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Supplementary Material for

Crystalline phosphino(silyl)carbenes that readily form transition metal complexes

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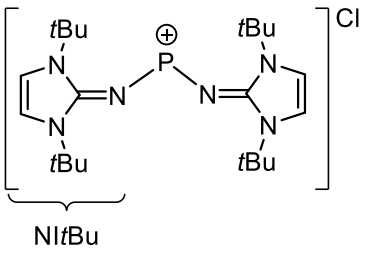
1 Experimental procedures

1.1 Synthetic Details

General remarks: All manipulations, if not stated differently, were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. All glassware was oven-dried at 160 °C prior to use. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 300 K on Agilent DD2 600, Bruker AVANCE I 400, Bruker AVANCE III 400 or Bruker AVANCE II 200 spectrometers. Chemical shifts are given in parts per million (ppm) relative to $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P) and they were referenced to the residual solvent signals (CD_3CN: ^{1}H δ_H = 1.94 ppm, ^{13}C δ_C = 118.26 ppm; C_6D_6: ^{1}H δ_H = 7.16 ppm, ^{13}C δ_C = 128.0 ppm; THF-d_8: ^{1}H δ_H = 3.58 ppm, ^{13}C δ_C = 67.21 ppm) or internally by the instrument after locking and shimming to the deuterated solvent (^{31}P). Chemical shifts (δ) are reported in ppm. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, p = pentet, sept = septet, m = multiplet, br = broad signal. Mass spectrometry was recorded using an Orbitrap LTQ XL (Thermo Scientific) spectrometer. HepatoChem EvoluChem™ LED 365PF (365 nm) was used for the irradiation experiments. Melting points were measured in glass capillaries sealed under argon gas by using a Stuart Melting Point Apparatus SMP3.

Reagents and Handling: All compounds were purchased from commercial sources (Sigma Aldrich, Alfa Aesar, Tokyo Chemical Industry) and used as received, if not stated differently. Au(tht)Cl[1] (tht = tetrahydrothiophene), CuO*t*Bu[2], NI*t*Bu(SiMe$_3$) (1,3-di-(*tert*-butyl)-N-(trimethylsilyl)-imidazol-2-imine)[3] and **1a**[4] were synthesized via literature procedures.

Preparation of 1b



NI*t*Bu(SiMe$_3$) (1,3-di-(*tert*-butyl)-N-(trimethylsilyl)-imidazol-2-imine) (15.1 mmol, 4.04 g, 2.00 eq) was dissolved in tetrahydrofuran (50 mL). At 21 °C, PCl_3 (7.5 mmol, 0.66 mL, 1.00 eq) was added to the stirred mixture. Immediately upon addition, a yellow precipitate formed. The mixture was further stirred for 16 h at 21 °C. Afterwards, the precipitate was isolated by filtration of the mixture. The product is recrystallized out of hot acetonitrile. The crystals were isolated by pipetting off the mother liquor and dried *in vacuo* ($1 \cdot 10^{-3}$ mbar) at 85 °C for 16 h. **1b** was obtained as a yellow crystalline solid.

Yield: 3.43 g (6.25 mmol, 83%).

^{1}H NMR (400 MHz, CD_3CN): δ = 7.09 (s, 4H, N-CH=CH-N), 1.64 (s, 36H, *t*Bu).

^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ = 146.1 (d, $^2J_{CP}$ = 25 Hz, C=N-P), 114.3 (N-CH=CH-N), 59.5 ($\underline{C}Me_3$), 30.1 ($C(\underline{C}H_3)_3$), 30.0 ($C(\underline{C}H_3)_3$).

^{31}P NMR (162 MHz, CD_3CN): δ = 296.8.

^{35}Cl NMR (39 MHz, CD_3CN): δ = 44.4.

HR-MS (ESI): Calculated for $[C_{22}H_{42}N_6O_2P]^+$ ([**1b**–Cl+H_2O]$^+$): m/z = 437.31522, found: m/z = 437.31534.

Single crystal X-ray diffraction analysis: Single crystals suitable for X-ray diffraction analysis were obtained (*vide supra*). The structure of **1b** was confirmed.

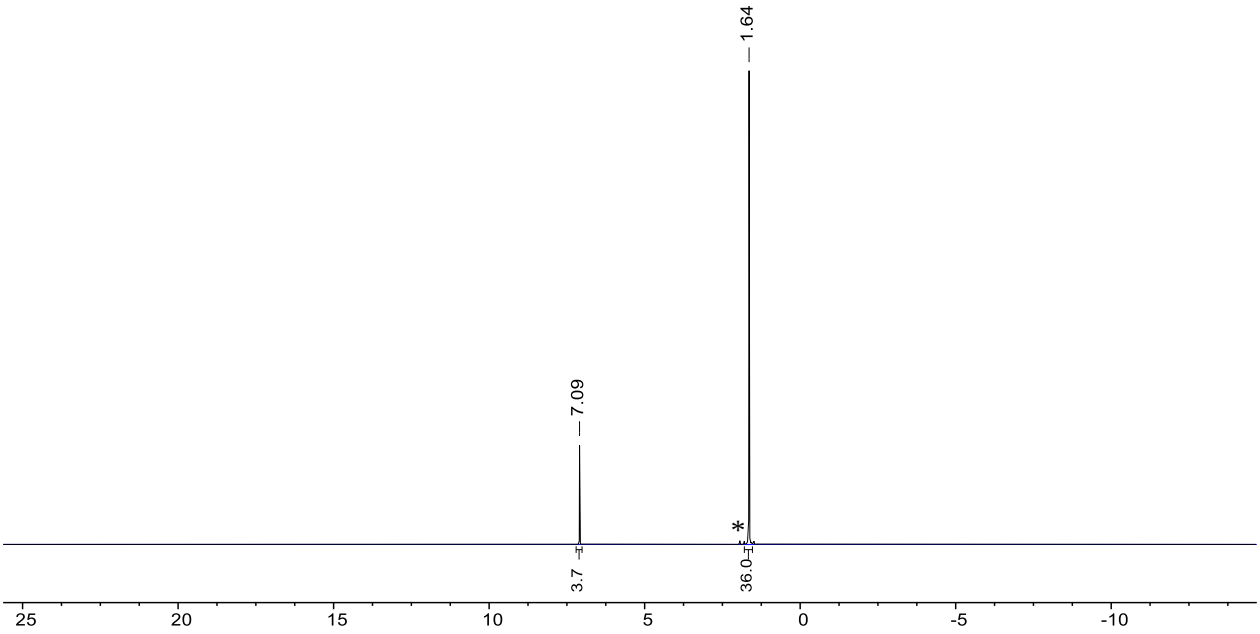


Figure S 1: ^{1}H NMR (400 MHz, 300K) spectrum of **1b** in CD_3CN. The asterisk (*) marks the solvent signal (too weak to be seen at the given amplification level).

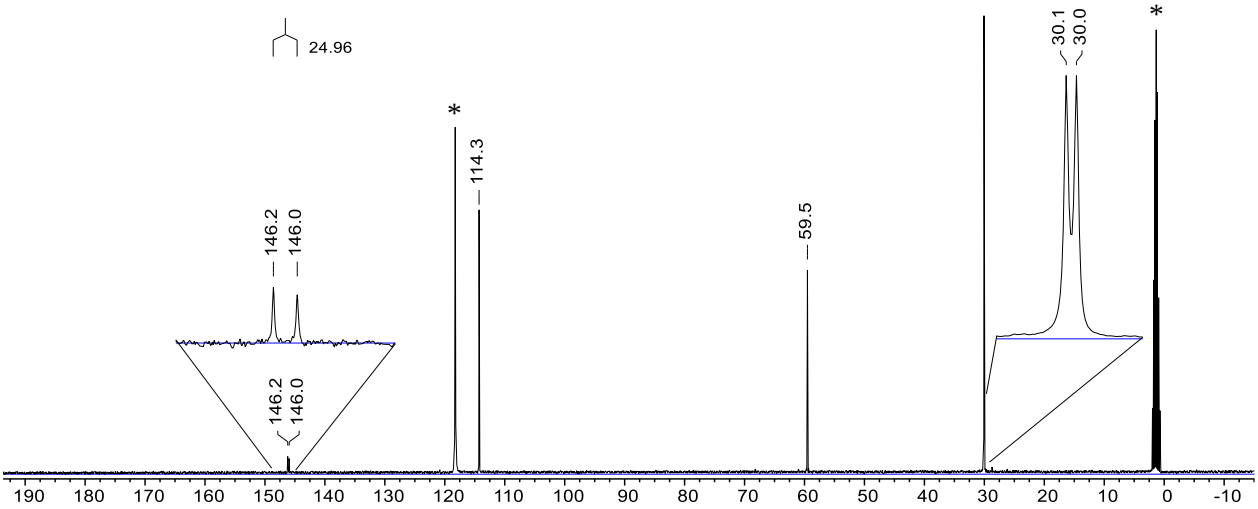


Figure S 2: $^{13}C\{^{1}H\}$ NMR (101 MHz, 300K) spectrum of **1b** in CD_3CN. The asterisks (*) mark the solvent signals.

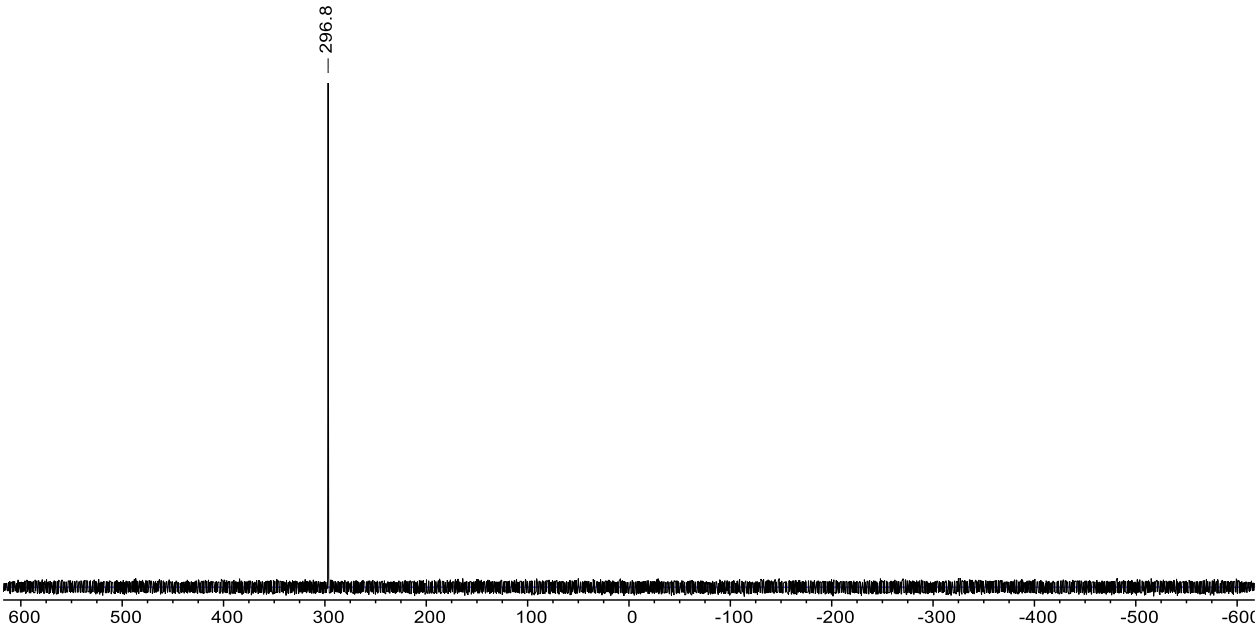


Figure S 3: ^{31}P NMR (162 MHz, 300K) spectrum of **1b** in CD_3CN.

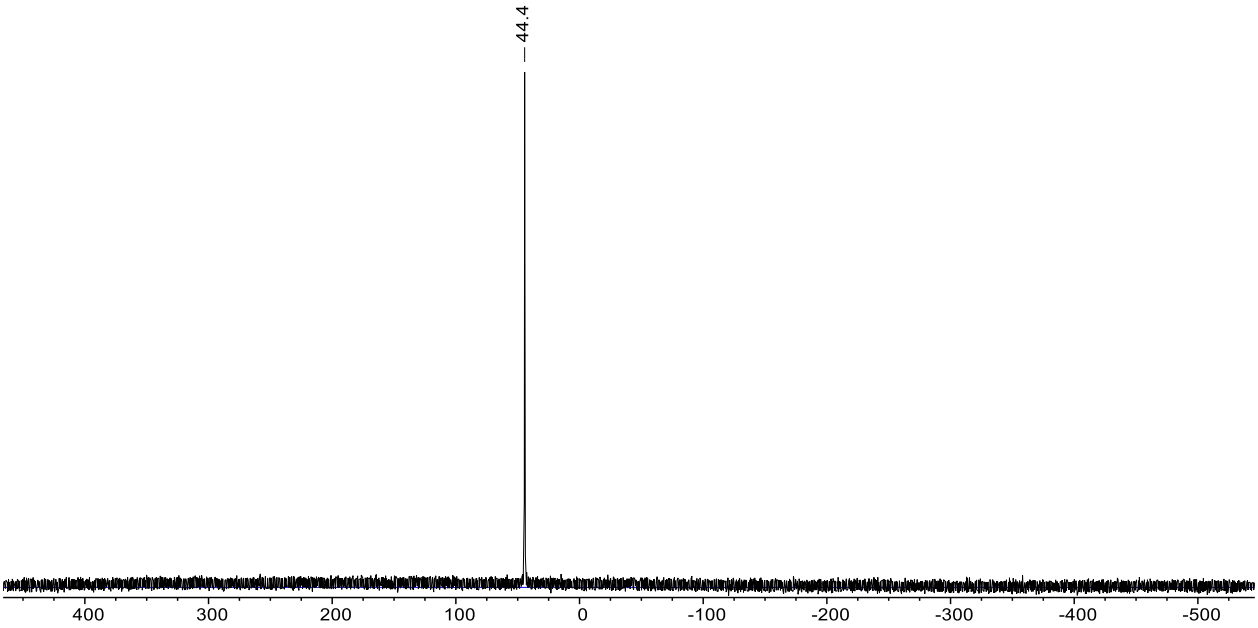


Figure S 4: ^{35}Cl NMR (39 MHz, 300K) spectrum of **1b** in CD_3CN.

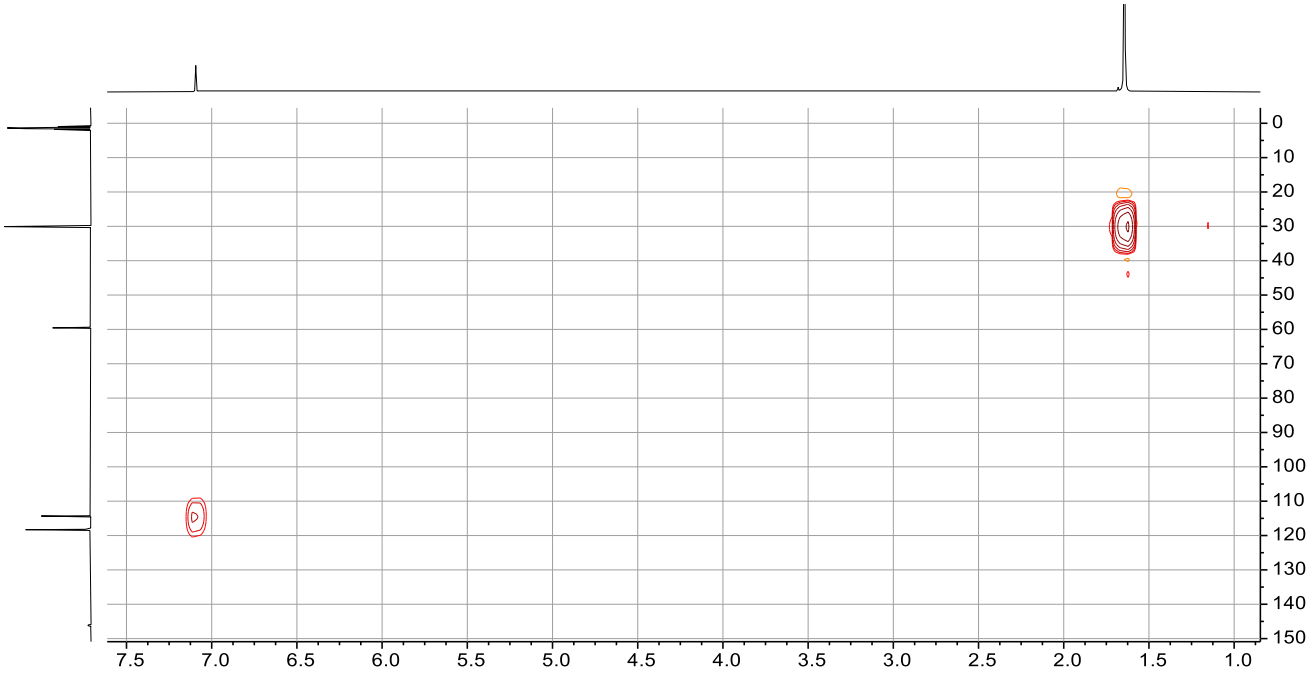


Figure S 5: ^{1}H/^{31}C{^{1}H} HSQC NMR spectrum of **1b** in CD_3CN.

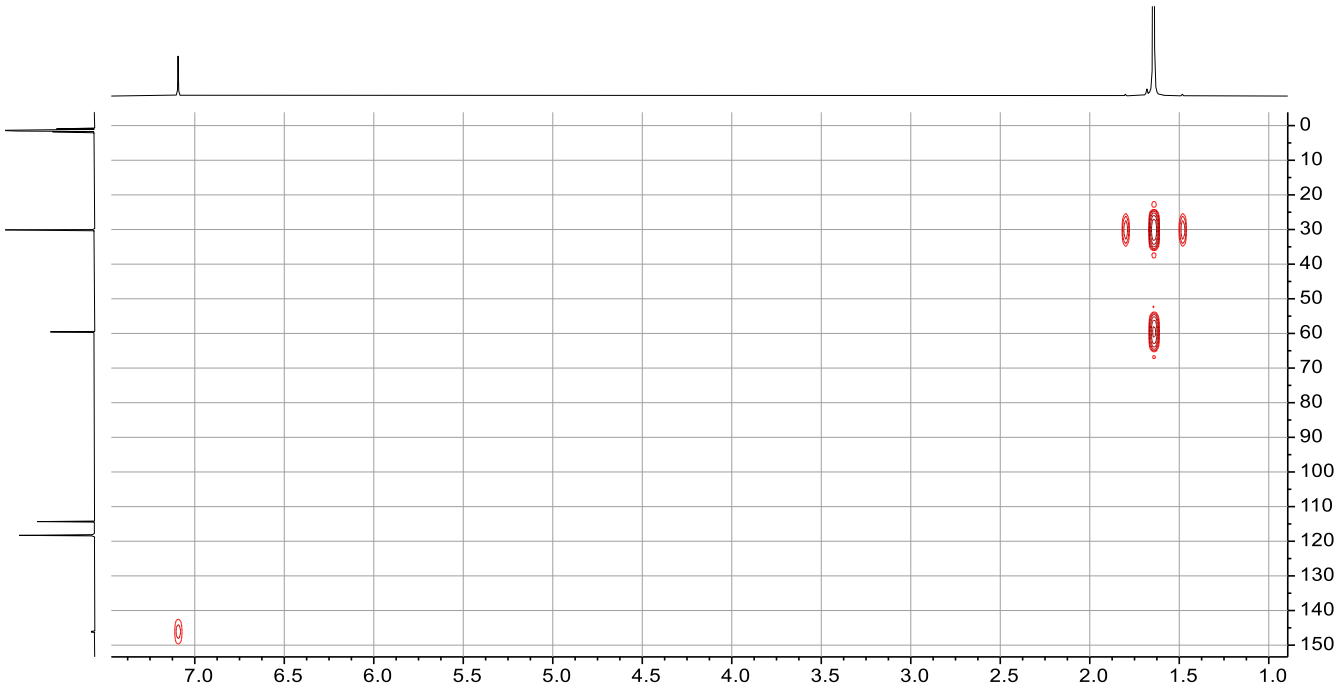
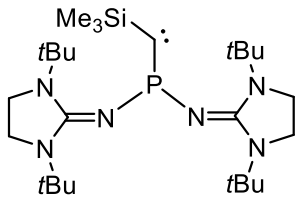


Figure S 6: $^{1}H/^{31}C\{^{1}H\}$ HMBC NMR spectrum of **1b** in CD_3CN.

1.2 **Preparation of 3a**



Note: Until the irradiation step, this reaction was performed in the dark.

Trimethylsilyldiazomethane (0.826 mL, 2.0 M in hexanes, 1.65 mmol, 1.00 eq.) was dissolved in THF (20 mL) and filled into a Schlenk tube. The solution was cooled to -78 °C using a dry ice/acetone bath and n-butyllithium (1.03 mL, 1.6 M in hexanes, 1.65 mmol, 1.00 eq.) was added to the solution. The mixture was stirred at -78 °C for 30 min and subsequently transferred (via a PTFE cannula) into a separate Schlenk flask containing a stirred suspension of **1a** (758 mg, 1.65 mmol, 1.00 eq.) in THF (30 mL), also cooled to -78 °C. The mixture was stirred for 80 min at -78 °C, then warmed to 0°C via an ice/water bath. While keeping the mixture cold, all volatiles were removed *in vacuo* and, subsequently, ice-cold n-hexane was added to the residue. The mixture was stirred for 5 minutes and then filtered into another Schlenk flask (via a PTFE cannula plucked with a glass filter). An orange solution was obtained (Figure S 7, left). The solution was irradiated with UV light (365 nm) for 3 h. Yellow crystals formed at the bottom of the Schlenk flask (Figure S 7, right). The mother liquor was pipetted off, the crystals washed four times with n-hexane (1.5 mL) and dried *in vacuo* at room temperature (Figure S 8).

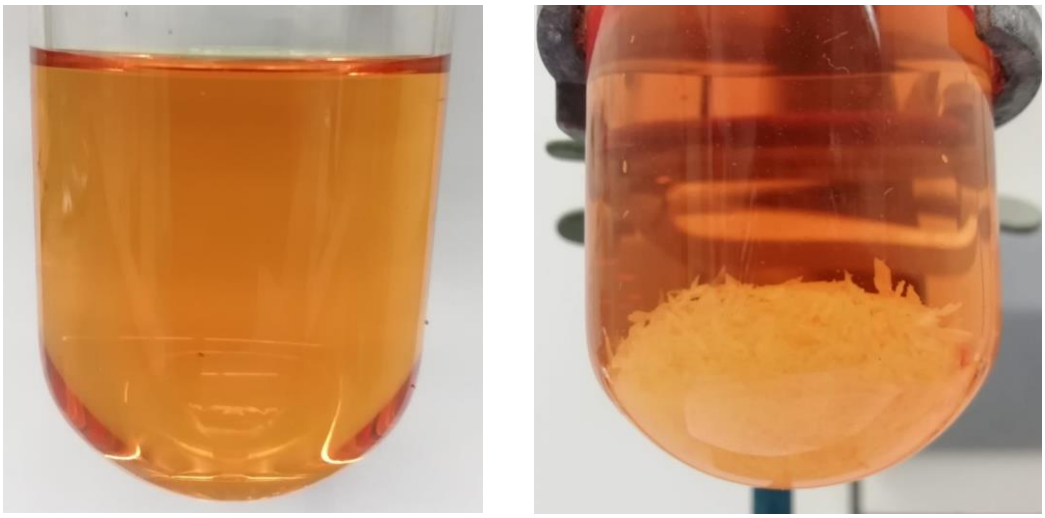


Figure S 7: *n*-Hexane solution before (left) and after irradiation (right).

Figure S 8: Isolated crystals of **3a**.

Yield: 218 mg (0.427 mmol, 26%).

Note: The NMR signals were assigned using 2D NMR experiments (*vide infra*).

^{1}H NMR (400 MHz, C_6D_6): δ = 2.76 (s, 8 H, N-CH_2-CH_2-N), 1.55 (s, 36 H, *t*Bu), 0.56 (d, $^{4}J_{HP}$ = 1.2 Hz, 9 H, $SiMe_3$),.

^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 153.1 (d, $^{2}J_{CP}$ = 16 Hz, C=N-P), 75.1 (d, $^{1}J_{CP}$ = 49 Hz, P-C), 54.7 ($\underline{C}Me_3$), 42.0 (N-CH_2-CH_2-N), 29.2 ($C(\underline{C}H_3)_3$), 5.6 (d, $^{3}J_{CP}$ = 14 Hz, $SiMe_3$).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6): δ = -21.4 (d, $^{2}J_{SiP}$ = 41 Hz).

^{31}P NMR (202 MHz, C_6D_6): δ = -7.3.

HR-MS (ESI): Calculated for $[C_{23}H_{46}N_6O_2P]^+$ ([**3a**+H+O+OH−$SiMe_3$]$^+$): m/z = 469.34144, found: m/z = 469.37502; calculated for $[C_{23}H_{46}N_6O_2P]^+$ ([**3a**+H+O_2]$^+$): m/z = 541.3810, found: m/z = 541.41399.

Elemental analysis: Calculated for $C_{26}H_{53}N_6PSi$ (**3a**): C 61.38 %, H 10.50 %, N 16.52 %, found: C 61.14 %, H 10.48 %, N 16.61 %.

Melting point: 172°C (decomposition).

Single crystal X-ray diffraction analysis: Single crystals suitable for X-ray diffraction analysis were obtained during the synthesis (*vide supra*). The structure of **3a** was confirmed.

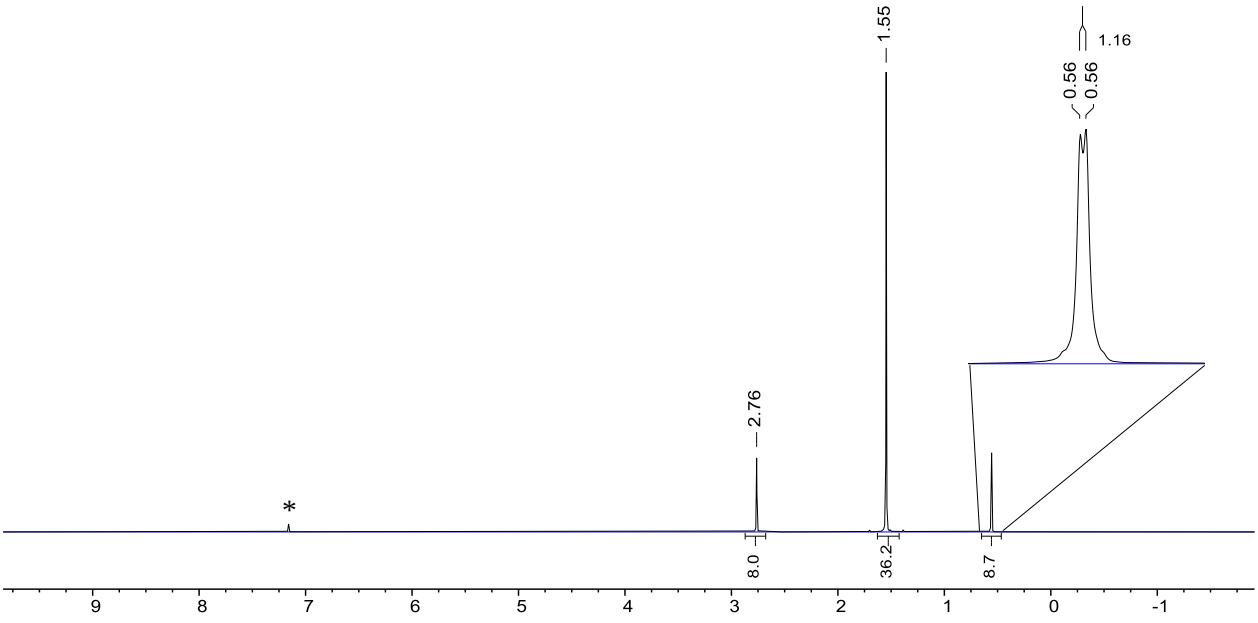


Figure S 9: ^{1}H NMR (400 MHz, 300K) spectrum of **3a** in C_6D_6. The asterisk (*) marks the solvent signal.

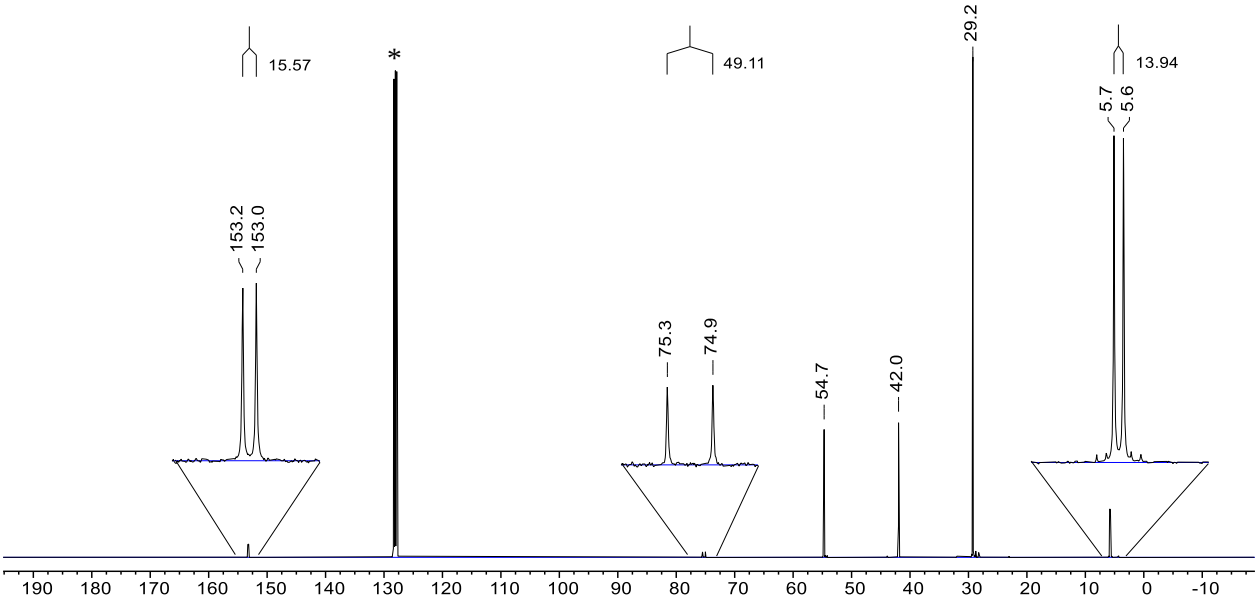


Figure S 10: $^{13}C\{^{1}H\}$ NMR (101 MHz, 300K) spectrum of **3a** in C_6D_6. The asterisk (*) marks the solvent signal.

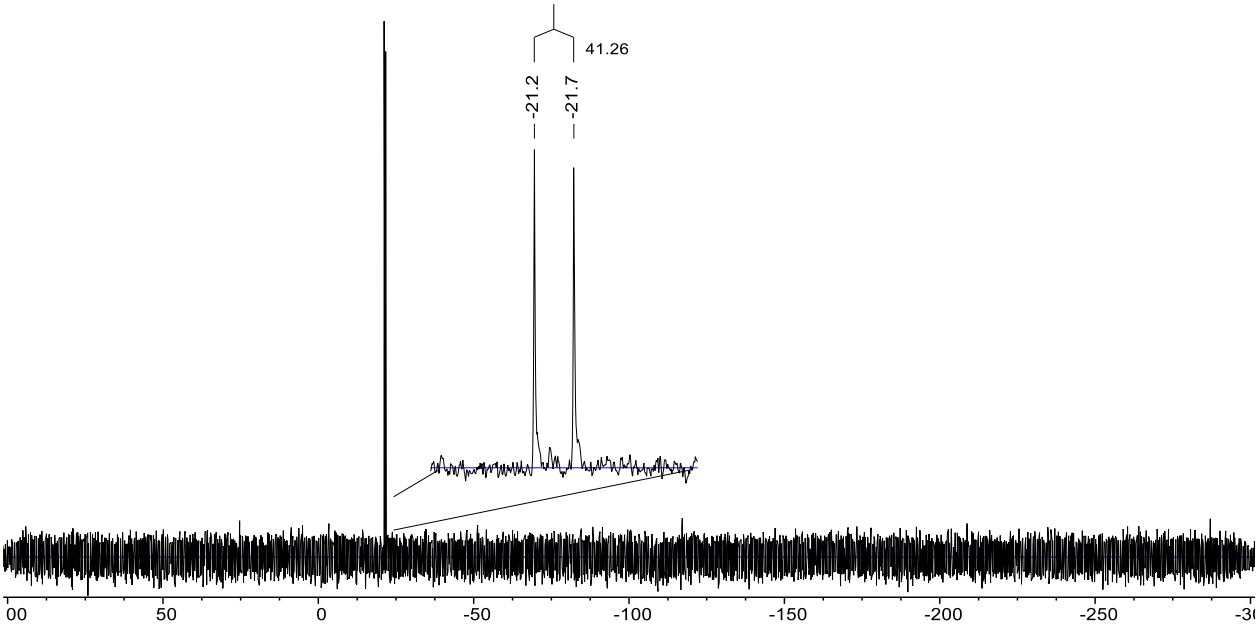


Figure S 11: $^{29}Si\{^{1}H\}$ NMR (80 MHz, 300K) spectrum of **3a** in C_6D_6.

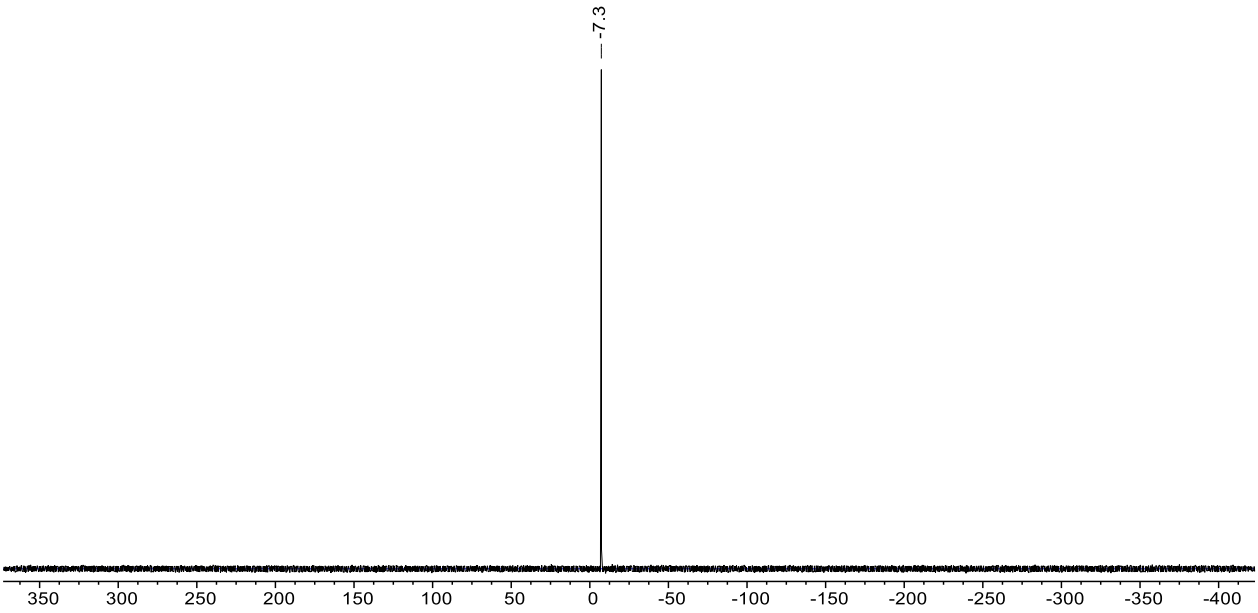


Figure S 12: ^{31}P NMR (202 MHz, 300K) spectrum of **3a** in C_6D_6.

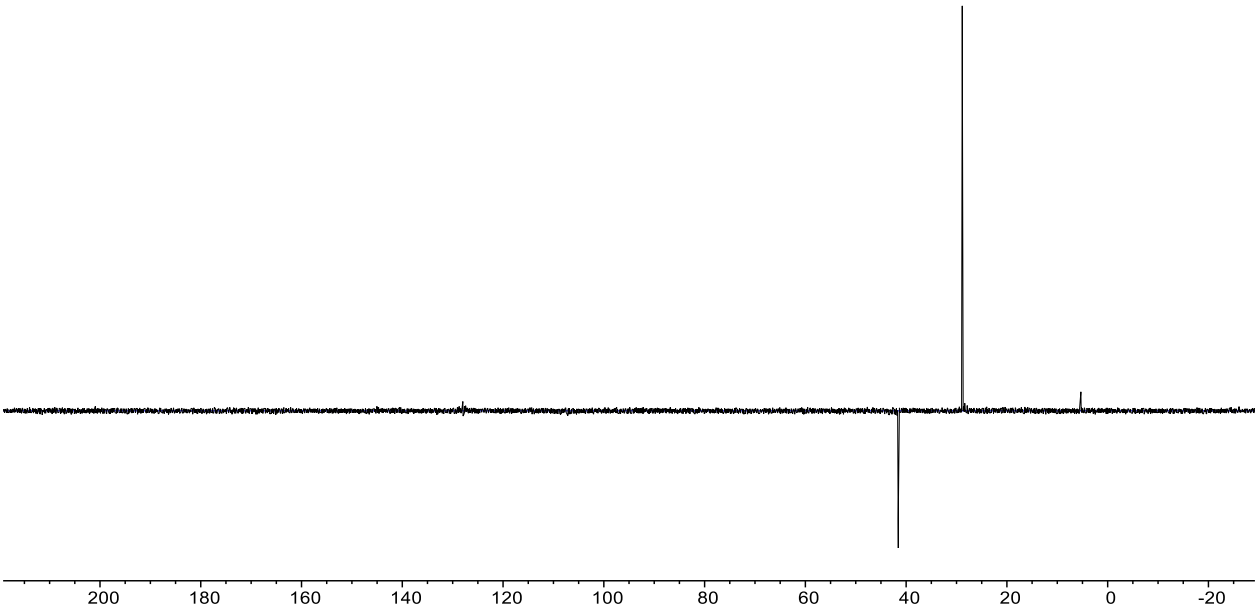


Figure S 13: $^{13}C\{^1H\}$ DEPT 135 NMR (101 MHz, 300K) spectrum of **3a** in C_6D_6.

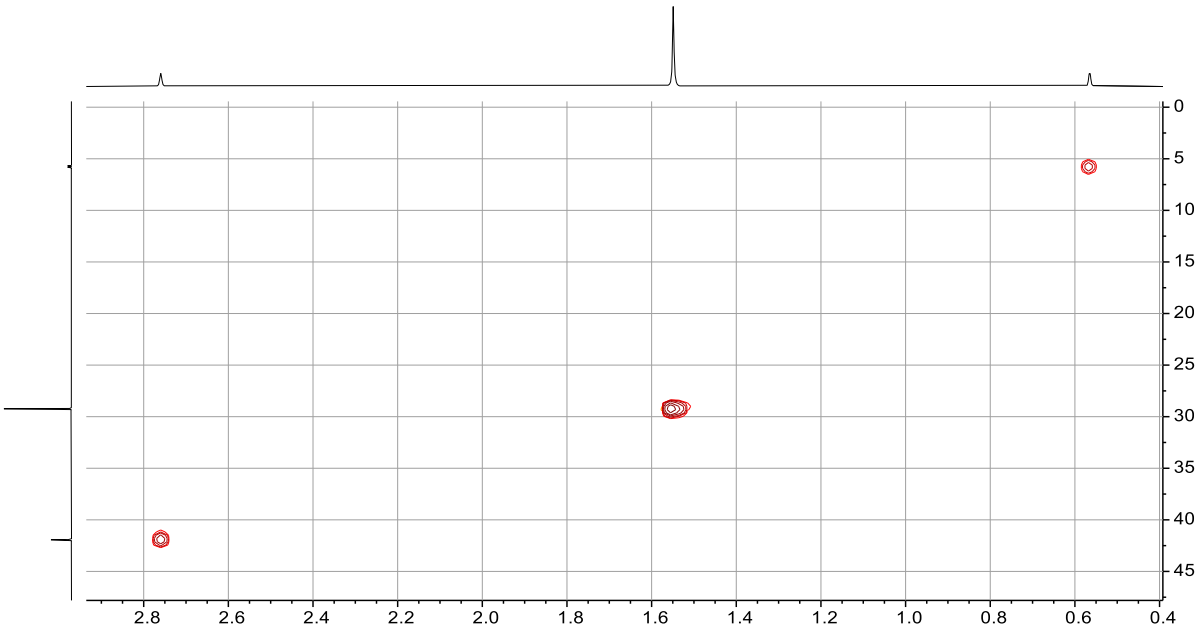


Figure S 14: $^{1}H/^{31}C\{^{1}H\}$ HSQC NMR spectrum of **3a** in C_6D_6 (excerpt). No spots are present outside of the shown area.

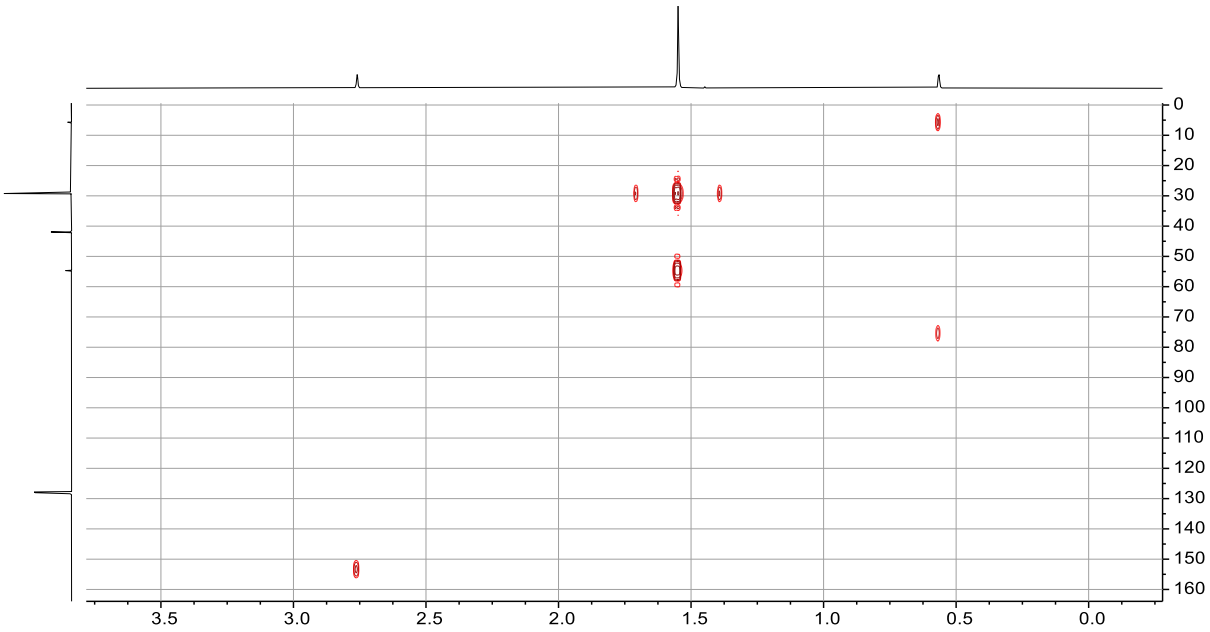
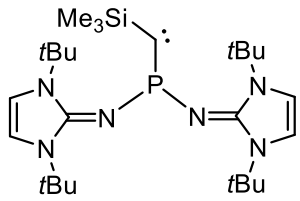


Figure S 15: $^{1}H/^{31}C\{^{1}H\}$ HMBC NMR spectrum of **3a** in C_6D_6.

1.3 **Preparation of 3b**



Note: Until the irradiation step, this reaction was performed in the dark.

A solution of (trimethylsilyl)diazomethane (2M in hexane, 0.9 mL, 1.80 mmol, 1.00 eq.) in THF (10 mL) was cooled to -78 °C using a dry ice/acetone bath and n-butyllithium (1.13 mL, 1.6 M in hexanes, 1.80 mmol, 1.00 eq.) was added to the solution. The mixture was stirred at -78 °C for 20 min and subsequently transferred (via a PTFE cannula) into a separate Schlenk flask containing a stirred suspension of **1b** (819 mg, 1.80 mmol, 1.00 eq.) in THF (30 mL) at -78 °C. After gradually warming the reaction mixture to 0 °C, the now clear solution was evaporated *in vacuo* and the residue extracted with hexane (3 x 10 mL). After exposure to sunlight for three consecutive cloudy days, crystals of the carbene **3b** formed. The supernatant hexane solution was decanted and the crystals washed with hexane (3 x 5 mL). After evaporation of the solvent, yellow, needle-like crystals of **3b** (229 mg, 0.45 mmol, 25%) could be obtained.

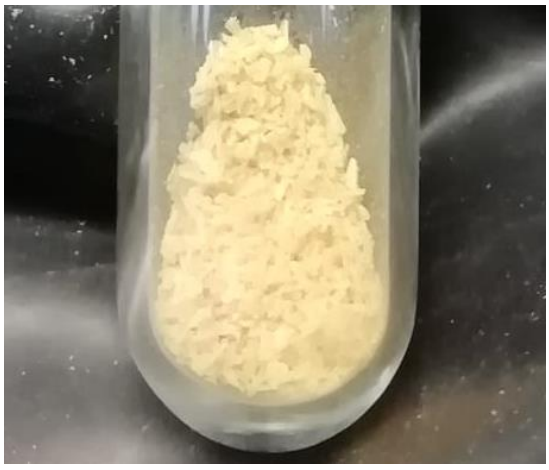


Figure S 16: Isolated crystals of **3b.**

Yield: 229 mg (0.45 mmol, 25%).

^{1}H NMR (400 MHz, C_6D_6): δ = 6.14 (s, 4 H, N-CH=CH-N), 1.73 (s, 36 H, *t*Bu), 0.38 (d, $^{4}J_{HP}$ = 1.0 Hz, 9 H, $SiMe_3$).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 145.6 (d, $^{2}J_{CP}$ = 12 Hz, C=N-P), 110.0 (N-CH=CH-N), 77.4 (d, $^{1}J_{CP}$ = 47 Hz, P-C), 55.2 ($\underline{C}Me_3$) 29.8 ($C(\underline{C}H_3)_3$), 5.5 (d, $^{3}J_{CP}$ = 13 Hz, $SiMe_3$).

^{29}Si{^{1}H} DEPT 19.5 NMR (99 MHz, C_6D_6): δ = -22.3 (d, $^{2}J_{SiP}$ = 41 Hz).

^{31}P NMR (162 MHz, C_6D_6): δ = 19.9.

Elemental analysis: Calculated for $C_{26}H_{49}N_6PSi$ (**3b**): C 61.87 %, H 9.78 %, N 16.65 %, found: C 61.87 %, H 9.91 %, N 16.80 %.

HR-MS (ESI): Calculated for $[C_{23}H_{42}N_6O_2P]^+$ ([**3b**+H+O+OH−$SiMe_3$]$^+$): m/z = 465.31014, found: m/z = 465.34439; calculated for $[C_{26}H_{50}N_6O_2PSi]^+$ ([**3b**+O_2+H]$^+$): m/z = 537.34966, found: m/z = 537.38512.

Melting point: 170°C (decomposition).

Single crystal X-ray diffraction analysis: Single crystals suitable for X-ray diffraction analysis were obtained during the synthesis (*vide supra*). The structure of **3b** was confirmed.

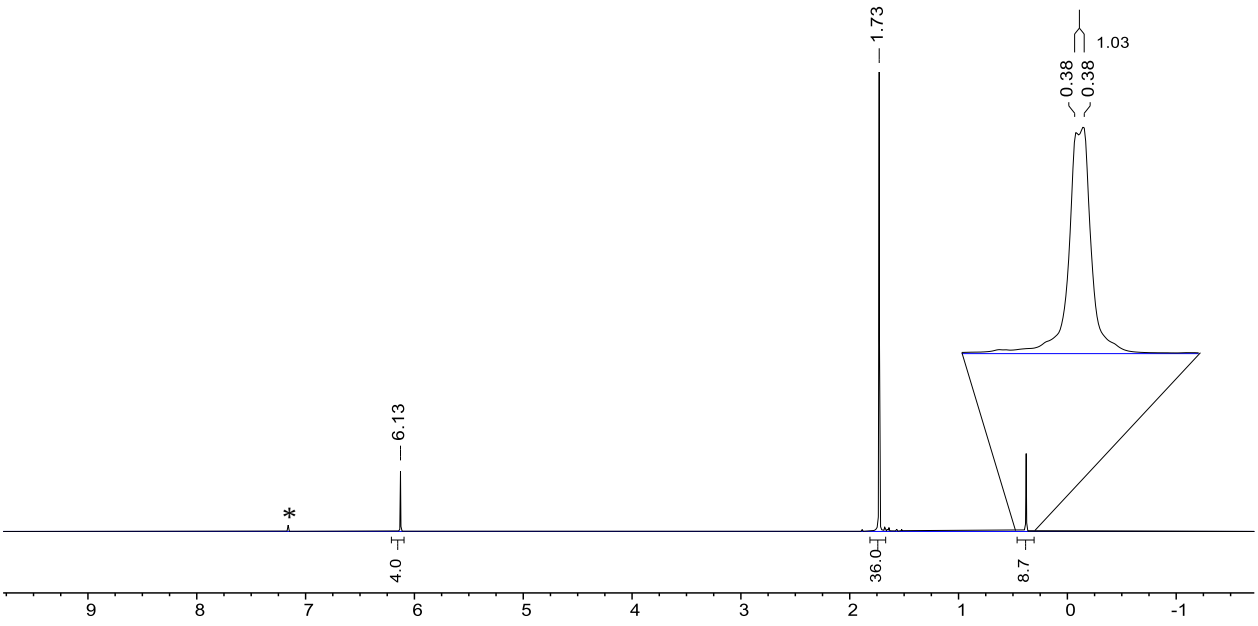


Figure S 17: ^{1}H NMR (400 MHz, 300K) spectrum of **3b** in C_6D_6. The asterisk (*) marks the solvent signal.

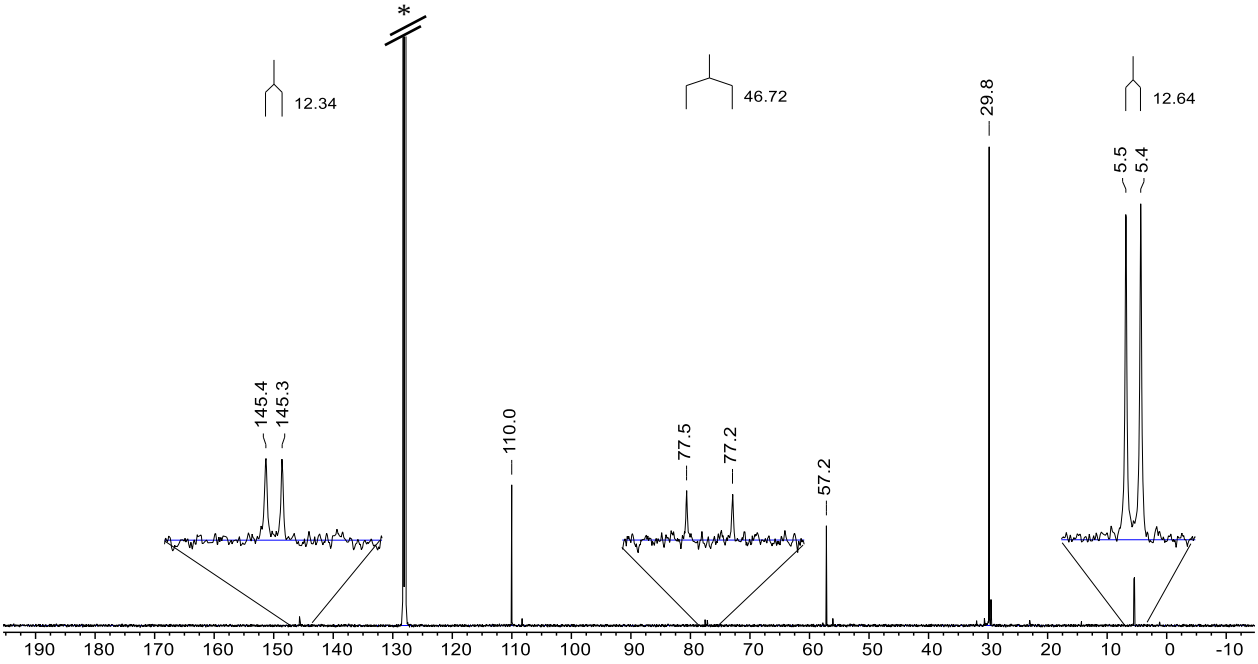


Figure S 18: $^{13}C\{^{1}H\}$ NMR (126 MHz, 300K) spectrum of **3b** in C_6D_6. The asterisk (*) marks the solvent signal. The solvent signal has been cut off due to the very low intensity of some sample signals.

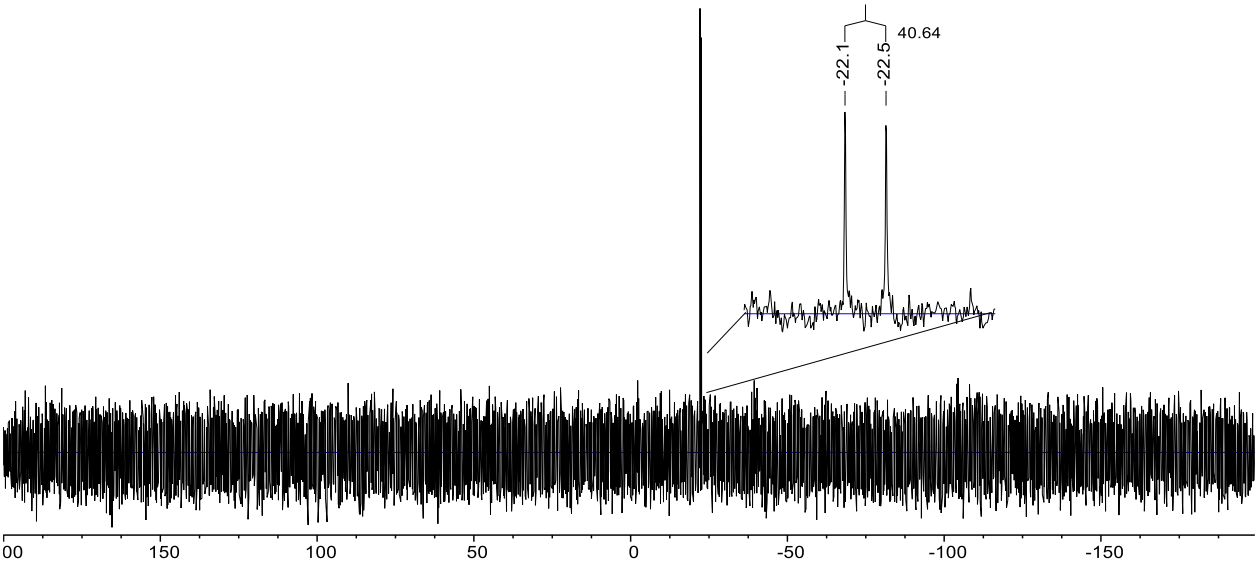


Figure S 19: $^{29}Si\{^{1}H\}$ DEPT 19.5 NMR (99 MHz, 300K) spectrum of **3b** in C_6D_6.

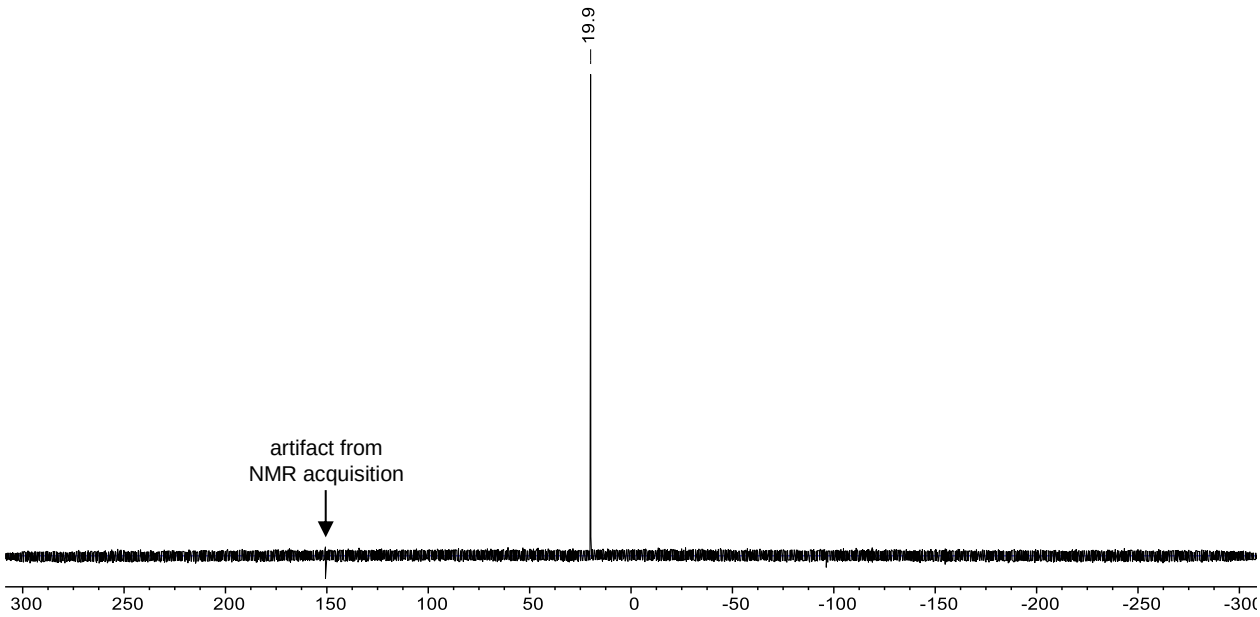
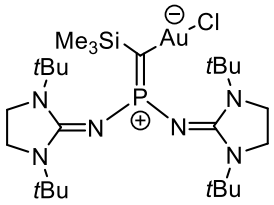


Figure S 20: ^{31}P NMR (162 MHz, 300K) spectrum of **3b** in C_6D_6.

1.4 **Preparation of 4**



Note: The reaction, as well as storage of the product, were conducted in the dark.

3a (100 mg, 0.197 mmol, 1.00 eq.) and chloro(tetrahydrothiophene)gold(I) (63 mg, 0.197 mmol, 1.00 eq.) were added into a vial. While stirring the mixture, THF (3 mL) was added and the suspension stirred for 30 minutes at 21 °C. Afterwards, the slightly cloudy suspension was passed through a glass filter and all volatiles of the yellow solution were removed *in vacuo*. The product is obtained as a light yellow solid.

Yield: 141 mg (0.190 mmol, 97%).

Note: Optionally, **4** can be recrystallized by storing a concentrated THF solution at -35 °C for one week.

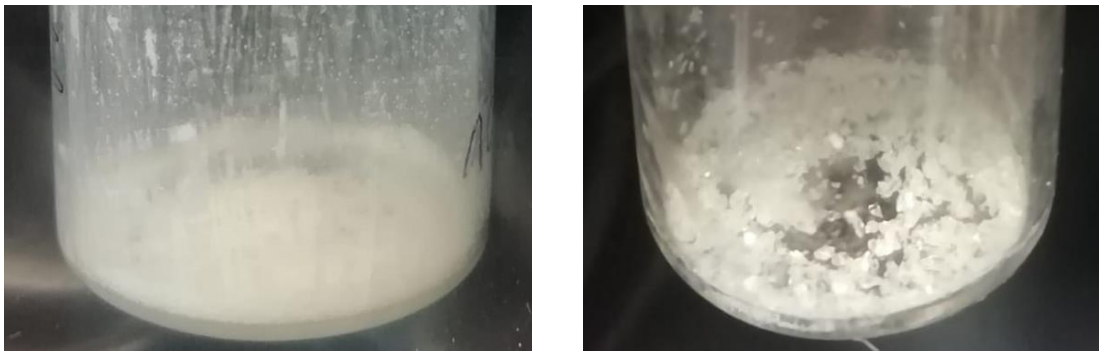


Figure S 21: **4** as obtained from the reaction (left) and recrystallized (right).

Remarks on the thermal stability of **4**: Gradual heating of solid **4** in the melting point apparatus resulted in slow color change from light yellow to purple starting at 137 °C, indicating thermal decomposition. In a separate experiment, a solution of **4** in THF was gradually heated. Heating at 60 °C for 2 h resulted in slight precipitation of a purple solid, indicating slow thermal decomposition. Further heating at 80 °C showed greatly accelerated decomposition.

Note: The NMR signals were assigned using 2D NMR and ^{31}P decoupled experiments (*vide infra*).

^{1}H NMR (400 MHz, THF-d_8): δ = 4.00–3.95 (m, 2 H, N-CH_2-CH_2-N), 3.50–3.46 (m, 6 H, N-CH_2-CH_2-N), 1.53 (s, 18 H, *t*Bu), 1.49 (s, 18 H, *t*Bu), 0.07 (d, $^{4}J_{HP}$ = 1.0 Hz, 9 H, $SiMe_3$).

^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 159.8 (d, $^{2}J_{CP}$ = 13 Hz, C=N-P), 152.1 (d, $^{2}J_{CP}$ = 20 Hz, C=N-P), 56.2 ($\underline{C}Me_3$), 55.6 ($\underline{C}Me_3$), 53.3 (d, $^{1}J_{CP}$ = 89 Hz, P-C), 43.0 (N-CH_2-CH_2-N), 42.5 (N-CH_2-CH_2-N), 29.4 (C($\underline{C}H_3$)$_3$), 28.8 (C($\underline{C}H_3$)$_3$), 4.8 (d, $^{3}J_{CP}$ = 9 Hz, $SiMe_3$).

^{29}Si{^{1}H} NMR (79 MHz, THF-d_8): δ = -11.5 (d, $^{2}J_{SiP}$ = 24 Hz).

^{31}P NMR (162 MHz, THF-d_8): δ = 70.0.

HR-MS (ESI): Calculated for $[C_{26}H_{54}AuClN_6PSi]^+$ ([**4**+H]$^+$): m/z = 741.32548, found: m/z = 741.32654; calculated for $[C_{26}H_{53}AuClN_6NaPSi]^+$ ([**4**+Na]$^+$): m/z = 763.30848, found: m/z = 763.30710.

Elemental analysis: Calculated for $C_{26}H_{53}AuClN_6PSi$ (**4**): C 42.13 %, H 7.21 %, N 11.34 %, found: C 42.36 %, H 7.25 %, N 11.41 %. Note: Elemental analysis data was acquired from the recrystallized product.

Single crystal X-ray diffraction analysis: Single crystals suitable for X-ray diffraction analysis were obtained by storing the filtrated reaction mixture at -35 °C for one week. The structure of **4** was confirmed.

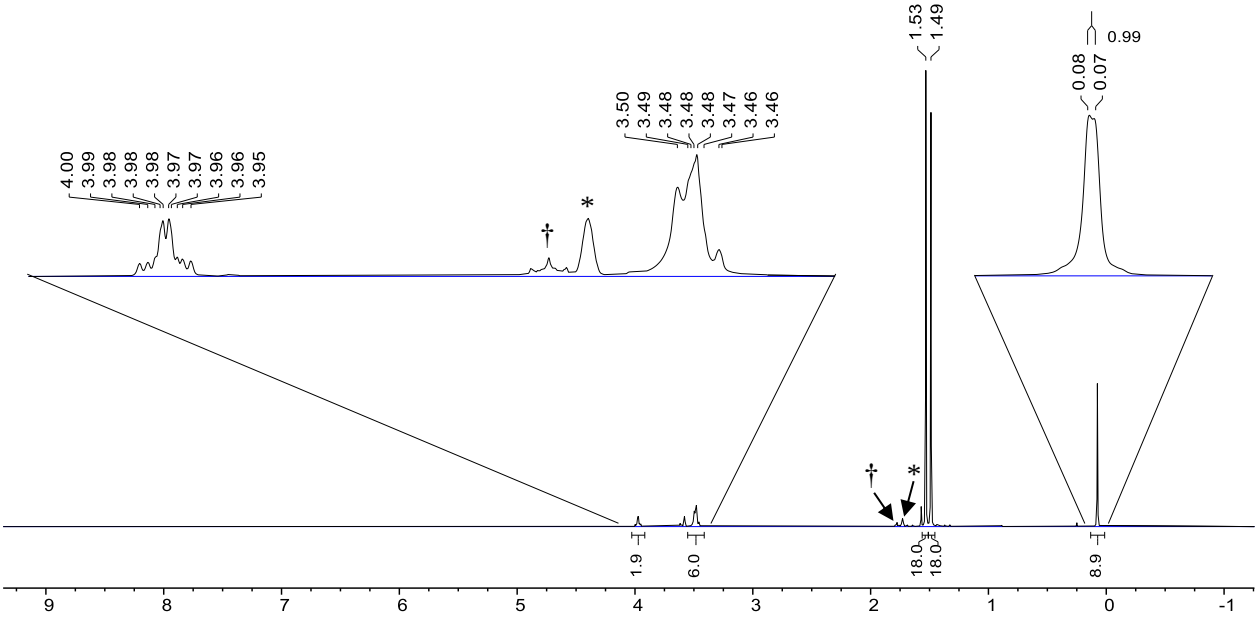


Figure S 22: ^{1}H NMR spectrum (400 MHz, 300 K) of **4** in THF-d_8. The asterisks (*) and daggers (†) mark the signals corresponding to THF-d_7 and THF, respectively.

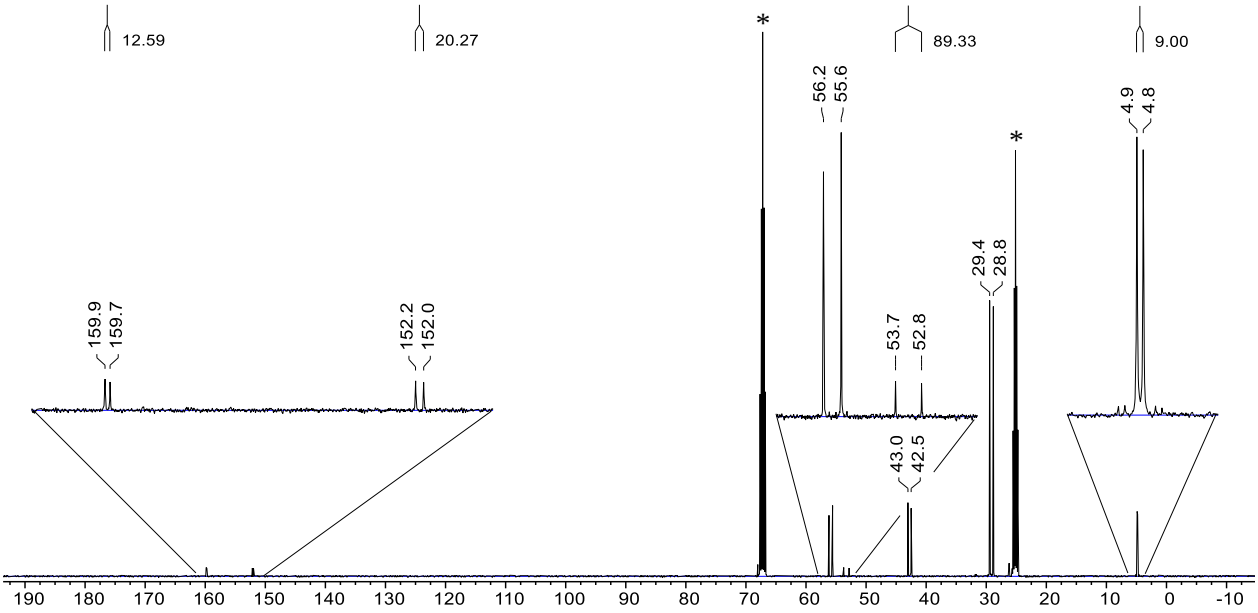


Figure S 23: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 300 K) of **4** in THF-d_8. The asterisks (*) mark the solvent signals.

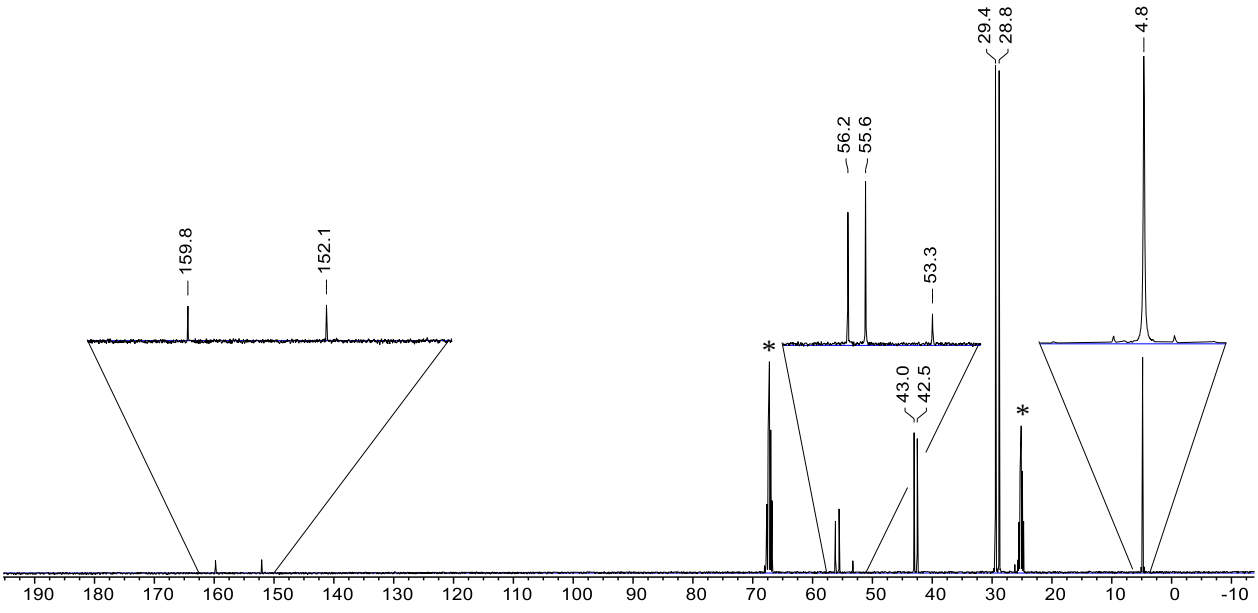


Figure S 24: $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum (101 MHz, 300 K) of **4** in THF-d_8. The asterisks (*) mark the solvent signals.

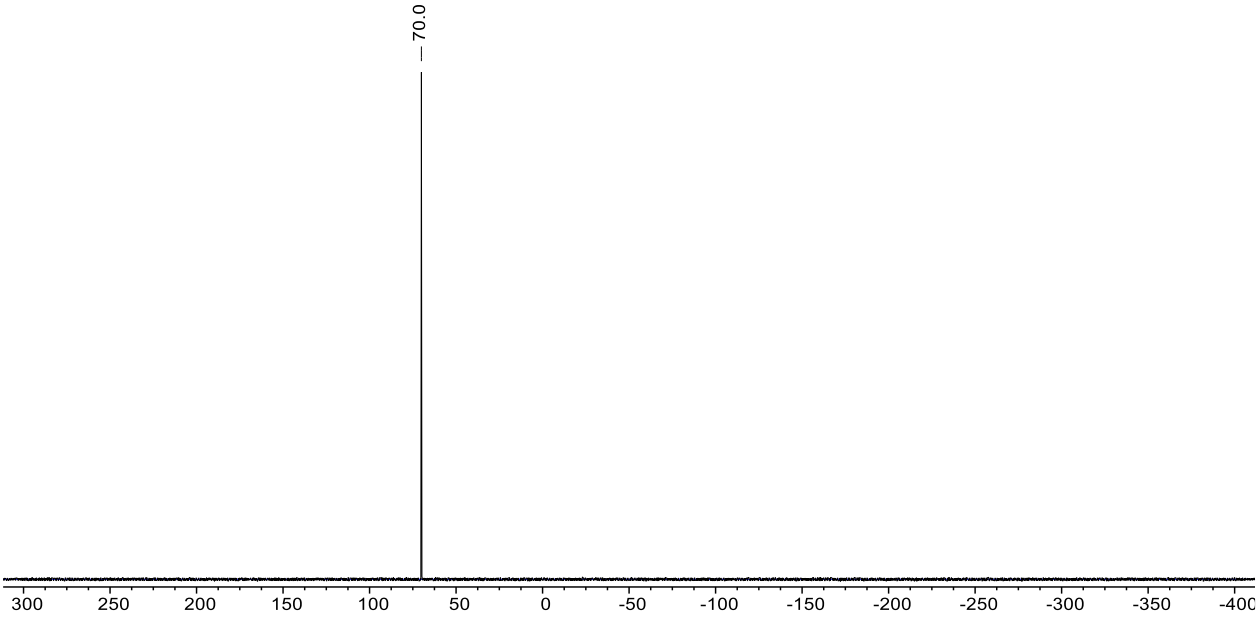


Figure S 25: ^{31}P NMR spectrum (162 MHz, 300 K) of **4** in THF-d_8.

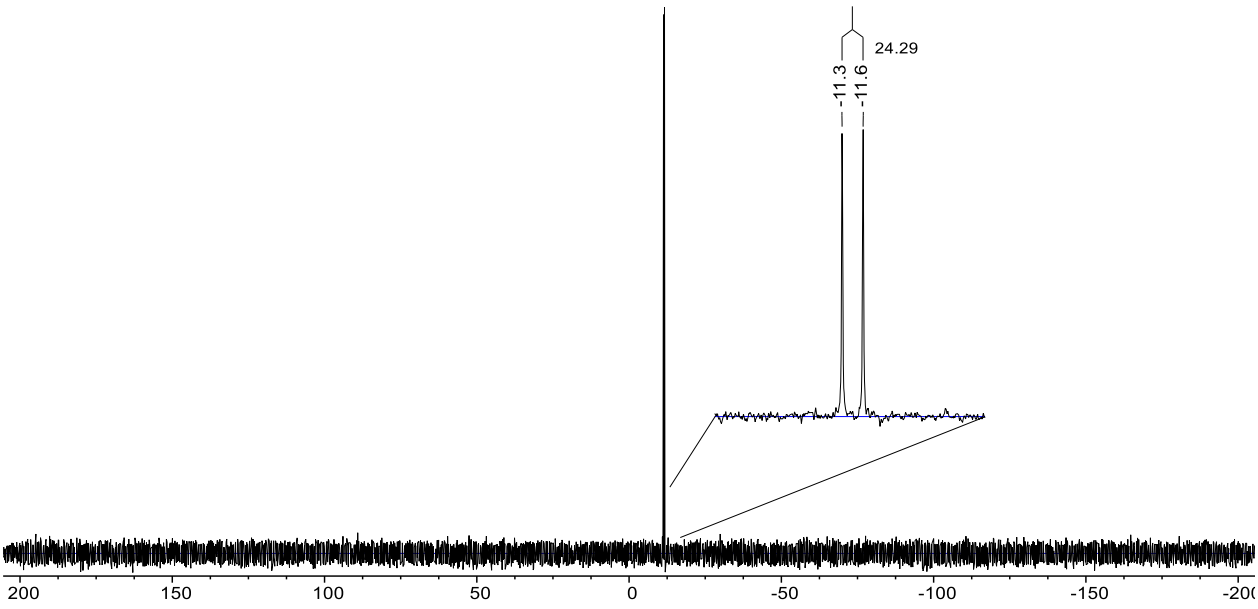


Figure S 26: ^{29}Si{^{1}H} DEPT 19.5 NMR spectrum (79 MHz, 300 K) of **4** in THF-d_8.

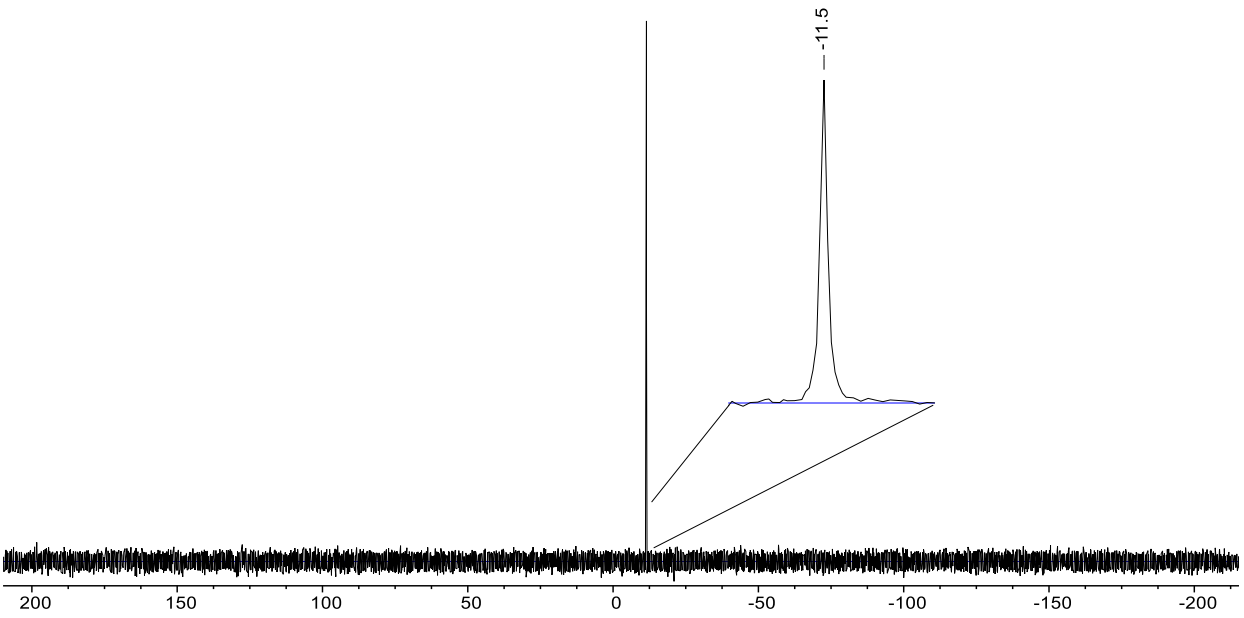


Figure S 27: $^{29}Si\{^{1}H, ^{31}P\}$ DEPT 19.5 NMR spectrum (79 MHz, 300 K) of **4** in THF-d_8.

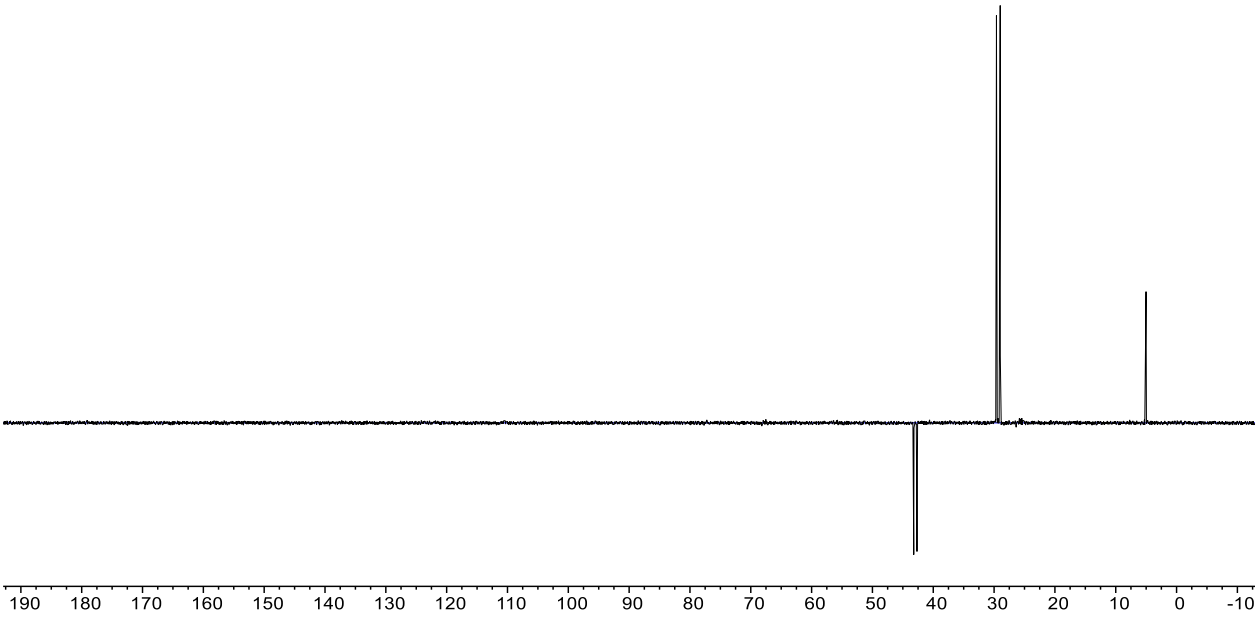


Figure S 28: $^{13}C\{^{1}H\}$ DEPT 135 NMR (101 MHz, 300K) spectrum of **4** in THF-d_8.

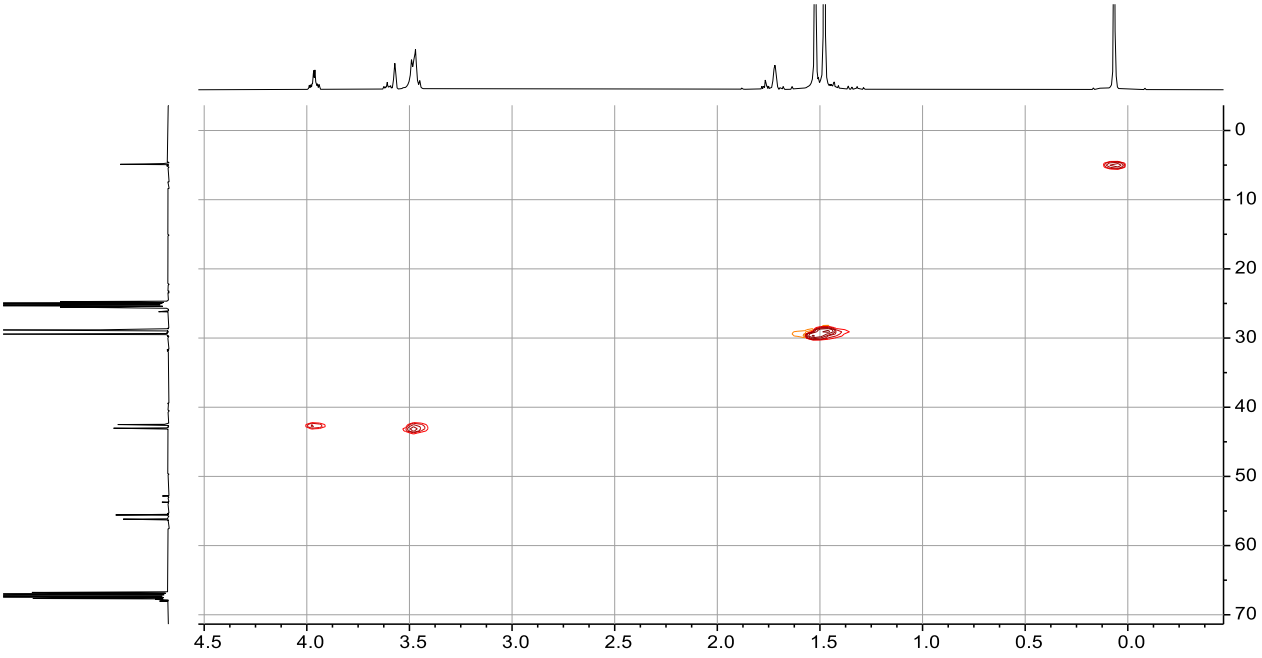
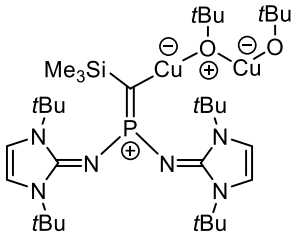


Figure S 29: $^{1}H/^{13}C\{^{1}H\}$ HSQC NMR spectrum of **4** in THF-d_8 (excerpt). No spots are present outside of the shown area. The correlation resonances corresponding to the solvent are too weak to be seen at the given amplification level.

1.5 **Preparation of 6**



3b (30.0 mg, 0.0590 mmol, 1.00 eq.) and Cu*O*tBu (16.3 mg, 0.118 mmol, 2.00 eq.) were dissolved in THF-d_8 (0.5 mL) and filled into an NMR-tube. The mixture immediately changed colour from yellow to light beige. A purification was not necessary.

NMR-Yield: Quantitative.

Optionally, **6** can be isolated as a white sold in quantitative yield after removal of all volatiles *in vacuo*.

Note: The NMR signals were assigned using 2D NMR experiments (*vide infra*).

^{1}H NMR (400 MHz, THF-d_8): δ = 7.15 (s, 2 H, N-CH-CH-N), 6.82 (s, 2 H, N-CH-CH-N), 1.85 (s, 18 H, N-*t*Bu), 1.73 (s, 18 H, N-*t*Bu), 1.25 (s, 9 H, O-*t*Bu), 1.14 (s, 9 H, O-*t*Bu), -0.12 (s, 9 H, $SiMe_3$).

^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ = 145.9 (d, $^{2}J_{CP}$ = 10 Hz, C=N-P), δ = 142.6 (d, $^{2}J_{CP}$ = 18 Hz, C=N-P), 114.0 (N-CH-CH-N), 111.5 (N-CH-CH-N), 72.0 (O-$\underline{C}Me_3$), 68.8 (O-$\underline{C}Me_3$), 59.0 (N-$\underline{C}Me_3$), 58.2 (N-$\underline{C}Me_3$), 53.1 (d, $^{1}J_{CP}$ = 57 Hz, P-C), 37.0 (O-C($\underline{C}H_3)_3$), 36.4 (O-C($\underline{C}H_3)_3$), 29.9 (N-C($\underline{C}H_3)_3$), 29.3 (N-C($\underline{C}H_3)_3$), 5.1 (d, $^{3}J_{CP}$ = 9 Hz, $SiMe_3$).

^{29}Si{^{1}H} NMR (80 MHz, THF-d_8): δ = -16.2 (d, $^{2}J_{SiP}$ = 17 Hz).

^{31}P NMR (202 MHz, THF-d_8): δ = 80.8.

Single crystal X-ray diffraction analysis: Single crystals suitable for X-ray diffraction analysis were obtained by attempting the reaction in C_6D_6: After initial addition of the reactants, a suspension was obtained. The mixture was heated until dissolution of the precipitate and then let cool down. Colourless crystals were obtained. The structure of **6** was confirmed.

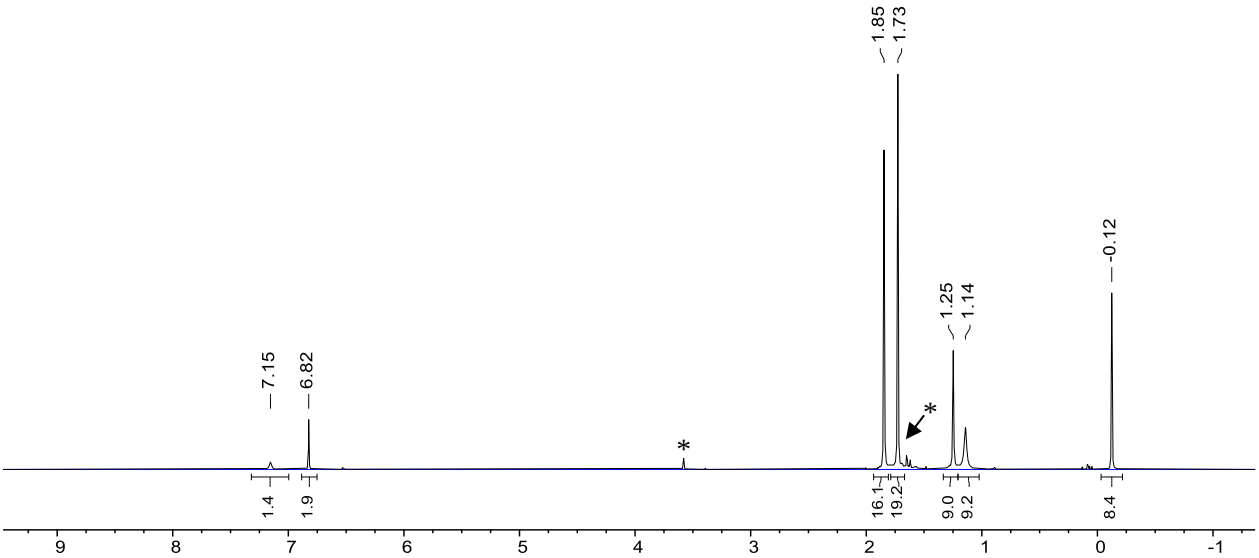


Figure S 30: ^{1}H NMR spectrum (400 MHz, 300 K) of **6** in THF-d_8. The asterisks (*) mark the solvent signals. Note: the solvent signal at δ = 1.73 ppm is overlayed by the signal corresponding to a *tert*-butyl group.

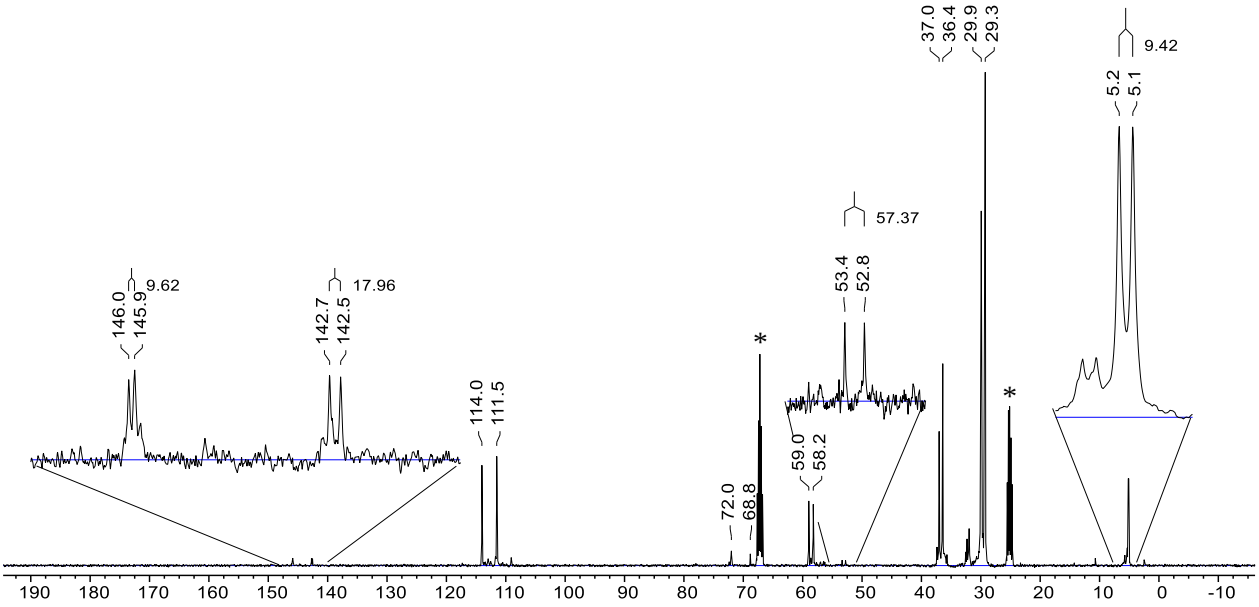


Figure S 31: ^{13}C{^{1}H} NMR spectrum (101 MHz, 300 K) of **6** in THF-d_8. The asterisks (*) mark the solvent signals.

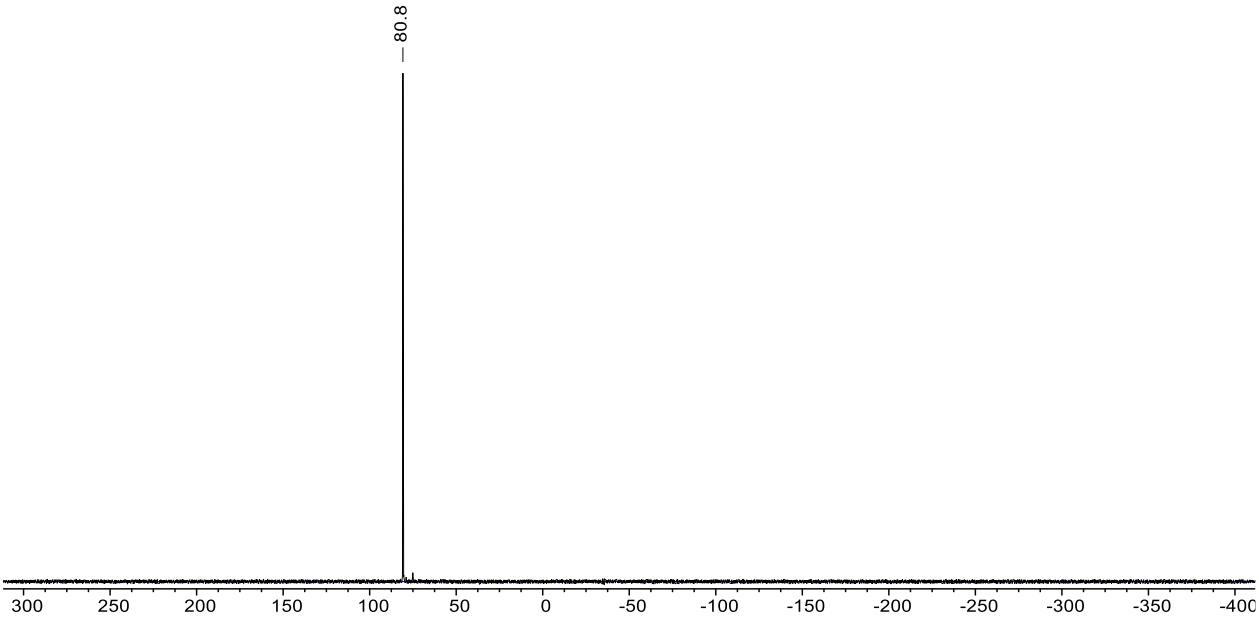


Figure S 32: ^{31}P NMR spectrum (162 MHz, 300 K) of **6** in THF-d_8.

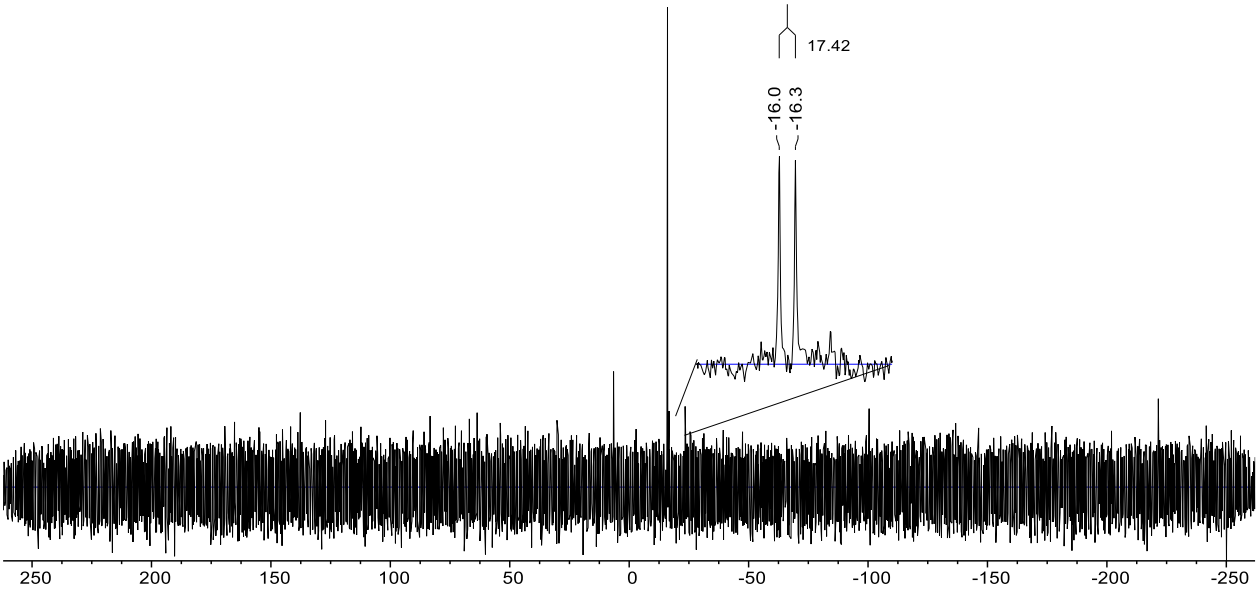


Figure S 33: ^{29}Si{^{1}H} DEPT 19.5 NMR spectrum (79 MHz, 300 K) of **6** in THF-d_8.

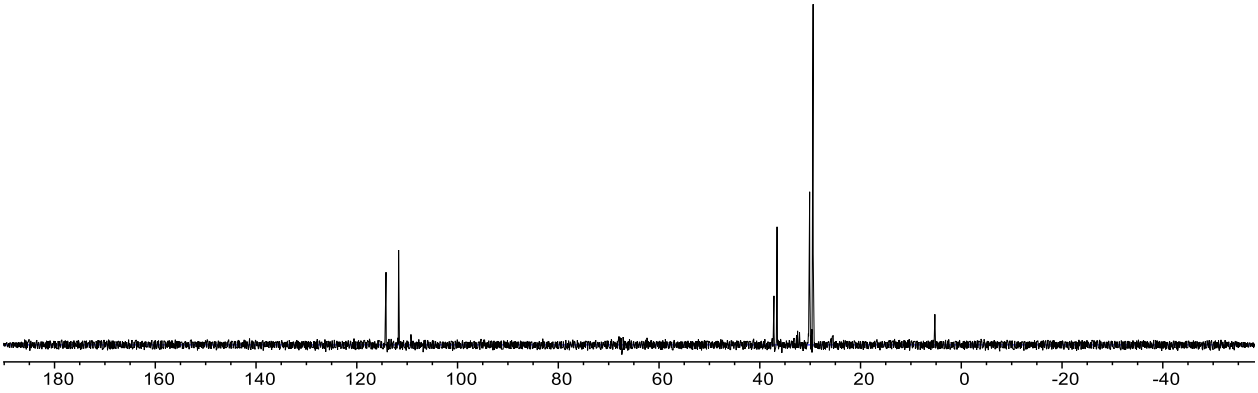


Figure S 34: $^{13}C\{^{1}H\}$ DEPT 135 NMR spectrum (101 MHz, 300 K) of **6** in THF-d_8.

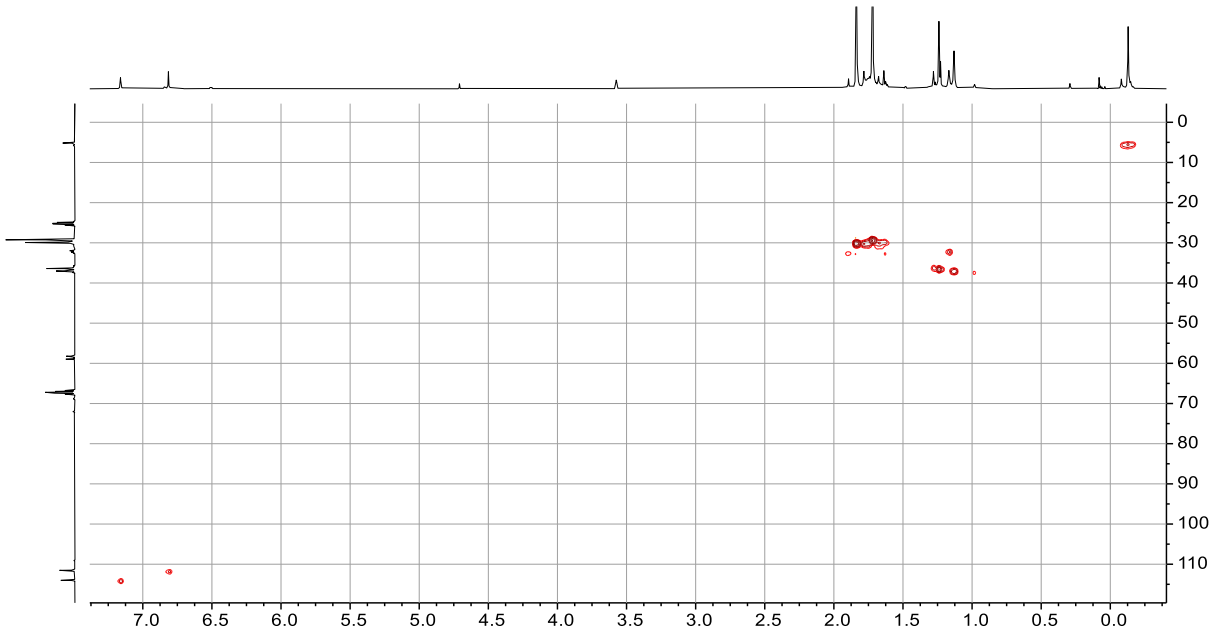


Figure S 35: $^{1}H/^{31}C\{^{1}H\}$ HSQC NMR spectrum of **6** in THF-d_8 (excerpt). No spots are present outside of the shown area. At the point of acquisition the compound partially decomposed in the NMR-tube, as seen by additional signals in the traces, presumably due to the presence of trace water or oxygen. The assignment of the product signals is not affected by this.

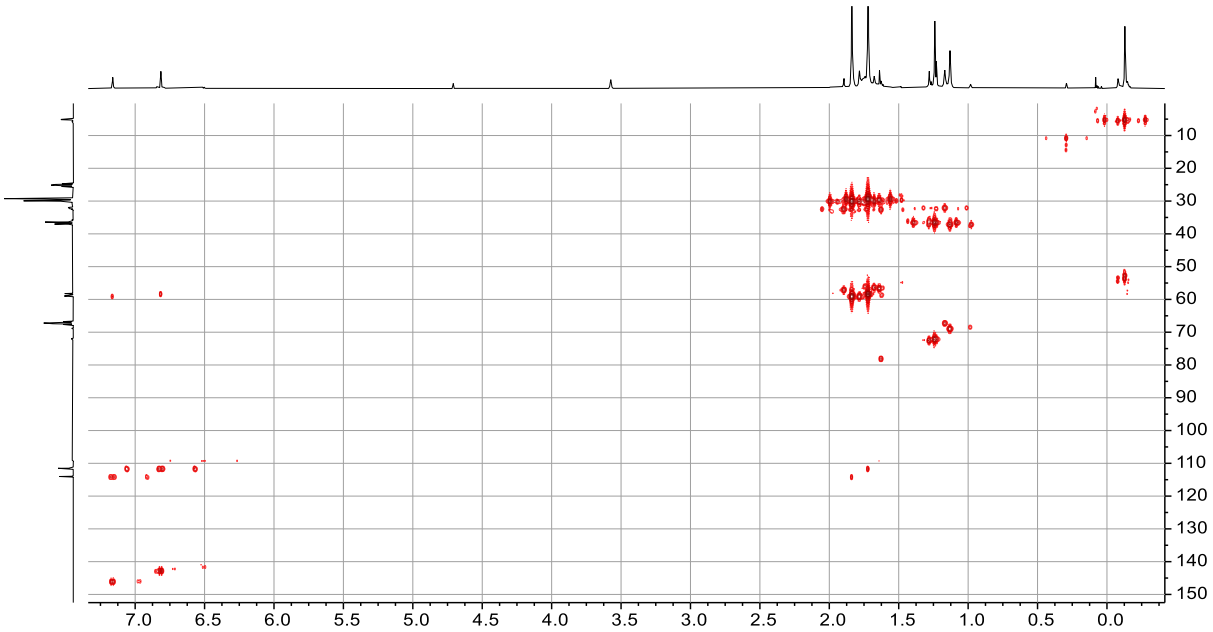


Figure S 36: $^{1}H/^{31}C\{^{1}H\}$ HMBC NMR spectrum of **6** in THF-d_8. At the point of acquisition the compound partially decomposed in the NMR-tube, as seen by additional signals in the traces, presumably due to the presence of trace water or oxygen. The assignment of the product signals is not affected by this.

1.6 Crystallization of 7 and attempt of its targeted synthesis

Compound **5** was first prepared in THF. Due to its low solubility in this solvent, an attempt was made to recrystallize it in 1,2-difluorobenzene. Storage of the mixture for four months at 21 °C resulted in the formation of few crystals of **7**, which were analyzed via X-ray diffraction analysis (*vide infra*).

To obtain **7** in a targeted synthesis, **5** (approx. 50 mg) was first prepared in THF (1 mL) by mixing equimolar amounts of **3b** and CuO*t*Bu. The supernatant THF solution was pipetted off and discarded. The remaining mixture was suspended in 1,2-difluorobenzene (0.5 mL) and monitored via ^{31}P NMR spectroscopy. After 2 h at 21 °C, no reaction was observed. However, heating at 60 °C for 16 h resulted in the formation of several species as indicated by ^{31}P NMR spectroscopy. Hence, a selective synthesis of **7** was not successful

2 Determination of %V_{bur} and steric maps

Computation of percent buried volume (%V_{bur}) values and steric maps was performed via the Samb*V*ca 2.1 web application.[5] The sphere are centered at the gold atom. Bond radii are scaled by 1.17, the sphere radius is set to 3.5 Å (if not stated differently), mesh spacing for numerical integration is set to 0.10 Å, H atoms are not included in the calculations. The investigated compounds are summarized in Figure S 37. The computed %V_{bur} values are summarized in Table S 1. The steric maps are depicted in chapters 0 to 2.3.

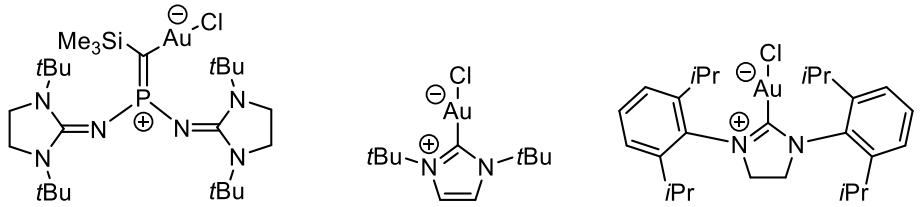


Figure S 37: Investigated gold complexes.[6,7]

Table S 1: Computed %V_{bur} values of the gold complexes shown in Figure S 37.

Compound	%V_{bur}	Reference
4	50.1	
(I*t*Bu)AuCl	39.3	[6]
(sIDipp)AuCl	47.4	[7]

2.1 **Steric map of compound 4**

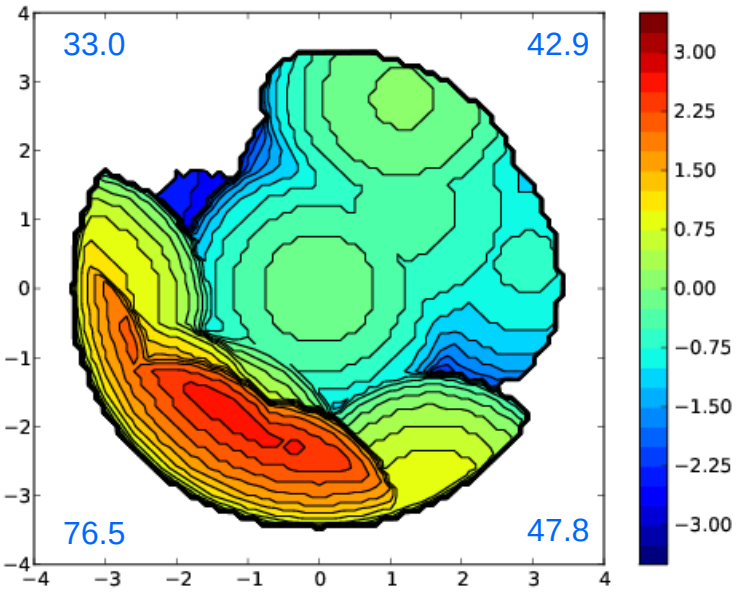


Figure S 38: Steric map of **4** (sphere radius is set to 3.5 Å). The blue numbers around the steric map indicate the %V_{bur} value of the corresponding quadrant

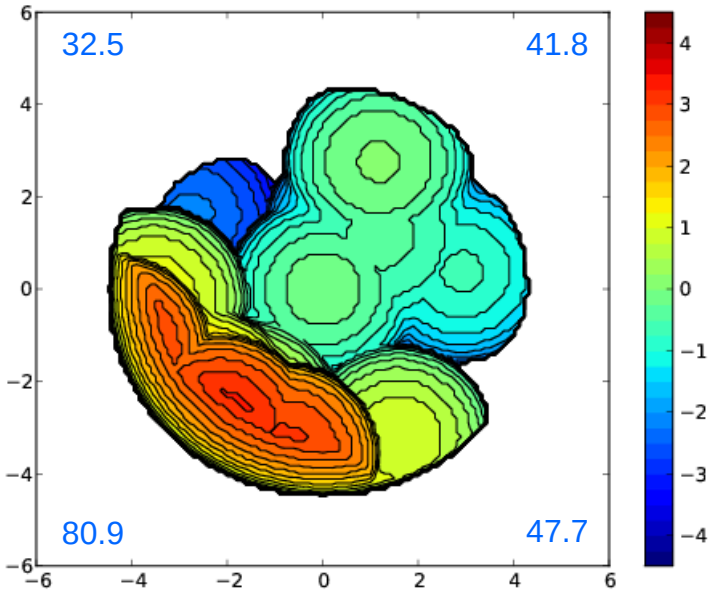


Figure S 39: Steric map of **4** (sphere radius is set to 4.5 Å). The blue numbers around the steric map indicate the %V_{bur} value of the corresponding quadrant.

2.2 Steric map of (I*t*Bu)AuCl

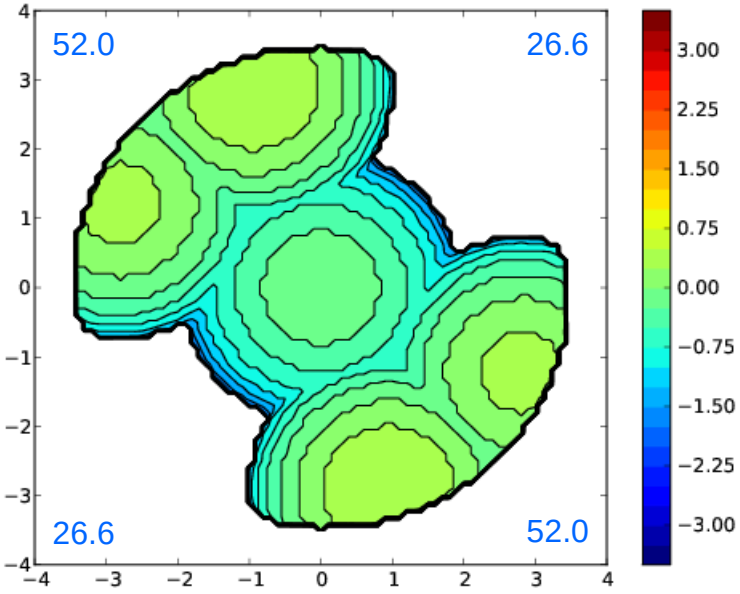


Figure S 40: Steric map of (I*t*Bu)AuCl (sphere radius is set to 3.5 Å). The blue numbers around the steric map indicate the %V_{bur} value of the corresponding quadrant.

2.3 Steric map of (sIDipp)AuCl

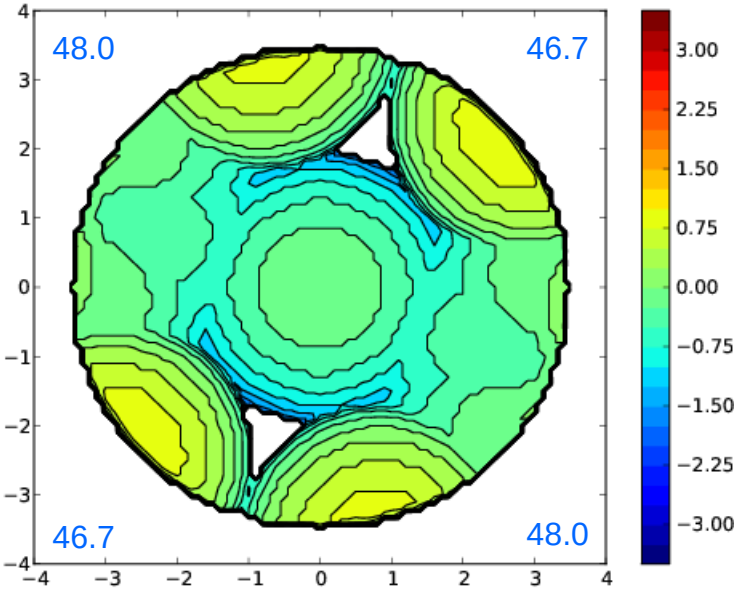


Figure S 41: Steric map of (sIDipp)AuCl (sphere radius is set to 3.5 Å). The blue numbers around the steric map indicate the %V_{bur} value of the corresponding quadrant.

3 X-ray Diffraction Studies

General: Single-crystal X-ray diffraction data of **1a**, **1b**, **3a**, **3b**, **4**, **6** and **7**: Crystals were selected under oil, mounted on glass capillaries, and then immediately placed in a cold stream of N_2 on a diffractometer. Data were collected on a Bruker AXS detector using Mo-K_α radiation (λ = 0.71073 Å). Using Olex2,[8] the structures were solved with the ShelXT[9] structure solution program using intrinsic phasing and refined with the ShelXL[10] refinement package using Least Squares minimization.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2190727 (**1a**), 2190728 (**1b**), 2190729 (**3a**), 2190730 (**3b**), 2190731 (**4**), 2190732 (**6**) and 2190733 (**7**). These data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

3.1 Crystal structure data of compound 1a

CCDC deposition number	2190727
Empirical formula	$C_{34}H_{54}ClF_2N_6P$
Formula weight	651.25
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	26.3923(6)
b/Å	5.86980(10)
c/Å	26.0141(6)
α/°	90
β/°	116.9270(10)
γ/°	90
Volume/Å^3	3593.12(13)
Z	4

ρ_{calc}g/cm^3	1.204
μ/mm^{-1}	0.193
F(000)	1400.0
Crystal size/mm^3	0.487 × 0.458 × 0.41
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.774 to 59.21
Index ranges	-36 ≤ h ≤ 36, -8 ≤ k ≤ 8, -36 ≤ l ≤ 36
Reflections collected	54469
Independent reflections	10031 [R_{int} = 0.0401, R_{sigma} = 0.0264]
Data/restraints/parameters	10031/0/436
Goodness-of-fit on F^2	1.194
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1227
Final R indexes [all data]	R_1 = 0.0497, wR_2 = 0.1238
Largest diff. peak/hole / e Å^{-3}	0.54/-0.45

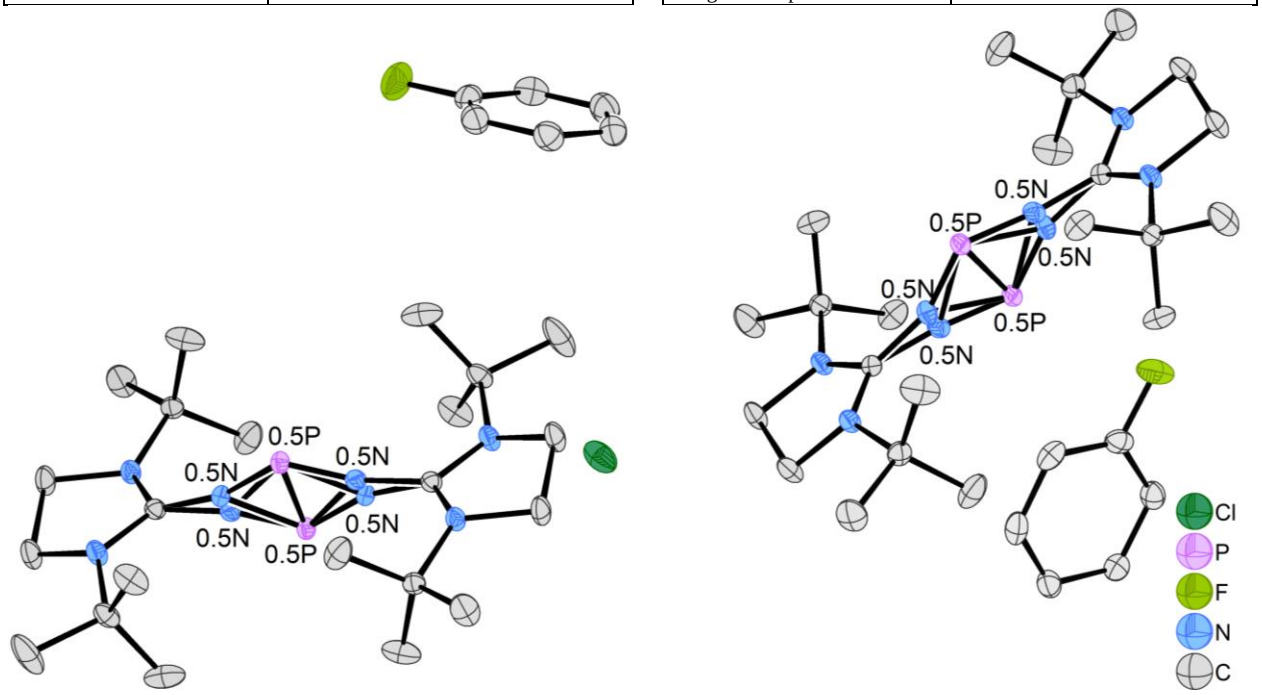


Figure S 42: Molecular view of **1a** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains two half molecules of **1a** and two molecules of fluorobenzene. The PN_2 fragments are disordered over two positions in a ratio of 1:1.

3.2 Crystal structure data of compound 1b

CCDC deposition number	2190728
Empirical formula	$C_{22}H_{40}ClN_6P$
Formula weight	455.02
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	10.3440(2)
b/Å	10.8041(2)
c/Å	12.4387(2)
α/°	66.9530(10)
β/°	81.9680(10)
γ/°	84.7670(10)
Volume/Å^3	1265.60(4)
Z	2

ρ_{calc}mg/mm^3	1.194
m/mm^{-1}	0.234
F(000)	492.0
Crystal size/mm^3	0.6 × 0.576 × 0.432
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.582 to 56.554°
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	19793
Independent reflections	6269 [R_{int} = 0.0173, R_{sigma} = 0.0177]
Data/restraints/parameters	6269/0/283
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0288, wR_2 = 0.0747
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0762
Largest diff. peak/hole / e Å^{-3}	0.41/-0.24

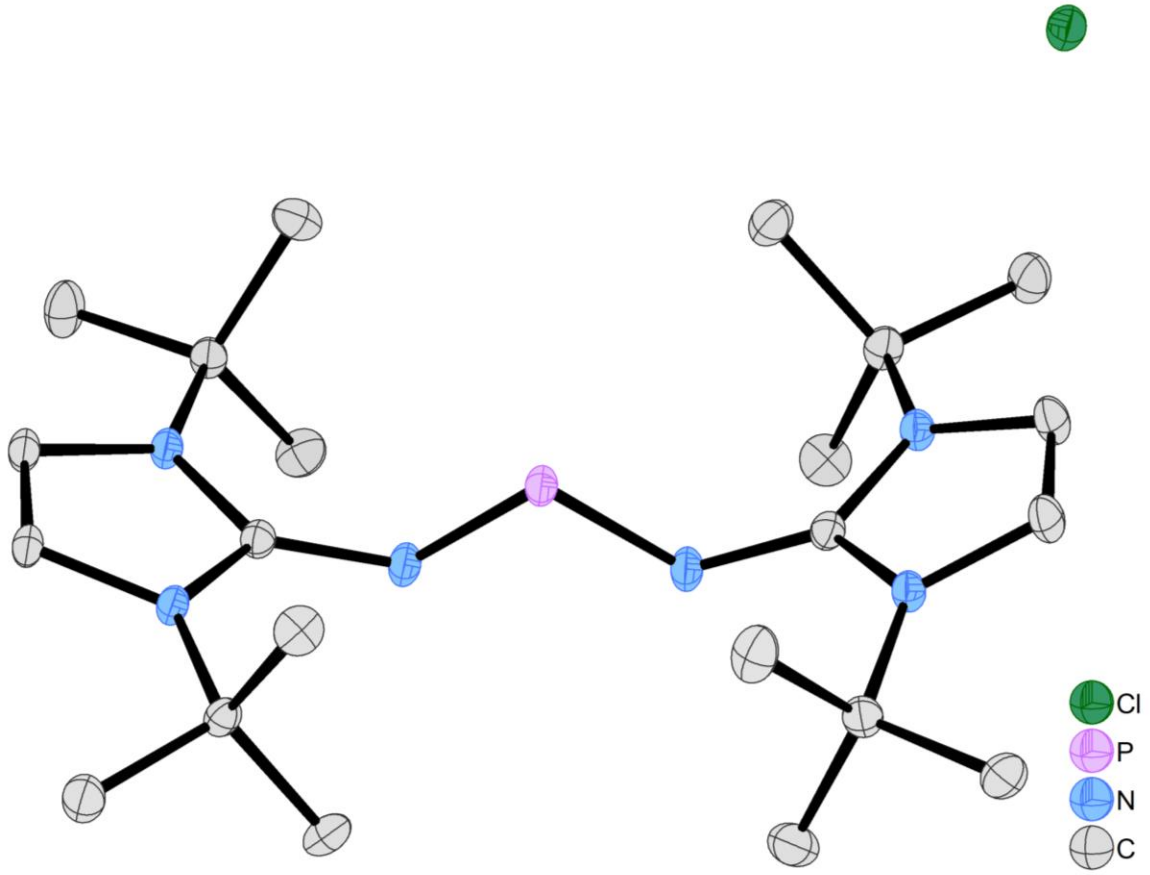


Figure S 43: Molecular view of **1b** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains one molecule of **1b**.

3.3 Crystal structure data of compound 3a

CCDC deposition number	2190729
Empirical formula	$C_{26}H_{53}N_6PSi$
Formula weight	508.80
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	11.0192(5)
b/Å	11.9241(5)
c/Å	12.4677(5)
α/°	79.803(3)
β/°	73.474(3)
γ/°	78.577(3)
Volume/Å^3	1526.65(12)
Z	2

ρ_{calc}g/cm^3	1.107
μ/mm^{-1}	0.153
F(000)	560.0
Crystal size/mm^3	0.263 × 0.19 × 0.167
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.436 to 59.186
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	24627
Independent reflections	8484 [R_{int} = 0.0437, R_{sigma} = 0.0491]
Data/restraints/parameters	8484/0/322
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1559
Final R indexes [all data]	R_1 = 0.0727, wR_2 = 0.1663
Largest diff. peak/hole / e Å^{-3}	0.65/-0.27

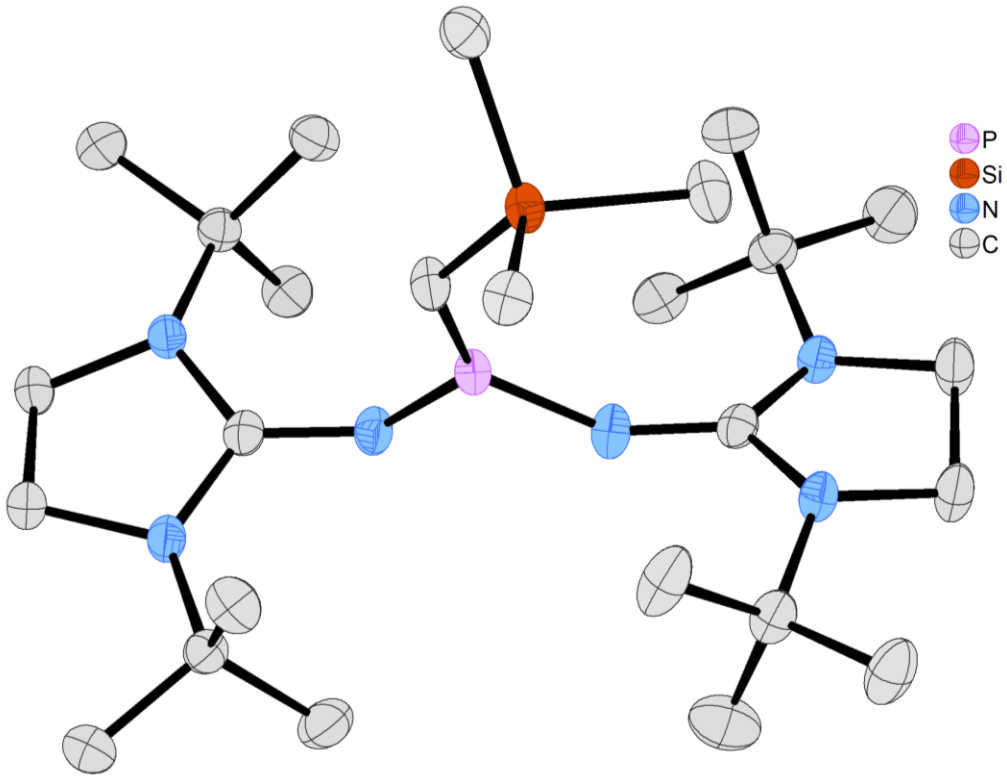


Figure S 44: Molecular view of **3a** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains one molecule of **3a**.

3.4 Crystal structure data of compound 3b

CCDC deposition number	2190730
Empirical formula	$C_{26}H_{49}N_6PSi$
Formula weight	504.77
Temperature/K	100.0
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	10.4710(2)
b/Å	11.9664(3)
c/Å	12.7029(3)
α/°	79.3550(10)
β/°	73.7850(10)
γ/°	74.4050(10)
Volume/Å^3	1461.71(6)
Z	2

ρ_{calc}g/cm^3	1.147
μ/mm^{-1}	0.160
F(000)	552.0
Crystal size/mm^3	0.315 × 0.162 × 0.087
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.558 to 55.93
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	22524
Independent reflections	7013 [R_{int} = 0.0515, R_{sigma} = 0.0522]
Data/restraints/parameters	7013/0/382
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0463, wR_2 = 0.1129
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.1216
Largest diff. peak/hole / e Å^{-3}	0.37/-0.41

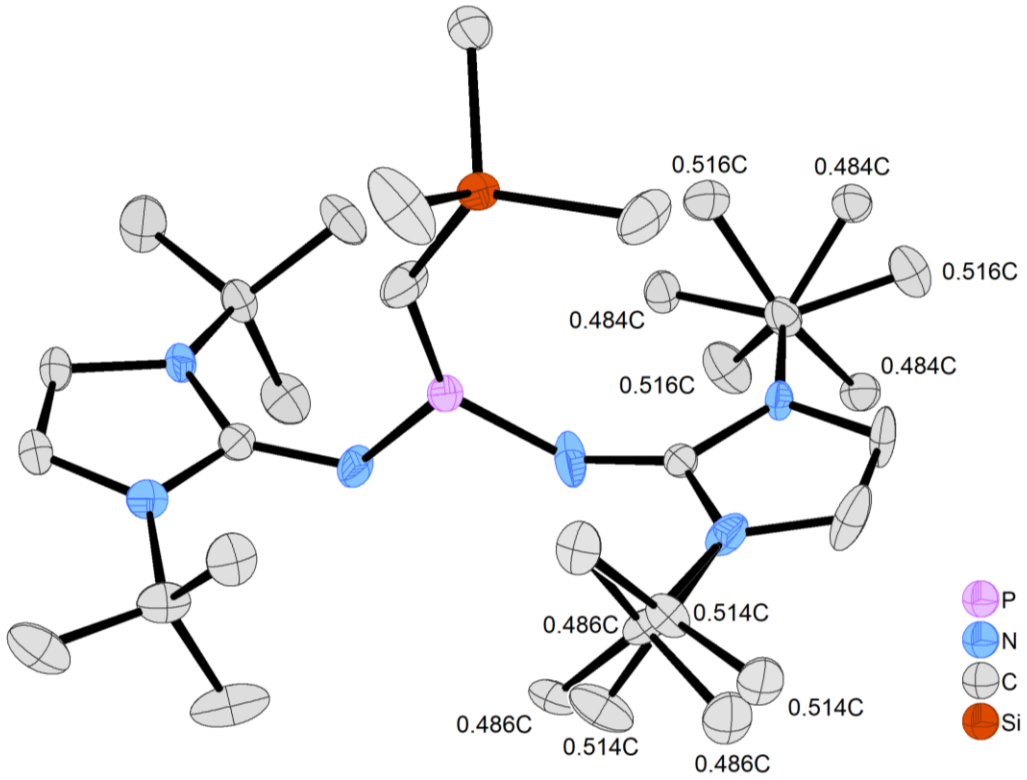


Figure S 45: Molecular view of **3b** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains one molecule of **3b**. Two tert-butyl groups are disordered over two positions, respectively. The occupancies are shown next to the corresponding atoms.

3.5 Crystal structure data of compound 4

CCDC deposition number	2190731
Empirical formula	$C_{26}H_{53}AuClN_6PSi$
Formula weight	741.22
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.5776(4)
b/Å	14.1333(4)
c/Å	18.1953(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3234.45(17)
Z	4

ρ_{calc}g/cm^3	1.522
μ/mm^{-1}	4.742
F(000)	1504.0
Crystal size/mm^3	0.182 × 0.165 × 0.155
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.648 to 58.05
Index ranges	-16 ≤ h ≤ 17, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24
Reflections collected	48349
Independent reflections	8586 [R_{int} = 0.0555, R_{sigma} = 0.0398]
Data/restraints/parameters	8586/0/340
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.0820
Final R indexes [all data]	R_1 = 0.0413, wR_2 = 0.0845
Largest diff. peak/hole / e Å^{-3}	2.03/-0.45

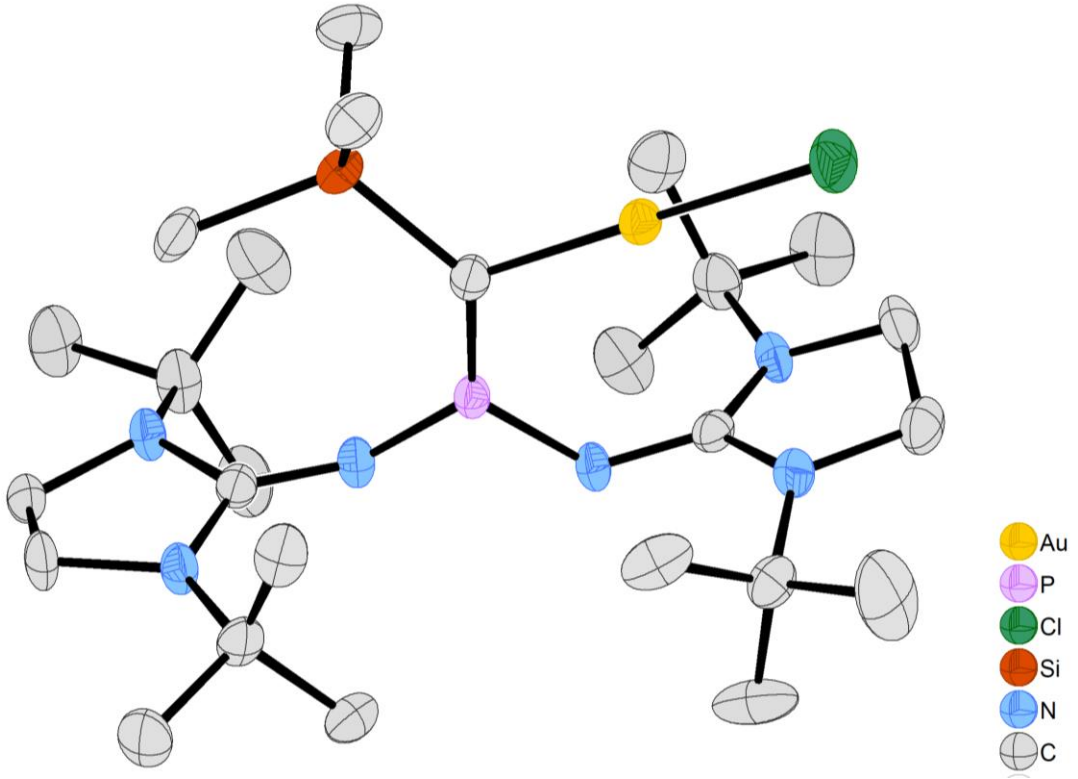


Figure S 46: Molecular view of **4** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains one molecule of **4**.

3.6 Crystal structure data of compound 6

CCDC deposition number	2190732
Empirical formula	$C_{40}H_{73}Cu_2N_6O_2PSi$
Formula weight	856.18
Temperature/K	100.0
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	21.6481(9)
b/Å	18.7415(8)
c/Å	22.4951(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9126.7(7)
Z	8

ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	1.032
F(000)	3664.0
Crystal size/mm^3	0.528 × 0.524 × 0.165
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.398 to 56.624
Index ranges	-28 ≤ h ≤ 28, -24 ≤ k ≤ 24, -29 ≤ l ≤ 29
Reflections collected	131767
Independent reflections	11234 [R_{int} = 0.0626, R_{sigma} = 0.0294]
Data/restraints/parameters	11234/0/490
Goodness-of-fit on F^2	1.121
Final R indexes [I>=2σ (I)]	R_1 = 0.0527, wR_2 = 0.1432
Final R indexes [all data]	R_1 = 0.0672, wR_2 = 0.1538
Largest diff. peak/hole / e Å^{-3}	2.24/-0.53

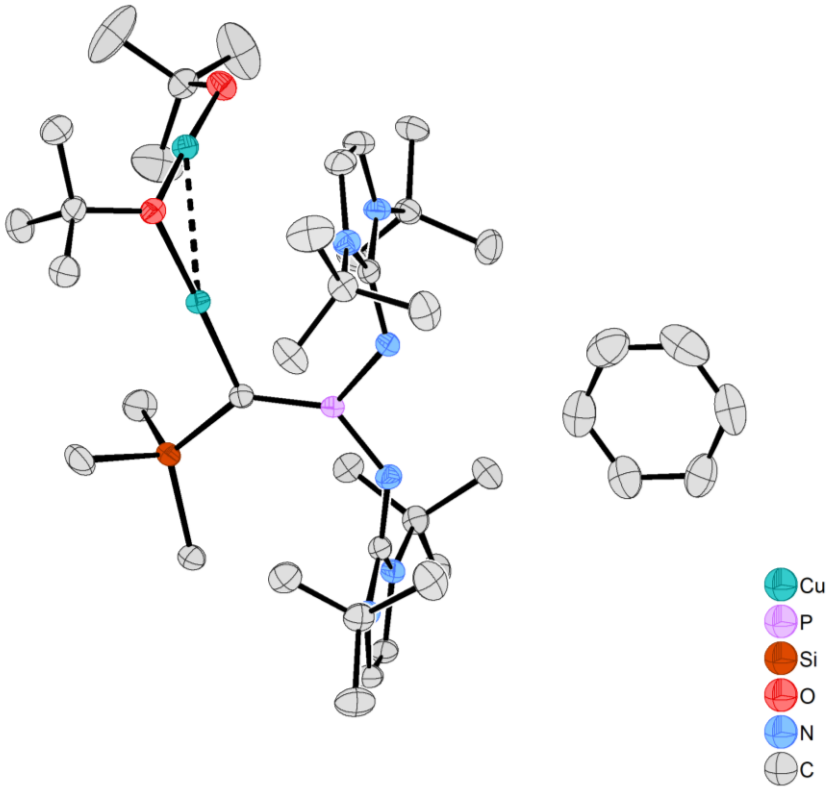


Figure S 47: Molecular view of **6** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains one molecule of **6** and one molecule of benzene.

Note: The highest residual electron density (Q1) is located about 1.8 Å adjacent to an imidazoline C atom, suggesting that it corresponds to a copper atom with an occupancy of 3%. One explanation would be that, similar to the formation of **7**, CH activation has occurred and that the metallated species is present at about 3% in the crystal lattice. Because of the low occupancy, the lighter atoms cannot be located on the residual electron density map.

3.7 Crystal structure data of compound 7

CCDC deposition number	2190732
Empirical formula	$C_{32}H_{52}CuF_2N_6PSi$
Formula weight	681.39
Temperature/K	100
Crystal system	orthorhombic
Space group	*Pna*2$_1$
a/Å	20.0953(8)
b/Å	10.1679(4)
c/Å	17.1211(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3498.3(2)
Z	4
ρ_{calc}g/cm^3	1.294

μ/mm^{-1}	0.746
F(000)	1448.0
Crystal size/mm^3	0.78 × 0.2 × 0.116
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.054 to 58.23
Index ranges	-27 ≤ h ≤ 26, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	45781
Independent reflections	9272 [R_{int} = 0.0591, R_{sigma} = 0.0510]
Data/restraints/parameters	9272/1/403
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0506, wR_2 = 0.1236
Final R indexes [all data]	R_1 = 0.0579, wR_2 = 0.1285
Largest diff. peak/hole / e Å^{-3}	1.56/-0.32
Flack parameter	0.012(5)

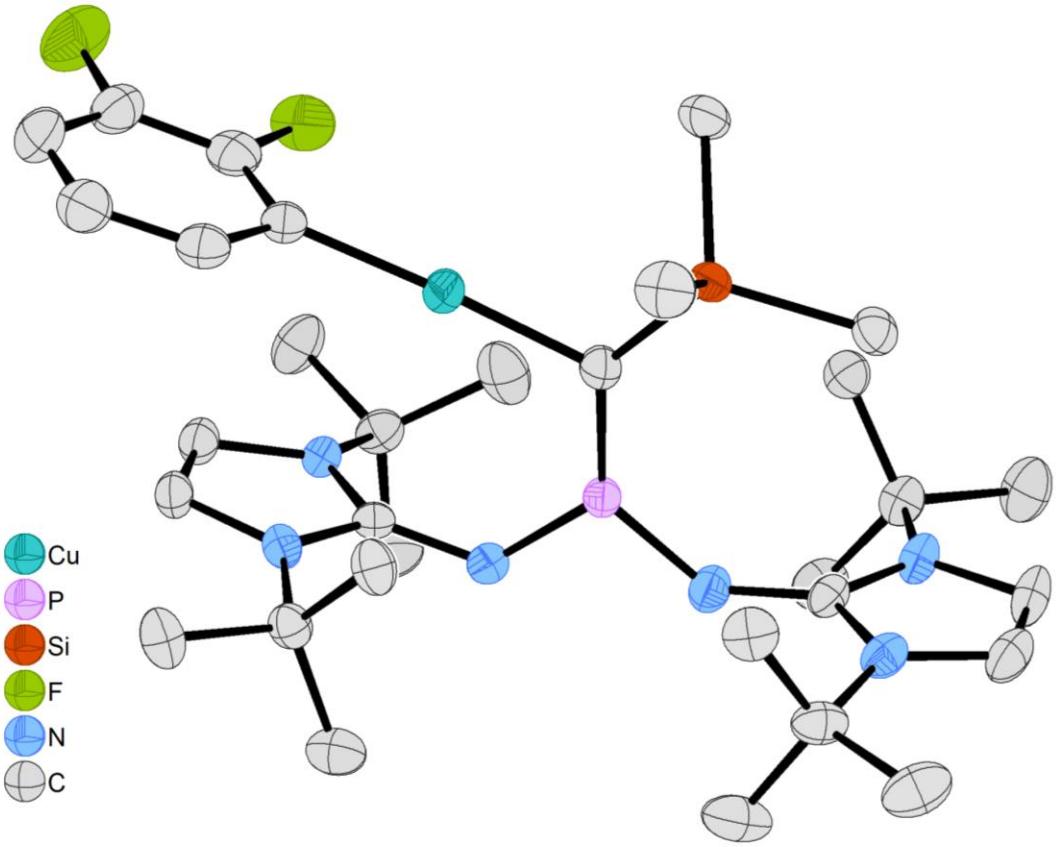


Figure S 48: Molecular view of **7** in the solid state (ellipsoids at 50% probability). The hydrogen atoms are omitted. The asymmetric unit contains one molecule of **7**.

4 Computational studies

4.1 General

The geometry optimizations and frequency calculations were performed with ORCA 5.0,[11] using the B3LYP[12] functional with a dispersion correction (D4)[13]. A triple zeta basis set (def2-TZVP)[14] with an RIJCOSX[15] approximation was used in all calculations. The absence of any imaginary frequencies confirmed that each optimized structure is at a local minimum.

4.2 Optimized structures

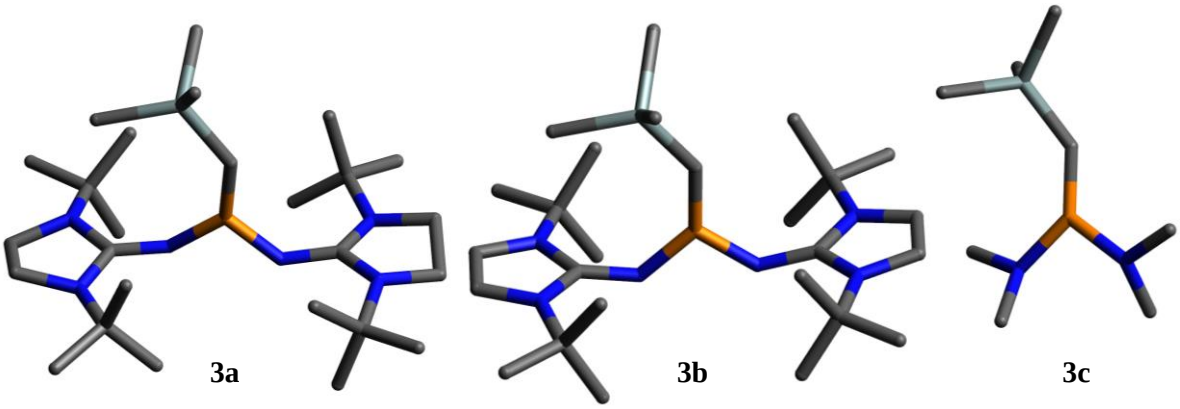
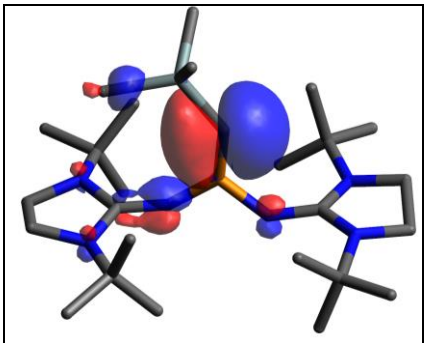
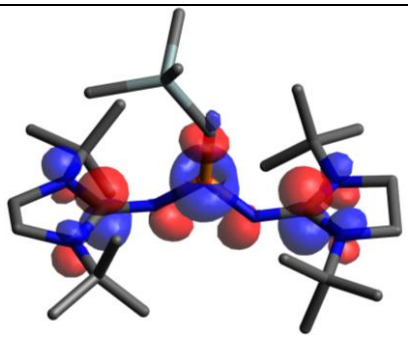


Figure S 49: Optimized structures of **3a** (left), **3b** (middle), and $(Me_2N)_2PCSiMe_3$ (**3c**, right). The hydrogen atoms are omitted for clarity.

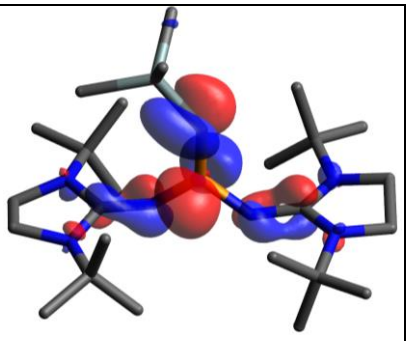
4.3 **Selected molecular orbitals**



HOMO (-4.216 eV)

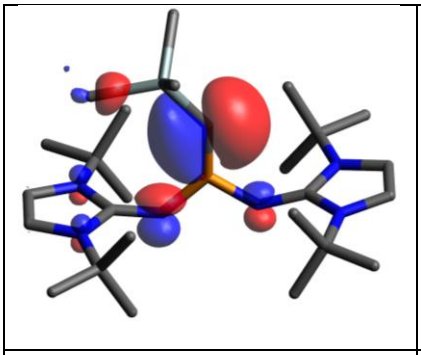


LUMO (0.053 eV)

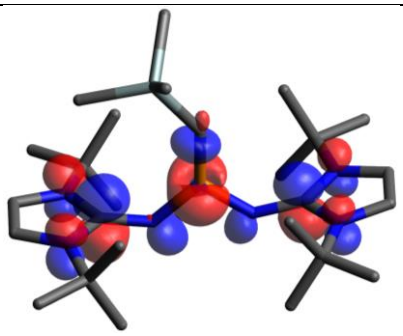


LUMO+5 (1.012 eV)

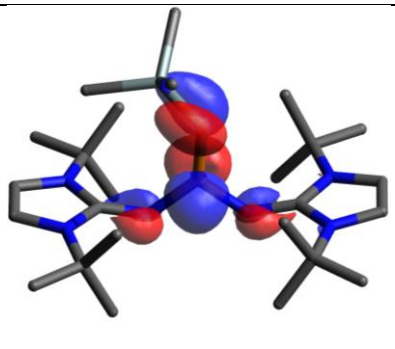
Figure S 50: Selected orbitals of **3a**.



HOMO (-4.035 eV)

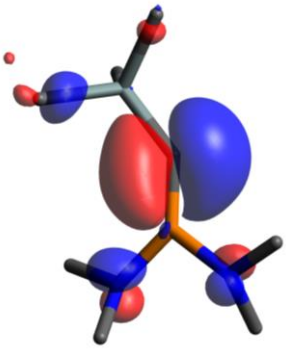


LUMO (0.193 eV)

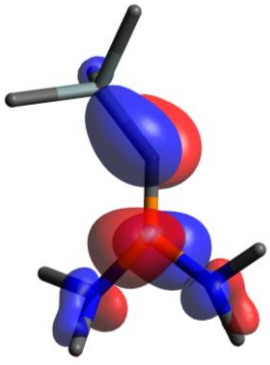


LUMO+7 (1.077 eV)

Figure S 51: Selected orbitals of **3b**.



HOMO (-5.143 eV)



LUMO (0.222 eV)

Figure S 52: Frontier orbitals of **3c**.

4.4 XYZ data of the optimized structures

3a

Number of atoms: 87

Charge = 0, multiplicity = 1

P	-0.07217	0.09037	-0.06233
Si	2.86093	-0.19903	0.96644
N	-2.97897	-0.02390	2.18365
N	0.89021	2.45781	-2.58493
N	-1.64513	-0.03817	0.24494
N	-2.66395	-1.99148	1.16777
N	1.43963	0.46344	-3.44528
N	-0.05649	0.49122	-1.62651
C	-2.33965	-0.65449	1.14414
C	0.71420	1.09830	-2.45824
C	0.39083	3.49822	-1.64959
C	-3.35404	-2.29073	2.41703
H	-2.64932	-2.64051	3.18193
H	-4.12818	-3.04179	2.28792
C	-3.14026	1.45106	2.29543
C	-2.01228	-3.07452	0.38246
C	-3.93606	-0.93873	2.78966
H	-4.93804	-0.81002	2.35780
H	-4.00412	-0.80720	3.86624
C	-3.95438	1.97565	1.10428
H	-3.45139	1.74860	0.16682
H	-4.07916	3.05758	1.18030
H	-4.94955	1.52455	1.08595
C	1.94483	1.45708	-4.38244
H	1.26467	1.58447	-5.23585
H	2.93071	1.19867	-4.76019
C	3.44074	-2.00004	1.00274
H	3.03143	-2.51533	1.87501
H	4.53142	-2.07490	1.04524
H	3.10038	-2.53752	0.11409
C	1.97403	2.71248	-3.52596
H	2.93481	2.81241	-3.00646
H	1.80183	3.60683	-4.11783
C	-1.77113	2.13691	2.37886
H	-1.14731	1.65818	3.13343
H	-1.91234	3.18487	2.65157
H	-1.23545	2.09772	1.43929
C	1.20422	-0.94618	-3.86102
C	1.15711	3.45997	-0.32142
H	1.05276	2.50350	0.18831
H	0.78820	4.24342	0.34393
H	2.22130	3.63837	-0.48756
C	1.06598	-0.14225	0.99961
C	-1.12012	3.33233	-1.43444
H	-1.64203	3.38945	-2.39164
H	-1.47994	4.14304	-0.79866
H	-1.38131	2.38891	-0.97002
C	3.56468	0.66193	2.49505
H	3.28092	1.71779	2.50968
H	4.65694	0.60696	2.52716
H	3.17277	0.20500	3.40682
C	-3.89092	1.75731	3.59765
H	-4.89958	1.34285	3.60702
H	-3.98030	2.83847	3.70148
H	-3.34723	1.38188	4.46655
C	-0.60205	-3.35343	0.91913
H	-0.64716	-3.69357	1.95653
H	0.03000	-2.46641	0.88683
H	-0.12885	-4.14364	0.33220
C	3.72659	0.61334	-0.51897
H	3.38536	0.19532	-1.46713
H	4.81048	0.47278	-0.45845
H	3.53620	1.68858	-0.54169
C	2.12389	-1.26759	-5.04545
H	3.17414	-1.13076	-4.78263
H	1.89915	-0.66444	-5.92587
H	1.98353	-2.31320	-5.31982
C	1.57364	-1.90450	-2.72237
H	1.41121	-2.93336	-3.04980
H	0.98665	-1.73205	-1.82810
H	2.62595	-1.79243	-2.46022
C	-2.86304	-4.34515	0.52759
H	-2.43765	-5.12220	-0.10728
H	-3.89308	-4.17499	0.20702
H	-2.87003	-4.72819	1.54833
C	-1.99181	-2.72172	-1.11053
H	-1.35647	-1.87697	-1.34139
H	-2.99926	-2.48658	-1.45892
H	-1.62810	-3.58615	-1.66861
C	0.60584	4.87264	-2.29873
H	1.66220	5.11004	-2.42900
H	0.17750	5.63454	-1.64758
H	0.10648	4.93990	-3.26718
C	-0.25702	-1.12758	-4.29791
H	-0.49178	-0.46795	-5.13698
H	-0.93742	-0.90232	-3.48040
H	-0.42790	-2.15576	-4.62252

3b

Number of atoms: 83

Charge = 0, multiplicity = 1

P	0.00213	-0.00757	0.11153
N	1.63189	-3.14847	0.88895
N	-2.72629	2.32796	-0.17106
N	-2.67630	1.13401	-2.01726
N	-1.57650	0.22218	-0.09325
C	1.00015	-2.07003	1.47186
C	-3.42471	2.27139	-2.26464
H	-3.88240	2.47539	-3.21144
C	1.29166	-3.72760	-0.44415
C	-2.22687	1.16544	-0.71581
C	-3.45427	3.00170	-1.13603
H	-3.94159	3.93771	-0.95189
C	-2.36207	0.07399	-3.02030
C	-1.01269	3.29528	1.30697
H	-0.84639	4.14240	0.63882
H	-0.30776	2.51668	1.01963
H	-0.79521	3.61696	2.32759
C	-2.72243	-1.30296	-2.44945
H	-2.16356	-1.52304	-1.54582
H	-2.50585	-2.06563	-3.19916
H	-3.78727	-1.34941	-2.21179
C	-0.88007	0.16825	-3.39702
H	-0.67096	1.13138	-3.86606
H	-0.63180	-0.62161	-4.10891
H	-0.22449	0.08609	-2.53270
C	-2.46862	2.82746	1.21273
C	-3.20872	0.30797	-4.27504
H	-4.27763	0.29178	-4.05489
H	-3.00039	-0.49610	-4.98045
H	-2.96029	1.24761	-4.77010
C	-3.39475	4.01475	1.49454
H	-4.44718	3.74445	1.39074
H	-3.18012	4.86762	0.84964
H	-3.23159	4.33619	2.52291
C	-2.78366	1.72602	2.23249
H	-2.62933	2.12080	3.23786
H	-2.15480	0.85416	2.09234
H	-3.82544	1.41069	2.14485
Si	2.91457	1.06324	-0.47825
C	1.12864	0.94605	-0.43654
C	3.52047	0.96082	-2.26819
H	3.25871	-0.00378	-2.71130
H	4.60563	1.08071	-2.34024
H	3.05076	1.73856	-2.87507
C	3.90395	-0.24805	0.47875
H	3.66060	-0.23939	1.54261
H	4.97957	-0.06719	0.38475
H	3.70660	-1.25565	0.10848
C	3.47072	2.73030	0.22311
H	2.99419	3.55174	-0.31704
H	4.55502	2.85931	0.15425
H	3.18864	2.82234	1.27569
C	1.37814	0.43482	3.38185
H	2.45580	0.58483	3.30969
N	0.01697	-1.38000	0.97173
N	1.53744	-1.95344	2.73695
C	2.54615	-3.67313	1.78611
H	3.18058	-4.50450	1.55388
C	2.48883	-2.94370	2.91392
H	3.06616	-3.04556	3.81049
C	2.10145	-5.00953	-0.65408
H	1.87949	-5.76298	0.10322
H	3.17543	-4.81772	-0.66316
H	1.83351	-5.42522	-1.62510
C	-0.20117	-4.08006	-0.46839
H	-0.81706	-3.20245	-0.29371
H	-0.42772	-4.82058	0.30163
H	-0.45618	-4.50723	-1.43951
C	1.65450	-2.73542	-1.55263
H	1.36860	-3.15342	-2.51953
H	2.72922	-2.55122	-1.56517
H	1.15854	-1.77700	-1.42905
H	0.98822	1.11784	4.13870
H	0.94548	0.70044	2.42155
C	1.79451	-1.31171	5.10010
H	2.87129	-1.16039	5.01088
H	1.60372	-2.32808	5.44789
H	1.42857	-0.62491	5.86299
C	-0.44079	-1.21839	4.00728
H	-0.79579	-0.52946	4.77521
H	-0.63389	-2.23810	4.34708
H	-1.00123	-1.04850	3.09227
C	1.06300	-1.00720	3.79031

$(Me_2N)_2PCSiMe_3$ (3c)

Number of atoms: 33

Charge = 0, multiplicity = 1

P	0.16563	-0.29049	-0.44265
Si	2.94634	1.21341	-0.76994
C	1.19288	0.78284	-0.92260
C	3.48386	2.25582	-2.24337
H	3.35630	1.70368	-3.17795
H	4.53482	2.54885	-2.16706
H	2.88080	3.16406	-2.31255
C	4.07105	-0.30375	-0.70695
H	3.87446	-0.90273	0.18545
H	5.12807	-0.02239	-0.69632
H	3.90414	-0.94204	-1.57826
C	3.21648	2.22896	0.79740
H	2.56657	3.10674	0.80797
H	4.25164	2.57543	0.86475
H	3.00195	1.64573	1.69616
N	-1.36614	-0.46465	-1.07536
N	0.18833	-1.47625	0.74065
C	-0.29153	-2.83362	0.51291
H	0.54333	-3.51527	0.31056
H	-0.82283	-3.20016	1.39666
H	-0.96976	-2.85765	-0.33581
C	1.17895	-1.36082	1.79997
H	0.75212	-1.72412	2.73933
H	2.07972	-1.94595	1.58214
H	1.46949	-0.32018	1.92561
C	-1.61916	0.14077	-2.37787
H	-2.41187	-0.41893	-2.88178
H	-1.93063	1.18717	-2.28483
H	-0.71542	0.11401	-2.98087
C	-2.54404	-0.52556	-0.21692
H	-3.30284	-1.16772	-0.67228
H	-2.28593	-0.93053	0.75801
H	-2.97961	0.47116	-0.07347

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