Supporting Information

Carbene-Dichlorosilylene Stabilized Phosphinidenes Exhibiting Strong Intramolecular Charge Transfer Transition

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Content:

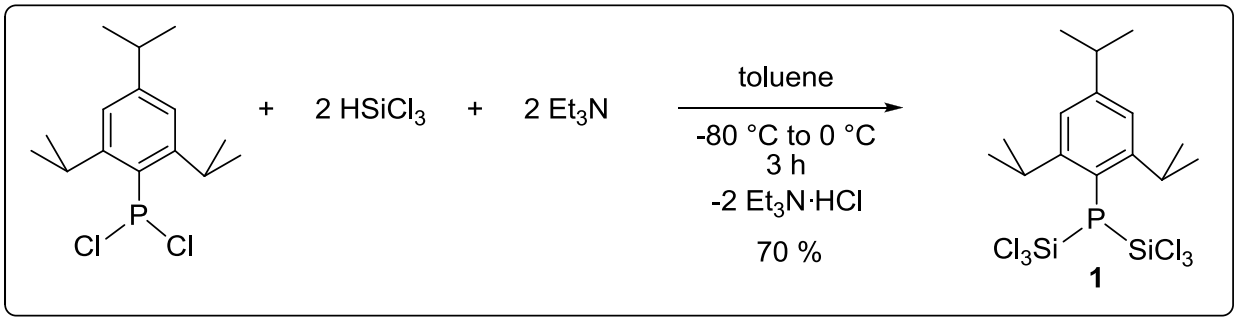
S1. Syntheses of compounds 1, 2a-c, and 3

General Remarks

All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and in a dinitrogen filled glove box where the O_2 and H_2O levels were usually kept below 1 ppm. $ArPCl_2$ [Ar = 2,4,6-*i*$Pr_3C_6H_2$],[S1] Cyclic alkyl(amino) carbenes [(cAAC), used as reported cAAC·LiOTf][S2] [Cy-cAAC: = :$C(CH_2)(CMe_2)(C_6H_{10})$N-2,6-*i*$Pr_2C_6H_3$, Et_2-cAAC: = :$C(CH_2)(CMe_2)(CEt_2)$N-2,6-*i*$Pr_2C_6H_3$ and Me_2-cAAC: = :$C(CH_2)(CMe_2)_2$N-2,6-*i*$Pr_2C_6H_3$], and the N-heterocyclic carbene, 1,3-bis(2,6- *i*$Pr_2C_6H_3$)-imidazol-2-ylidene[S3a] were prepared according to the literature reported procedures. All solvents were dried initially with the M-Braun solvent drying system and then deoxygenated by stirring for 4-5 hours over Na/K alloy followed by distillation in vacuum and degassed. ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker Avance 500 MHz NMR spectrometer. Deuterated NMR solvent C_6D_6 was dried prior to use by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. EI-MS spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV) by EI-MS methods. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus.

Synthesis of compound 1:

Scheme S1. Synthesis of compound **1**



To a pre-cooled solution of $ArPCl_2$ (Ar = 2,4,6-*i*$Pr_3C_6H_2$) (4.273 g, 14 mmol) in 100 mL toluene at -90 to -80 ^oC (cooling bath was prepared by using *i*-PrOH and liquid nitrogen), triethylamine (4.3 mL, 30.8 mmol) and trichlorosilane (2.82 mL, 28 mmol) were added sequentially. The temperature of the reaction mixture was then slowly raised to 0 ^oC over 3-4 h with continuous stirring. The white precipitate ($Et_3NH^+Cl^-$) formed was filtered through a celite pad. The light

yellow filtrate was concentrated under vacuo to 5mL to immediately obtain the colorless block-shaped crystals of compound **1** in 70% yield (4.95 g). The crystals of compound **1** are stable at room temperature under an inert atmosphere for several months. Suitable single crystals of compound **1** for X-ray crystallographic studies were grown from a concentrated toluene solution at room temperature.

Compound 1: Melting range: 87-88 °C

^{1}H NMR (500 MHz, C_6D_6) δ: 7.10 (d, J = 3.9 Hz, $2H_{Ar}$), 3.95 (dq, J = 13.3, 6.6 Hz, 2H, *o*-$CHMe_2$), 2.61 (dt, J = 13.8, 6.9 Hz, 1H, *m*-$CHMe_2$), 1.26 (d, J = 6.7 Hz, 12H), 1.05 (d, J = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, C_6D_6) δ: 157.68 (*o*-C_{sp2}), 157.56 (*o*-C_{sp2}), 153.40 (*p*-C_{sp2}), 123.72 (*m*-C_{sp2}), 123.67 (*m*-C_{sp2}), 122.39 (C_{sp2}-P).

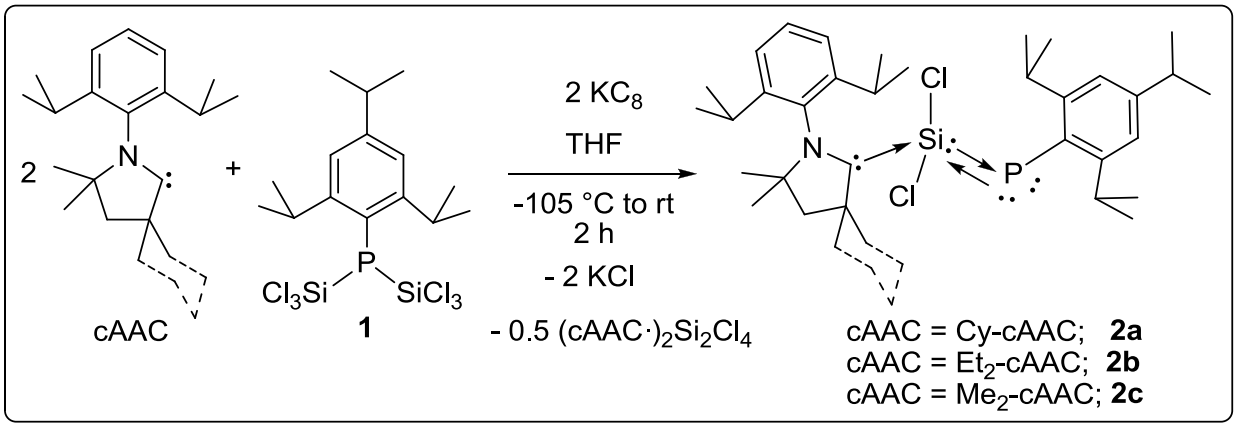
^{31}P NMR (202 MHz, C_6D_6) δ: -101.60 (with two satellites at -101.48 and -101.74).

^{29}Si NMR (99 MHz, C_6D_6, 25 °C) δ: 2.73 (d, J_{Si-P} = 51.7 Hz)

EI-MS for $C_{15}H_{23}Cl_6PSi_2$: m/z (%) 501.9 (100%)[M^+], 503.9 (81%)[M^+]. Mass spectrometry was performed on a solid sample of **1**.

Syntheses of compounds 2a-c:

Scheme S2. Syntheses of compounds **2a-c**



The reaction of **1** with cAAC at different molar ratios always produces a solution having light to dark blue colors depending upon the ratio of cAAC which disappear when the reaction is stirred

for a longer period of time (for 2 days). Several synthetic attempts led to the conclusion that a reducing agent such as KC_8 is required for the successful syntheses of **2a-c**.

Synthesis of compound 2a: Tetrahydrofuran (50 mL) was cooled to -105 °C and added to a 2:1:2 molar mixture of Cy-cAAC: [:C(CH_2)(CMe_2)(C_6H_{10})N-2,6-*i*$Pr_2C_6H_3$] (962 mg, 2 mmol), compound **1** (503 mg, 1 mmol), and KC_8 (270 mg, 2 mmol) resulting in an immediate color change to dark green. The temperature of the reaction mixture was kept at -78 °C for 30-45 minutes and then slowly raised to room temperature over 20 minutes (Note: Cooling of the reaction mixture for the above mentioned time is very important in order to reduce the amount of the byproduct.). After 35 minutes the color of the reaction mixture slowly turned to dark blue. The mixture was stirred for 1 h at room temperature and then the graphite was separated out by filtration. The dark blue filtrate was brought to the dryness and extracted with *n*-hexane (50 mL) and the resulting volume was reduced (to 2-3 mL) under vacuo. The concentrated solution was stored in a refrigerator at 0 °C and blue-black rods of compound **2a** were obtained in 45% yield (294 mg). The crystals of **2a** are stable at 0 ^oC under an inert atmosphere for at least 3 months and in air for 45 minutes and then slowly decompose to a white mass within one day. The crystals of **2a** are soluble in THF, toluene, benzene and *n*-hexane. **2a** slowly decomposes in THF.

Compound 2a: Elemental analysis found % (cal.) for $C_{38}H_{58}Cl_2NPSi$; C: 70.01 (69.27), H: 9.13 (8.87), N: 2.41 (2.13).

Decomposition: above 170 °C; UV-visible absorption bands found at 412 and 665 nm (in THF).

^{1}H NMR (500 MHz, C_6D_6, 25 ^oC) δ ppm: 7.22 (d, J = 1.5 Hz, 2H, *m*-H_{Ar}(Tip)), 7.10–7.07 (m, 1H, *p*-H_{Ar}(Dip)), 6.93 (d, J = 7.7 Hz, 2H, *m*-H_{Ar}(Dip)), 5.06–4.96 (m, 2H, *o*-C*H*Me_2(Tip)), 3.75 (dt, J = 13.5, 6.8 Hz, 1H, C*H*Me_2(cAAC-Dip)), 3.56 (dt, J = 13.1, 6.6 Hz, 1H, C*H*Me_2(cAAC-Dip)), 3.46–3.34 (m, 2H, CH_2(cyclohexane)), 2.87–2.82 (m, 1H, *p*-C*H*Me_2(Tip)), 2.77 (dt, J = 13.1, 6.6 Hz, 2H), 2.44 (td, J = 13.3, 3.0 Hz, 1H), 2.09 (t, J = 13.7 Hz, 1H), 2.00 (d, J = 12.5 Hz, 1H), 1.86 (d, J = 12.0 Hz, 1H), 1.71 (dd, J = 40.8, 12.2 Hz, 4H, 2 x CH_2(cyclohexane)), 1.54 (d, J = 6.9 Hz, 12H, *o*-CH*Me*$_2$(Tip)), 1.53–1.50 (m, 6H, CH*Me*$_2$(cAAC-Dip)), 1.26 (d, J = 6.9 Hz, 6H, CH*Me*$_2$(cAAC-Dip), 1.07 (d, J = 6.6 Hz, 6H, *p*-CH*Me*$_2$(Tip)), 0.84 (s, 6H, NC*Me*$_2$).

^{13}C NMR (126 MHz, C_6D_6, 25 ^oC) δ ppm: 208.05 (carbene C), 156.31, 147.07, 146.44, 134.12, 133.68, 133.16, 131.19, 128.79, 127.38, 126.21, 121.31, 81.79, 68.87, 61.69, 51.11, 45.43, 35.20, 35.03, 32.41, 29.91, 29.78, 29.36, 27.52, 27.49, 27.25, 26.80, 26.42, 25.58, 25.51, 25.37, 25.03, 24.91, 23.50, 23.34.

^{31}P NMR (202 MHz, C_6D_6, 25 ^oC) δ ppm: -123.09 (with two satellites at -122.62 and -123.60).

^{29}Si NMR (99 MHz, C_6D_6, 25 °C) δ ppm: -6.56 (d, J_{Si-P} = 198.4 Hz).

Synthesis of compound 2b: Tetrahydrofuran (30 mL) was cooled to -105 °C and added to a 2:1:2 molar mixture of Et_2-cAAC: [:C(CH_2)(CMe_2)(CEt_2)N-2,6-*i*$Pr_2C_6H_3$] (470 mg, 1 mmol), compound **1** (252 mg, 0.5 mmol), and KC_8 (135 mg, 1 mmol) resulting in an immediate color change to dark blue. The mixture was slowly warmed to room temperature over 1 h (Note: Cooling of the reaction mixture for the above mentioned time is very important in order to reduce the amount of the byproduct.) and then allowed to stir for another 1 h. The graphite was separated out through filtration. The dark blue filtrate was brought to dryness and extracted with *n*-hexane (50-60 mL) and the resulting volume was reduced (to 3 mL) under vacuo. The concentrated solution was kept overnight at 0 ^oC in a refrigerator to produce blue-black rods of compound **2b** in around 44% yield (143 mg). The crystals of **2b** are stable at 0 ^oC under an inert atmosphere for at least 1 month, and in air for 30 minutes and then slowly decompose to a white mass within one day. The crystals of **2b** are soluble in THF, toluene, benzene and *n*-hexane. **2b** slowly decomposes in THF.

Compound 2b: Elemental analysis found % (cal.) for $C_{37}H_{58}Cl_2NPSi$; C: 67.70 (68.70), H: 8.57 (9.04), N: 1.93 (2.17).

Melting range: 165-166 °C to a blue liquid; UV-visible absorption bands found at 412 and 680 nm (in THF).

^{1}H NMR (500 MHz, C_6D_6, 25 ^oC) δ ppm: 7.23 (d, J = 1.6 Hz, 2H, *m*-H_{Ar}(Tip)), 7.02–6.98 (t, J = 7.0 Hz, 1H, *p*-H_{Ar}(Dip)), 6.92 (d, J = 7.4 Hz, 2H, *m*-H_{Ar}(Dip)), 5.04–4.94 (m, 2H, *o*-C*H*Me_2(Tip)), 2.89–2.80 (m, 1H, *m*-C*H*Me_2(Tip)), 2.72 (dt, J = 13.1, 6.5 Hz, 2H, C*H*Me_2(cAAC-Dip)), 2.61–2.53 (m, 2H, CH_2Me), 2.47 (dqd, J = 14.6, 7.3, 1.9 Hz, 2H, CH_2Me), 1.56 (t, J = 7.3 Hz, 18H, *o*-CHMe_2(Tip) + CHMe_2(cAAC-Dip)), 1.45 (s, 2H, NCMe_2CH_2), 1.25 (d, J = 6.9 Hz, 6H, CHMe_2(cAAC-Dip)), 1.07 (d, J = 6.5 Hz, 6H, *m*-CHMe_2(Tip)), 0.88 (t, J = 7.4 Hz, 6H, *p*-CHMe_2(Tip)), 0.81 (s, 6H, NCMe_2).

^{13}C NMR (126 MHz, C_6D_6, 25 ^oC) δ ppm: 211.44 (carbene C), 155.91, 146.53, 145.57, 133.08, 132.87, 132.65, 130.72, 125.79, 120.76, 82.14, 64.40, 41.28, 34.71, 34.34, 34.27, 34.13, 33.99, 29.57, 28.64, 27.17, 25.15, 24.81, 24.42, 11.01.

^{31}P NMR (202 MHz, C_6D_6, 25 ^oC) δ ppm: -121.83 (with two satellites at -122.30 and -122.83).

^{29}Si NMR (99 MHz, C_6D_6, 25 °C) δ ppm: -7.48 (d, J_{Si-P} = 203.6 Hz).

Synthesis of compound 2c: Tetrahydrofuran (30 mL) was cooled to -105 °C and added to a 2:1:2 molar mixture of Me_2-cAAC: [:C(CH_2)(CMe_2)$_2$N-2,6-*i*$Pr_2C_6H_3$] (440 mg, 1 mmol), compound **1** (252 mg, 0.5 mmol), and KC_8 (135 mg, 1 mmol) resulting in an immediate color change to dark purple. The mixture was slowly warmed to room temperature over 1 h (Note: Cooling of the reaction mixture for the above mentioned time is very important in order to

reduce the amount of the byproduct.) and then allowed to stir for another 1 h. The graphite was separated out through filtration. The purple-blue filtrate was brought to dryness and extracted with *n*-hexane (30 mL) and this *n*-hexane solution was discarded. The residue contains highly crystalline compound **2c** which was completely dissolved in THF (10 mL). The concentrated THF solution was stored at 0 °C in a refrigerator to form dark blue rods of compound **2c** in 50% yield (308 mg) at room temperature. The crystals of **2c** are stable at 0 ^{o}C under an inert atmosphere for 3 months, and in air for 45 minutes and then slowly decompose to a white mass within one day. The crystals of **2c** are soluble in THF, toluene, benzene and *n*-hexane. **2c** slowly decomposes in THF.

Alternative procedure for the synthesis of compound 2c: Compound **1** (252 mg, 0.5 mmol) was dissolved in 30 mL of tetrahydrofuran to produce a light yellow solution which was then cooled to -105 °C and passed through a cannula to a 2:2 solid molar mixture of Me_2-cAAC: [:C(CH_2)(CMe_2)$_2$N-2,6-*i*Pr$_2$C$_6$H$_3$] (440 mg, 1 mmol) and KC_8 (135 mg, 1 mmol) (maintaining the temperature at -105 °C while addition). The temperature of the reaction mixture was slowly raised to room temperature over 1 h. The resulting dark purple-blue solution was allowed to stir for 2 h using *i*-PrOH bath (*i*-PrOH frozen with liquid nitrogen). The graphite was separated out through filtration. The purple-blue filtrate was brought to dryness and extracted with *n*-hexane (50 mL) and the resulting volume was reduced (to 3 mL) under vacuo. The concentrated solution was kept overnight at 0 ^{o}C in a refrigerator to produce blue-black rods of compound **2c** in around 50% yield (152 mg).

Compound 2c: Elemental analysis found % (cal.) for $C_{35}H_{54}Cl_2NPSi$; C: 68.29 (67.94), H: 9.02 (8.80), N: 2.42 (2.26).

Decomposition: above 165 °C; UV-visible absorption bands found at 437 and 669 nm (in *n*-hexane).

^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C) δ ppm: 7.23 (d, J = 1.4 Hz, 2H, *m*-H_{Ar}(Tip)), 6.99 (t, J = 7.5 Hz, 1H, *p*-H_{Ar}(Dip)), 6.91 (d, J = 7.7 Hz, 2H, *m*-H_{Ar}(Dip)), 5.01–4.94 (m, 2H, *o*-C*H*Me_2(Tip)), 2.85 (dt, J = 13.9, 7.0 Hz, 1H, *m*-C*H*Me_2(Tip)), 2.71 (dt, J = 13.1, 6.5 Hz, 2H, C*H*Me_2(cAAC-Dip)), 1.84 (d, J = 12.4 Hz, 6H), 1.64 (d, J = 12.4 Hz, 6H, CH*Me*$_2$(cAAC-Dip)), 1.51 (d, J = 6.7 Hz, 12H, *o*-CH*Me*$_2$(Tip)), 1.36 (s, 2H, NCMe_2C*H*$_2$), 1.26 (d, J = 6.9 Hz, 6H, CH*Me*$_2$(cAAC-Dip)), 1.05 (d, J = 6.6 Hz, 6H, *m*-CH*Me*$_2$(Tip)), 0.79 (s, 6H, NC*Me*$_2$).

^{13}C NMR (126 MHz, C_6D_6, 25 ^{o}C) δ ppm: 208.95 (carbene C), 156.30, 146.44, 143.77, 131.23, 127.64, 126.22, 126.07, 124.61, 121.35, 68.19, 58.91, 35.20, 35.02, 32.41, 29.88, 29.62, 29.01, 28.82, 28.25, 27.86, 27.43, 26.79, 26.52, 25.91, 25.60, 25.52, 25.31, 24.92, 23.50.

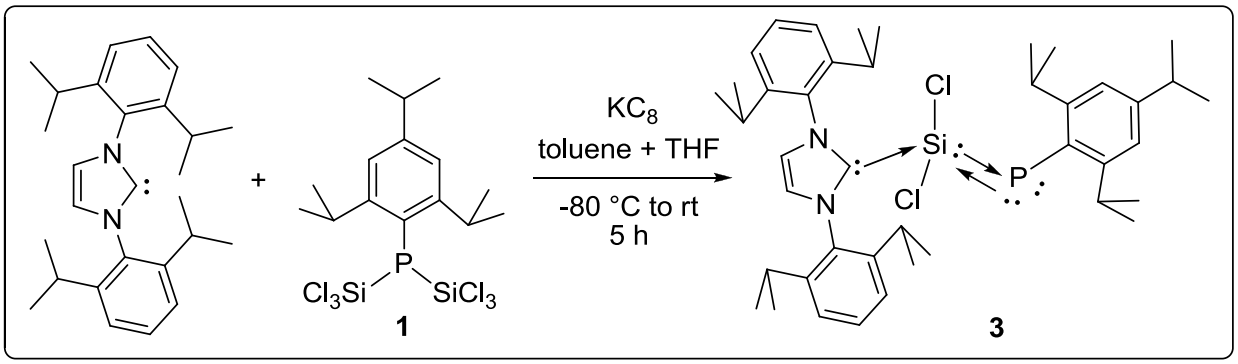
^{31}P NMR (202 MHz, C_6D_6, 25 ^{o}C) δ ppm: -123.27 (with two satellites at -122.82 and -123.78).

^{29}Si NMR (99 MHz, C_6D_6, 25 °C) δ ppm: -7.89 (d, J_{Si-P} = 195.5 Hz).

Important point: Cooling (from -105 ^{o}C to slowly room temperature over a period of at least 1 h using a frozen THF bath initially and then a frozen *i*-PrOH bath) of the reaction mixture during the syntheses of compound **2a-c** is very crucial otherwise lack of cooling enhances the formation of $(cAAC)_2SiCl_2$ as the side product.

Synthesis of compound 3:

Scheme S3. Synthesis of compound **3**



Synthesis of compound 3: Tetrahydrofuran (30 mL) was cooled to -78 °C which was then added to a solution of N-heterocyclic carbene [1,3-bis(2,6- iPr$_2$C$_6$H$_3$)-imidazol-2-ylidene] (388 mg, 1 mmol) in toluene (15 mL). The resulting mixture was then cooled to -78 °C, and added to a 1:2 molar mixture of compound **1** (252 mg, 0.5 mmol), and KC_8 (135 mg, 1 mmol). The mixture was slowly warmed to room temperature over 45-60 minutes. The initial yellow solution was turned to dark red after 1.5 h. The reaction mixture was allowed to stir for another 3.5 h at room temperature, and then filtered to separate out the graphite. The dark-red filtrate was brought to dryness and extracted with *n*-hexane (30 mL) and the resulting volume was reduced (5 mL) under vacuo. The concentrated solution produced tiny dark-red crystals of compound **3** in 90% yield (326 mg) at room temperature. The crystals of **3** are stable at room temperature under an inert atmosphere for 3 months and in air for less than a minute and then readily decompose to a white mass with fume. Suitable single crystals of compound **3** for X-ray crystallographic studies were grown from a dilute C_6D_6 solution at room temperature.

Compound 3: Elemental analysis found % (cal.) for $C_{42}H_{59}Cl_2N_2PSi$; C 69.72 (69.88), H 8.36 (8.24), N 3.95 (3.88).

Decomposition: above 201 °C (decomposed to a brown liquid); UV-visible absorption band found at 475 nm (in THF).

^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ ppm: 7.20 (t, J = 7.7 Hz, 2H, p-H_{Ar}), 7.12 (s, 2H, m-$H_{Ar\text{-}Tip}$), 7.07 (d, J = 7.8 Hz, 4H, m-H_{Ar}), 6.35 (s, 2H, NC*H*), 4.68–4.61 (m, 2H, C*H*Me_2(Tip)), 2.84–2.73 (m, 5H, C*H*Me_2(NHC + Tip)), 1.53 (d, J = 6.7 Hz, 12H, CH*Me*$_2$(Tip)), 1.41 (d, J = 6.9 Hz, 12H, CH*Me*$_2$(NHC)), 1.22 (d, J = 6.9 Hz, 6H, CH*Me*$_2$(Tip)), 0.96 (d, J = 6.9 Hz, 12H, CH*Me*$_2$(NHC)).

^{13}C NMR (126 MHz, C_6D_6, 25 °C) δ ppm: 156.59, 156.54, 146.57, 146.40, 134.23, 132.39, 132.17, 129.81, 129.01, 126.02, 124.94, 121.01, 68.27, 35.19, 34.24, 34.17, 29.98, 29.96, 26.50, 25.10, 24.92, 23.28, 23.25.

^{31}P NMR (202 MHz, C_6D_6, 25 °C) δ ppm: -141.24 (with two satellites at -140.77 and -141.75).

^{29}Si NMR (99 MHz, C_6D_6, 25 °C) δ ppm: -19.12 (d, $J_{Si\text{-}P}$ = 197.7 Hz).

S2. Stability of compounds 2a-c, and 3 in air

The cAAC containing compounds **2a, 2b** and **2c** are stable in air for several hours. The blue color of the powder samples is retained for several hours. In contrast the red colored powder of NHC analogue **3** immediately turns into colorless solid (within 2-3 minutes) on exposure to air with the formation of colorless smoke.

Figure S1. Solid samples of compounds **2c** (left) and **3** (right). The picture is taken within 20-30 seconds after the samples being exposed to air.

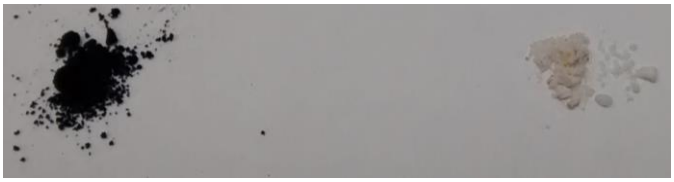
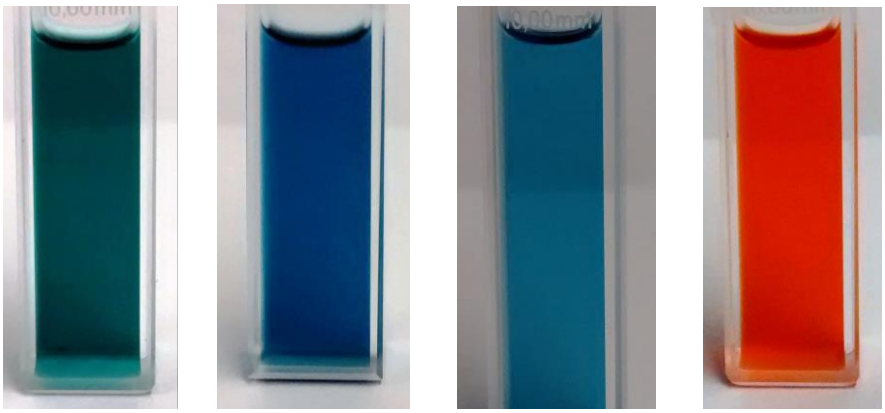


Figure S2. Solid samples of compounds **2c** (left) and **3** (right). The picture is taken after 2-3 minutes from the time of samples being exposed to air.

S3. UV-visible spectra of compounds 2a-c and 3



2a **2b** **2c** **3**

Figure S3. Color of compounds **2a**, **2b, 2c** (~10^{-4} M solutions) and **3** (~10^{-3} M solution).

UV-visible spectra of compounds 2a:

The absorption bands of **2a** (of 2.16×10^{-4} M *n*-hexane solution) are observed at 438 nm (band I) (the molar extinction coefficient, ε = 1402 L mol^{-1} cm^{-1}) and at 677 nm (band II) (ε = 3965 L mol^{-1} cm^{-1}).

It should be noted that the band II (due to intramolecular charge transfer; ICT), observed at 677 nm (ε = 3965 L mol^{-1} cm^{-1}) in *n*-hexane was red-shifted in polar and poorly coordinating solvent toluene to 679 nm and blue-shifted in polar coordinating solvent THF to 665 nm (ε = 3032 L mol^{-1} cm^{-1} in tetrahydrofuran (THF) (c = 4.55×10^{-4} M)]. The shift of maxima at 677nm (in *n*-hexane) of the band II (500-900 nm) for compound **2a** is in line with those blue colored anthracenyl-substituted trialkyldisilene [S3b] and 3-silylene-2-silaaziridine [S3c] show ICT due to electronic transitions from $\pi_{Si=Si}\rightarrow\pi^*_{anthracene}$ and $\pi_{Si=C}\rightarrow\pi^*_{anthracene,}$ respectively.

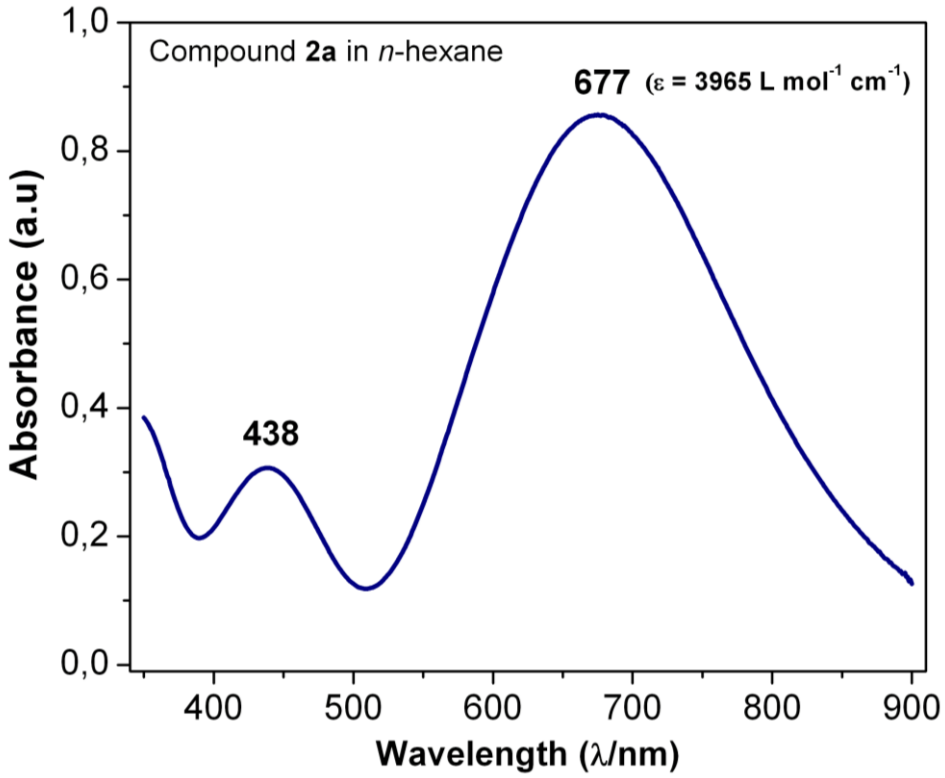


Figure S4. UV-vis spectrum of compound **2a** in *n*-hexane (of 2.16×10^{-4} M solution). The molar extinction coefficient, ε = 3965 L mol^{-1} cm^{-1}.

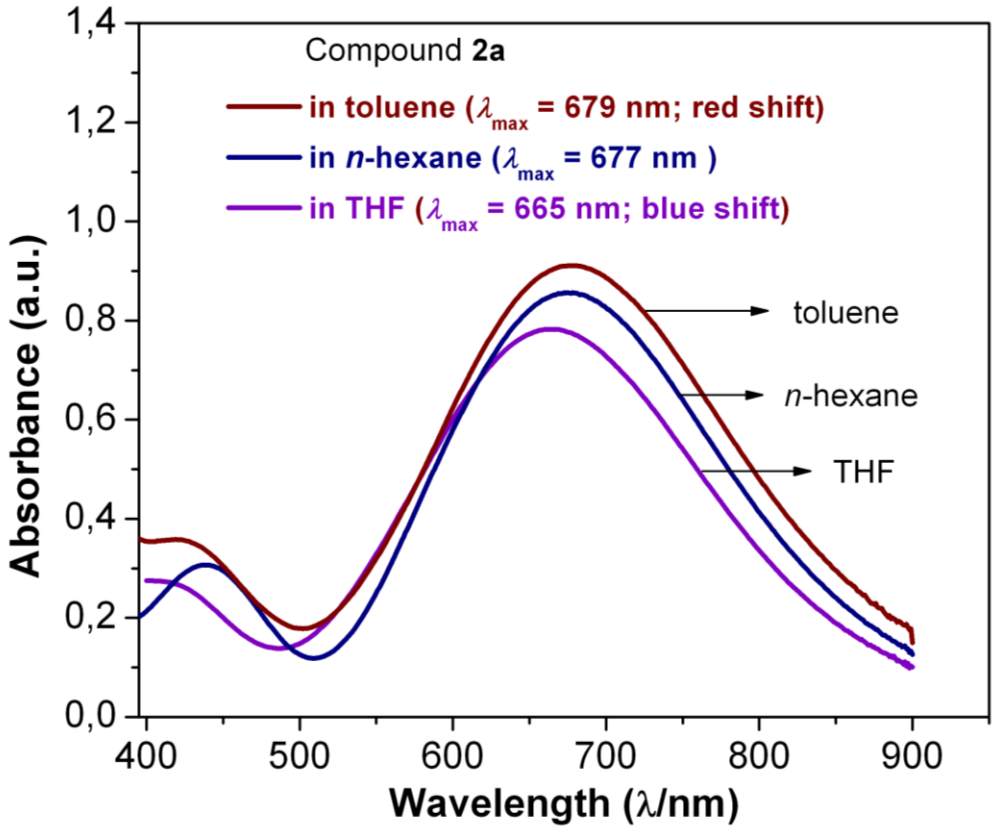


Figure S5. Comparative UV-vis spectra of compound **2a** in toluene, *n*-hexane, and THF.

UV-visible spectrum of compound 2b:

The absorption bands of **2b** (in THF solution) are observed at 412 nm (band I) and at 680 nm (band II).

UV-visible spectrum of compound 2c:

The absorption bands of **2c** (in THF solution) are observed at 437 nm (band I) and at 669 nm (band II).

UV-visible spectrum of compound 3:

The absorption band of **3** (of 4.15 $\times 10^{-4}$ M THF solution) is observed at 475 nm (ε = 1102 L mol^{-1} cm^{-1}).

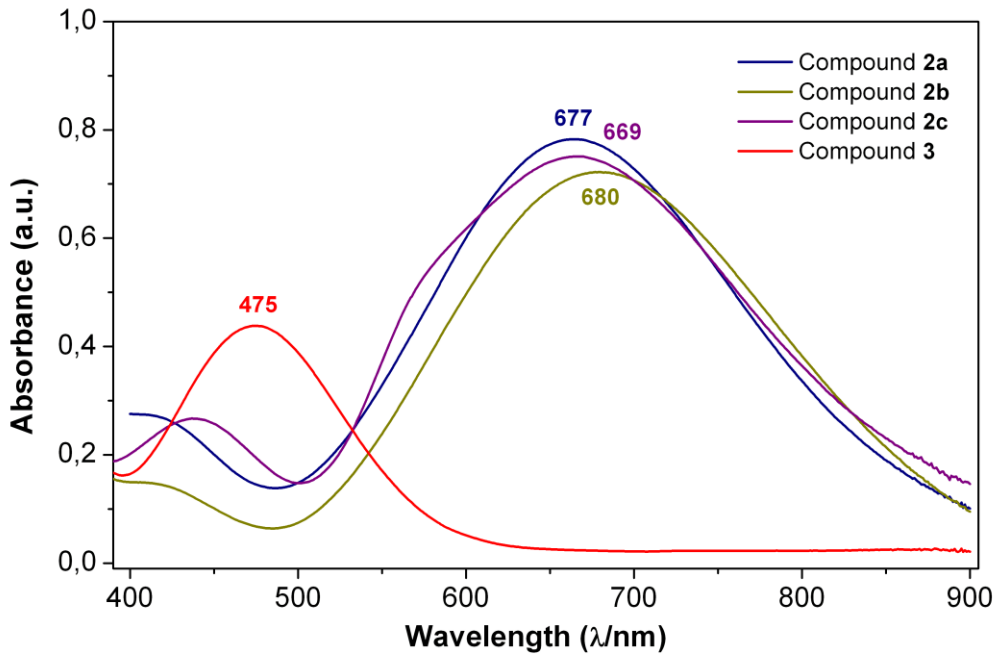


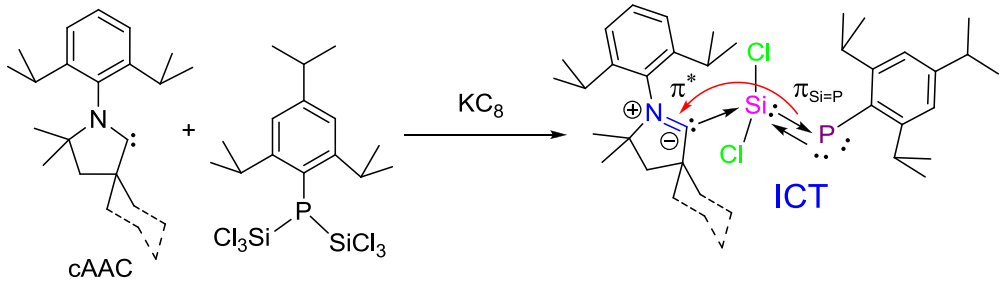
Figure S6. UV-vis spectra of compounds **2a-b** (in THF), **2c** (in *n*-hexane) and **3** (in THF).

Intramolecular charge transfer transition (ICT):

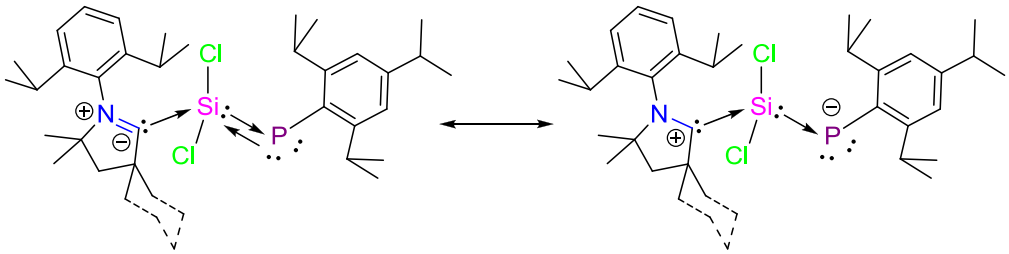
The dark blue color of **2a-c** arises due to the strong intramolecular charge transfer (ICT) transition from $\pi_{Si=P} \rightarrow \pi^*_{cAAC}$, and the absorption band II observed in the UV-vis spectra of compounds **2a-c** is assigned for this particular transition from the theoretical calculations.

Scheme S4. (a) Strong intramolecular charge transfer (ICT with λ_{max} at 677 (**2a**), 680 (**2b**), 679 (**2c**) nm; Figure S6) transition from $\pi_{Si=P} \rightarrow \pi^*_{cAAC}$; (b) Resonance structures of compound **2a-c**.

(a)



(b)



The dramatic change in color of the compounds **2a-c** and **3** from red (**3**, NHC) to blue (**2**, cAAC) is due to the difference in energy of the LUMO within the carbenes due to a lower lying LUMO of cAAC.

When one of the π–donating and σ–accepting nitrogen atoms in NHC (N-heterocyclic carbene) is replaced by a σ–donating quaternary carbon atom, the ligand field is drastically changed and the resultant carbene is called the cyclic alkyl(amino) carbene (cAAC). Theoretical studies showed that the HOMO-LUMO energy gap is smaller in cAAC than that of NHC (Figure S7).

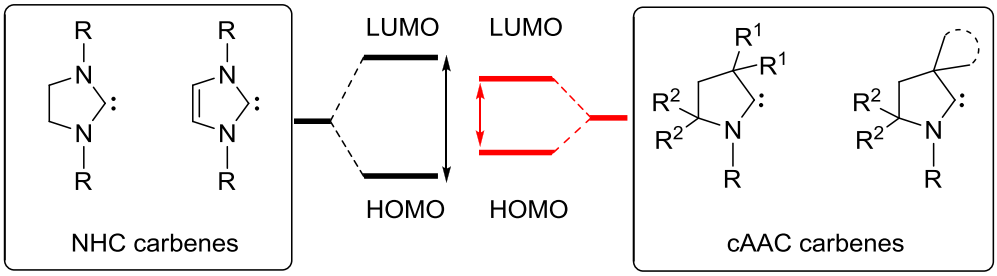
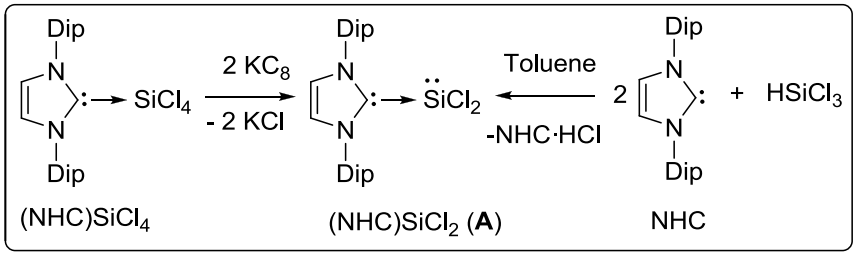


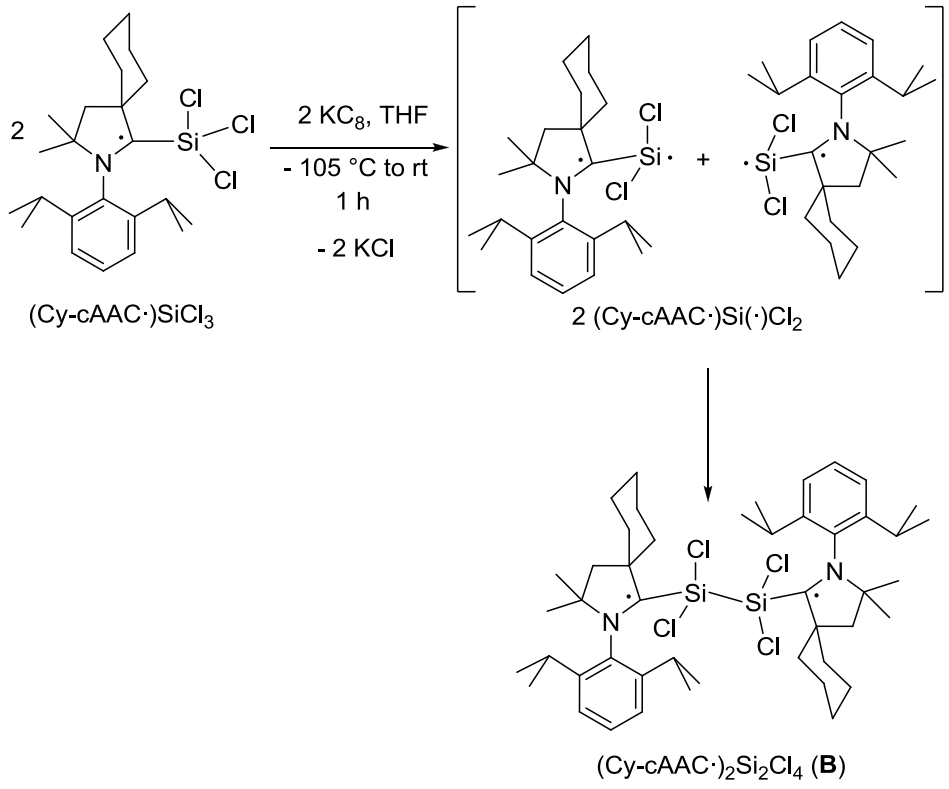
Figure S7. Comparison between NHC (left) and cAAC (right) carbenes.

Scheme S5. Known synthetic routes of (a) non-radical (NHC)$SiCl_2$ (**A**) and (b) singlet diradical (Cy-cAAC)Si_2Cl_4 (**B**).

(a)


Dip
N
SiCl4
2 KC8
- 2 KCl
SiCl2
Toluene
-NHC·HCl
2
+ HSiCl3
(NHC)SiCl4
(NHC)SiCl2 (A)
NHC

(b)


2
Cl
Si
N
2 KC8, THF
- 105 °C to rt
1 h
- 2 KCl
+
(Cy-cAAC·)SiCl3
2 (Cy-cAAC·)Si(·)Cl2
(Cy-cAAC·)2Si2Cl4 (B)

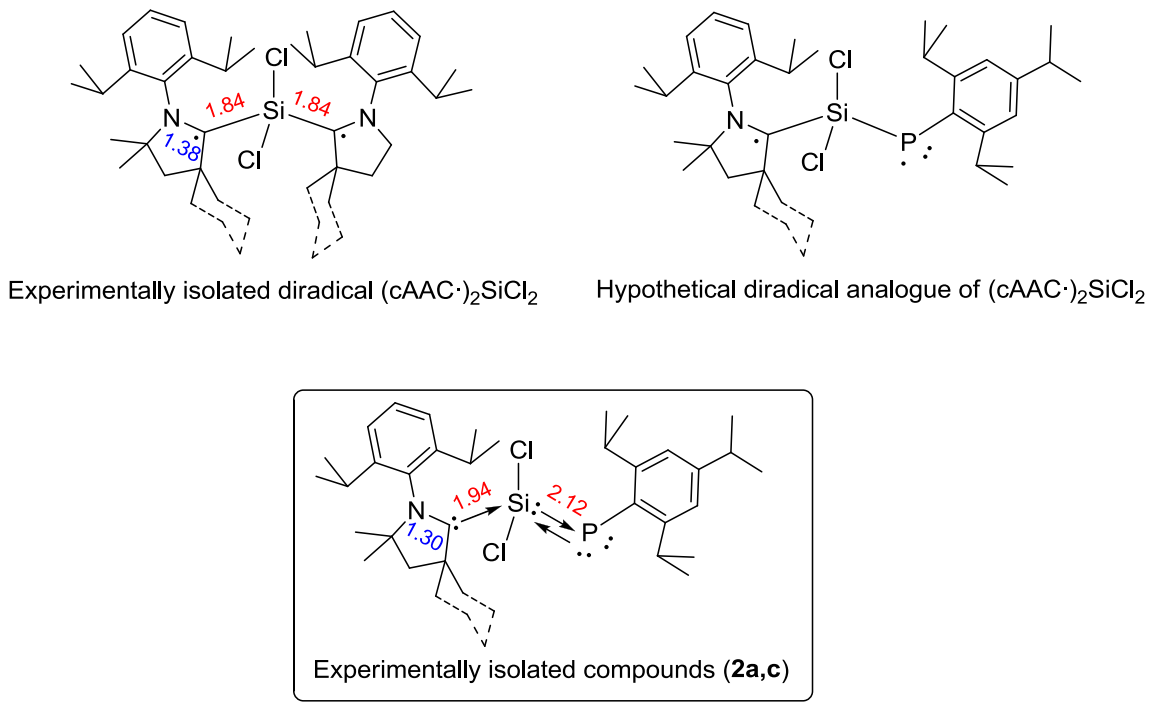


Figure S8. Selected bond lengths in $(cAAC\cdot)_2SiCl_2$ (top left; C-Si electron sharing covalent bond; C-Si = 1.84 Å and C-N = 1.38 Å) and cAAC→$SiCl_2$→P-Tip (**2a,c**) (top right and bottom; C→Si dative bond; C-Si = 1.94 Å and C-N = 1.30 Å).

S4. Crystal data of 1, 2a, 2c and 3

Suitable crystals for single crystal X–ray diffraction analysis of compounds **1**, **2a**, **2c** and **3** were selected under an argon atmosphere and transferred in perfluorated oil on a microscope slide. Crystals were mounted to the tip of a MiTeGen©MicroMount using a polarizer microscope. The data were collected either on a BRUKER D8 three circle diffractometer equipped with a SMART APEX II QUAZAR detector and an INCOATEC Mo or Ag microsource[S1] with mirror optics, or a BRUKER TXS-Mo rotating anode with mirror optics and a SMART APEX II ULTRA detector. The data were integrated with SAINT[S2] and a semi-empirical absorption correction with SADABS[S3] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods against F^2 (SHELXL-2014)[S4] within the SHELXLE-GUI[S5]. All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. The disordered moieties were refined using distance restraints and restraints for the anisotropic displacement parameter[S6].

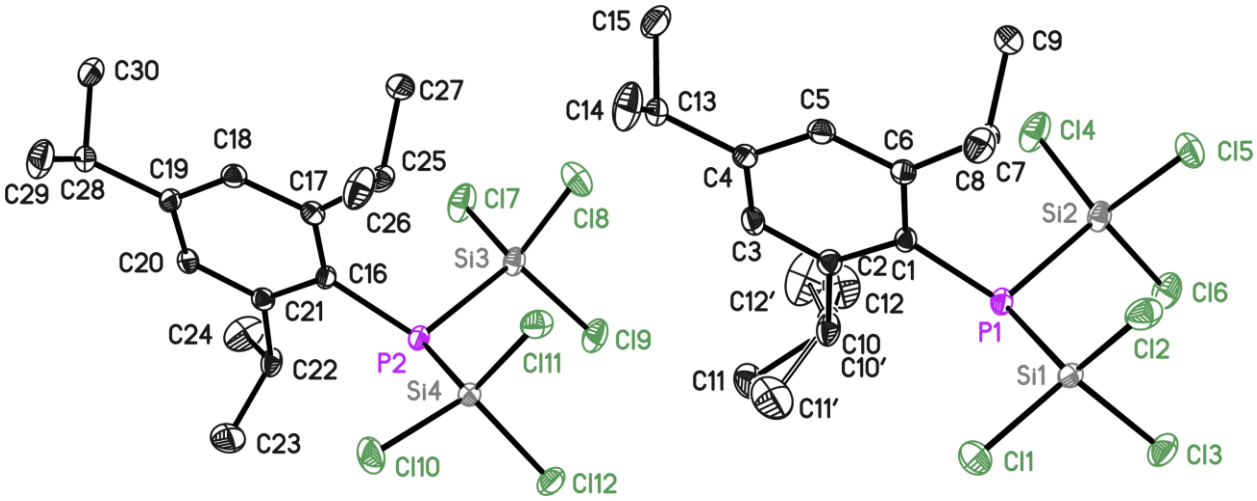


Figure S9. Molecular structure of **1** with thermal ellipsoid drawn at the 50 % probability level. The hydrogen atoms are omitted for clarity.

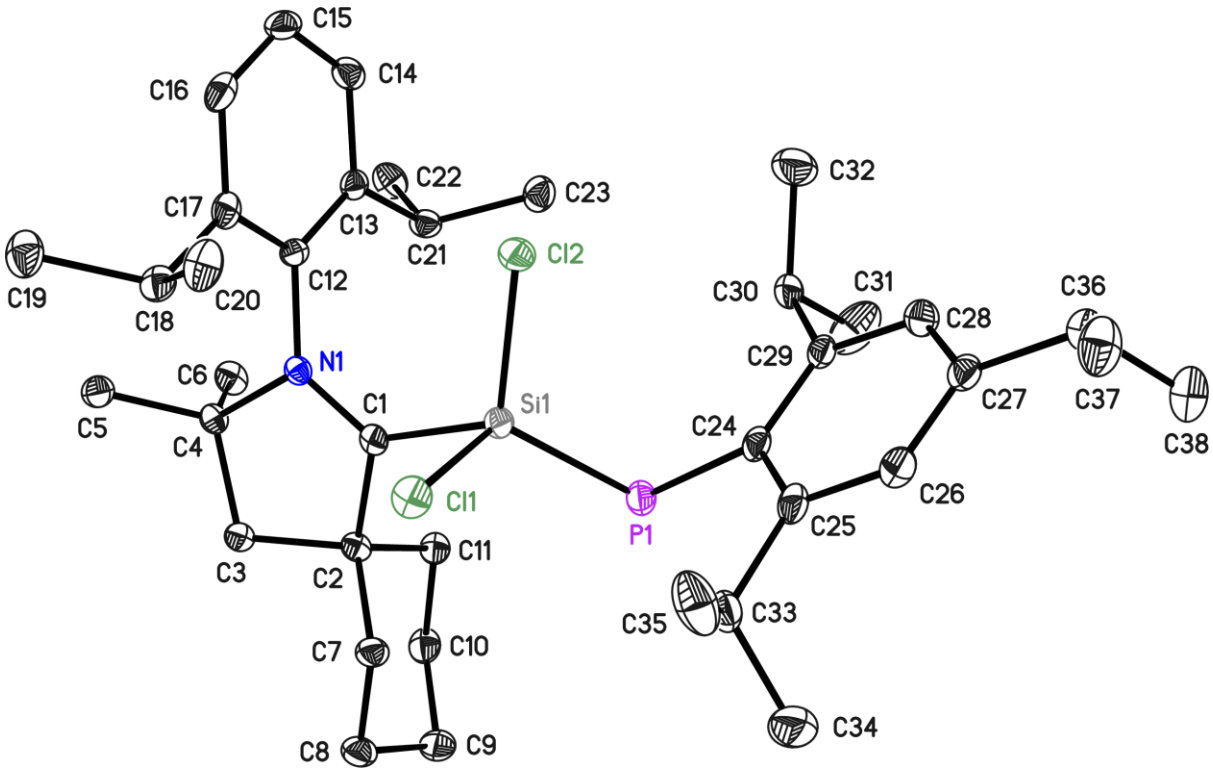


Figure S10. Molecular structure of **2a** with thermal ellipsoid drawn at the 50 % probability level. The hydrogen atoms are omitted for clarity. Selected experimental [calculated at the M06-2X/def2-SVP level of theory] bond lengths [Å] and angles [°]. Si1-C1 1.945(2) [1.969], Si1-Cl1 2.1247(9) [2.138], Si1-Cl2 2.0772(9) [2.107], P1-C24 1.874(2) [1.885], P1-Si1 2.1225(9) [2.116], N1-C1 1.308(3) [1.299]; C24-P1-Si1 99.64(8) [90.7],N1-C1-Si1 130.00(17) [129.2], C1-Si1-Cl2 112.18(7) [109.6], C1-Si1-P1 110.69(7) [93.3], Cl2-Si1-P1 116.76(4) [117.3], C1-Si1-Cl1 94.72(7) [93.3], Cl2-Si1-Cl1 99.00(4) [99.5], P1-Si1-Cl1 121.19(4) [121.7], N1-C1-C2 110.03(19) [110.5], C2-C1-Si1 119.95(16) [120.3].

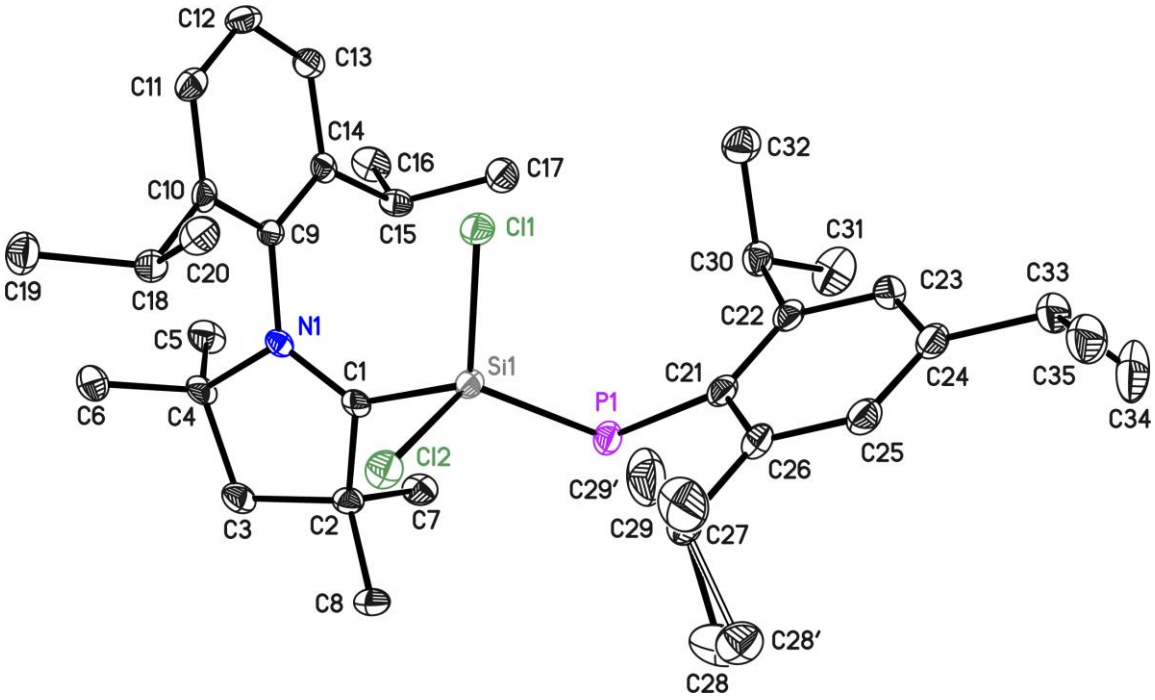


Figure S11. Molecular structure of **2c** with thermal ellipsoid drawn at the 50 % probability level. The hydrogen atoms are omitted for clarity.

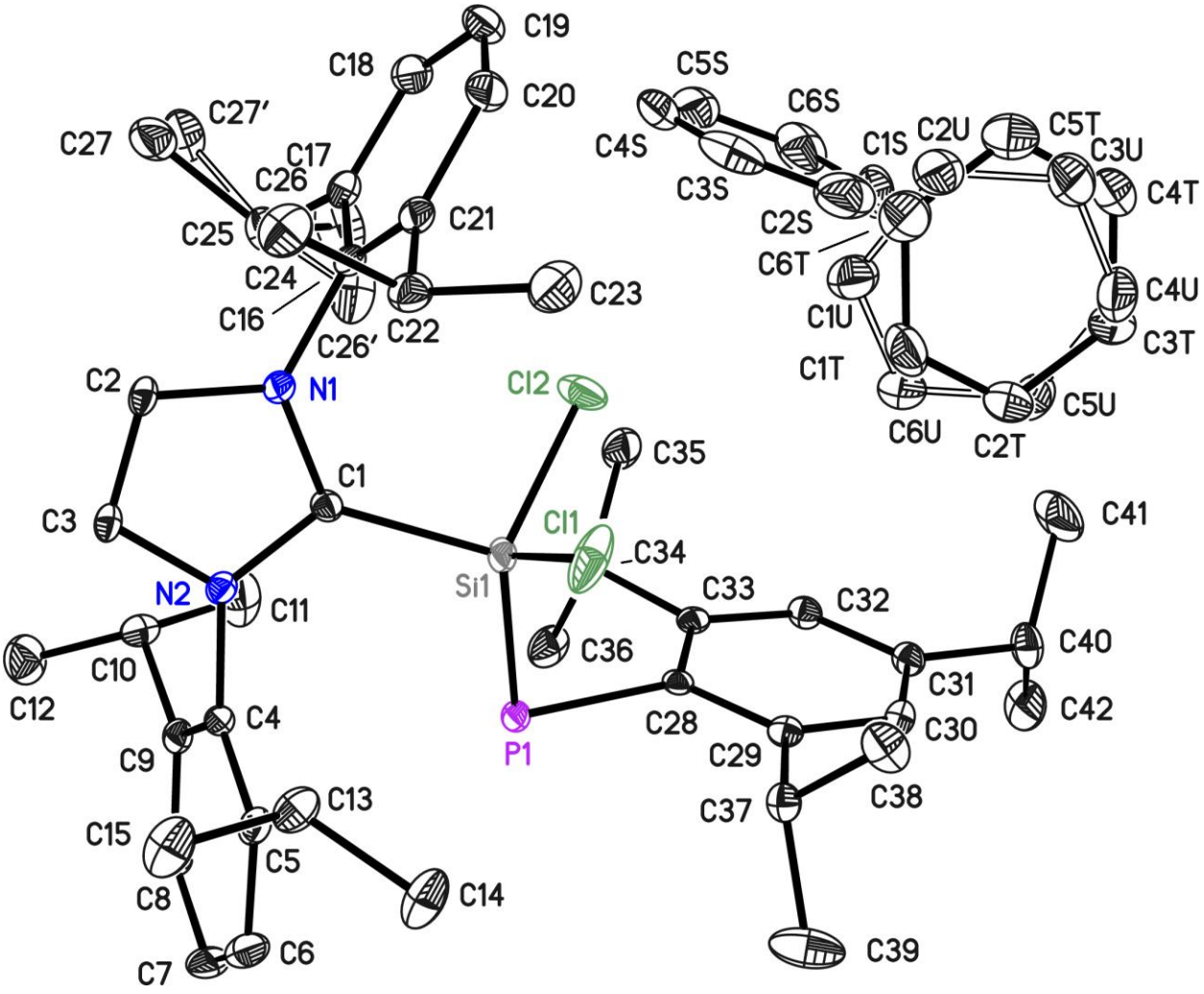


Figure S12. Molecular structure of **3** with thermal ellipsoid drawn at the 50 % probability level. The hydrogen atoms are omitted for clarity.

Table S1. Selected bond lengths [Å] and angles [°] for compounds **1**, **2a**, **2c** and **3**.

Compound	**1**	**2a**	**2c**	**3**
P-C_{Tip} (Å)	1.8423(17)-1.8424(17)	1.874(2)	1.874(2)	1.884(3)
Si-P (Å)	2.2125(8)-2.2155(8)	2.1225(9)	2.1205(9)	2.1129(10)
Si-$C_{carbene}$ (Å)	1.8423(17)-1.8424(17)	1.945(2)	1.944(2)	1.928(3)
N-$C_{carbene}$ (Å)	-	1.308(3)	1.304(2)	1.362(3)-1.383(3)
C_{Tip}-P-Si (°)	111.46(6)-112.40(6)	99.64(8)	105.62(7)	95.01(8)

Table S2. Crystallographic data for compounds **1**, **2a**, **2c** and **3**.

	1	**2a**	**2c**	**3**
empirical formula	$C_{15}H_{23}Cl_6PSi_2$	$C_{38}H_{58}Cl_2NPSi$	$C_{35}H_{54}Cl_2NPSi$	$C_{54}H_{71}Cl_2N_2PSi$
CCDC no.	1035413	1035414	1035415	1035416
M [g/mol]	503.18	658.81	618.75	878.08
crystal system	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
space group	$P\bar{1}$	Pbca	$P2_1/c$	$P2_12_12_1$
λ [Å]	0.71073	0.71073	0.56086	0.71073
T [K]	100(2)	100(2)	100(2)	100(2)
a [Å]	9.812(2)	17.079(2)	14.001(2)	10.414(2)
b [Å]	13.784(2)	18.335(2)	15.439(4)	17.913(2)
c [Å]	18.184(3)	24.196(3)	17.768(5)	27.306(3)
α [°]	79.47(2)	90	90	90
β [°]	82.48(2)	90	113.065(7)	90
γ [°]	75.52(2)	90	90	90
V [Å^3]	2331.7(8)	7576.8(15)	3533.7(15)	5093.8(13)
Z	4	8	4	4
ρ_{calc} [Mg/m^{-3}]	1.433	1.155	1.163	1.145
μ [mm^{-1}]	0.907	0.271	0.153	0.218
F(000)	1032	2848	1336	1888
crystal size [mm]	0.431 x 0.164 x 0.083	0.096 x 0.080 x 0.072	0.196 x 0.177 x 0.068	0.194 x 0.165 x 0.058
θ-min, max [°]	1.144 - 26.155	1.683 - 25.363	2.302 - 19.769	1.360 - 25.355
max. / min. transm.	0.5701 / 0.5160	0.6742 / 0.6358	0.9514 / 0.9016	0.9420 / 0.9420
refl. collected	52866	44461	87687	69636
unique refl.	9269	6944	6456	9335
restraints	124	0	67	730
parameters	465	400	396	627
GooF	1.052	1.004	1.032	1.071
$R1$ / w$R2$ [$I > 2\sigma(I)$] [a,b]	0.0274 / 0.0658	0.0408 / 0.0765	0.0389 / 0.0761	0.0334 / 0.0696
$R1$ / $wR2$ (all data)	0.0345 / 0.0697	0.0790 / 0.0904	0.0661 / 0.0854	0.0420 / 0.0738
largest diff. peak, hole [e Å^{-3}]	0.493 / -0.278	0.283 / -0.269	0.311 / -0.255	0.238 / -0.319

a) $R1 = \frac{\sum \| |F_o| - |F_c| \|}{\sum |F_o|}$ b) $wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$ with $w = \frac{1}{\sigma^2(F_o^2) + (g_1 P)^2 + g_2 P}$; $P = \frac{(F_o^2 + 2F_c^2)}{3}$.

Table S3. Bond lengths [Å], bond angles [°] and torsion angles [°] for **1**.

Cl(1)-Si(1)	2.0197(8)
Cl(2)-Si(1)	2.0324(8)
Cl(3)-Si(1)	2.0356(8)
Cl(4)-Si(2)	2.0250(8)
Cl(5)-Si(2)	2.0327(8)
Cl(6)-Si(2)	2.0296(8)
Cl(7)-Si(3)	2.0222(8)
Cl(8)-Si(3)	2.0356(8)
Cl(9)-Si(3)	2.0307(8)
Cl(10)-Si(4)	2.0203(8)
Cl(11)-Si(4)	2.0330(7)
Cl(12)-Si(4)	2.0340(8)
Si(1)-P(1)	2.2125(8)
Si(2)-P(1)	2.2155(8)
Si(3)-P(2)	2.2132(8)
Si(4)-P(2)	2.2131(8)
P(1)-C(1)	1.8423(17)
P(2)-C(16)	1.8424(17)
C(1)-C(6)	1.410(2)
C(1)-C(2)	1.417(2)
C(4)-C(3)	1.388(2)
C(4)-C(5)	1.390(2)
C(4)-C(13)	1.520(2)
C(5)-C(6)	1.395(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.518(2)
C(7)-C(8)	1.531(2)
C(7)-C(9)	1.535(2)

C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(2)-C(3)	1.388(2)
C(2)-C(10)	1.524(5)
C(2)-C(10')	1.538(12)
C(3)-H(3)	0.9500
C(10)-C(11)	1.522(7)
C(10)-C(12)	1.530(6)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(10')-C(11')	1.532(13)
C(10')-C(12')	1.537(13)
C(10')-H(10')	1.0000
C(11')-H(11D)	0.9800
C(11')-H(11E)	0.9800
C(11')-H(11F)	0.9800
C(12')-H(12D)	0.9800
C(12')-H(12E)	0.9800
C(12')-H(12F)	0.9800
C(13)-C(15)	1.524(3)
C(13)-C(14)	1.526(3)
C(13)-H(13)	1.0000
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.414(2)
C(16)-C(21)	1.416(2)
C(17)-C(18)	1.391(2)
C(17)-C(25)	1.516(2)
C(18)-C(19)	1.391(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.386(2)
C(19)-C(28)	1.517(2)
C(20)-C(21)	1.395(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.524(2)
C(22)-C(23)	1.525(3)
C(22)-C(24)	1.527(3)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(27)	1.530(3)
C(25)-C(26)	1.533(3)
C(25)-H(25)	1.0000
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(30)	1.524(3)
C(28)-C(29)	1.527(3)
C(28)-H(28)	1.0000

C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800

Cl(1)-Si(1)-Cl(2)	107.55(4)
Cl(1)-Si(1)-Cl(3)	109.67(4)
Cl(2)-Si(1)-Cl(3)	104.93(4)
Cl(1)-Si(1)-P(1)	106.17(3)
Cl(2)-Si(1)-P(1)	123.39(3)
Cl(3)-Si(1)-P(1)	104.69(4)
Cl(4)-Si(2)-Cl(6)	109.98(4)
Cl(4)-Si(2)-Cl(5)	107.72(4)
Cl(6)-Si(2)-Cl(5)	106.12(4)
Cl(4)-Si(2)-P(1)	106.93(3)
Cl(6)-Si(2)-P(1)	105.94(4)
Cl(5)-Si(2)-P(1)	119.96(3)
Cl(7)-Si(3)-Cl(9)	110.23(4)
Cl(7)-Si(3)-Cl(8)	107.27(4)
Cl(9)-Si(3)-Cl(8)	106.08(4)
Cl(7)-Si(3)-P(2)	105.46(3)
Cl(9)-Si(3)-P(2)	106.45(4)
Cl(8)-Si(3)-P(2)	121.17(3)
Cl(10)-Si(4)-Cl(11)	108.76(4)
Cl(10)-Si(4)-Cl(12)	108.89(4)
Cl(11)-Si(4)-Cl(12)	105.07(3)
Cl(10)-Si(4)-P(2)	106.87(3)
Cl(11)-Si(4)-P(2)	121.62(3)
Cl(12)-Si(4)-P(2)	105.09(4)
C(1)-P(1)-Si(1)	112.40(6)
C(1)-P(1)-Si(2)	111.46(6)
Si(1)-P(1)-Si(2)	106.13(3)
C(16)-P(2)-Si(4)	113.18(6)

C(16)-P(2)-Si(3)	110.09(6)
Si(4)-P(2)-Si(3)	106.33(3)
C(6)-C(1)-C(2)	119.82(15)
C(6)-C(1)-P(1)	126.23(13)
C(2)-C(1)-P(1)	113.96(12)
C(3)-C(4)-C(5)	117.63(16)
C(3)-C(4)-C(13)	120.30(15)
C(5)-C(4)-C(13)	122.06(16)
C(4)-C(5)-C(6)	122.38(16)
C(4)-C(5)-H(5)	118.8
C(6)-C(5)-H(5)	118.8
C(5)-C(6)-C(1)	118.77(15)
C(5)-C(6)-C(7)	117.58(15)
C(1)-C(6)-C(7)	123.65(15)
C(6)-C(7)-C(8)	112.06(14)
C(6)-C(7)-C(9)	111.14(14)
C(8)-C(7)-C(9)	110.93(15)
C(6)-C(7)-H(7)	107.5
C(8)-C(7)-H(7)	107.5
C(9)-C(7)-H(7)	107.5
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(3)-C(2)-C(1)	118.52(16)
C(3)-C(2)-C(10)	118.4(4)
C(1)-C(2)-C(10)	123.1(4)

C(3)-C(2)-C(10')	117.0(9)
C(1)-C(2)-C(10')	124.3(9)
C(4)-C(3)-C(2)	122.84(16)
C(4)-C(3)-H(3)	118.6
C(2)-C(3)-H(3)	118.6
C(11)-C(10)-C(2)	114.0(6)
C(11)-C(10)-C(12)	110.0(5)
C(2)-C(10)-C(12)	108.8(4)
C(11)-C(10)-H(10)	107.9
C(2)-C(10)-H(10)	107.9
C(12)-C(10)-H(10)	107.9
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11')-C(10')-C(12')	114.5(15)
C(11')-C(10')-C(2)	108.8(12)
C(12')-C(10')-C(2)	112.0(12)
C(11')-C(10')-H(10')	107.0
C(12')-C(10')-H(10')	107.0
C(2)-C(10')-H(10')	107.0
C(10')-C(11')-H(11D)	109.5
C(10')-C(11')-H(11E)	109.5
H(11D)-C(11')-H(11E)	109.5
C(10')-C(11')-H(11F)	109.5
H(11D)-C(11')-H(11F)	109.5
H(11E)-C(11')-H(11F)	109.5

C(10')-C(12')-H(12D)	109.5
C(10')-C(12')-H(12E)	109.5
H(12D)-C(12')-H(12E)	109.5
C(10')-C(12')-H(12F)	109.5
H(12D)-C(12')-H(12F)	109.5
H(12E)-C(12')-H(12F)	109.5
C(4)-C(13)-C(15)	111.20(15)
C(4)-C(13)-C(14)	112.49(15)
C(15)-C(13)-C(14)	110.93(16)
C(4)-C(13)-H(13)	107.3
C(15)-C(13)-H(13)	107.3
C(14)-C(13)-H(13)	107.3
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(21)	119.68(15)
C(17)-C(16)-P(2)	126.47(13)
C(21)-C(16)-P(2)	113.84(13)
C(18)-C(17)-C(16)	118.82(15)
C(18)-C(17)-C(25)	117.44(15)
C(16)-C(17)-C(25)	123.73(15)
C(17)-C(18)-C(19)	122.54(16)
C(17)-C(18)-H(18)	118.7
C(19)-C(18)-H(18)	118.7
C(20)-C(19)-C(18)	117.67(16)
C(20)-C(19)-C(28)	120.75(15)

C(18)-C(19)-C(28)	121.56(16)
C(19)-C(20)-C(21)	122.66(16)
C(19)-C(20)-H(20)	118.7
C(21)-C(20)-H(20)	118.7
C(20)-C(21)-C(16)	118.56(16)
C(20)-C(21)-C(22)	117.33(15)
C(16)-C(21)-C(22)	124.08(15)
C(21)-C(22)-C(23)	109.62(15)
C(21)-C(22)-C(24)	112.50(16)
C(23)-C(22)-C(24)	111.43(17)
C(21)-C(22)-H(22)	107.7
C(23)-C(22)-H(22)	107.7
C(24)-C(22)-H(22)	107.7
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(17)-C(25)-C(27)	110.81(15)
C(17)-C(25)-C(26)	111.96(15)
C(27)-C(25)-C(26)	111.39(16)
C(17)-C(25)-H(25)	107.5
C(27)-C(25)-H(25)	107.5
C(26)-C(25)-H(25)	107.5
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5

H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(19)-C(28)-C(30)	111.05(15)
C(19)-C(28)-C(29)	112.24(15)
C(30)-C(28)-C(29)	111.13(16)
C(19)-C(28)-H(28)	107.4
C(30)-C(28)-H(28)	107.4
C(29)-C(28)-H(28)	107.4
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(28)-C(30)-H(30A)	109.5
C(28)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5

Si(1)-P(1)-C(1)-C(6)	57.37(16)
Si(2)-P(1)-C(1)-C(6)	-61.63(16)
Si(1)-P(1)-C(1)-C(2)	-122.72(12)
Si(2)-P(1)-C(1)-C(2)	118.27(12)
C(3)-C(4)-C(5)-C(6)	-0.6(3)
C(13)-C(4)-C(5)-C(6)	-179.57(16)
C(4)-C(5)-C(6)-C(1)	-1.0(3)
C(4)-C(5)-C(6)-C(7)	178.58(15)

C(2)-C(1)-C(6)-C(5)	1.8(2)
P(1)-C(1)-C(6)-C(5)	-178.31(13)
C(2)-C(1)-C(6)-C(7)	-177.74(15)
P(1)-C(1)-C(6)-C(7)	2.2(2)
C(5)-C(6)-C(7)-C(8)	58.9(2)
C(1)-C(6)-C(7)-C(8)	-121.61(18)
C(5)-C(6)-C(7)-C(9)	-65.9(2)
C(1)-C(6)-C(7)-C(9)	113.64(18)
C(6)-C(1)-C(2)-C(3)	-1.0(2)
P(1)-C(1)-C(2)-C(3)	179.07(13)
C(6)-C(1)-C(2)-C(10)	179.7(3)
P(1)-C(1)-C(2)-C(10)	-0.2(4)
C(6)-C(1)-C(2)-C(10')	173.0(7)
P(1)-C(1)-C(2)-C(10')	-6.9(7)
C(5)-C(4)-C(3)-C(2)	1.4(3)
C(13)-C(4)-C(3)-C(2)	-179.59(16)
C(1)-C(2)-C(3)-C(4)	-0.6(3)
C(10)-C(2)-C(3)-C(4)	178.7(3)
C(10')-C(2)-C(3)-C(4)	-175.1(6)
C(3)-C(2)-C(10)-C(11)	-36.0(7)
C(1)-C(2)-C(10)-C(11)	143.2(5)
C(10')-C(2)-C(10)-C(11)	-113(13)
C(3)-C(2)-C(10)-C(12)	87.2(6)
C(1)-C(2)-C(10)-C(12)	-93.6(6)
C(10')-C(2)-C(10)-C(12)	10(12)
C(3)-C(2)-C(10')-C(11')	-66.8(18)
C(1)-C(2)-C(10')-C(11')	119.1(16)
C(10)-C(2)-C(10')-C(11')	39(11)
C(3)-C(2)-C(10')-C(12')	60.9(17)
C(1)-C(2)-C(10')-C(12')	-113.3(16)
C(10)-C(2)-C(10')-C(12')	167(14)
C(3)-C(4)-C(13)-C(15)	-104.35(19)
C(5)-C(4)-C(13)-C(15)	74.6(2)
C(3)-C(4)-C(13)-C(14)	130.53(18)
C(5)-C(4)-C(13)-C(14)	-50.5(2)

Si(4)-P(2)-C(16)-C(17)	49.99(16)
Si(3)-P(2)-C(16)-C(17)	-68.85(15)
Si(4)-P(2)-C(16)-C(21)	-128.47(11)
Si(3)-P(2)-C(16)-C(21)	112.69(12)
C(21)-C(16)-C(17)-C(18)	2.8(2)
P(2)-C(16)-C(17)-C(18)	-175.57(13)
C(21)-C(16)-C(17)-C(25)	-175.86(16)
P(2)-C(16)-C(17)-C(25)	5.8(2)
C(16)-C(17)-C(18)-C(19)	-0.8(3)
C(25)-C(17)-C(18)-C(19)	178.00(16)
C(17)-C(18)-C(19)-C(20)	-1.3(3)
C(17)-C(18)-C(19)-C(28)	-179.81(16)
C(18)-C(19)-C(20)-C(21)	1.4(3)
C(28)-C(19)-C(20)-C(21)	179.88(16)
C(19)-C(20)-C(21)-C(16)	0.6(3)
C(19)-C(20)-C(21)-C(22)	178.55(16)
C(17)-C(16)-C(21)-C(20)	-2.7(2)
P(2)-C(16)-C(21)-C(20)	175.83(13)
C(17)-C(16)-C(21)-C(22)	179.49(16)
P(2)-C(16)-C(21)-C(22)	-1.9(2)
C(20)-C(21)-C(22)-C(23)	-74.2(2)
C(16)-C(21)-C(22)-C(23)	103.6(2)
C(20)-C(21)-C(22)-C(24)	50.4(2)
C(16)-C(21)-C(22)-C(24)	-131.85(18)
C(18)-C(17)-C(25)-C(27)	-62.9(2)
C(16)-C(17)-C(25)-C(27)	115.76(19)
C(18)-C(17)-C(25)-C(26)	62.1(2)
C(16)-C(17)-C(25)-C(26)	-119.21(18)
C(20)-C(19)-C(28)-C(30)	-108.16(19)
C(18)-C(19)-C(28)-C(30)	70.3(2)
C(20)-C(19)-C(28)-C(29)	126.76(18)
C(18)-C(19)-C(28)-C(29)	-54.8(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Bond lengths [Å], bond angles [°] and torsion angles [°] for **2a**.

Cl(1)-Si(1)	2.1247(9)
Cl(2)-Si(1)	2.0772(9)
P(1)-C(24)	1.874(2)
P(1)-Si(1)	2.1225(9)
Si(1)-C(1)	1.945(2)
N(1)-C(1)	1.308(3)
N(1)-C(12)	1.474(3)
N(1)-C(4)	1.552(3)
C(1)-C(2)	1.532(3)
C(2)-C(3)	1.539(3)
C(2)-C(7)	1.543(3)
C(2)-C(11)	1.555(3)
C(3)-C(4)	1.526(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(6)	1.518(3)
C(4)-C(5)	1.524(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(8)	1.532(3)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.520(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.525(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900

C(10)-C(11)	1.533(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.406(3)
C(12)-C(17)	1.409(3)
C(13)-C(14)	1.391(3)
C(13)-C(21)	1.520(3)
C(14)-C(15)	1.378(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.380(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.392(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.524(3)
C(18)-C(19)	1.540(3)
C(18)-C(20)	1.540(3)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(23)	1.528(3)
C(21)-C(22)	1.540(3)
C(21)-H(21)	1.0000
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.411(3)

C(24)-C(29)	1.422(3)
C(25)-C(26)	1.395(3)
C(25)-C(33)	1.523(3)
C(26)-C(27)	1.384(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.389(3)
C(27)-C(36)	1.526(3)
C(28)-C(29)	1.393(3)
C(28)-H(28)	0.9500
C(29)-C(30)	1.517(3)
C(30)-C(32)	1.529(3)
C(30)-C(31)	1.529(4)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(34)	1.526(3)
C(33)-C(35)	1.531(3)
C(33)-H(33)	1.0000
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-C(38)	1.527(3)
C(36)-C(37)	1.528(3)
C(36)-H(36)	1.0000
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800

C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800

C(24)-P(1)-Si(1)	99.64(8)
C(1)-Si(1)-Cl(2)	112.18(7)
C(1)-Si(1)-P(1)	110.69(7)
Cl(2)-Si(1)-P(1)	116.76(4)
C(1)-Si(1)-Cl(1)	94.72(7)
Cl(2)-Si(1)-Cl(1)	99.00(4)
P(1)-Si(1)-Cl(1)	121.19(4)
C(1)-N(1)-C(12)	126.08(19)
C(1)-N(1)-C(4)	114.18(18)
C(12)-N(1)-C(4)	119.57(17)
N(1)-C(1)-C(2)	110.03(19)
N(1)-C(1)-Si(1)	130.00(17)
C(2)-C(1)-Si(1)	119.95(16)
C(1)-C(2)-C(3)	102.13(18)
C(1)-C(2)-C(7)	114.49(18)
C(3)-C(2)-C(7)	110.69(18)
C(1)-C(2)-C(11)	107.72(18)
C(3)-C(2)-C(11)	112.89(18)
C(7)-C(2)-C(11)	108.87(19)
C(4)-C(3)-C(2)	107.38(18)
C(4)-C(3)-H(3A)	110.2
C(2)-C(3)-H(3A)	110.2
C(4)-C(3)-H(3B)	110.2
C(2)-C(3)-H(3B)	110.2
H(3A)-C(3)-H(3B)	108.5
C(6)-C(4)-C(5)	108.25(19)
C(6)-C(4)-C(3)	113.38(19)
C(5)-C(4)-C(3)	112.68(19)
C(6)-C(4)-N(1)	111.43(18)
C(5)-C(4)-N(1)	111.05(18)
C(3)-C(4)-N(1)	99.93(17)
C(4)-C(5)-H(5A)	109.5

C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-C(2)	111.10(19)
C(8)-C(7)-H(7A)	109.4
C(2)-C(7)-H(7A)	109.4
C(8)-C(7)-H(7B)	109.4
C(2)-C(7)-H(7B)	109.4
H(7A)-C(7)-H(7B)	108.0
C(9)-C(8)-C(7)	111.0(2)
C(9)-C(8)-H(8A)	109.4
C(7)-C(8)-H(8A)	109.4
C(9)-C(8)-H(8B)	109.4
C(7)-C(8)-H(8B)	109.4
H(8A)-C(8)-H(8B)	108.0
C(8)-C(9)-C(10)	111.1(2)
C(8)-C(9)-H(9A)	109.4
C(10)-C(9)-H(9A)	109.4
C(8)-C(9)-H(9B)	109.4
C(10)-C(9)-H(9B)	109.4
H(9A)-C(9)-H(9B)	108.0
C(9)-C(10)-C(11)	111.2(2)
C(9)-C(10)-H(10A)	109.4
C(11)-C(10)-H(10A)	109.4
C(9)-C(10)-H(10B)	109.4
C(11)-C(10)-H(10B)	109.4
H(10A)-C(10)-H(10B)	108.0

C(10)-C(11)-C(2)	112.44(19)
C(10)-C(11)-H(11A)	109.1
C(2)-C(11)-H(11A)	109.1
C(10)-C(11)-H(11B)	109.1
C(2)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8
C(13)-C(12)-C(17)	122.2(2)
C(13)-C(12)-N(1)	118.4(2)
C(17)-C(12)-N(1)	119.4(2)
C(14)-C(13)-C(12)	117.4(2)
C(14)-C(13)-C(21)	117.7(2)
C(12)-C(13)-C(21)	124.9(2)
C(15)-C(14)-C(13)	121.6(2)
C(15)-C(14)-H(14)	119.2
C(13)-C(14)-H(14)	119.2
C(14)-C(15)-C(16)	119.9(2)
C(14)-C(15)-H(15)	120.1
C(16)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	121.7(2)
C(15)-C(16)-H(16)	119.2
C(17)-C(16)-H(16)	119.2
C(16)-C(17)-C(12)	117.2(2)
C(16)-C(17)-C(18)	117.4(2)
C(12)-C(17)-C(18)	125.3(2)
C(17)-C(18)-C(19)	111.5(2)
C(17)-C(18)-C(20)	110.5(2)
C(19)-C(18)-C(20)	108.68(19)
C(17)-C(18)-H(18)	108.7
C(19)-C(18)-H(18)	108.7
C(20)-C(18)-H(18)	108.7
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5

H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(13)-C(21)-C(23)	110.56(19)
C(13)-C(21)-C(22)	111.1(2)
C(23)-C(21)-C(22)	110.24(19)
C(13)-C(21)-H(21)	108.3
C(23)-C(21)-H(21)	108.3
C(22)-C(21)-H(21)	108.3
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(29)	118.7(2)
C(25)-C(24)-P(1)	121.25(18)
C(29)-C(24)-P(1)	119.52(18)
C(26)-C(25)-C(24)	119.4(2)
C(26)-C(25)-C(33)	117.7(2)
C(24)-C(25)-C(33)	122.8(2)
C(27)-C(26)-C(25)	122.6(2)
C(27)-C(26)-H(26)	118.7
C(25)-C(26)-H(26)	118.7
C(26)-C(27)-C(28)	117.5(2)

C(26)-C(27)-C(36)	122.7(2)
C(28)-C(27)-C(36)	119.7(2)
C(27)-C(28)-C(29)	122.6(2)
C(27)-C(28)-H(28)	118.7
C(29)-C(28)-H(28)	118.7
C(28)-C(29)-C(24)	119.1(2)
C(28)-C(29)-C(30)	118.8(2)
C(24)-C(29)-C(30)	122.1(2)
C(29)-C(30)-C(32)	112.9(2)
C(29)-C(30)-C(31)	111.8(2)
C(32)-C(30)-C(31)	110.2(2)
C(29)-C(30)-H(30)	107.2
C(32)-C(30)-H(30)	107.2
C(31)-C(30)-H(30)	107.2
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(25)-C(33)-C(34)	111.3(2)
C(25)-C(33)-C(35)	112.3(2)
C(34)-C(33)-C(35)	110.7(2)
C(25)-C(33)-H(33)	107.4
C(34)-C(33)-H(33)	107.4
C(35)-C(33)-H(33)	107.4
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5

C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(27)-C(36)-C(38)	110.0(2)
C(27)-C(36)-C(37)	114.1(2)
C(38)-C(36)-C(37)	109.7(2)
C(27)-C(36)-H(36)	107.6
C(38)-C(36)-H(36)	107.6
C(37)-C(36)-H(36)	107.6
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5

C(12)-N(1)-C(1)-C(2)	-171.86(19)
C(4)-N(1)-C(1)-C(2)	3.3(2)
C(12)-N(1)-C(1)-Si(1)	9.7(3)
C(4)-N(1)-C(1)-Si(1)	-175.09(16)
N(1)-C(1)-C(2)-C(3)	-17.6(2)
Si(1)-C(1)-C(2)-C(3)	161.03(15)
N(1)-C(1)-C(2)-C(7)	-137.2(2)

Si(1)-C(1)-C(2)-C(7)	41.4(2)
N(1)-C(1)-C(2)-C(11)	101.5(2)
Si(1)-C(1)-C(2)-C(11)	-79.9(2)
C(1)-C(2)-C(3)-C(4)	25.1(2)
C(7)-C(2)-C(3)-C(4)	147.43(19)
C(11)-C(2)-C(3)-C(4)	-90.2(2)
C(2)-C(3)-C(4)-C(6)	95.9(2)
C(2)-C(3)-C(4)-C(5)	-140.69(19)
C(2)-C(3)-C(4)-N(1)	-22.8(2)
C(1)-N(1)-C(4)-C(6)	-107.7(2)
C(12)-N(1)-C(4)-C(6)	67.9(2)
C(1)-N(1)-C(4)-C(5)	131.6(2)
C(12)-N(1)-C(4)-C(5)	-52.9(3)
C(1)-N(1)-C(4)-C(3)	12.4(2)
C(12)-N(1)-C(4)-C(3)	-172.04(18)
C(1)-C(2)-C(7)-C(8)	-176.97(19)
C(3)-C(2)-C(7)-C(8)	68.3(2)
C(11)-C(2)-C(7)-C(8)	-56.4(2)
C(2)-C(7)-C(8)-C(9)	58.7(3)
C(7)-C(8)-C(9)-C(10)	-57.2(3)
C(8)-C(9)-C(10)-C(11)	55.0(3)
C(9)-C(10)-C(11)-C(2)	-54.7(3)
C(1)-C(2)-C(11)-C(10)	179.57(19)
C(3)-C(2)-C(11)-C(10)	-68.5(2)
C(7)-C(2)-C(11)-C(10)	54.9(2)
C(1)-N(1)-C(12)-C(13)	83.6(3)
C(4)-N(1)-C(12)-C(13)	-91.3(2)
C(1)-N(1)-C(12)-C(17)	-97.3(3)
C(4)-N(1)-C(12)-C(17)	87.7(2)
C(17)-C(12)-C(13)-C(14)	-0.4(3)
N(1)-C(12)-C(13)-C(14)	178.7(2)
C(17)-C(12)-C(13)-C(21)	176.5(2)
N(1)-C(12)-C(13)-C(21)	-4.4(3)
C(12)-C(13)-C(14)-C(15)	-1.4(3)
C(21)-C(13)-C(14)-C(15)	-178.5(2)

C(13)-C(14)-C(15)-C(16)	1.6(4)
C(14)-C(15)-C(16)-C(17)	0.0(4)
C(15)-C(16)-C(17)-C(12)	-1.7(3)
C(15)-C(16)-C(17)-C(18)	175.7(2)
C(13)-C(12)-C(17)-C(16)	1.9(3)
N(1)-C(12)-C(17)-C(16)	-177.1(2)
C(13)-C(12)-C(17)-C(18)	-175.3(2)
N(1)-C(12)-C(17)-C(18)	5.7(3)
C(16)-C(17)-C(18)-C(19)	59.2(3)
C(12)-C(17)-C(18)-C(19)	-123.6(2)
C(16)-C(17)-C(18)-C(20)	-61.8(3)
C(12)-C(17)-C(18)-C(20)	115.4(2)
C(14)-C(13)-C(21)-C(23)	61.7(3)
C(12)-C(13)-C(21)-C(23)	-115.2(2)
C(14)-C(13)-C(21)-C(22)	-61.1(3)
C(12)-C(13)-C(21)-C(22)	122.1(2)
Si(1)-P(1)-C(24)-C(25)	87.33(19)
Si(1)-P(1)-C(24)-C(29)	-100.91(18)
C(29)-C(24)-C(25)-C(26)	-0.2(3)
P(1)-C(24)-C(25)-C(26)	171.60(18)
C(29)-C(24)-C(25)-C(33)	-179.8(2)
P(1)-C(24)-C(25)-C(33)	-8.0(3)
C(24)-C(25)-C(26)-C(27)	-0.1(4)
C(33)-C(25)-C(26)-C(27)	179.5(2)
C(25)-C(26)-C(27)-C(28)	0.2(4)
C(25)-C(26)-C(27)-C(36)	-179.1(2)
C(26)-C(27)-C(28)-C(29)	0.0(4)
C(36)-C(27)-C(28)-C(29)	179.3(2)
C(27)-C(28)-C(29)-C(24)	-0.3(4)
C(27)-C(28)-C(29)-C(30)	-179.9(2)
C(25)-C(24)-C(29)-C(28)	0.4(3)
P(1)-C(24)-C(29)-C(28)	-171.57(17)
C(25)-C(24)-C(29)-C(30)	-179.9(2)
P(1)-C(24)-C(29)-C(30)	8.1(3)
C(28)-C(29)-C(30)-C(32)	-46.7(3)

C(24)-C(29)-C(30)-C(32)	133.6(2)
C(28)-C(29)-C(30)-C(31)	78.1(3)
C(24)-C(29)-C(30)-C(31)	-101.5(3)
C(26)-C(25)-C(33)-C(34)	-73.2(3)
C(24)-C(25)-C(33)-C(34)	106.4(3)
C(26)-C(25)-C(33)-C(35)	51.6(3)
C(24)-C(25)-C(33)-C(35)	-128.8(2)
C(26)-C(27)-C(36)-C(38)	92.5(3)
C(28)-C(27)-C(36)-C(38)	-86.8(3)
C(26)-C(27)-C(36)-C(37)	-31.2(3)
C(28)-C(27)-C(36)-C(37)	149.5(2)

Symmetry transformations used to generate equivalent atoms:

Table S5. Bond lengths [Å], bond angles [°] and torsion angles [°] for **2c**.

Cl(1)-Si(1)	2.0763(8)
Cl(2)-Si(1)	2.1366(10)
P(1)-C(21)	1.874(2)
P(1)-Si(1)	2.1205(9)
Si(1)-C(1)	1.944(2)
N(1)-C(1)	1.304(2)
N(1)-C(9)	1.475(2)
N(1)-C(4)	1.552(2)
C(1)-C(2)	1.541(3)
C(2)-C(8)	1.534(3)
C(2)-C(3)	1.539(3)
C(2)-C(7)	1.552(3)
C(3)-C(4)	1.533(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(6)	1.520(3)
C(4)-C(5)	1.528(3)
C(5)-H(5A)	0.9800

C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(14)	1.409(3)
C(9)-C(10)	1.411(3)
C(10)-C(11)	1.398(3)
C(10)-C(18)	1.530(3)
C(11)-C(12)	1.386(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.383(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.399(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.523(3)
C(15)-C(17)	1.535(3)
C(15)-C(16)	1.537(3)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(20)	1.537(3)
C(18)-C(19)	1.541(3)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800

C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(26)	1.416(3)
C(21)-C(22)	1.420(3)
C(22)-C(23)	1.402(3)
C(22)-C(30)	1.524(3)
C(23)-C(24)	1.388(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.389(3)
C(24)-C(33)	1.529(3)
C(25)-C(26)	1.402(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.528(3)
C(27)-C(29')	1.490(7)
C(27)-C(28)	1.509(9)
C(27)-C(28')	1.532(8)
C(27)-C(29)	1.592(8)
C(27)-H(27)	1.0000
C(27)-H(27')	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(28')-H(28D)	0.9800
C(28')-H(28E)	0.9800
C(28')-H(28F)	0.9800
C(29')-H(29D)	0.9800
C(29')-H(29E)	0.9800
C(29')-H(29F)	0.9800
C(30)-C(31)	1.530(3)

C(30)-C(32)	1.535(3)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(35)	1.524(3)
C(33)-C(34)	1.531(3)
C(33)-H(33)	1.0000
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800

C(21)-P(1)-Si(1)	105.62(7)
C(1)-Si(1)-Cl(1)	113.87(7)
C(1)-Si(1)-P(1)	109.11(7)
Cl(1)-Si(1)-P(1)	115.50(3)
C(1)-Si(1)-Cl(2)	92.37(6)
Cl(1)-Si(1)-Cl(2)	100.19(3)
P(1)-Si(1)-Cl(2)	123.78(3)
C(1)-N(1)-C(9)	126.17(16)
C(1)-N(1)-C(4)	114.44(16)
C(9)-N(1)-C(4)	118.79(15)
N(1)-C(1)-C(2)	110.32(17)
N(1)-C(1)-Si(1)	128.61(15)
C(2)-C(1)-Si(1)	120.96(14)
C(8)-C(2)-C(3)	111.03(17)
C(8)-C(2)-C(1)	115.20(17)
C(3)-C(2)-C(1)	102.40(16)
C(8)-C(2)-C(7)	108.36(17)

C(3)-C(2)-C(7)	111.45(17)
C(1)-C(2)-C(7)	108.32(16)
C(4)-C(3)-C(2)	107.91(16)
C(4)-C(3)-H(3A)	110.1
C(2)-C(3)-H(3A)	110.1
C(4)-C(3)-H(3B)	110.1
C(2)-C(3)-H(3B)	110.1
H(3A)-C(3)-H(3B)	108.4
C(6)-C(4)-C(5)	108.80(18)
C(6)-C(4)-C(3)	111.89(17)
C(5)-C(4)-C(3)	114.65(18)
C(6)-C(4)-N(1)	110.64(16)
C(5)-C(4)-N(1)	110.16(16)
C(3)-C(4)-N(1)	100.49(15)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(2)-C(8)-H(8A)	109.5
C(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5

C(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(14)-C(9)-C(10)	122.62(18)
C(14)-C(9)-N(1)	116.92(17)
C(10)-C(9)-N(1)	120.40(17)
C(11)-C(10)-C(9)	116.76(19)
C(11)-C(10)-C(18)	117.84(18)
C(9)-C(10)-C(18)	125.11(18)
C(12)-C(11)-C(10)	122.1(2)
C(12)-C(11)-H(11)	118.9
C(10)-C(11)-H(11)	118.9
C(13)-C(12)-C(11)	119.4(2)
C(13)-C(12)-H(12)	120.3
C(11)-C(12)-H(12)	120.3
C(12)-C(13)-C(14)	121.8(2)
C(12)-C(13)-H(13)	119.1
C(14)-C(13)-H(13)	119.1
C(13)-C(14)-C(9)	117.14(19)
C(13)-C(14)-C(15)	118.17(18)
C(9)-C(14)-C(15)	124.61(18)
C(14)-C(15)-C(17)	110.47(17)
C(14)-C(15)-C(16)	113.15(17)
C(17)-C(15)-C(16)	109.98(17)
C(14)-C(15)-H(15)	107.7
C(17)-C(15)-H(15)	107.7
C(16)-C(15)-H(15)	107.7
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5

H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(10)-C(18)-C(20)	109.18(17)
C(10)-C(18)-C(19)	113.07(17)
C(20)-C(18)-C(19)	108.68(17)
C(10)-C(18)-H(18)	108.6
C(20)-C(18)-H(18)	108.6
C(19)-C(18)-H(18)	108.6
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(26)-C(21)-C(22)	118.35(19)
C(26)-C(21)-P(1)	122.35(16)
C(22)-C(21)-P(1)	118.48(16)
C(23)-C(22)-C(21)	119.32(19)
C(23)-C(22)-C(30)	117.31(19)
C(21)-C(22)-C(30)	123.36(18)
C(24)-C(23)-C(22)	122.9(2)
C(24)-C(23)-H(23)	118.6
C(22)-C(23)-H(23)	118.6
C(23)-C(24)-C(25)	117.13(19)
C(23)-C(24)-C(33)	119.11(19)
C(25)-C(24)-C(33)	123.76(19)
C(24)-C(25)-C(26)	122.7(2)

C(24)-C(25)-H(25)	118.7
C(26)-C(25)-H(25)	118.7
C(25)-C(26)-C(21)	119.6(2)
C(25)-C(26)-C(27)	117.64(19)
C(21)-C(26)-C(27)	122.76(19)
C(29')-C(27)-C(26)	110.2(5)
C(28)-C(27)-C(26)	112.7(8)
C(29')-C(27)-C(28')	113.4(6)
C(26)-C(27)-C(28')	112.8(7)
C(28)-C(27)-C(29)	108.0(6)
C(26)-C(27)-C(29)	112.1(5)
C(28)-C(27)-H(27)	107.9
C(26)-C(27)-H(27)	107.9
C(29)-C(27)-H(27)	107.9
C(29')-C(27)-H(27')	106.7
C(26)-C(27)-H(27')	106.7
C(28')-C(27)-H(27')	106.7
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(27)-C(28')-H(28D)	109.5
C(27)-C(28')-H(28E)	109.5
H(28D)-C(28')-H(28E)	109.5
C(27)-C(28')-H(28F)	109.5
H(28D)-C(28')-H(28F)	109.5
H(28E)-C(28')-H(28F)	109.5

C(27)-C(29')-H(29D)	109.5
C(27)-C(29')-H(29E)	109.5
H(29D)-C(29')-H(29E)	109.5
C(27)-C(29')-H(29F)	109.5
H(29D)-C(29')-H(29F)	109.5
H(29E)-C(29')-H(29F)	109.5
C(22)-C(30)-C(31)	112.26(18)
C(22)-C(30)-C(32)	110.72(17)
C(31)-C(30)-C(32)	109.55(19)
C(22)-C(30)-H(30)	108.1
C(31)-C(30)-H(30)	108.1
C(32)-C(30)-H(30)	108.1
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(35)-C(33)-C(24)	113.96(19)
C(35)-C(33)-C(34)	110.74(19)
C(24)-C(33)-C(34)	109.96(18)
C(35)-C(33)-H(33)	107.3
C(24)-C(33)-H(33)	107.3
C(34)-C(33)-H(33)	107.3
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5

H(34B)-C(34)-H(34C)	109.5
C(33)-C(35)-H(35A)	109.5
C(33)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(33)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5

C(9)-N(1)-C(1)-C(2)	-166.06(17)
C(4)-N(1)-C(1)-C(2)	5.0(2)
C(9)-N(1)-C(1)-Si(1)	17.7(3)
C(4)-N(1)-C(1)-Si(1)	-171.26(14)
N(1)-C(1)-C(2)-C(8)	-136.84(18)
Si(1)-C(1)-C(2)-C(8)	39.7(2)
N(1)-C(1)-C(2)-C(3)	-16.2(2)
Si(1)-C(1)-C(2)-C(3)	160.35(14)
N(1)-C(1)-C(2)-C(7)	101.64(19)
Si(1)-C(1)-C(2)-C(7)	-81.80(19)
C(8)-C(2)-C(3)-C(4)	144.71(17)
C(1)-C(2)-C(3)-C(4)	21.2(2)
C(7)-C(2)-C(3)-C(4)	-94.4(2)
C(2)-C(3)-C(4)-C(6)	-135.69(18)
C(2)-C(3)-C(4)-C(5)	99.8(2)
C(2)-C(3)-C(4)-N(1)	-18.3(2)
C(1)-N(1)-C(4)-C(6)	126.85(19)
C(9)-N(1)-C(4)-C(6)	-61.4(2)
C(1)-N(1)-C(4)-C(5)	-112.82(19)
C(9)-N(1)-C(4)-C(5)	58.9(2)
C(1)-N(1)-C(4)-C(3)	8.5(2)
C(9)-N(1)-C(4)-C(3)	-179.77(16)
C(1)-N(1)-C(9)-C(14)	80.1(2)
C(4)-N(1)-C(9)-C(14)	-90.6(2)
C(1)-N(1)-C(9)-C(10)	-102.5(2)
C(4)-N(1)-C(9)-C(10)	86.8(2)
C(14)-C(9)-C(10)-C(11)	3.5(3)

N(1)-C(9)-C(10)-C(11)	-173.75(17)
C(14)-C(9)-C(10)-C(18)	-170.23(18)
N(1)-C(9)-C(10)-C(18)	12.5(3)
C(9)-C(10)-C(11)-C(12)	-1.1(3)
C(18)-C(10)-C(11)-C(12)	173.11(18)
C(10)-C(11)-C(12)-C(13)	-1.7(3)
C(11)-C(12)-C(13)-C(14)	2.2(3)
C(12)-C(13)-C(14)-C(9)	0.1(3)
C(12)-C(13)-C(14)-C(15)	-176.78(18)
C(10)-C(9)-C(14)-C(13)	-3.0(3)
N(1)-C(9)-C(14)-C(13)	174.29(16)
C(10)-C(9)-C(14)-C(15)	173.66(18)
N(1)-C(9)-C(14)-C(15)	-9.0(3)
C(13)-C(14)-C(15)-C(17)	68.1(2)
C(9)-C(14)-C(15)-C(17)	-108.5(2)
C(13)-C(14)-C(15)-C(16)	-55.7(2)
C(9)-C(14)-C(15)-C(16)	127.7(2)
C(11)-C(10)-C(18)-C(20)	-60.3(2)
C(9)-C(10)-C(18)-C(20)	113.4(2)
C(11)-C(10)-C(18)-C(19)	60.9(2)
C(9)-C(10)-C(18)-C(19)	-125.5(2)
Si(1)-P(1)-C(21)-C(26)	76.83(17)
Si(1)-P(1)-C(21)-C(22)	-113.74(15)
C(26)-C(21)-C(22)-C(23)	2.6(3)
P(1)-C(21)-C(22)-C(23)	-167.20(15)
C(26)-C(21)-C(22)-C(30)	-176.39(18)
P(1)-C(21)-C(22)-C(30)	13.8(3)
C(21)-C(22)-C(23)-C(24)	-0.2(3)
C(30)-C(22)-C(23)-C(24)	178.91(19)
C(22)-C(23)-C(24)-C(25)	-1.6(3)
C(22)-C(23)-C(24)-C(33)	177.77(19)
C(23)-C(24)-C(25)-C(26)	0.9(3)
C(33)-C(24)-C(25)-C(26)	-178.4(2)
C(24)-C(25)-C(26)-C(21)	1.5(3)
C(24)-C(25)-C(26)-C(27)	-177.6(2)

C(22)-C(21)-C(26)-C(25)	-3.3(3)
P(1)-C(21)-C(26)-C(25)	166.14(16)
C(22)-C(21)-C(26)-C(27)	175.83(19)
P(1)-C(21)-C(26)-C(27)	-14.7(3)
C(25)-C(26)-C(27)-C(29')	67.5(7)
C(21)-C(26)-C(27)-C(29')	-111.6(6)
C(25)-C(26)-C(27)-C(28)	-77.7(8)
C(21)-C(26)-C(27)-C(28)	103.2(8)
C(25)-C(26)-C(27)-C(28')	-60.3(7)
C(21)-C(26)-C(27)-C(28')	120.6(6)
C(25)-C(26)-C(27)-C(29)	44.4(7)
C(21)-C(26)-C(27)-C(29)	-134.7(7)
C(23)-C(22)-C(30)-C(31)	54.9(3)
C(21)-C(22)-C(30)-C(31)	-126.1(2)
C(23)-C(22)-C(30)-C(32)	-67.9(2)
C(21)-C(22)-C(30)-C(32)	111.1(2)
C(23)-C(24)-C(33)-C(35)	159.3(2)
C(25)-C(24)-C(33)-C(35)	-21.4(3)
C(23)-C(24)-C(33)-C(34)	-75.7(3)
C(25)-C(24)-C(33)-C(34)	103.6(3)

Symmetry transformations used to generate equivalent atoms:

Table S6. Bond lengths [Å], bond angles [°] and torsion angles [°] for **3**

Cl(1)-Si(1)	2.1095(12)
Cl(2)-Si(1)	2.0663(11)
P(1)-C(28)	1.884(3)
P(1)-Si(1)	2.1129(10)
Si(1)-C(1)	1.928(3)
N(1)-C(1)	1.362(3)
N(1)-C(2)	1.383(3)
N(1)-C(16)	1.464(3)
N(2)-C(1)	1.358(3)

N(2)-C(3)	1.382(3)
N(2)-C(4)	1.453(3)
C(1S)-C(6S)	1.370(6)
C(1S)-C(2S)	1.380(6)
C(1S)-H(1S)	0.9500
C(2S)-C(3S)	1.379(6)
C(2S)-H(2S)	0.9500
C(3S)-C(4S)	1.370(5)
C(3S)-H(3S)	0.9500
C(4S)-C(5S)	1.355(5)
C(4S)-H(4S)	0.9500
C(5S)-C(6S)	1.374(5)
C(5S)-H(5S)	0.9500
C(6S)-H(6S)	0.9500
C(1T)-C(2T)	1.365(11)
C(1T)-C(6T)	1.375(10)
C(1T)-H(1T)	0.9500
C(2T)-C(3T)	1.392(10)
C(2T)-H(2T)	0.9500
C(3T)-C(4T)	1.390(9)
C(3T)-H(3T)	0.9500
C(4T)-C(5T)	1.384(8)
C(4T)-H(4T)	0.9500
C(5T)-C(6T)	1.381(9)
C(5T)-H(5T)	0.9500
C(6T)-H(6T)	0.9500
C(1U)-C(2U)	1.374(12)
C(1U)-C(6U)	1.387(11)
C(1U)-H(1U)	0.9500
C(2U)-C(3U)	1.369(13)
C(2U)-H(2U)	0.9500
C(3U)-C(4U)	1.376(13)
C(3U)-H(3U)	0.9500
C(4U)-C(5U)	1.376(15)
C(4U)-H(4U)	0.9500

C(5U)-C(6U)	1.381(13)
C(5U)-H(5U)	0.9500
C(6U)-H&U	0.9500
C(2)-C(3)	1.340(4)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-C(5)	1.399(4)
C(4)-C(9)	1.400(4)
C(5)-C(6)	1.396(4)
C(5)-C(13)	1.524(4)
C(6)-C(7)	1.372(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.385(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.400(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.519(4)
C(10)-C(11)	1.522(4)
C(10)-C(12)	1.524(4)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(15)	1.533(4)
C(13)-C(14)	1.536(4)
C(13)-H(13)	1.0000
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800

C(16)-C(21)	1.399(4)
C(16)-C(17)	1.400(4)
C(18)-C(19)	1.374(4)
C(18)-C(17)	1.391(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.385(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.397(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.515(4)
C(22)-C(23)	1.535(4)
C(22)-C(24)	1.539(4)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(17)-C(25)	1.522(4)
C(25)-C(27')	1.488(16)
C(25)-C(26)	1.525(6)
C(25)-C(27)	1.552(6)
C(25)-C(26')	1.585(15)
C(25)-H(25)	1.0000
C(25)-H(25')	1.0000
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(26')-H(26D)	0.9800
C(26')-H(26E)	0.9800
C(26')-H(26F)	0.9800

C(27')-H(27D)	0.9800
C(27')-H(27E)	0.9800
C(27')-H(27F)	0.9800
C(28)-C(29)	1.414(4)
C(28)-C(33)	1.420(4)
C(29)-C(30)	1.400(4)
C(29)-C(37)	1.525(4)
C(30)-C(31)	1.391(4)
C(30)-H(30)	0.9500
C(31)-C(32)	1.391(4)
C(31)-C(40)	1.521(4)
C(32)-C(33)	1.395(4)
C(32)-H(32)	0.9500
C(33)-C(34)	1.526(4)
C(34)-C(35)	1.529(4)
C(34)-C(36)	1.529(4)
C(34)-H(34)	1.0000
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(38)	1.522(4)
C(37)-C(39)	1.524(4)
C(37)-H(37)	1.0000
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-C(42)	1.514(4)
C(40)-C(41)	1.532(5)
C(40)-H(40)	1.0000

C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800

C(28)-P(1)-Si(1)	95.01(8)
C(1)-Si(1)-Cl(2)	104.92(9)
C(1)-Si(1)-Cl(1)	98.94(9)
Cl(2)-Si(1)-Cl(1)	100.39(5)
C(1)-Si(1)-P(1)	115.11(8)
Cl(2)-Si(1)-P(1)	116.12(5)
Cl(1)-Si(1)-P(1)	118.78(5)
C(1)-N(1)-C(2)	110.2(2)
C(1)-N(1)-C(16)	127.4(2)
C(2)-N(1)-C(16)	122.0(2)
C(1)-N(2)-C(3)	110.2(2)
C(1)-N(2)-C(4)	126.9(2)
C(3)-N(2)-C(4)	122.8(2)
C(6S)-C(1S)-C(2S)	120.5(4)
C(6S)-C(1S)-H(1S)	119.7
C(2S)-C(1S)-H(1S)	119.7
C(3S)-C(2S)-C(1S)	119.3(4)
C(3S)-C(2S)-H(2S)	120.4
C(1S)-C(2S)-H(2S)	120.4
C(4S)-C(3S)-C(2S)	119.7(4)
C(4S)-C(3S)-H(3S)	120.1
C(2S)-C(3S)-H(3S)	120.1
C(5S)-C(4S)-C(3S)	120.6(4)
C(5S)-C(4S)-H(4S)	119.7
C(3S)-C(4S)-H(4S)	119.7
C(4S)-C(5S)-C(6S)	120.5(4)
C(4S)-C(5S)-H(5S)	119.8
C(6S)-C(5S)-H(5S)	119.8

C(1S)-C(6S)-C(5S)	119.4(4)
C(1S)-C(6S)-H(6S)	120.3
C(5S)-C(6S)-H(6S)	120.3
C(2T)-C(1T)-C(6T)	121.2(7)
C(2T)-C(1T)-H(1T)	119.4
C(6T)-C(1T)-H(1T)	119.4
C(1T)-C(2T)-C(3T)	120.4(9)
C(1T)-C(2T)-H(2T)	119.8
C(3T)-C(2T)-H(2T)	119.8
C(4T)-C(3T)-C(2T)	118.6(8)
C(4T)-C(3T)-H(3T)	120.7
C(2T)-C(3T)-H(3T)	120.7
C(5T)-C(4T)-C(3T)	120.4(6)
C(5T)-C(4T)-H(4T)	119.8
C(3T)-C(4T)-H(4T)	119.8
C(6T)-C(5T)-C(4T)	120.3(7)
C(6T)-C(5T)-H(5T)	119.9
C(4T)-C(5T)-H(5T)	119.9
C(1T)-C(6T)-C(5T)	119.1(7)
C(1T)-C(6T)-H(6T)	120.4
C(5T)-C(6T)-H(6T)	120.4
C(2U)-C(1U)-C(6U)	119.4(10)
C(2U)-C(1U)-H(1U)	120.3
C(6U)-C(1U)-H(1U)	120.3
C(3U)-C(2U)-C(1U)	121.2(11)
C(3U)-C(2U)-H(2U)	119.4
C(1U)-C(2U)-H(2U)	119.4
C(2U)-C(3U)-C(4U)	119.4(11)
C(2U)-C(3U)-H(3U)	120.3
C(4U)-C(3U)-H(3U)	120.3
C(3U)-C(4U)-C(5U)	120.2(13)
C(3U)-C(4U)-H(4U)	119.9
C(5U)-C(4U)-H(4U)	119.9
C(4U)-C(5U)-C(6U)	120.3(14)
C(4U)-C(5U)-H(5U)	119.8

C(6U)-C(5U)-H(5U)	119.8
C(5U)-C(6U)-C(1U)	119.4(11)
C(5U)-C(6U)-H&U	120.3
C(1U)-C(6U)-H&U	120.3
N(2)-C(1)-N(1)	105.1(2)
N(2)-C(1)-Si(1)	125.49(18)
N(1)-C(1)-Si(1)	129.12(18)
C(3)-C(2)-N(1)	107.1(2)
C(3)-C(2)-H(2)	126.5
N(1)-C(2)-H(2)	126.5
C(2)-C(3)-N(2)	107.3(2)
C(2)-C(3)-H(3)	126.3
N(2)-C(3)-H(3)	126.3
C(5)-C(4)-C(9)	123.6(2)
C(5)-C(4)-N(2)	118.7(2)
C(9)-C(4)-N(2)	117.6(2)
C(6)-C(5)-C(4)	116.6(3)
C(6)-C(5)-C(13)	120.7(3)
C(4)-C(5)-C(13)	122.6(3)
C(7)-C(6)-C(5)	121.7(3)
C(7)-C(6)-H(6)	119.2
C(5)-C(6)-H(6)	119.2
C(6)-C(7)-C(8)	120.3(3)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	121.1(3)
C(7)-C(8)-H(8)	119.5
C(9)-C(8)-H(8)	119.5
C(4)-C(9)-C(8)	116.7(3)
C(4)-C(9)-C(10)	123.5(2)
C(8)-C(9)-C(10)	119.8(3)
C(9)-C(10)-C(11)	111.7(2)
C(9)-C(10)-C(12)	112.1(2)
C(11)-C(10)-C(12)	109.9(3)
C(9)-C(10)-H(10)	107.7

C(11)-C(10)-H(10)	107.7
C(12)-C(10)-H(10)	107.7
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(5)-C(13)-C(15)	109.3(2)
C(5)-C(13)-C(14)	111.7(2)
C(15)-C(13)-C(14)	111.6(3)
C(5)-C(13)-H(13)	108.1
C(15)-C(13)-H(13)	108.1
C(14)-C(13)-H(13)	108.1
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(21)-C(16)-C(17)	123.9(3)
C(21)-C(16)-N(1)	118.7(2)
C(17)-C(16)-N(1)	117.4(2)

C(19)-C(18)-C(17)	121.7(3)
C(19)-C(18)-H(18)	119.2
C(17)-C(18)-H(18)	119.2
C(18)-C(19)-C(20)	120.2(3)
C(18)-C(19)-H(19)	119.9
C(20)-C(19)-H(19)	119.9
C(19)-C(20)-C(21)	121.3(3)
C(19)-C(20)-H(20)	119.4
C(21)-C(20)-H(20)	119.4
C(20)-C(21)-C(16)	116.3(3)
C(20)-C(21)-C(22)	120.8(3)
C(16)-C(21)-C(22)	122.8(3)
C(21)-C(22)-C(23)	112.7(3)
C(21)-C(22)-C(24)	110.0(2)
C(23)-C(22)-C(24)	109.9(2)
C(21)-C(22)-H(22)	108.1
C(23)-C(22)-H(22)	108.1
C(24)-C(22)-H(22)	108.1
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(18)-C(17)-C(16)	116.5(3)
C(18)-C(17)-C(25)	119.9(3)
C(16)-C(17)-C(25)	123.5(3)
C(27')-C(25)-C(17)	117.4(13)
C(17)-C(25)-C(26)	112.5(4)

C(17)-C(25)-C(27)	107.9(4)
C(26)-C(25)-C(27)	109.1(4)
C(27')-C(25)-C(26')	110.7(12)
C(17)-C(25)-C(26')	110.2(9)
C(17)-C(25)-H(25)	109.1
C(26)-C(25)-H(25)	109.1
C(27)-C(25)-H(25)	109.1
C(27')-C(25)-H(25')	105.9
C(17)-C(25)-H(25')	105.9
C(26')-C(25)-H(25')	105.9
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(26')-H(26D)	109.5
C(25)-C(26')-H(26E)	109.5
H(26D)-C(26')-H(26E)	109.5
C(25)-C(26')-H(26F)	109.5
H(26D)-C(26')-H(26F)	109.5
H(26E)-C(26')-H(26F)	109.5
C(25)-C(27')-H(27D)	109.5
C(25)-C(27')-H(27E)	109.5
H(27D)-C(27')-H(27E)	109.5
C(25)-C(27')-H(27F)	109.5
H(27D)-C(27')-H(27F)	109.5
H(27E)-C(27')-H(27F)	109.5
C(29)-C(28)-C(33)	118.3(2)

C(29)-C(28)-P(1)	121.5(2)
C(33)-C(28)-P(1)	119.9(2)
C(30)-C(29)-C(28)	119.7(2)
C(30)-C(29)-C(37)	117.5(2)
C(28)-C(29)-C(37)	122.8(2)
C(31)-C(30)-C(29)	122.5(3)
C(31)-C(30)-H(30)	118.8
C(29)-C(30)-H(30)	118.8
C(32)-C(31)-C(30)	117.2(2)
C(32)-C(31)-C(40)	121.7(3)
C(30)-C(31)-C(40)	121.1(3)
C(31)-C(32)-C(33)	122.8(3)
C(31)-C(32)-H(32)	118.6
C(33)-C(32)-H(32)	118.6
C(32)-C(33)-C(28)	119.5(3)
C(32)-C(33)-C(34)	118.3(2)
C(28)-C(33)-C(34)	122.2(2)
C(33)-C(34)-C(35)	112.9(2)
C(33)-C(34)-C(36)	111.1(2)
C(35)-C(34)-C(36)	110.5(3)
C(33)-C(34)-H(34)	107.4
C(35)-C(34)-H(34)	107.4
C(36)-C(34)-H(34)	107.4
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5

C(38)-C(37)-C(39)	109.7(3)
C(38)-C(37)-C(29)	112.2(2)
C(39)-C(37)-C(29)	111.6(2)
C(38)-C(37)-H(37)	107.7
C(39)-C(37)-H(37)	107.7
C(29)-C(37)-H(37)	107.7
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(37)-C(39)-H(39A)	109.5
C(37)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(37)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(42)-C(40)-C(31)	112.1(2)
C(42)-C(40)-C(41)	109.9(3)
C(31)-C(40)-C(41)	111.3(3)
C(42)-C(40)-H(40)	107.8
C(31)-C(40)-H(40)	107.8
C(41)-C(40)-H(40)	107.8
C(40)-C(41)-H(41A)	109.5
C(40)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(40)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(40)-C(42)-H(42A)	109.5
C(40)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(40)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5

H(42B)-C(42)-H(42C)	109.5

C(6S)-C(1S)-C(2S)-C(3S)	0.0(6)
C(1S)-C(2S)-C(3S)-C(4S)	0.6(5)
C(2S)-C(3S)-C(4S)-C(5S)	-0.7(5)
C(3S)-C(4S)-C(5S)-C(6S)	0.1(5)
C(2S)-C(1S)-C(6S)-C(5S)	-0.6(6)
C(4S)-C(5S)-C(6S)-C(1S)	0.5(5)
C(6T)-C(1T)-C(2T)-C(3T)	-0.4(15)
C(1T)-C(2T)-C(3T)-C(4T)	0.3(15)
C(2T)-C(3T)-C(4T)-C(5T)	-0.8(12)
C(3T)-C(4T)-C(5T)-C(6T)	1.4(11)
C(2T)-C(1T)-C(6T)-C(5T)	1.0(14)
C(4T)-C(5T)-C(6T)-C(1T)	-1.5(13)
C(6U)-C(1U)-C(2U)-C(3U)	-0.6(16)
C(1U)-C(2U)-C(3U)-C(4U)	-1.5(19)
C(2U)-C(3U)-C(4U)-C(5U)	2(3)
C(3U)-C(4U)-C(5U)-C(6U)	0(3)
C(4U)-C(5U)-C(6U)-C(1U)	-2(2)
C(2U)-C(1U)-C(6U)-C(5U)	2.3(19)
C(3)-N(2)-C(1)-N(1)	-0.5(3)
C(4)-N(2)-C(1)-N(1)	176.3(2)
C(3)-N(2)-C(1)-Si(1)	173.6(2)
C(4)-N(2)-C(1)-Si(1)	-9.6(4)
C(2)-N(1)-C(1)-N(2)	0.4(3)
C(16)-N(1)-C(1)-N(2)	-173.7(2)
C(2)-N(1)-C(1)-Si(1)	-173.4(2)
C(16)-N(1)-C(1)-Si(1)	12.5(4)
C(1)-N(1)-C(2)-C(3)	-0.1(3)
C(16)-N(1)-C(2)-C(3)	174.4(2)
N(1)-C(2)-C(3)-N(2)	-0.3(3)
C(1)-N(2)-C(3)-C(2)	0.5(3)
C(4)-N(2)-C(3)-C(2)	-176.5(2)
C(1)-N(2)-C(4)-C(5)	85.8(3)
C(3)-N(2)-C(4)-C(5)	-97.7(3)

C(1)-N(2)-C(4)-C(9)	-97.4(3)
C(3)-N(2)-C(4)-C(9)	79.0(3)
C(9)-C(4)-C(5)-C(6)	1.6(4)
N(2)-C(4)-C(5)-C(6)	178.1(2)
C(9)-C(4)-C(5)-C(13)	-175.4(3)
N(2)-C(4)-C(5)-C(13)	1.1(4)
C(4)-C(5)-C(6)-C(7)	-0.2(4)
C(13)-C(5)-C(6)-C(7)	176.8(3)
C(5)-C(6)-C(7)-C(8)	-1.0(4)
C(6)-C(7)-C(8)-C(9)	0.9(4)
C(5)-C(4)-C(9)-C(8)	-1.7(4)
N(2)-C(4)-C(9)-C(8)	-178.2(2)
C(5)-C(4)-C(9)-C(10)	178.3(3)
N(2)-C(4)-C(9)-C(10)	1.7(4)
C(7)-C(8)-C(9)-C(4)	0.4(4)
C(7)-C(8)-C(9)-C(10)	-179.5(2)
C(4)-C(9)-C(10)-C(11)	100.7(3)
C(8)-C(9)-C(10)-C(11)	-79.4(3)
C(4)-C(9)-C(10)-C(12)	-135.5(3)
C(8)-C(9)-C(10)-C(12)	44.5(3)
C(6)-C(5)-C(13)-C(15)	-77.8(3)
C(4)-C(5)-C(13)-C(15)	99.0(3)
C(6)-C(5)-C(13)-C(14)	46.1(4)
C(4)-C(5)-C(13)-C(14)	-137.0(3)
C(1)-N(1)-C(16)-C(21)	-94.0(3)
C(2)-N(1)-C(16)-C(21)	92.5(3)
C(1)-N(1)-C(16)-C(17)	88.5(3)
C(2)-N(1)-C(16)-C(17)	-85.0(3)
C(17)-C(18)-C(19)-C(20)	-2.0(5)
C(18)-C(19)-C(20)-C(21)	2.3(4)
C(19)-C(20)-C(21)-C(16)	0.4(4)
C(19)-C(20)-C(21)-C(22)	-176.0(3)
C(17)-C(16)-C(21)-C(20)	-3.6(4)
N(1)-C(16)-C(21)-C(20)	179.0(2)
C(17)-C(16)-C(21)-C(22)	172.7(3)

N(1)-C(16)-C(21)-C(22)	-4.7(4)
C(20)-C(21)-C(22)-C(23)	-39.4(4)
C(16)-C(21)-C(22)-C(23)	144.5(3)
C(20)-C(21)-C(22)-C(24)	83.6(3)
C(16)-C(21)-C(22)-C(24)	-92.6(3)
C(19)-C(18)-C(17)-C(16)	-1.1(4)
C(19)-C(18)-C(17)-C(25)	176.0(3)
C(21)-C(16)-C(17)-C(18)	4.0(4)
N(1)-C(16)-C(17)-C(18)	-178.6(2)
C(21)-C(16)-C(17)-C(25)	-173.0(3)
N(1)-C(16)-C(17)-C(25)	4.4(4)
C(18)-C(17)-C(25)-C(27')	-47.4(16)
C(16)-C(17)-C(25)-C(27')	129.5(16)
C(18)-C(17)-C(25)-C(26)	51.2(7)
C(16)-C(17)-C(25)-C(26)	-131.9(6)
C(18)-C(17)-C(25)-C(27)	-69.1(5)
C(16)-C(17)-C(25)-C(27)	107.8(5)
C(18)-C(17)-C(25)-C(26')	80.6(18)
C(16)-C(17)-C(25)-C(26')	-102.5(18)
Si(1)-P(1)-C(28)-C(29)	90.4(2)
Si(1)-P(1)-C(28)-C(33)	-96.5(2)
C(33)-C(28)-C(29)-C(30)	-2.0(4)
P(1)-C(28)-C(29)-C(30)	171.2(2)
C(33)-C(28)-C(29)-C(37)	177.3(2)
P(1)-C(28)-C(29)-C(37)	-9.5(4)
C(28)-C(29)-C(30)-C(31)	0.3(4)
C(37)-C(29)-C(30)-C(31)	-179.0(3)
C(29)-C(30)-C(31)-C(32)	0.8(4)
C(29)-C(30)-C(31)-C(40)	178.8(2)
C(30)-C(31)-C(32)-C(33)	-0.1(4)
C(40)-C(31)-C(32)-C(33)	-178.0(3)
C(31)-C(32)-C(33)-C(28)	-1.7(4)
C(31)-C(32)-C(33)-C(34)	178.7(3)
C(29)-C(28)-C(33)-C(32)	2.7(4)
P(1)-C(28)-C(33)-C(32)	-170.7(2)

C(29)-C(28)-C(33)-C(34)	-177.7(2)
P(1)-C(28)-C(33)-C(34)	8.9(3)
C(32)-C(33)-C(34)-C(35)	-42.0(4)
C(28)-C(33)-C(34)-C(35)	138.4(3)
C(32)-C(33)-C(34)-C(36)	82.8(3)
C(28)-C(33)-C(34)-C(36)	-96.8(3)
C(30)-C(29)-C(37)-C(38)	51.5(3)
C(28)-C(29)-C(37)-C(38)	-127.8(3)
C(30)-C(29)-C(37)-C(39)	-72.1(3)
C(28)-C(29)-C(37)-C(39)	108.6(3)
C(32)-C(31)-C(40)-C(42)	-63.2(4)
C(30)-C(31)-C(40)-C(42)	118.9(3)
C(32)-C(31)-C(40)-C(41)	60.4(4)
C(30)-C(31)-C(40)-C(41)	-117.5(3)

Symmetry transformations used to generate equivalent atoms:

S5. Theoretical calculations

The geometries of the full complexes **2a** and **3** have been optimized using the functional M06-2X[S10] with the def2-SVP basis set.[S11] The geometries of the model compounds **2M** and **3M** were optimized at M06-2X with the basis sets def2-TZVPP[S12]. Stationary points were located with the Berny algorithm[S13] using redundant coordinates. Analytical Hessians were computed to determinate the nature of the stationary points.[S14] All geometry optimizations computations were performed using the Gaussian 09 suite of programs.[S15] The NBO[S16] analyses have been carried out with the internal module of Gaussian09 at the M06-2X/def2-TZVPP level of theory. The TD-DFT[S17] calculations of **2M** and **3M** were also carried out at the M06-2X/def2-TZVPP level.

The energy decomposition analyses of **2M** and **3M** were carried at the M06-2X/def2-TZVPP optimized geometries with the program package ADF2013.01[S18] using the functional BP86[S19] in conjunction with uncontracted Slater-type orbitals (STOs) as basis functions.[S20] The latter basis sets for all elements have triple-ζ quality augmented by two sets of polarization functions. This level of theory is denoted BP86/TZ2P+. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[S21] The BP86/TZ2P+ calculations have been carried out using the frozen core approximation.

The interatomic interactions were investigated by means of an energy decomposition analysis (EDA, also termed extended transition state method - ETS) developed independently by Morokuma[S22] and by Ziegler and Rauk.[S23] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A–B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Eq. (1)].

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (1)$$

The term ΔE_{elstat} corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion ΔE_{Pauli} is the energy change associated with the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wavefunction

$\Psi^0 = N\hat{A}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization (N = constant) of the product wavefunction. ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects. The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. Further details on the EDA/ETS method[S18] and its application to the analysis of the chemical bond[S24] can be found in the literature.

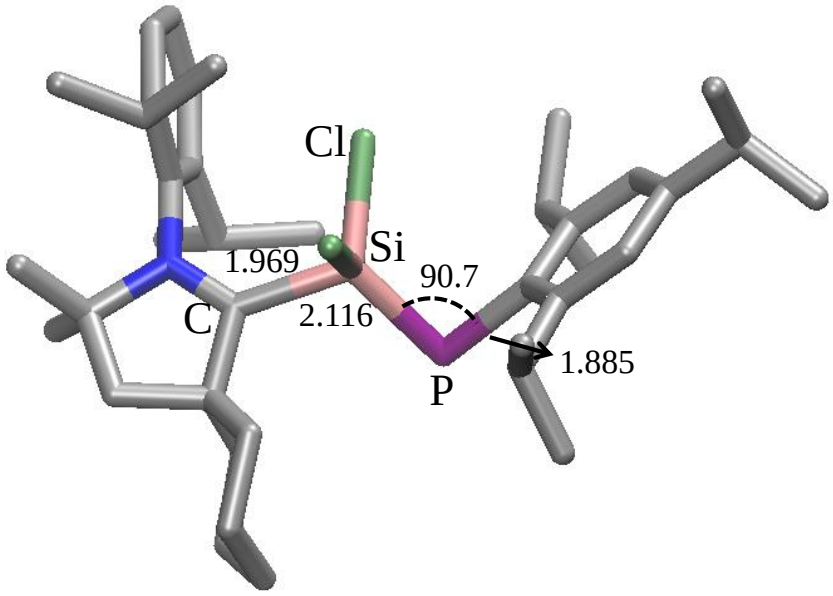
The EDA-NOCV[S25] method combines charge (NOCV) and energy (EDA) decomposition schemes to decompose the deformation density which is associated with the bond formation, $\Delta\rho$, into different components of the chemical bond. The EDA-NOCV calculations provide pairwise energy contributions for each pair of interacting orbitals to the total bond energy. NOCV (Natural Orbital for Chemical Valence)[S26] is defined as the eigenvector of the valence operator, $\hat{V}$, given by Equation (2):

$$\hat{V}\Psi_i = v_i\Psi_i \tag{2}$$

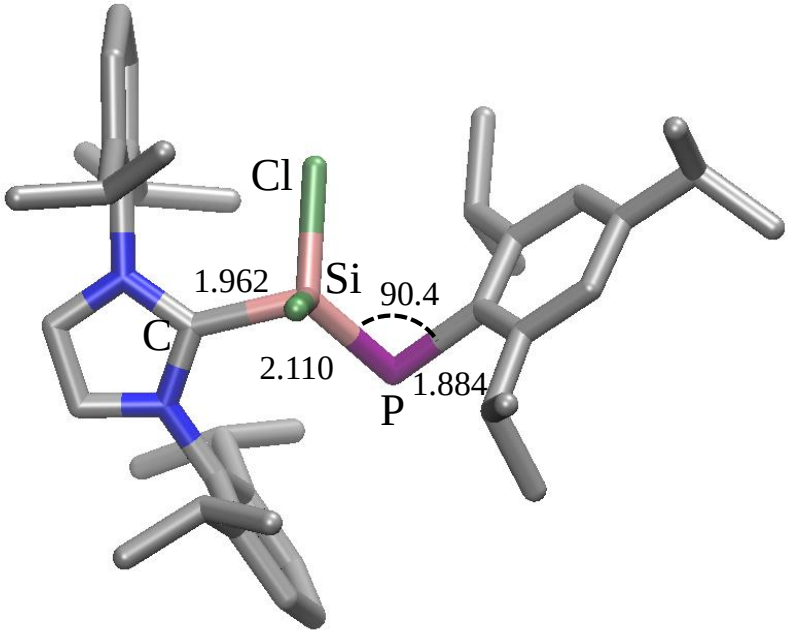
In the EDA-NOCV scheme the orbital interaction term, ΔE_{orb}, is given by Equation (3):

$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{\frac{N}{2}} v_k \left[-F_{-k,-k}^{TS} + F_{k,k}^{TS}\right] \tag{3}$$

In which $F_{-k,-k}^{TS}$ and $F_{k,k}^{TS}$ are diagonal transition state Kohn-Sham matrix elements corresponding to NOCVs with the eigenvalues $-v_k$ and v_k, respectively. The ΔE_k^{orb} term of a particular type of bond are assigned by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV scheme thus provides both qualitative ($\Delta\rho_{orb}$) and quantitative (ΔE_{orb}) information about the strength of orbital interactions in chemical bonds, also in molecules with C_1 symmetry.[S27]

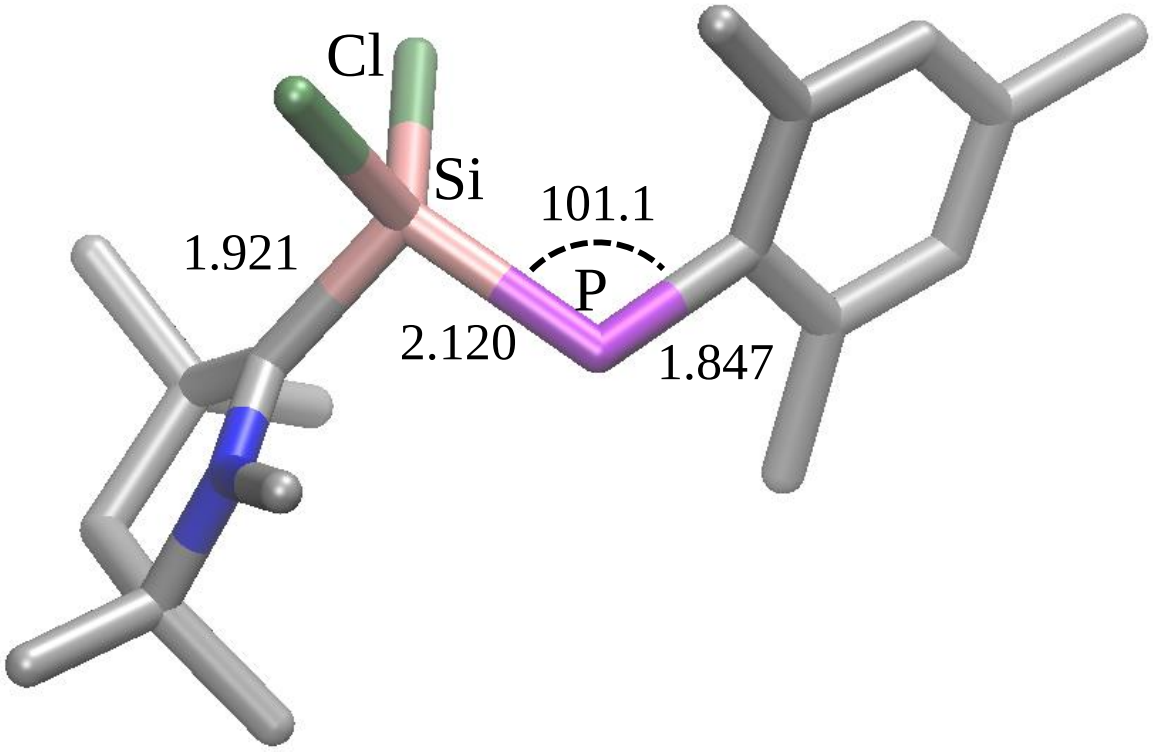


(a)

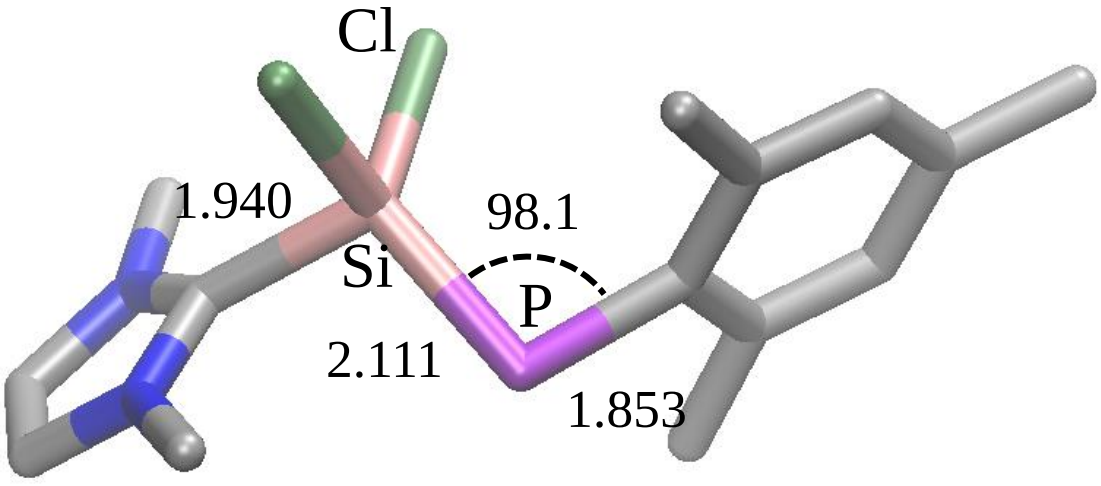


(b)

Figure S13. Optimized geometries at the M06-2X/def2-SVP level of theory of (a) **2a** and (b) **3**. Bond length are given in [Å] an angles in [°].



(a)



(b)

Figure S14. Optimized geometries at the M06-2X/def2-TZVPP level of theory of (a) **2M** and (b) **3M**. Bond length are given in [Å] an angles in [°].

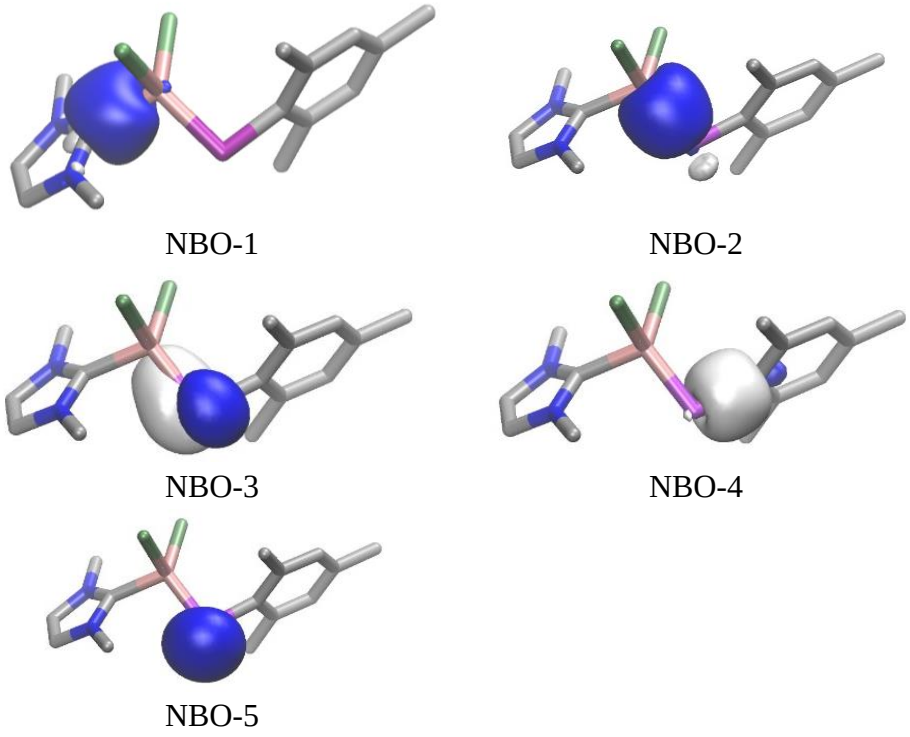


Figure S15. Shape of relevant natural bond orbitals of **3M** at M06-2X/def2-TZVPP.

Table S7. Energy decomposition analysis using the EDA-NOCV method of the (L)$SiCl_2$→PAr bonds in **2M** and **3M** at the BP86/TZ2P+ level of theory. The interacting fragments are $LSiCl_2$ (L = CAAC, NHC) and P-Ar in the electronic singlet states. Energy values are given in kcal mol^{-1}.

	2M	**3M**
ΔE_{int}	-76.3	-75.0

ΔE_{Pauli}	263.0	271.1
ΔE_{elstat}[a]	-152.1 (44.8 %)	-161.0 (46.5 %)
ΔE_{orb}[a]	-187.2 (55.2 %)	-185.1 (53.5 %)
ΔE_{σ} (donation)[b]	-137.4 (73.3 %)	-140.8 (76.1 %)
$\Delta E_{\pi\perp}$ (π backdonation)[b]	-29.0 (15.5 %)	-23.8 (12.9 %)
ΔE_{rest}[b]	-20.8 (11.1 %)	-20.5 (11.1 %)
ΔE_{prep}	33.0	33.5
$-D_e$	-44.3	-41.5

[a] The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.

[b] The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

Table S8. Cartesian coordinates [Å] of the optimized geometries.

2a (M06-2X/def2-SVP)

Cl	-0.320784000000	0.728923000000	2.169077000000
Cl	-0.172849000000	-1.880539000000	0.253529000000
P	-1.231912000000	1.139245000000	-1.408647000000
Si	-0.077745000000	0.218931000000	0.106835000000
N	2.882543000000	0.090559000000	0.242367000000
C	1.804912000000	0.794464000000	0.067640000000
C	2.154832000000	2.260903000000	-0.141361000000
C	3.617116000000	2.328999000000	0.342957000000
H	4.230352000000	3.013886000000	-0.257306000000
H	3.634669000000	2.691365000000	1.382063000000
C	4.170404000000	0.901605000000	0.287303000000
C	4.978840000000	0.556398000000	1.529920000000
H	4.403967000000	0.729325000000	2.447690000000
H	5.862411000000	1.210073000000	1.552784000000
H	5.323663000000	-0.486772000000	1.506058000000
C	5.031980000000	0.627327000000	-0.944993000000
H	4.561513000000	0.960411000000	-1.877816000000
H	5.269212000000	-0.442434000000	-1.023979000000
H	5.976285000000	1.176802000000	-0.828384000000
C	1.255694000000	3.243175000000	0.635665000000
H	0.205257000000	3.053953000000	0.366325000000
H	1.353083000000	3.051515000000	1.714481000000
C	1.593716000000	4.692501000000	0.294771000000
H	0.944297000000	5.359695000000	0.879867000000
H	2.631885000000	4.927153000000	0.591596000000
C	1.415534000000	4.945457000000	-1.200416000000
H	1.640647000000	5.992951000000	-1.449897000000
H	0.360725000000	4.765268000000	-1.469181000000

C	2.302551000000	4.004239000000	-2.011528000000
H	3.362843000000	4.248568000000	-1.824246000000
H	2.137789000000	4.148564000000	-3.089391000000
C	2.025902000000	2.540168000000	-1.666582000000
H	2.705745000000	1.881241000000	-2.228278000000
H	1.003419000000	2.286940000000	-1.986548000000
C	2.946707000000	-1.361224000000	0.290731000000
C	3.003723000000	-2.056822000000	-0.934282000000
C	3.106177000000	-3.449502000000	-0.881216000000
H	3.138003000000	-4.014338000000	-1.814376000000
C	3.144891000000	-4.125670000000	0.330880000000
H	3.226081000000	-5.213344000000	0.348029000000
C	3.046765000000	-3.416299000000	1.520418000000
H	3.030769000000	-3.956209000000	2.468767000000
C	2.926755000000	-2.023739000000	1.534539000000
C	2.673031000000	-1.350370000000	2.877905000000
H	2.525281000000	-0.272974000000	2.707425000000
C	3.827559000000	-1.559966000000	3.866977000000
H	3.626866000000	-1.010747000000	4.798548000000
H	4.799536000000	-1.233733000000	3.477367000000
H	3.915632000000	-2.625230000000	4.127951000000
C	1.381724000000	-1.888287000000	3.513671000000
H	0.533138000000	-1.837729000000	2.823165000000
H	1.133898000000	-1.298135000000	4.408068000000
H	1.515126000000	-2.935325000000	3.826031000000
C	2.883986000000	-1.401051000000	-2.304283000000
H	2.941932000000	-0.313067000000	-2.180495000000
C	4.016656000000	-1.828498000000	-3.244781000000
H	3.983130000000	-1.232825000000	-4.168521000000
H	3.910957000000	-2.884175000000	-3.535115000000
H	5.009658000000	-1.704569000000	-2.789957000000
C	1.522427000000	-1.700057000000	-2.947074000000

H	1.507342000000	-1.319830000000	-3.979389000000
H	0.699749000000	-1.216510000000	-2.404279000000
H	1.329762000000	-2.783318000000	-2.975571000000
C	-2.797798000000	0.334068000000	-0.736069000000
C	-3.572214000000	0.999297000000	0.249373000000
C	-4.765513000000	0.420917000000	0.688578000000
H	-5.356528000000	0.941137000000	1.445455000000
C	-5.225308000000	-0.800448000000	0.194093000000
C	-4.453489000000	-1.444553000000	-0.769546000000
H	-4.803638000000	-2.402694000000	-1.160818000000
C	-3.253118000000	-0.905668000000	-1.245354000000
C	-2.501276000000	-1.640573000000	-2.345414000000
H	-1.440702000000	-1.386957000000	-2.225979000000
C	-2.943535000000	-1.120320000000	-3.717036000000
H	-2.774553000000	-0.036323000000	-3.794032000000
H	-4.016346000000	-1.313870000000	-3.875009000000
H	-2.381077000000	-1.616163000000	-4.523846000000
C	-2.617020000000	-3.161756000000	-2.268629000000
H	-3.626996000000	-3.516569000000	-2.525883000000
H	-2.367847000000	-3.525942000000	-1.261312000000
H	-1.920545000000	-3.624202000000	-2.984593000000
C	-3.175410000000	2.363972000000	0.798403000000
H	-2.078702000000	2.409219000000	0.783773000000
C	-3.692974000000	3.469455000000	-0.128001000000
H	-4.793414000000	3.450941000000	-0.171115000000
H	-3.306076000000	3.334011000000	-1.148459000000
H	-3.378652000000	4.461617000000	0.232551000000
C	-3.617170000000	2.604330000000	2.241253000000
H	-4.708070000000	2.725367000000	2.328848000000
H	-3.159346000000	3.529547000000	2.622269000000
H	-3.307589000000	1.774325000000	2.892928000000
C	-6.524502000000	-1.407054000000	0.689300000000

H	-6.646508000000	-2.372865000000	0.171676000000
C	-6.481183000000	-1.685548000000	2.194335000000
H	-6.384383000000	-0.748069000000	2.763238000000
H	-5.625952000000	-2.325336000000	2.453579000000
H	-7.404119000000	-2.185294000000	2.525661000000
C	-7.724844000000	-0.526979000000	0.328284000000
H	-7.653137000000	0.451374000000	0.828192000000
H	-8.667092000000	-0.999493000000	0.644967000000
H	-7.771453000000	-0.347703000000	-0.755047000000

3 (M06-2X/def2-SVP)

Cl	0.263422000000	0.182591000000	-2.417979000000
Cl	0.223153000000	-2.194406000000	-0.241604000000
P	1.083068000000	1.079606000000	1.081383000000
Si	0.022591000000	-0.100642000000	-0.308913000000
N	-2.949969000000	-0.605412000000	-0.449507000000
C	-1.909870000000	0.222392000000	-0.213512000000
N	-2.454358000000	1.445318000000	-0.026803000000
C	-3.822010000000	1.389945000000	-0.168474000000
H	-4.440583000000	2.274463000000	-0.055269000000
C	-4.136162000000	0.094912000000	-0.436300000000
C	-2.906475000000	-2.046343000000	-0.540224000000
C	-3.034925000000	-2.768429000000	0.657219000000
C	-2.964352000000	-4.160066000000	0.564368000000
H	-3.041444000000	-4.763453000000	1.469654000000
C	-2.786999000000	-4.787199000000	-0.665557000000
H	-2.729176000000	-5.875589000000	-0.713902000000
C	-2.680023000000	-4.037619000000	-1.831611000000
H	-2.536551000000	-4.543089000000	-2.787357000000
C	-2.731444000000	-2.641746000000	-1.795063000000
C	-2.600472000000	-1.824994000000	-3.067293000000

H	-2.322538000000	-0.798883000000	-2.785107000000
C	-3.942258000000	-1.770408000000	-3.806481000000
H	-3.855493000000	-1.165054000000	-4.720591000000
H	-4.732485000000	-1.332125000000	-3.178769000000
H	-4.265798000000	-2.782324000000	-4.095257000000
C	-1.484002000000	-2.349482000000	-3.971906000000
H	-0.548601000000	-2.464273000000	-3.407161000000
H	-1.302675000000	-1.637859000000	-4.790029000000
H	-1.749922000000	-3.317004000000	-4.424310000000
C	-3.184153000000	-2.087166000000	2.010070000000
H	-3.591730000000	-1.076516000000	1.843178000000
C	-4.171161000000	-2.820404000000	2.921427000000
H	-4.367574000000	-2.219088000000	3.820570000000
H	-3.766097000000	-3.785357000000	3.260244000000
H	-5.128677000000	-3.009921000000	2.415346000000
C	-1.824475000000	-1.928000000000	2.705050000000
H	-1.962160000000	-1.492541000000	3.706711000000
H	-1.138844000000	-1.274085000000	2.146001000000
H	-1.330653000000	-2.905799000000	2.816464000000
C	2.679304000000	0.175302000000	0.652122000000
C	3.519011000000	0.667077000000	-0.379793000000
C	4.732398000000	0.024701000000	-0.640297000000
H	5.374756000000	0.406127000000	-1.437627000000
C	5.151090000000	-1.091007000000	0.085987000000
C	4.315710000000	-1.564527000000	1.094972000000
H	4.634525000000	-2.440329000000	1.664679000000
C	3.090591000000	-0.958619000000	1.392833000000
C	2.257608000000	-1.500209000000	2.546125000000
H	1.206119000000	-1.307976000000	2.294683000000
C	2.570006000000	-0.719608000000	3.827341000000
H	2.402336000000	0.357094000000	3.676353000000
H	3.622088000000	-0.864778000000	4.119462000000

H	1.930512000000	-1.056534000000	4.658640000000
C	2.405829000000	-3.004037000000	2.768744000000
H	3.399836000000	-3.271741000000	3.159237000000
H	2.239941000000	-3.559072000000	1.833751000000
H	1.667038000000	-3.346588000000	3.509276000000
C	3.158319000000	1.918751000000	-1.169668000000
H	2.061877000000	1.960086000000	-1.213306000000
C	3.620036000000	3.169576000000	-0.415124000000
H	4.714730000000	3.167020000000	-0.292651000000
H	3.158196000000	3.210747000000	0.582259000000
H	3.335999000000	4.081707000000	-0.964302000000
C	3.674196000000	1.918473000000	-2.607289000000
H	4.768459000000	2.030832000000	-2.657228000000
H	3.238770000000	2.765326000000	-3.159830000000
H	3.397255000000	0.990631000000	-3.128761000000
C	6.469182000000	-1.775668000000	-0.223378000000
H	6.586254000000	-2.592345000000	0.507898000000
C	6.459168000000	-2.395754000000	-1.623477000000
H	6.344159000000	-1.615845000000	-2.392035000000
H	5.625378000000	-3.102793000000	-1.736459000000
H	7.400396000000	-2.930352000000	-1.822949000000
C	7.655467000000	-0.822389000000	-0.055089000000
H	7.596747000000	0.006509000000	-0.777048000000
H	8.607205000000	-1.348005000000	-0.225762000000
H	7.674187000000	-0.388045000000	0.954434000000
H	-5.087908000000	-0.401927000000	-0.596247000000
H	-3.605718000000	3.708719000000	-2.022119000000
C	-2.699678000000	4.004731000000	-2.571522000000
H	-2.569920000000	5.090117000000	-2.441701000000
H	-2.865981000000	3.803899000000	-3.639984000000
C	-1.461033000000	3.253647000000	-2.068341000000
H	-1.632177000000	2.175991000000	-2.206474000000

C	-0.226467000000	3.611749000000	-2.896639000000
H	0.675595000000	3.140670000000	-2.481398000000
H	-0.069936000000	4.700229000000	-2.940978000000
H	-0.352401000000	3.252790000000	-3.928156000000
C	-1.258843000000	3.510217000000	-0.585642000000
C	-1.754838000000	2.639425000000	0.394219000000
C	-1.605031000000	2.849597000000	1.775504000000
C	-2.132657000000	1.862624000000	2.806963000000
H	-2.155800000000	0.868381000000	2.332554000000
C	-1.222813000000	1.738381000000	4.029347000000
H	-0.191981000000	1.509960000000	3.723087000000
H	-1.583257000000	0.925920000000	4.677344000000
H	-1.225115000000	2.658179000000	4.633553000000
C	-3.559664000000	2.229671000000	3.234519000000
H	-3.948323000000	1.490314000000	3.951092000000
H	-3.568786000000	3.216034000000	3.723351000000
H	-4.250948000000	2.272133000000	2.380958000000
C	-0.591379000000	4.652565000000	-0.138057000000
C	-0.941433000000	4.014157000000	2.166320000000
H	-0.789802000000	4.214479000000	3.226959000000
H	0.094549000000	5.796472000000	1.549645000000
C	-0.437672000000	4.902395000000	1.221356000000
H	-0.177424000000	5.351198000000	-0.865986000000

2M (M06-2X/def2-TZVPP)

N	2.813896000000	0.042809000000	-0.731186000000
C	1.987183000000	0.203941000000	0.258227000000
C	2.477601000000	-0.542843000000	1.484309000000
C	3.888743000000	-0.970199000000	-0.494364000000
C	2.650174000000	0.418434000000	2.666153000000
H	3.157128000000	-0.109791000000	3.475556000000

H	1.693652000000	0.779085000000	3.034582000000
H	3.260560000000	1.277945000000	2.384899000000
C	3.485286000000	-2.260372000000	-1.207009000000
H	4.191491000000	-3.049844000000	-0.950576000000
H	3.501087000000	-2.134081000000	-2.289642000000
H	2.482599000000	-2.572785000000	-0.914318000000
C	3.848746000000	-1.088365000000	1.030585000000
H	4.645421000000	-0.479700000000	1.460583000000
H	4.002774000000	-2.117076000000	1.353878000000
C	1.510140000000	-1.672647000000	1.861661000000
H	1.911728000000	-2.196478000000	2.730853000000
H	1.390809000000	-2.386119000000	1.047271000000
H	0.526624000000	-1.282654000000	2.115637000000
C	5.240868000000	-0.476208000000	-0.989914000000
H	5.451360000000	0.524691000000	-0.611848000000
H	5.307374000000	-0.470484000000	-2.076971000000
H	6.012360000000	-1.150467000000	-0.617835000000
C	2.608527000000	0.532820000000	-2.088201000000
H	3.572808000000	0.747443000000	-2.540997000000
H	2.081972000000	-0.227642000000	-2.664930000000
H	2.008347000000	1.437425000000	-2.074031000000
Si	0.278940000000	1.054235000000	0.032695000000
Cl	0.860270000000	3.059477000000	-0.276468000000
Cl	-0.663027000000	1.178558000000	1.874518000000
P	-0.584993000000	-0.223849000000	-1.421825000000
C	-2.300944000000	-0.360199000000	-0.753466000000
C	-2.771230000000	-1.632418000000	-0.375593000000
C	-3.185315000000	0.732109000000	-0.698813000000
C	-4.082979000000	-1.782991000000	0.058041000000
C	-4.490439000000	0.536527000000	-0.255804000000
C	-4.959975000000	-0.709159000000	0.132803000000
H	-4.429866000000	-2.769980000000	0.344778000000

H	-5.161977000000	1.387803000000	-0.222829000000
C	-2.771427000000	2.119661000000	-1.105540000000
H	-2.167863000000	2.105153000000	-2.012948000000
H	-3.647500000000	2.746343000000	-1.268286000000
H	-2.169142000000	2.599617000000	-0.329353000000
C	-1.883332000000	-2.846766000000	-0.423912000000
H	-1.027695000000	-2.726111000000	0.242682000000
H	-2.435926000000	-3.738108000000	-0.130153000000
H	-1.477334000000	-3.003623000000	-1.424487000000
C	-6.364254000000	-0.889617000000	0.638974000000
H	-6.749246000000	-1.877926000000	0.388893000000
H	-6.400911000000	-0.787776000000	1.725737000000
H	-7.035543000000	-0.142937000000	0.216139000000

3M (M06-2X/def2-TZVPP)

N	3.384047000000	-0.047260000000	-0.978186000000
C	2.569336000000	-0.267679000000	0.070295000000
N	3.157490000000	-1.238218000000	0.792430000000
C	4.470970000000	-0.882073000000	-0.922058000000
C	4.330789000000	-1.630412000000	0.193419000000
H	4.956751000000	-2.394631000000	0.615329000000
C	2.643441000000	-1.840251000000	2.017434000000
H	3.363123000000	-2.583293000000	2.348340000000
H	1.685064000000	-2.314555000000	1.822751000000
H	2.516391000000	-1.081073000000	2.782583000000
C	3.112860000000	0.858840000000	-2.090001000000
H	4.057390000000	1.093637000000	-2.573121000000
H	2.432336000000	0.380374000000	-2.791727000000
H	2.657498000000	1.771369000000	-1.713760000000
Si	0.844633000000	0.598773000000	0.232609000000

Cl	1.582585000000	2.531146000000	0.702211000000
Cl	0.027082000000	0.036129000000	2.054720000000
P	-0.191188000000	0.097516000000	-1.537752000000
C	-1.887059000000	-0.068422000000	-0.808952000000
C	-2.478513000000	-1.345602000000	-0.770298000000
C	-2.637838000000	1.037492000000	-0.373663000000
C	-3.780196000000	-1.489454000000	-0.303769000000
C	-3.937156000000	0.848194000000	0.090063000000
C	-4.527631000000	-0.405339000000	0.136730000000
H	-4.222342000000	-2.479980000000	-0.281741000000
H	-4.504888000000	1.712318000000	0.418494000000
C	-2.075909000000	2.432013000000	-0.378988000000
H	-1.542693000000	2.639308000000	-1.306830000000
H	-2.869329000000	3.166349000000	-0.245932000000
H	-1.357320000000	2.573701000000	0.432438000000
C	-1.731144000000	-2.575141000000	-1.210551000000
H	-0.841749000000	-2.726169000000	-0.595555000000
H	-2.366482000000	-3.456937000000	-1.137801000000
H	-1.378780000000	-2.482085000000	-2.238555000000
C	-5.920721000000	-0.591601000000	0.671724000000
H	-6.446773000000	-1.382262000000	0.136938000000
H	-5.896630000000	-0.870254000000	1.727551000000
H	-6.501394000000	0.326166000000	0.586381000000
H	5.240316000000	-0.866253000000	-1.671860000000

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