548      -3.50862
C          2.82331       0.84927       2.84632
H          3.91167       0.83998       2.95868
H          2.57196       1.38501       1.92928
H          2.41017       1.41107       3.68940
C          2.48126      -1.29693       4.15881
H          2.02035      -2.28763       4.15422
H          3.55029      -1.42393       4.35479
H          2.05192      -0.72547       4.98739
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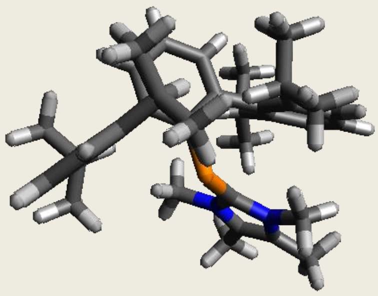
6.5.31 $^{Dip}TerPIMe_4$



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89
DipTerPIMe4, C1, B3LYP-D3/6-311G(d,p)
C         -4.51980      -1.44771      -2.96069
C         -2.36145       0.64204      -2.96085
C          3.08021       2.68468      -2.03598
C         -3.27566      -1.55665      -2.14916
C         -0.61774       4.00045      -1.51895
C          4.86963       0.25715      -1.51122
C          5.30563      -1.05972      -1.56608
C         -2.86304      -2.51463      -1.27499
C         -1.25874      -0.90116      -1.33059
C         -3.47254      -3.82970      -0.92290
C          3.36729       2.09012      -0.64768
C          3.78050       0.62365      -0.71536
C          4.65539      -2.03325      -0.81700
C          4.41985       2.91821       0.11046
C         -0.54019       3.24332      -0.18690
C         -3.02917       2.80179      -0.28540
C         -1.76358       2.38587       0.12874
C          3.11894      -0.37114       0.03541
C         -4.17630       2.11105       0.09410
C          3.56103      -1.70870      -0.01262
C          2.60096      -4.06913       0.02158
C         -0.78508      -2.85667       0.12489
C         -0.28061       4.22792       0.97066
C          0.66222       0.19021       0.47902
C         -1.65165       1.22232       0.93360
C          2.89301      -2.79065       0.82554
C         -4.06801       1.01473       0.93584
C          1.99646       0.03528       0.94823
C         -0.28368       0.77382       1.37240
C         -2.81809       0.56498       1.38053
C         -3.74251      -1.72028       2.06165
C          3.73168      -3.11325       2.07553
C          2.33206       0.34649       2.26678
C         -2.76996      -0.57597       2.39187
C          0.09207       1.06973       2.68759
C          1.38128       0.84129       3.15152
C         -3.06459      -0.06093       3.81521
H         -4.29795      -1.33396      -4.02623
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H          -2.20043        0.42302       -4.01921
H           3.97902        2.71163       -2.65934
H          -5.13290       -2.34074       -2.83989
H          -1.57525        1.30558       -2.60814
H          -5.11958       -0.58516       -2.65263
H          -3.33203        1.11770       -2.81982
H           2.31802        2.10056       -2.55529
H          -0.81482        3.32559       -2.35438
H           2.71699        3.71225       -1.93774
H           5.38805        1.01452       -2.08870
H           6.15367       -1.32739       -2.18736
H           0.33693        4.49507       -1.71453
H          -1.38888        4.77657       -1.51096
H          -2.89958       -4.66088       -1.34771
H          -4.48806       -3.89307       -1.31422
H           5.38325        2.90046       -0.40817
H          -3.12738        3.68535       -0.90424
H           5.00763       -3.05771       -0.85815
H           2.07211       -3.84010       -0.90637
H           4.10063        3.96156        0.19689
H           0.31817        2.57816       -0.25661
H           2.44217        2.15155       -0.07395
H          -5.15174        2.44863       -0.24058
H          -0.95068       -3.92248       -0.02675
H           3.52100       -4.59807       -0.24196
H          -3.52186       -3.98048        0.15796
H           0.62190        4.81578        0.77616
H           0.24566       -2.60266       -0.11714
H           4.57351        2.52380        1.11820
H          -1.12129        4.91927        1.08613
H           1.98844       -4.75825        0.61171
H          -0.97578       -2.60116        1.16808
H          -3.71095       -1.96631        1.00309
H           1.93962       -2.38728        1.17406
H          -4.96770        0.50848        1.26556
H          -0.14099        3.69825        1.91449
H           4.71870       -3.49048        1.79127
H          -4.77459       -1.45391        2.30691
H          -1.75400       -0.97744        2.38909
H           3.35993        0.21464        2.58666
H          -3.49423       -2.61266        2.64380
H           3.87613       -2.22229        2.69039
H           3.23934       -3.87491        2.68874
H          -0.63519        1.53462        3.34163
H          -4.06709        0.37552        3.85814
H           1.64973        1.08515        4.17307
H          -2.35513        0.70453        4.12896
H          -3.01970       -0.88172        4.53799
P           0.36729       -0.11120       -1.32563
N          -2.29025       -0.57402       -2.16625
N          -1.63505       -2.09234       -0.76851
```

6.5.32 Mes*PHC$_3$H$_3$IDip$_2$

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120
Mes*PHC3H3IDip2, C1, B3LYP-D3/6-311G(d,p)
C           4.96878       -0.41814       -0.59541
C           4.87175        0.91728       -0.72052
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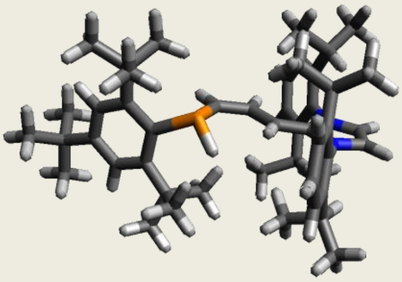
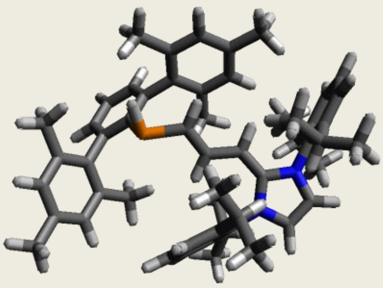


N	3.70469	-0.90550	-0.25412
N	3.54398	1.27772	-0.45096
H	5.60421	1.66239	-0.97473
H	5.80636	-1.08182	-0.71574
C	2.79612	0.14758	-0.14713
C	1.47558	-0.00792	0.19983
H	1.20057	-1.03779	0.38508
C	3.38422	-2.26993	0.03154
C	3.30856	-2.68012	1.37339
C	3.11940	-3.14200	-1.04156
C	2.96546	-4.01101	1.62785
C	2.78309	-4.46211	-0.73479
C	2.70539	-4.89205	0.58641
H	2.89967	-4.35749	2.65272
H	2.57118	-5.16219	-1.53284
H	2.43701	-5.92021	0.80300
C	3.06697	2.62605	-0.43461
C	2.49489	3.15265	-1.60432
C	3.15986	3.36021	0.76044
C	2.01316	4.46320	-1.55671
C	2.65914	4.66436	0.75904
C	2.09263	5.21093	-0.38748
H	1.55944	4.89727	-2.44021
H	2.70148	5.25373	1.66733
H	1.70568	6.22382	-0.36748
C	2.35025	2.31997	-2.86999
C	3.08246	2.96266	-4.06008
C	0.86737	2.06296	-3.19309
H	2.81443	1.34962	-2.68473
H	4.14146	3.11734	-3.83684
H	3.00954	2.31999	-4.94210
H	2.64901	3.93281	-4.31947
H	0.35663	1.59405	-2.35104
H	0.34763	2.99642	-3.42962
H	0.77684	1.39945	-4.05779
C	3.72288	2.74615	2.03503
C	2.59299	2.43509	3.03492
C	4.81052	3.62540	2.67364
H	4.19159	1.79638	1.77048
H	1.84983	1.76696	2.59648
H	3.00074	1.95446	3.92926
H	2.08419	3.35244	3.34615
H	5.61426	3.83940	1.96413
H	4.40707	4.58011	3.02223
H	5.24510	3.11726	3.53903
C	3.13632	-2.64135	-2.48139
C	1.75169	-2.08355	-2.86542
C	3.59909	-3.70075	-3.49210
H	3.84633	-1.81218	-2.53694
H	1.44525	-1.27851	-2.19676
H	1.76554	-1.69433	-3.88823
H	0.99282	-2.87000	-2.81036
H	4.55333	-4.14663	-3.19937
H	2.86792	-4.50658	-3.60223
H	3.72372	-3.24310	-4.47709
C	3.58616	-1.72605	2.52700
C	4.83728	-2.15811	3.31216
C	2.36441	-1.58295	3.45142
H	3.78942	-0.73977	2.10782
H	5.71107	-2.22334	2.65823

H	5.05634	-1.43691	4.10489
H	4.69442	-3.13657	3.77967
H	1.48557	-1.25486	2.89353
H	2.12289	-2.52912	3.94434
H	2.56722	-0.84272	4.23066
C	0.46104	0.99017	0.36937
H	0.73521	2.02799	0.21846
C	-0.83160	0.74230	0.69510
H	-1.52387	1.56807	0.80922
H	-0.94003	-1.60551	-0.01173
P	-1.50463	-0.91509	1.07876
C	-3.26792	-0.67384	0.47637
C	-4.21360	-0.21609	1.44986
C	-3.67324	-0.77803	-0.88845
C	-5.43707	0.28333	0.99775
C	-4.92912	-0.27080	-1.24789
C	-5.80845	0.30537	-0.34229
H	-6.13992	0.67129	1.71603
H	-5.22760	-0.32032	-2.27929
C	-4.01353	-0.27830	3.00113
C	-3.69819	-1.72952	3.43912
H	-2.76580	-2.09523	3.01444
H	-3.61155	-1.77610	4.52946
H	-4.50626	-2.40017	3.13325
C	-5.30085	0.11509	3.76714
H	-5.12191	-0.01519	4.83725
H	-5.57656	1.16156	3.61212
H	-6.15168	-0.51577	3.49782
C	-2.92084	0.69844	3.49856
H	-2.90686	0.70691	4.59327
H	-1.92228	0.42759	3.16390
H	-3.13190	1.71514	3.15487
C	-2.85077	-1.45471	-2.03001
C	-1.60773	-0.61896	-2.41760
H	-0.89897	-0.47689	-1.60951
H	-1.08053	-1.10053	-3.24691
H	-1.92202	0.37426	-2.74969
C	-2.49181	-2.91338	-1.64646
H	-1.89037	-3.36908	-2.43956
H	-1.93424	-3.00495	-0.71872
H	-3.40726	-3.50182	-1.53641
C	-3.66743	-1.59246	-3.34090
H	-4.59450	-2.15267	-3.19549
H	-3.90955	-0.62474	-3.78704
H	-3.06326	-2.13971	-4.06927
C	-7.15907	0.91347	-0.75395
C	-8.30559	0.13550	-0.06877
H	-8.22692	0.17613	1.01995
H	-9.27539	0.55768	-0.35080
H	-8.28973	-0.91638	-0.36665
C	-7.20610	2.39318	-0.30949
H	-8.16080	2.84665	-0.59426
H	-7.09714	2.49342	0.77267
H	-6.40095	2.96331	-0.78084
C	-7.38718	0.86359	-2.27506
H	-6.61141	1.41083	-2.81749
H	-7.40746	-0.16393	-2.64794
H	-8.34957	1.32232	-2.51790

6.5.33 $^{Mes}TerPHC_3H_3IDip_2$



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122
MesTerPHC3H3IDip2, C1, B3LYP-D3/6-311G(d,p)
C          -4.09293        -2.44047        0.78160
C          -3.04648        -3.28423        0.81483
N          -3.60895        -1.17709        0.42763
N          -1.89697        -2.55961        0.47150
H          -2.98782        -4.33158        1.05150
H          -5.13821        -2.60348        0.97322
C          -2.23862        -1.24288        0.18158
C          -1.48334        -0.19315       -0.28504
H          -2.03788         0.71201       -0.49817
C          -4.40935        -0.01803        0.17358
C          -4.60422         0.91109        1.21471
C          -4.93913         0.16832       -1.11328
C          -5.39887         2.02651        0.94475
C          -5.72183         1.30623       -1.33570
C          -5.95662         2.21894       -0.31642
H          -5.57597         2.76255        1.71828
H          -6.14208         1.48206       -2.31906
H          -6.56486         3.09632       -0.50671
C          -0.59998        -3.14262        0.29173
C          -0.19097        -3.49873       -1.00347
C           0.22809        -3.29699        1.41951
C           1.10918        -3.98723       -1.16051
C           1.51601        -3.79208        1.20889
C           1.95743        -4.11963       -0.06975
H           1.46330        -4.25308       -2.14934
H           2.19002        -3.91303        2.04649
H           2.97096        -4.47596       -0.21380
C          -1.10882        -3.35569       -2.20951
C          -1.49546        -4.73882       -2.76372
C          -0.49455        -2.46427       -3.30203
H          -2.02766        -2.87052       -1.87713
H          -1.97469        -5.35293       -1.99650
H          -2.19114        -4.63307       -3.60139
H          -0.61513        -5.27892       -3.12400
H          -0.22244        -1.48599       -2.90302
H           0.40259        -2.91872       -3.73221
H          -1.21397        -2.31899       -4.11314
C          -0.25740        -2.88482        2.80566
C          -0.07434        -1.37044        3.02614
C           0.40300        -3.67741        3.94255
H          -1.33095        -3.08997        2.85132
H          -0.57668        -0.78532        2.25597
H          -0.48129        -1.07613        3.99839
H           0.98577        -1.10431        3.00953
H           0.32822        -4.75570        3.77943
H           1.46100        -3.42273        4.05257
H          -0.08549        -3.44056        4.89135
C          -4.64993        -0.80118       -2.25099
C          -3.71063        -0.16107       -3.28992
C          -5.93931        -1.32380       -2.90614
H          -4.12965        -1.66450       -1.83301
H          -2.76949         0.14410       -2.82923
H          -3.48233        -0.87677       -4.08490
H          -4.17241         0.71800       -3.74936
H          -6.59805        -1.78854       -2.16784
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H	-6.49781	-0.52182	-3.39664
H	-5.69803	-2.07087	-3.66739
C	-3.97171	0.68850	2.58411
C	-4.82518	-0.26801	3.44052
C	-3.71819	1.98824	3.36231
H	-3.00220	0.21121	2.41318
H	-4.94721	-1.24076	2.96371
H	-4.35273	-0.42974	4.41383
H	-5.81890	0.15687	3.61172
H	-3.18593	2.73004	2.76469
H	-4.65263	2.44015	3.70762
H	-3.11480	1.77555	4.24835
C	-0.07840	-0.17025	-0.54596
H	0.52665	-0.99089	-0.17295
C	0.56302	0.82604	-1.20601
H	2.51355	1.73218	-2.40006
H	-0.01039	1.64712	-1.62156
P	2.36716	0.80325	-1.33087
C	3.02043	1.96063	0.01040
C	4.27875	1.61810	0.54994
C	2.35688	3.10359	0.51312
C	4.86449	2.41939	1.53704
C	2.96391	3.88275	1.50237
C	4.21544	3.55188	2.01040
H	5.83350	2.13558	1.93366
H	2.43767	4.75695	1.87122
C	5.02221	0.38871	0.12056
C	4.76741	-0.83514	0.76152
C	5.99524	0.46539	-0.88998
C	5.48661	-1.96691	0.37539
C	6.69396	-0.68811	-1.24847
C	6.45186	-1.91536	-0.62999
H	5.28597	-2.91207	0.87220
H	7.44364	-0.62791	-2.03237
C	0.99417	3.50652	0.04615
C	0.83867	4.28143	-1.11254
C	-0.13585	3.07331	0.76522
C	-0.45170	4.56224	-1.57179
C	-1.40552	3.37397	0.27539
C	-1.58524	4.10441	-0.90111
H	-0.57131	5.14413	-2.48122
H	-2.27835	2.99585	0.79681
H	4.67545	4.16758	2.77567
C	0.02701	2.22984	2.00378
H	0.58442	1.31987	1.76997
H	0.58747	2.75959	2.77899
H	-0.93977	1.93712	2.41344
C	-2.97511	4.39571	-1.41378
H	-3.62210	3.52000	-1.31988
H	-3.44303	5.20559	-0.84294
H	-2.95827	4.69798	-2.46348
C	2.04472	4.79541	-1.86211
H	1.74706	5.36502	-2.74456
H	2.65479	5.44339	-1.22591
H	2.69197	3.97637	-2.18665
C	3.69393	-0.93947	1.81533
H	3.77515	-0.14349	2.55940
H	2.70379	-0.85082	1.35684
H	3.73604	-1.90204	2.32799
C	6.26291	1.77336	-1.59612

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H          7.04878          1.66403         -2.34592
H          5.36160          2.13740         -2.09877
H          6.56467          2.55408         -0.89248
C          7.19177         -3.15884         -1.06211
H          6.69770         -3.62934         -1.91956
H          8.21727         -2.92973         -1.36322
H          7.23236         -3.89949         -0.25955
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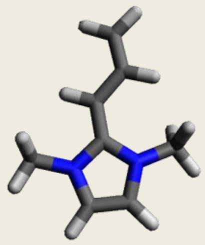
6.5.34 $C_3H_4IMe_2$



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22
C3H4IMe2, C1, B3LYP-D3/6-311G(d,p)
C         -2.40717         -0.08924         -0.02262
C         -1.98342          1.18669         -0.04875
N         -1.28213         -0.90861          0.01096
N         -0.58561          1.17926         -0.03274
H         -2.53912          2.10728         -0.08131
H         -3.40319         -0.49591         -0.03063
C         -0.12303         -0.13418          0.00553
C          1.15136         -0.65094          0.03950
H          1.20781         -1.72801          0.14779
C          2.41388          0.02893         -0.07656
H          2.40209          1.09858         -0.25737
C          3.62696         -0.55418         -0.00501
H          3.73758         -1.62073          0.16610
C          0.22560          2.37209          0.08512
H          0.89886          2.29600          0.94297
H          0.82081          2.54671         -0.81568
H         -0.43407          3.22698          0.23499
C         -1.28473         -2.35191          0.01174
H         -0.72649         -2.73990         -0.84693
H         -0.82897         -2.74725          0.92600
H         -2.31420         -2.70411         -0.04734
H          4.53638          0.02223         -0.11980
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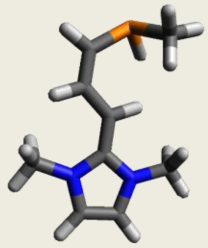
6.5.35 $MePHC_3H_3IMe_2$ *cis*



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27
MePHC3H3IMe2, C1, B3LYP-D3/6-311G(d,p)
C         -3.22670          1.03830          0.00641
C         -3.43517         -0.28583         -0.11140
N         -1.85355          1.24218          0.09142
N         -2.19090         -0.92029         -0.09952
H         -4.34933         -0.84481         -0.20604
H         -3.92375          1.85730          0.03294
C         -1.18393          0.02674          0.02574
C          0.19100         -0.09600          0.09066
H          0.71295          0.82679          0.30155
C          0.99592         -1.26092         -0.09354
H          0.48905         -2.17809         -0.37767
C          2.34893         -1.35905          0.02656
H          2.79960         -2.32915         -0.15645
H          2.69543          0.69733          1.37703
P          3.53651         -0.06089          0.50594
C         -1.19121          2.52325          0.19709
H         -0.49748          2.66747         -0.63685
H         -1.94258          3.31171          0.17391
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H          -0.62854          2.59841          1.13306
C          -2.02077         -2.35936         -0.07526
H          -1.56453         -2.72621         -0.99858
H          -1.39598         -2.65515          0.77066
H          -3.00145         -2.82184          0.03577
C           3.44390          1.13177         -0.94376
H           4.01168          0.71100         -1.77596
H           2.41998          1.30969         -1.27785
H           3.90653          2.08219         -0.66304
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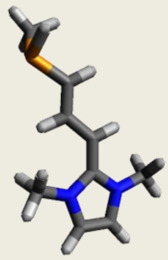
6.5.36 $MePHC_3H_3IMe_2$ *trans*



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27
      Energy: -503861.2583339
C           3.75864         -0.11615          0.22156
C           3.33242          1.15900          0.27003
N           2.64437         -0.92506          0.01969
N           1.94657          1.15767          0.09669
H           3.87903          2.07449          0.41210
H           4.74797         -0.52812          0.31541
C           1.49620         -0.14654         -0.05897
C           0.22805         -0.65561         -0.26013
H           0.18430         -1.71931         -0.46198
C          -1.02545          0.02755         -0.20212
H          -1.02374          1.07745          0.07289
C          -2.24502         -0.52404         -0.43348
H          -4.43982          0.05060         -1.45472
H          -2.31315         -1.57720         -0.70508
P          -3.76061          0.45548         -0.26396
C           1.15144          2.36151         -0.04859
H           0.55098          2.31323         -0.95978
H           0.48615          2.51241          0.80549
H           1.82590          3.21481         -0.11918
C           2.64710         -2.36884         -0.04892
H           1.98703         -2.79078          0.71549
H           2.30912         -2.71765         -1.03003
H           3.66137         -2.72845          0.12104
C          -4.78019         -0.60663          0.89560
H          -5.81417         -0.25073          0.90319
H          -4.77071         -1.66247          0.61428
H          -4.37675         -0.51019          1.90579
```

7 References

[1] B. Buster, A. A. Diaz, T. Graham, R. Khan, M. A. Khan, D. R. Powell, R. J. Wehmschulte, Inorg. Chim. Acta **2009**, *362*, 3465.

[2] K. Powers, C. Hering-Junghans, R. McDonald, M. J. Ferguson, E. Rivard, *Polyhedron* **2016**, *108*, 8.

[3] C. E. I. Knappke, J. M. Neudörfl, A. Jacobi von Wangelin, *Org. Biomol. Chem.* **2010**, *8*, 1695.

[4] T. Schaub, U. Radius, *Chem. – Eur. J.* **2005**, *11*, 5024.

[5] N. Kuhn, T. Kratz, *Synthesis* **1993**, *6*, 561.

[6] X. Bantreil, S. P. Nolan, *Nat. Protoc.* **2011**, *6*, 69.

[7] S. Urban, M. Tursky, R. Fröhlich, F. Glorius, *Dalton Trans.* **2009**, *35*, 6934.

[8] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.

[9] a) J. Bresien, C. Hering, A. Schulz, A. Villinger, *Chem. Eur. J.* **2014**, *20*, 12607; b) C. M. E. Graham, T. E. Pritchard, P. D. Boyle, J. Valjus, H. M. Tuononen, P. J. Ragogna, *Angew. Chem. Int. Ed.* **2017**, 56, 6236; c) J.-E. Siewert, A. Schumann, M. Fischer, C. Schmidt, T. Täufer, C. Hering-Junghans, *Dalton Trans.* **2020**, *49*, 12354.

[10] P. Wucher, J. B. Schwaderer, S. Mecking, *ACS Catalysis* **2014**, *4*, 2672.

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

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

[13] G. M. Sheldrick, *SADABS Version 2*, University of Göttingen, Germany, **2004**.

[14] A. L. Spek, *Acta Cryst. C* **2015**, *71*, 9.

[15] M. Duncan, M. J. Gallagher, *Org. Mag. Res.* **1981**, *15*, 37.

[16] S. O. Grim, R. P. Molenda, J. D. Mitchell, *J. Org. Chem.* **1980**, *45*, 250.

[17] H. Schmidbaur, C. M. Frazão, G. Reber, G. Müller, *Chem. Ber.* 1989, *122*, 259.

[18] *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, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

[19] a) E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, **2013**; b) J. E. Carpenter, F. Weinhold, *J. Mol. Struct.: THEOCHEM* **1988**, *169*, 41–62; c) F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum Press, **1988**; d) F. Weinhold, C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005**.

[20] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648

[21] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[22] V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378

[23] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580.

[24] a) F. London, *J. Phys. Radium* **1937**, *8*, 397; b) R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028; c) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789; d) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251; e) J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497.

[25] C. J. Jameson, A. De Dios, A. Keith Jameson, *Chem. Phys. Lett.* **1990**, *167*, 575.

[26] C. van Wüllen, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2137.