Supporting Information

An Isolable 2,5-Disila-3,4-Diphosphapyrrole and a Conjugated Si=Si=P=Si=N Chain Through Degradation of White Phosphorus with a N,N-Bis(Silylenyl)Aniline

Y. Xiong, S. Dong, S. Yao, C. Dai, J. Zhu, S. Kemper, M. Driess*
# Table of Content

A **Experimental Section** ........................................................................................................................................3
   A1 General considerations .......................................................................................................................................3
   A2 Single-crystal X-ray structure determination.................................................................................................3
   A3 Synthesis, characterization and reactivity .........................................................................................................3
      A3.1 Synthesis and characterization of 1 - 4 ......................................................................................................3
      A3.2 Reactivity of 2, 3 and 4 .............................................................................................................................15
   A4 Details of the single crystal X-ray diffraction analyses ..................................................................................17
B **Computational Section** ..................................................................................................................................28
C **References** ......................................................................................................................................................46
A. Experimental Section

A1. General considerations
All experiments and manipulations were carried out under dry nitrogen using standard Schlenk techniques or in an MBrIan inert atmosphere dry box containing an atmosphere of purified N₂. Solvents were deoxygenated and dried by standard methods, saturated with purified N₂ and freshly distilled prior to use. The precursor compounds PhNLiz ¹ and PhC[(tBu)N]₂SiCl ² were prepared according to literature procedure. The ¹H, ¹³C, ³¹P, ²⁹Si-NMR spectra were recorded on Brucker AV200, AV400, AV500 spectrometers referenced to residual solvent signals as internal standards (¹H NMR: C₆D₆, 7.16 ppm; THF-d₈, 1.76 and 3.62 ppm; ¹³C(¹H) NMR: C₆D₆, 128.06 ppm; THF-d₈, 26.19 and 68.26 ppm) or an external standard (²⁹Si NMR: SiMe₄, 0.0 ppm; ³¹P NMR: 85% H₃PO₄, 0.0 ppm). ¹H NMR spectrum of 2 was calibrated using TMS as external standard, the other nuclei (¹³C, ²⁹Si and ³¹P) of this compound were calibrated using the unified scale. Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; m = multiplet; br = broad; dd = doublet of doublets, dt = doublet of triplets and so on. IR spectra were measured with a Nicolet iS5 FT-IR Spectrometer from the company of Thermo Scientific. UV/Vis spectra were recorded on an Analytik Jena Specord S600 diode array spectrometer. Elemental analyses were performed on a Flash EA 1112 CHNS Analyzer. Melting points were measured on a Stuart SMP30 melting point apparatus.

A2. Single-crystal X-ray structure determinations
Crystals were each mounted on a glass capillary in per-fluorinated oil and measured in a cold N₂ flow. The data of 1-4 were collected on an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu- Kα-radiation, λ = 1.5418 Å). The structures were solved by direct method and refined on F2 with the SHELX-97 ³ software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. Several co-crystallized free THF molecules in 2 and 3, Et₂O in 4 within the asymmetric unit are highly disordered and treated using the SQUEEZE routine in PLATON. CCDC 2175471 (1), CCDC 2175474 (2), CCDC 2175473 (3), and CCDC 2175472 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

A3. Synthesis, characterization and reactivity of 1 - 4

A3.1 Synthesis and characterization of 1 - 4

Compound 1: To a 250 mL flask with 100 mL Et₂O solution of PhC[(tBu)N]₂SiCl (6.50 g, 22.0 mmol) at −30 °C was added slowly PhNLiz (1.16 g, 11.0 mmol) under stirring. The reaction mixture was allowed to warm to ambient temperature slowly and stirring for 4 h. A brown solution and precipitate (containing 1 and LiCl) were formed. Compound 1 was extracted with Et₂O (3x50 mL) from the isolated precipitate. The concentrated extraction yielded at 4 °C yellow crystals of 1 (4.37 g, 7.15 mmol, 65 % yield). M.p. 181 °C (decomp.); ¹H NMR (200.13 MHz,
THF-\(d_8\), 298 K): \(\delta\) (ppm) = 1.04 (s, 36 H; Si-NC(CH\(_3\))\(_3\)), 6.83 – 7.48 (m, 15 H; Ph); \(^{13}\)C\({^1}\)H NMR (50.32 MHz, THF-\(d_8\), 298 K): \(\delta\) (ppm) = 32.65 (CH\(_3\))\(_3\)), 54.22 (C(CH\(_3\))\(_3\)), 121.88, 125.32, 128.84, 129.10, 129.36, 130.06, 130.96 132.28 (Ph), 136,33, 151.34 (quaternary Ph), 162.93 (NCN);
\(^{29}\)Si\({^1}\)H NMR (79.49 MHz, THF-\(d_8\), 298 K): \(\delta\) (ppm) = -12.9 ppm (s); Elemental analysis calcd (%) for C\(_{36}\)H\(_{51}\)N\(_5\)Si\(_2\) (610.0 g/mol) C 70.88, H 8.43, N 11.48, found: C 70.43, H 8.30, N 11.60. IR (cm\(^{-1}\)): 2959\(m\), 1587\(m\), 1479\(m\), 1443\(w\), 1410\(vs\), 1390 \(s\), 1359\(s\), 1267\(m\), 1214\(vs\), 1166\(m\), 1070\(m\), 1021\(m\), 1000\(m\), 927\(m\), 898\(s\), 833\(vs\), 827\(vs\), 794\(m\), 749\(s\), 738\(vs\), 709\(vs\), 697\(vs\), 659\(m\), 615\(m\), 604\(m\).

Scheme S1. Synthesis of 1

Figure S1. \(^1\)H NMR spectrum (200.13 MHz, \(d_8\)-THF, 298 K) of 1.
Figure S2. $^{13}$C($^1$H) NMR spectrum (50.32 MHz, $d_8$-THF, 298 K) of 1.

Figure S3. $^{29}$Si($^1$H) NMR spectrum (79.49 MHz, $d_8$-THF, 298 K) of 1.
**Compound 2**: A colorless solution of $P_4$ (0.11 g, 0.90 mmol) in 20 mL THF was added rapidly to a yellow solution of $1$ (1.17 g, 1.92 mmol) in 50 mL THF at -20 °C under stirring. The solution turned to black immediately. The reaction mixture was stirred for one hour at that temperature. The volatiles were removed under reduced pressure. 10 mL Et₂O was added to the residue. From Et₂O solution at 4 °C black crystals of $2$ (0.20 g, 0.30 mmol, 17% yield) were obtained. 

**M.p.**: 206 °C (decomp.); **$^1$H NMR** (400.13 MHz, THF-$d_8$/C₆D₆, 298 K): $\delta$(ppm) = 1.24 (s, 36 H, CH₃), 7.13 (t, 1H, $J$ = 7.4 Hz), 7.29 (d, 4H, $J$ = 7.4 Hz), 7.41 – 7.58 (m, 10H); **$^{13}$C($^1$H) NMR** (100.61 MHz, THF-$d_8$/C₆D₆, 298 K): $\delta$(ppm) = 33.01 (C(CH₃)₃), 55.98 (CMe₃), 124.12, 125.43, 129.51, 129.62, 129.91, 130.37, 130.42, 132.11(Ph), 132.88, 149.68 (quaternary Ph), 176.06 (NCN); **$^{31}$P($^1$H) NMR** (161.98 MHz, THF-$d_8$/C₆D₆, 298 K): $\delta$(ppm) = -328.0 (with Si satellite, non-first order spectrum); **$^{29}$Si($^1$H) NMR** (79.49 MHz, THF-$d_8$/C₆D₆, 298 K): $\delta$(ppm) = 5.7 (non-first order spectrum, $^1$J$_{PSi}$ = 206 Hz, $^2$J$_{PSi}$ = −9.5 Hz); Elemental analysis calcd (%) for C₃₆H₅₁N₅Si₂P₂: (671.95 g/mol) C 64.35, H 7.65, N 10.42, found: C 64.09, H 7.45, N 10.78. **IR** (cm⁻¹): 2969(w), 1592(w), 1494(w), 1474(w), 1447(w), 1401(vs), 1393(vs), 1363(s), 1279(w), 1248(s), 1202(s), 1090(w), 1024(w), 1001(w), 926(vs), 910(w), 866(vs), 796(w), 767(vs), 751 (vs), 705(s), 698(s), 684(vs), 661(m), 643(vs). UV-Vis: 426nm, $\varepsilon = 1.5 \times 10^5$; 568 nm, $\varepsilon = 9.6\times10^4$.

![Scheme S2. Synthesis of 2.](image-url)

![Figure S4. $^1$H NMR spectrum (400.13 MHz, THF-$d_8$/C₆D₆, 298 K) of 2.](image-url)
Figure S5. $^{13}\text{C}^1\text{H}$ (bottom) and DEPT-135 NMR (top) spectra (100.61 MHz, THF-$d_8$/C$_6$D$_6$, 298 K) of 2.

Figure S6. $^{31}\text{P}^1\text{H}$ NMR spectrum (161.98 MHz, THF-$d_8$/C$_6$D$_6$, 298 K) of 2.
**Figure S7.** $^{31}$P($^1$H) NMR spectrum (161.98 MHz, THF-$d_8$/C$_6$D$_6$, 298 K) for 2 (top) and simulated spectrum (bottom, only the $^{29}$Si isotopologue).

**Figure S8.** $^{29}$Si($^1$H) NMR spectrum (79.49 MHz, THF-$d_8$/C$_6$D$_6$, 298 K) of 2.
Figure S9. $^{29}$Si{$^1$H} NMR spectrum (79.49 MHz, THF-d$_8$/C$_6$D$_6$, 298 K) of 2 (top) and simulated $^{29}$Si NMR spectrum (bottom).

Simulated $^{31}$P{$^1$H} and $^{29}$Si{$^1$H} NMR spectra for 2 ($^{29}$Si isotopologue)

\[ \delta = -327.9628 \text{ (P1), } -327.9463 \text{ (P2)} \]
\[ \delta = 5.6871 \text{ (Si)} \]
\[ ^1J_{PP} = +/- 158.98736; \]
\[ ^1J_{PSi} = 206.08895 \]
\[ ^2J_{PSi} = -9.52608 \]

Spin simulation was done using Spinworks and NUMMRIT simulation. $^1J_{PSi}$ and $^2J_{PSi}$ have opposite signs. The sign of the $^2J_{PSi}$ coupling was set negative according to Berger, S.; Braun, S.; Kalinowski, H.-O. NMR Spectroscopy of the non-metallic elements, 1st ed.; Wiley, 1997.
**Compound 3**: 50 mL Et2O was added to a mixture of 1 (0.91 g, 1.49 mmol) and P4 (0.14 g, 1.14 mmol) at room temperature. After the reaction mixture was stirred overnight, the volatiles were removed under vacuum and the residue was washed with n-hexane (25 mL), yielding 0.77 g (0.55 mmol, 74% yield) of 3 as orange crystals. The X-ray analysis qualified crystals were obtained from THF solution. M.p. 132 °C (decomp.); 1H NMR (500.25 MHz, THF-d8/C6D6, 298 K): δ (ppm) = 0.87 (s, 18 H, CH3), 0.92 (s, 18 H, CH3), 1.50 (s, 18 H, CH3), 1.65 (s, 18 H, CH3), 7.17 (t, 2H, J = 7.3 Hz), 7.22 (d, 2H, J = 7.3 Hz), 7.73 (d, 4H, J = 7.7 Hz), 7.29 – 7.49 (m, 20H), 8.27 (d, 2H, J = 7.3 Hz); 13C{1H} NMR (125.79 MHz, THF-d8/C6D6, 298 K): δ (ppm) = 32.24, 33.10, 33.25, 35.06 (C(CH3)3), 55.43, 55.66, 55.75, 57.90 (OMe3), 124.86, 127.69, 129.34 (presumably 3x), 129.39, 129.48, 129.78, 130.18, 130.56, 131.80, 131.96 (Ph), 133.33 (quaternary Ph), 134.95 (Ph), 138.59, 151.53 (quaternary Ph), 167.01, 174.37 (CN); 31P{1H} NMR (81.01 MHz, THF-d8/C6D6, 298 K): δ (ppm) = 40.2 (ddm, J = 192 Hz, 339 Hz, P2(P5)), -34.2 (dm, J = 192 Hz, P3(P4)), -247 (dm, J= P = 15.6 Hz, 339 Hz, P1(P6)); 29Si{1H} NMR (99.39 MHz, THF-d8/C6D6, 298 K): δ (ppm) = 7.2 (dd, Si1, 1JSi1P1 = 200Hz, 3JSi1P2 = 10.5 Hz), -57.5 ppm (m, Si2); Elemental analysis calc (%) for C12H102N10Si4P4: (1405.85 g/mol) C 61.51, H 7.31, N 9.96, found: C 61.09, H 7.40, N 10.09. IR (cm⁻¹): 2966(m), 1590(m), 1546(m), 1480(s), 1445(w), 1404(s), 1393 (s), 1362(s), 1274(w), 1208(vs), 1114(m), 1091(m), 1071(m), 1022(m), 1003(w), 928(vs), 895(vs), 833(vs), 868(vs), 794(m), 765(vs), 733 (w), 722(w), 708(vs), 699(vs), 669(vs), 640(s), 615(w), 594(s). UV-Vis: 370nm, ε = 2.4x10⁶.

![Scheme S3. Syntheses of 3](image-url)

1. **Scheme S3. Syntheses of 3**
Figure S10. $^1$H NMR spectrum (500.25 MHz, THF-d$_8$/C$_6$D$_6$, 298 K) of 3.

Figure S11. $^{13}$C($^1$H) (top) and DEPT-135 (bottom) NMR Spectra of 3 (100.61 MHz, THF-d$_8$/C$_6$D$_6$, 298 K).
**Compound 4:** A 20 mL THF solution of 1 (1.13 g, 1.85 mmol) was added to a 20 mL THF solution of P₄ (0.057 g, 0.46 mmol) at room temperature. The reaction mixture was stirred for 16 h. From the concentrated THF solution yellow crystals of 4 was obtained with yield of 85% (1.01 g, 0.79 mmol). M.p. 167 °C (decomp.); ¹H NMR (200.13 MHz, THF-d₈, 298 K): δ (ppm) 1.13 (s, 18 H, C₆H₃), 1.28 (s, 18 H, C₆H₃), 1.35 (s, 18 H, C₆H₃), 1.51 (s, 18 H, C₆H₃), 6.27 (t, 1H, J = 6.8Hz), 6.82 (d, 2H, J = 8.2 Hz), 6.93 (t, 2H, J = 7.7Hz), 7.09 – 7.65 (m, 23H), 8.46 (d, 1H, J = 8.0Hz), 9.29 (t, 1H, J = 7.8Hz); ¹³C[¹H] NMR (100.61 MHz, THF-d₈, 298 K): δ (ppm) = 32.59, 32.80,
32.88, 33.04 (C(CH₃)₃), 54.47, 54.92, 55.99, 56.49 (CMe₃), 112.89, 124.19, 125.30, 127.47, 127.96, 128.83, 128.85, 129.11, 129.15, 129.28, 129.33, 129.55, 129.70, 129.82, 129.91, 130.07, 130.61, 130.86, 131.00, 131.04, 131.11, 131.27, 131.43, 131.49, 132.14, 132.20 (Ph), 132.70, 134.56, 134.67, 136.14, 149.72, 162.21, 162.93, 172.63, 172.91, 176.39 (quaternary Ph) and (NCN); ³¹P{¹H} NMR (81.01 MHz, THF-d₈, 298 K): δ(ppm) = -263.8 (d, ²J_{PH} = 47.6 Hz P1), -287.6 (d, ²J_{PH} = 47.6 Hz P2); ²⁹Si{¹H} NMR (79.49 MHz, THF-d₈, 298 K): δ (ppm) = 46.2 (dd, ¹J_{SiP} = 115Hz, ¹J_{SiP} = 188Hz Si3), 9.91 (dd, ¹J_{SiP} = 138Hz, ¹J_{SiP} = 7.8Hz Si2), -27.4 (dd, ¹J_{SiP} = 113Hz, ³J_{SiP} = 10.9Hz Si1), -31.6 (dd, ¹J_{SiP} = 98.3Hz, ³J_{SiP} = 3.5Hz Si4); Elemental analysis calcd (%) for C_{72}H_{102}N_{10}Si_{4}P_{2}: (1281.96 g/mol) C 67.46, H 8.02, N 10.93, found: C 66.98, H 8.23, N 11.24. IR (cm⁻¹): 2969(m), 1580(m), 1522(w), 1475(s), 1444(w), 1406(vs), 1361(s), 1304(s), 1275(m), 1210(vs), 1162(w), 1088(w), 1024(m), 1003(m), 927(s), 899(m), 842(s), 792(s), 766(s), 753(m), 744(m), 724(m), 708(vs), 700(s), 695(s), 662(s), 649(w), 640(w), 617(m), 612(m), 573(s). UV-Vis: 275 nm, ε = 5.9x10⁵.

**Scheme S4. Syntheses of 4**

**Figure S14.** ¹H NMR spectrum (200.13 MHz, THF-d₈, 298 K) of 4.
Figure S15. $\text{^{13}C}[^1\text{H}]$ NMR spectrum (100.61 MHz, THF-$d_8$, 298 K) of 4.

Figure S16. $\text{^{31}P}[^1\text{H}]$ NMR spectrum (81.01 MHz, THF-$d_8$, 298 K) of 4.
A3.2 Reactivity of 2, 3, and 4

Reactivity of 2 toward P₄ and 1 respectively:
a) The isolated compound 2 reacts with P₄ to afford 3: To a colorless solution of P₄ (0.0008 g, 0.0065 mmol) in 0.30 mL d₈-THF in an NMR tube was added a black solution of 2 (0.0175 g, 0.0260 mmol) in 0.20 mL d₈-THF at room temperature (molar ratio of 2 : P₄ = 4 : 1). After 1 h the reaction was completed and 3 was afforded quantitatively.
b) The isolated compound 2 reacts with 1 to afford 4: when a yellow solution of 1 (0.0145 g, 0.0238 mmol) in 0.30 mL d₈-THF was added to a black solution of the isolated 2 (0.0160 g, 0.0238 mmol) in 0.30 mL d₈-THF in an NMR tube at room temperature. The reaction solution turned to yellow immediately. The ³¹P{¹H} NMR spectrum of the reaction mixture confirmed the formation of 4.

Reactivity of 3 toward bis(silylenes) 1:
Reaction of 3 with 1 to give 2, which reacts with 1 further to give 4: 0.50 mL d₈-THF was added to a mixture of 3 (0.0250 g, 0.0178 mmol) and 1 (0.0134 g, 0.0220 mmol) in an NMR tube at room temperature (molar ratio of 3 and 1 = 1.00 : 1.24). Since 3 needs four molar equivalents of 1 to convert to 4 completely (Figure S18), the added 1.24 molar equivalents of 1 can result only a mixture of unreacted 3, reaction intermediate 2 and product 4. As expected, the ³¹P{¹H} NMR spectrum showed a signal at δ = -328.0 ppm for 2 along with the signals for product 4 and unreacted 3 as well as unidentified species (Figure S18). The subsequent addition of 1 (0.0490 g) to the mixture yielded complete conversion of 3 and 2 to 4.
Figure S18. Compound 2 as intermediate in the conversion of 3 to 4 [Si: = Si(N(tBu))2CPh] (3 is in excess).

Reactivity of 3 toward (Xant)Si₂:
Reaction of 3 with (Xant)Si₂ to give 2 and B: 0.50 mL d₆-THF was added to a mixture of 3 (0.0032 g, 0.023 mmol) and (Xant)Si₂ (0.0066g, 0.0090 mmol) in an NMR tube at room temperature. After three days the 3¹P{¹H} NMR spectrum of the resulting mixture exhibited a signal at δ = -282.4 ppm for B and a signal at δ = -328.0 ppm for 2 (Figure S19).

Figure S19. 3¹P{¹H} spectrum of the reaction mixture of 3 and (Xant)Si₂ [Si: = Si(N(tBu))2CPh].
Reactivity of 4 toward P₄:

d₈-THF (0.50 mL) was added to an NMR tube with 4 (0.0110 g, 0.0085 mmol) and P₄ (0.0010 g, 0.0081 mmol) at room temperature. The ³¹P{¹H} NMR spectrum of the reaction mixture showed that compound 4 converted to 3.

A4. Details of the single crystal X-ray diffraction analyses

Table S1. Crystal data and structure refinement for 1.

| Property                                      | Value                |
|-----------------------------------------------|----------------------|
| Empirical formula                            | C₃₆H₅₁N₅Si₂         |
| Formula weight                                | 609.99               |
| Temperature                                   | 150(2) K             |
| Wavelength                                    | 1.54184 Å            |
| Crystal system                                | Monoclinic           |
| Space group                                   | P2₁/c                |
| Unit cell dimensions                          | a = 11.39940(10) Å  |
|                                              | α = 90°.             |
|                                              | b = 17.8390(2) Å     |
|                                              | β = 102.8530(10)°.   |
|                                              | c = 18.3255(3) Å     |
|                                              | γ = 90°.             |
| Volume                                        | 3633.19(8) Å³       |
| Z                                             | 4                    |
| Density (calculated)                          | 1.115 Mg/m³          |
| Absorption coefficient                        | 1.109 mm⁻¹           |
| F(000)                                        | 1320                 |
| Crystal size                                  | 0.320 x 0.210 x 0.120 mm³ |
| Theta range for data collection               | 3.501 to 67.497°.    |
| Index ranges                                  | -13<=h<=10, -21<=k<=21, -21<=l<=21 |
| Reflections collected                         | 25325                |
| Independent reflections                       | 6555 [R(int) = 0.0285] |
| Completeness to theta = 67.497°              | 100.0 %              |
| Absorption correction                         | Semi-empirical from equivalents |
| Max. and min. transmission                    | 1.00000 and 0.33248 |
| Refinement method                             | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 6555 / 0 / 400       |
| Goodness-of-fit on F²                         | 1.013                |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0362, wR2 = 0.0892 |
| R indices (all data)                          | R1 = 0.0436, wR2 = 0.0952 |
| Extinction coefficient                        | n/a                  |
| Largest diff. peak and hole                   | 0.325 and -0.245 e.Å⁻³ |
**Figure S20.** Molecular structure of 1. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

**Table S2.** Bond lengths [Å] and angles [°] for 1.

| Bond                  | Length [Å] | Angle [°] |
|-----------------------|------------|-----------|
| Si2-N5                | 1.765(1)   |           |
| Si2-N3                | 1.875(1)   |           |
| Si2-N4                | 1.893(1)   |           |
| Si1-N5                | 1.781(1)   |           |
| Si1-N2                | 1.881(1)   |           |
| Si1-N1                | 1.908(1)   |           |
| N5-C1                 | 1.425(2)   |           |
| N3-C22                | 1.339(2)   |           |
| N4-C22                | 1.334(2)   |           |
| N1-C7                 | 1.333(2)   |           |
| N2-C7                 | 1.336(2)   |           |
| N5-Si2-N3             | 102.9(1)   |           |
| N5-Si2-N4             | 106.2(1)   |           |
| N3-Si2-N4             | 68.8(1)    |           |
| N5-Si1-N2             | 101.6(1)   |           |
| N5-Si1-N1             | 105.0(1)   |           |
| N2-Si1-N1             | 68.6(1)    |           |
| C1-N5-Si2             | 124.5(1)   |           |
| C1-N5-Si1             | 126.0(1)   |           |
| Si2-N5-Si1            | 109.4(1)   |           |
| C22-N3-Si2            | 92.1(1)    |           |
| C22-N4-Si2            | 91.4(1)    |           |
| C7-N1-Si1             | 91.3(1)    |           |
| C7-N2-Si1             | 92.4(1)    |           |
Table S3. Crystal data and structure refinement for 2.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C36 H51 N5 P2 Si2                          |
| Formula weight                                | 671.93                                     |
| Temperature                                   | 150(2) K                                   |
| Wavelength                                    | 1.54184 Å                                  |
| Crystal system                                | Monoclinic                                 |
| Space group                                   | P2\(\alpha/c\)                            |
| Unit cell dimensions                          |                                           |
| \(a = 20.9035(5)\) Å                         | \(\alpha = 90^\circ\).                    |
| \(b = 15.2852(2)\) Å                         | \(\beta = 109.653(2)^\circ\).             |
| \(c = 18.3172(4)\) Å                         | \(\gamma = 90^\circ\).                    |
| Volume                                        | 5511.7(2) Å\(^3\)                         |
| \(Z\)                                         | 4                                         |
| Density (calculated)                          | 0.810 Mg/m\(^3\)                          |
| Absorption coefficient                        | 1.294 mm\(^{-1}\)                         |
| \(F(000)\)                                    | 1440                                       |
| Crystal size                                  | 0.390 x 0.140 x 0.110 mm\(^3\)             |
| Theta range for data collection               | 3.661 to 67.499\(^\circ\).                 |
| Index ranges                                  | -22\(\leq h \leq \) 25, -18\(\leq k \leq 18\), -21\(\leq l \leq 16\) |
| Reflections collected                         | 39502                                      |
| Independent reflections                       | 9922 \([R(int) = 0.0395]\)                 |
| Completeness to theta = 67.499\(^\circ\)     | 99.9 \%                                    |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 1.00000 and 0.54814                       |
| Refinement method                             | Full-matrix least-squares on F\(^2\)      |
| Data / restraints / parameters                 | 9922 / 0 / 418                            |
| Goodness-of-fit on F\(^2\)                    | 1.078                                      |
| Final R indices \([I > 2\sigma(I)]\)          | \(R1 = 0.0429\), w\(R2 = 0.1133\)         |
| R indices (all data)                          | \(R1 = 0.0520\), w\(R2 = 0.1182\)         |
| Extinction coefficient                        | n/a                                        |
| Largest diff. peak and hole                   | 0.372 and -0.337 e.Å\(^{-3}\)             |
**Figure S21.** Molecular structure of 2. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

**Table S4.** Bond lengths [Å] and angles [°] for 2.

| Bond Pair    | Length [Å] |
|--------------|------------|
| Si2-N5       | 1.736(1)   |
| Si2-N3       | 1.829(1)   |
| Si2-N4       | 1.853(1)   |
| Si2-P2       | 2.115(1)   |
| Si1-N5       | 1.749(1)   |
| Si1-N2       | 1.820(1)   |
| Si1-N1       | 1.855(1)   |
| Si1-P1       | 2.108(1)   |
| P2-P1        | 2.265(1)   |
| N3-C2        | 1.340(2)   |
| N4-C2        | 1.338(2)   |
| N2-C1        | 1.339(2)   |
| N1-C1        | 1.341(2)   |

| Bond Pair    | Angle [°] |
|--------------|-----------|
| N5-Si2-N3    | 111.8(1)  |
| N5-Si2-N4    | 111.6(1)  |
| N3-Si2-N4    | 71.0(1)   |
| N5-Si2-P2    | 112.1(1)  |
| N3-Si2-P2    | 120.5(1)  |
| N4-Si2-P2    | 123.8(1)  |
| N5-Si1-N2    | 109.1(1)  |
| N5-Si1-N1    | 109.6(1)  |
N2-Si1-N1  71.4 (1)
N5-Si1-P1  113.8(1)
N2-Si1-P1  120.8(1)
N1-Si1-P1  124.9(1)
Si2-P2-P1  95.5(1)
Si1-P1-P2  92.4(1)
C2-N3-Si2  91.8(1)
Si2-N5-Si1  109.6(1)
C2-N4-Si2  90.8(1)
C1-N2-Si1  91.8(1)
C1-N1-Si1  90.2(1)

Symmetry transformations used to generate equivalent atoms:

Table S5. Crystal data and structure refinement for 3.

| Property                              | Value                  |
|---------------------------------------|------------------------|
| Empirical formula                     | C72 H102 N10 P6 Si4    |
| Formula weight                        | 1405.81                |
| Temperature                           | 150(2) K               |
| Wavelength                            | 1.54184 Å              |
| Crystal system                        | Triclinic              |
| Space group                           | P-1                    |
| Unit cell dimensions                  | a = 16.6668(7) Å       |
|                                       | b = 24.3254(10) Å      |
|                                       | c = 25.1425(12) Å      |
|                                       | α = 86.969(4)°         |
|                                       | β = 70.922(4)°         |
|                                       | γ = 82.502(3)°         |
| Volume                                | 9550.6(8) Å³           |
| Z                                      | 4                      |
| Density (calculated)                  | 0.978 Mg/m³            |
| Absorption coefficient                | 1.819 mm⁻¹             |
| F(000)                                | 3000                   |
| Crystal size                          | 0.380 x 0.120 x 0.090 mm³ |
| Theta range for data collection       | 2.625 to 67.500°       |
| Index ranges                          | -19<h<13, -29<k<29, -30<l<29 |
| Reflections collected                 | 67899                  |
| Independent reflections               | 34245 [R(int) = 0.0817] |
| Completeness to theta = 67.500°       | 99.6 %                 |
| Absorption correction                 | Semi-empirical from equivalents |
| Max. and min. transmission            | 1.00000 and 0.16222    |
| Refinement method                     | Full-matrix least-squares on F² |
| Data / restraints / parameters        | 34245 / 128 / 1760     |
Goodness-of-fit on $F^2$ 0.925
Final $R$ indices [I>2sigma(I)] $R_1 = 0.0792$, $wR_2 = 0.1902$
$R$ indices (all data) $R_1 = 0.1309$, $wR_2 = 0.2240$
Extinction coefficient n/a
Largest diff. peak and hole 0.768 and -0.444 e.Å$^{-3}$

**Figure S22.** Molecular structure of 3. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

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

| Bonds       | Lengths [Å]  |
|-------------|--------------|
| P5-P6       | 2.192(1)     |
| P5-P4       | 2.249(2)     |
| P5-Si3      | 2.330(2)     |
| Si3-N8      | 1.770(3)     |
| Si3-P3      | 2.275(1)     |
| P6-Si4      | 2.121(2)     |
| P4-P3       | 2.218(2)     |
| P4-Si2      | 2.273(2)     |
| P3-P2       | 2.234(2)     |
| P2-P1       | 2.192(1)     |
| P2-Si2      | 2.335(2)     |
| Bond                  | Distance (Å) |
|----------------------|--------------|
| P1-Si1               | 2.119(2)     |
| Si1-N3               | 1.732(4)     |
| Si1-N2               | 1.833(4)     |
| Si1-N1               | 1.866(5)     |
| Si2-N3               | 1.771(4)     |
| Si2-N4               | 1.798(4)     |
| Si2-N5               | 2.200(4)     |
| P6-P5-P4             | 105.5(1)     |
| P6-P5-Si3            | 107.7(1)     |
| P4-P5-Si3            | 85.0(1)      |
| N8-Si3-P3            | 116.8(1)     |
| N8-Si3-P5            | 99.5(1)      |
| P3-Si3-P5            | 87.8(1)      |
| Si4-P6-P5            | 90.7(1)      |
| P3-P4-P5             | 91.2(1)      |
| P3-P4-Si2            | 87.2(1)      |
| P5-P4-Si2            | 100.1(1)     |
| P4-P3-P2             | 90.4(1)      |
| P4-P3-Si3            | 87.0(1)      |
| P2-P3-Si3            | 98.3(1)      |
| P1-P2-P3             | 105.2(1)     |
| P1-P2-Si2            | 108.2(1)     |
| P3-P2-Si2            | 85.3(1)      |
| Si1-P1-P2            | 91.6(1)      |
| N3-Si1-N2            | 110.6(2)     |
| N3-Si1-N1            | 110.2(2)     |
| N3-Si1-P1            | 119.4(1)     |
| N3-Si2-P4            | 120.8(1)     |
| N3-Si2-P2            | 99.2(1)      |
| N4-Si2-P2            | 109.3(2)     |
| P4-Si2-P2            | 86.5(1)      |
| Si4-N8-Si3           | 117.8(2)     |
| Si1-N3-Si2           | 119.0(2)     |
| **Table S7. Crystal data and structure refinement for 4.** |
|----------------------------------------------------------|
| Empirical formula | C72 H102 N10 P2 Si4 |
| Formula weight | 1281.93 |
| Temperature | 150(2) K |
| Wavelength | 1.54184 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions |  
| a = 15.2767(4) Å | α = 91.142(3)°. |
| b = 15.8862(5) Å | β = 105.873(3)°. |
| c = 18.9658(6) Å | γ = 95.745(2)°. |
| Volume | 4399.7(2) Å³ |
| Z | 2 |
| Density (calculated) | 0.968 Mg/m³ |
| Absorption coefficient | 1.269 mm⁻¹ |
| F(000) | 1380 |
| Crystal size | 0.470 x 0.250 x 0.190 mm³ |
| Theta range for data collection | 2.425 to 67.499°. |
| Index ranges | -18≤h≤16, -18≤k≤19, -22≤l≤22 |
| Reflections collected | 32145 |
| Independent reflections | 15815 [R(int) = 0.0402] |
| Completeness to theta = 67.499° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.56658 |
| Refinement method | Full-matrix least-squares on F² |
| Data / restraints / parameters | 15815 / 0 / 817 |
| Goodness-of-fit on F² | 1.032 |
| Final R indices [I>2sigma(I)] | R1 = 0.0525, wR2 = 0.1452 |
| R indices (all data) | R1 = 0.0618, wR2 = 0.1542 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.590 and -0.353 e.Å⁻³ |
Figure S23. Molecular structure of for 4. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S8. Bond lengths [Å] and angles [°] for 4.

| Bond          | Length [Å]  |
|---------------|-------------|
| P2-Si3        | 2.145(1)    |
| P2-Si4        | 2.178(1)    |
| Si2-N3        | 1.728(2)    |
| Si2-N4        | 1.832(1)    |
| Si2-N5        | 1.846(1)    |
| Si2-P1        | 2.127(1)    |
| Si2-C2        | 2.284(1)    |
| Si3-N7        | 1.845(2)    |
| Si3-N6        | 1.850(2)    |
| Si3-P1        | 2.186(1)    |
| Si3-C3        | 2.299(2)    |
| Si4-N10       | 1.625(2)    |
| Si4-N9        | 1.871(2)    |
| Si4-N8        | 1.881(2)    |
| Si4-C4        | 2.326(2)    |
| Si1-N3        | 1.803(1)    |
| Si1-N1        | 1.879(2)    |
| Si1-N2        | 1.903(2)    |
| Si1-C1        | 2.333(2)    |
| N5-C2         | 1.329(3)    |
| N9-C4         | 1.328(3)    |
| N4-C2         | 1.341(2)    |
| N2-C1         | 1.327(3)    |
\begin{table}
\centering
\begin{tabular}{ll}
N1-C1 & 1.340(3) \\
N6-C3 & 1.336(3) \\
N8-C4 & 1.330(3) \\
N7-C3 & 1.322(3) \\
Si3-P2-Si4 & 104.1(1) \\
N3-Si2-N4 & 108.3(1) \\
N3-Si2-N5 & 112.1(1) \\
N4-Si2-N5 & 71.5(1) \\
N3-Si2-P1 & 108.6(1) \\
N4-Si2-P1 & 128.6(1) \\
N5-Si2-P1 & 123.1(1) \\
N3-Si2-C2 & 116.7(1) \\
N4-Si2-C2 & 35.9(1) \\
N5-Si2-C2 & 35.6(1) \\
P1-Si2-C2 & 134.7(1) \\
N7-Si3-N6 & 70.6(1) \\
N7-Si3-P2 & 119.7(1) \\
N6-Si3-P2 & 120.1(1) \\
N7-Si3-P1 & 104.4(1) \\
N6-Si3-P1 & 105.5(1) \\
P2-Si3-P1 & 123.9(1) \\
N7-Si3-C3 & 35.1(1) \\
N6-Si3-C3 & 35.5(1) \\
P2-Si3-C3 & 127.4(1) \\
P1-Si3-C3 & 108.8(1) \\
Si2-P1-Si3 & 108.7(1) \\
N10-Si4-N9 & 114.2(1) \\
N10-Si4-N8 & 118.6(1) \\
N9-Si4-N8 & 69.6(1) \\
N10-Si4-P2 & 125.8(1) \\
N9-Si4-P2 & 108.1(1) \\
N8-Si4-P2 & 106.7(1) \\
N10-Si4-C4 & 124.2(1) \\
N9-Si4-C4 & 34.8(1) \\
N8-Si4-C4 & 34.9(1) \\
P2-Si4-C4 & 109.8(1) \\
N3-Si1-N1 & 101.3(1) \\
N3-Si1-N2 & 105.0(1) \\
\end{tabular}
\caption{Bond lengths (Å) for the given compound.}
\end{table}
| Bond                  | Angle (°) |
|-----------------------|-----------|
| N1-Si1-N2             | 68.8(1)   |
| N3-Si1-C1             | 111.8(1)  |
| N1-Si2-C1             | 35.0(1)   |
| N2-Si1-C1             | 34.7(1)   |
| C2-N5-Si2             | 90.5(1)   |
| C4-N9-Si4             | 91.7(1)   |
| C2-N4-Si2             | 90.8(1)   |
| C1-N2-Si1             | 90.7(1)   |
| Si2-N3-Si1            | 115.7(1)  |
| C1-N1-Si1             | 91.4(1)   |
| C3-N6-Si3             | 90.9(1)   |
| C4-N8-Si4             | 91.2(1)   |
| C3-N7-Si3             | 91.6(1)   |
| N5-C2-N4              | 107.1(1)  |
| N5-C2-Si2             | 53.9(1)   |
| N4-C2-Si2             | 53.3(1)   |
| N9-C4-N8              | 107.3(2)  |
| N9-C4-Si4             | 53.5(1)   |
| N8-C4-Si4             | 53.9(1)   |
| N2-C1-N1              | 106.6(2)  |
| N2-C1-Si1             | 54.6(1)   |
| N1-C1-Si1             | 53.6(1)   |
| N7-C3-N6              | 106.9(2)  |
| N7-C3-Si3             | 53.4(1)   |
| N6-C3-Si3             | 53.6(1)   |
**B Computational Section**

**Computational details.** All the calculations were performed using the Gaussian 16 software package.\(^4\) Geometry optimization of the compounds was conducted at the TPSS-D3BJ\(^5\) density functional theory level, according to the best agreement with the metric data from X-ray structure analyses (Table S9, S10, S11). The Def2-SVP\(^6\) basis set is used to describe C, N, H atoms, whereas ma-TZVP\(^7,8\) basis set is used to Si and P atoms. In addition, frequency calculations are carried out at the same level of theory to confirm the stationary points are minima with no imaginary frequencies. Furthermore, the B97-2\(^9\)/Def2-TZVP\(^10\) method is used to calculate the \(^{31}\)P NMR chemical shifts, where the solvent effect (solvent = THF) is taken into account by SMD model. The calculated \(^{31}\)P absolute shielding constants are converted to \(^{31}\)P NMR chemical shifts, with 85% water solution of H\(_3\)PO\(_4\) as reference. Here, we use \(\sigma(\text{H}_3\text{PO}_4) = 328.35\) ppm suggested by Jameson et al.\(^11\) The calculated \(^{29}\)Si absolute shielding constants are converted to \(^{29}\)Si NMR chemical shifts, with that of tetramethylsilane (TMS) calculated at the same level (\(\sigma(\text{TMS}) = 338.2\) ppm) as reference. Viewing of optimized structures and rendering of molecular orbitals were performed using the program CYLview\(^12\) and VMD,\(^13\) respectively. NMR spectra were drawn in the Multiwfn program.\(^14\) EDBD and NICS calculations were performed at the CAM-B3LYP/def2-TZVP level. Here, the more representative NICS(1)\(_{ZZ}\) was employed to aromaticity calculation because it has been proven as a good index for both the \(S_0\) and \(T_1\) states.\(^15\) Since the 6/5MR in compounds D and 2 are nonplanar, their NICS(1)\(_{ZZ}\) values are averaged at 1Å above and below the ring center. For TD-DFT, PBE0 is used for UV/vis absorption simulation calculation at gas phase because König et al.\(^16\) indicates that PBE0 performs well in the calculation of excitation energy. 

![Diagram](image)

**Table S9.** Key distances (Å) of experimental and DFT-optimized structures of compound 2\(^a\)

| Functional | Exp. | TPSS | PBE0 | B3LYP |
|------------|------|------|------|-------|
| N1-Si1     | 1.736| 1.752| 1.743| 1.745 |
| Si1-P1     | 2.114| 2.113| 2.103| 2.106 |
| P1-P2      | 2.265| 2.281| 2.271| 2.297 |
| P2-Si2     | 2.108| 2.113| 2.103| 2.106 |
| Si2-N      | 1.749| 1.752| 1.743| 1.745 |
| N1-C       | 1.432| 1.408| 1.398| 1.407 |
| RD(%)\(^a\) | 0    | 0.75 | 0.83 | 0.88  |

\(^a\) RD = \[\frac{\sum_{i=1}^{n} |d_i(\text{calc}) - d_i(\text{exp})|}{n d_i(\text{exp})} \times 100\%\], BL means bond length.

**NMR analysis.** According to the DFT calculation, the peak located at -340.1 (\(\sigma_{\text{exp}} = -330\) ppm of 2) is assigned to the P1 and P2 atoms (Figure S24).
Figure S24. Calculated $^{31}$P NMR spectrum of 2.

Figure S25. Structural parameters of compound 2 at TPSS-D3BJ / def2-SVP – ma-TZVP level. Bond length (a, black) are in Å; Wiberg bond index (a, blue). (b) The natural population analysis of the charges in 2. Hydrogen atoms and substituents are omitted for clarity in the 3D structure and the NPA diagram, respectively.
Figure S26. PIO analysis on the bonding modes of between Si/P and P atoms in compound 2. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed by cutting the Si/P-P bonds. The isosurface 0.050 au is plotted.
Figure S27. The electron density of delocalized bonds (EDDB) analyses for pyrrole, D, and 2. Delocalized electrons of the specified fragments are listed below the corresponding plots. Hydrogen atoms in 3D structures are omitted for clarity (isovalue = 0.005 a.u.).
**Figure S28.** HOMO and LUMO orbitals of the compound 2. Hydrogen atoms in 3D structures are omitted for clarity. The isosurface 0.030 a.u. is plotted.

**The calculation of UV absorption spectrum.** According to the DFT calculation, the maximum absorption wavelength located at 600.2 nm ($\lambda_{\text{exp.}} = 568$ nm) of 2 (Figure S29), and the oscillator strength (f) is 0.0361. The HOMO was mainly localized on the five-membered ring moiety, whereas the LUMO was mostly localized on the benzene rings of the both side (Figure S28). The computed absorption band ($\lambda = 600.2$) can be assigned to the electronic transitions HOMO$\rightarrow$LUMO$+2$ (19.2%), HOMO$\rightarrow$LUMO$+5$ (72.2%). In addition, we also located an absorption peak at 421.2 nm ($\lambda_{\text{exp.}} = 426$ nm) with f = 0.0151, and the computed absorption band can be assigned to the electronic transition HOMO$-1$$\rightarrow$LUMO (77.8%).

![UV absorption spectrum](image)

**Figure S29.** The UV/vis absorption spectrums of the compound 2. The basis set is def2-TZVP.

**Table S10** Key distances (Å) of experimental and DFT-optimized structures of compound 3.$^a$

| Functional  | Exp.  | PBE0 | TPSS  | B3LYP |
|-------------|-------|------|-------|-------|
| Si1-P1      | 2.119 | 2.117| 2.124 | 2.119 |
| P1-P2       | 2.192 | 2.18 | 2.196 | 2.191 |
| P2-Si2      | 2.335 | 2.344| 2.349 | 2.333 |
| P2-P3       | 2.234 | 2.222| 2.239 | 2.247 |
| P3-P4       | 2.218 | 2.19 | 2.205 | 2.234 |
| P4-Si2      | 2.273 | 2.287| 2.292 | 2.286 |
| RD(%)$^b$   | 0     | 0.4  | 0.3   | 0.6   |

$^a$ RD = $\frac{\sum_{i=1}^{n} |B(L\text{Exp}) - B(L\text{Opt})| \times 100%}{B(L\text{Exp}) \times n}$, BL means bond length.
Figure S30. Calculated $^{31}$P NMR Spectrum of 3. According to the DFT calculation, the peaks located at 41.5 ($\delta_{\text{exp}} = 41.2$), -26.7 ($\delta_{\text{exp}} = -33.2$) and -235.1 ($\delta_{\text{exp}} = -246$) ppm of 3 are assigned to the P2 (P5), P3 (P4), and P1 (P6) atoms, respectively.

Figure S31. Calculated $^{29}$Si NMR Spectrum of 3. According to the DFT calculation, the $^{29}$Si NMR peaks located at -1.6 and -70.4 ppm of 3 are assigned to the Si1 (Si4) and Si2 (Si3) atoms, respectively.

Figure S32. Structural parameters of compound 3 at TPSS-D3BJ / def2-SVP – ma-TZVP level. Bond length (a, black) are in Å; Wiberg bond index (a, blue). The natural population analysis of the charges in 3 (b). Hydrogen atoms and substituents are omitted for clarity in the 3D structure and the NPA diagram, respectively.
Figure S33. PIO analysis on the bonding modes of Si1-P1 in compound 3. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed to the Si and P atoms. Each PIO pair leads to a bonding PIMO (principal interacting molecular orbital). The PBI quantifies the strength of the interaction. The isosurface 0.050 au is plotted.

Si1-P1 bonding

Total PBI: 1.349

1.12 e

1st PIO pair
PBI = 0.88
65.4 %

0.90 e

2nd PIO pair
PBI = 0.48
24.8 %

Figure S34. PIO analysis on the bonding modes of Si2-P2 in compound 3. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed to the Si and P atoms. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurface 0.050 au is plotted.

Si2-P2 bonding

Total PBI: 0.732

1.36 e

1st PIO pair
PBI = 0.67
91.0 %

0.73 e

Figure S34. PIO analysis on the bonding modes of Si2-P4 in compound 3. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed to the Si and P atoms. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurface 0.050 au is plotted.

Si2-P4 bonding

Total PBI: 0.775

0.79 e

1st PIO pair
PBI = 0.71
92.0 %

1.31 e
Figure S35. PIO analysis on the bonding modes of Si2-P4 in compound 3. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed to the Si and P atoms. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurface 0.050 au is plotted.

![Image of PIO analysis](image)

Figure S36. HOMO and LUMO orbitals of the compound 3. Hydrogen atoms in 3D structures are omitted for clarity. The isosurface 0.050 au is plotted.

![Image of HOMO and LUMO orbits](image)

Table S11 Key distances (Å) of experimental and DFT-optimized structures of compound 4.\(^a\)

| Functional | Exp.  | TPSS |
|------------|-------|------|
| Si1-N2     | 1.803 | 1.810 |
| N2-Si3     | 1.728 | 1.739 |
| Si3-P4     | 2.127 | 2.124 |
| P4-Si5     | 2.186 | 2.189 |
| Si5-P6     | 2.145 | 2.144 |
| P6-Si7     | 2.178 | 2.165 |
| Si7-N8     | 1.625 | 1.644 |
| RD(%)\(^a\) | 0     | 0.4  |

\(^a\) \text{RD} = \frac{\sum_{i=1}^{n} \frac{BL_{DFT} - BL_{Exp}}{BL_{Exp}} \times 100\%}{n}, \text{ BL means bond length.}

Figure S37. Calculated \(^{31}\)P NMR Spectrum of 4. According to the DFT calculation, the \(^{31}\)P NMR peaks located at -263.9 (\(\delta_{\exp} = -262.8\)), -293.2 (\(\delta_{\exp} = -286.6\)) ppm of 4 are assigned to the P4 and P6 atoms, respectively.

![Image of 31P NMR Spectrum](image)
Figure S38. Calculated $^{29}\text{Si}$ NMR Spectrum of 4. According to DFT calculations, the $^{29}\text{Si}$ NMR peaks located at 46.7 ($\delta_{\text{exp.}} = 47.2$), 12.1 ($\delta_{\text{exp.}} = 10.9$), -19.6 ($\delta_{\text{exp.}} = -26.4$) and -29.3 ($\delta_{\text{exp.}} = -30.6$) ppm of 4 are assigned to the Si5, Si3, Si7 and Si1 atoms, respectively.

Figure S39. Structural parameters of compound 4 at TPSS-D3BJ / def2-SVP – ma-TZVP level. Bond length (a, black) are in Å; Wiberg bond index (a, blue). The natural population analysis of the charges in 4 (b). Hydrogen atoms and substituents are omitted for clarity in the 3D structure and the NPA diagram, respectively.
Figure S40. PIO analysis on the bonding modes of Si2-P1 bond in compound 4. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed by cutting the Si2-P1 bond. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurfaces with the isovalue of 0.050 au are plotted.

Figure S41. PIO analysis on the bonding modes of P1-Si3 bond in compound 4. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed by cutting the P4-Si5 bond. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurfaces with the isovalue of 0.050 au are plotted.

Figure S42. PIO analysis on the bonding modes of Si3-P2 bond in compound 4. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed by cutting the Si5-P6 bond. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurfaces with the isovalue of 0.050 au are plotted.
Figure S43. PIO analysis on the bonding modes of P2-Si4 bond in compound 4. Hydrogen atoms in 3D structures are omitted for clarity. The PIO analysis is performed by cutting the P6-Si7 bond. Each PIO pair leads to a bonding PIMO. The PBI quantifies the strength of the interaction. The isosurfaces with the isovalue of 0.050 au are plotted.

Figure S44. HOMO and LUMO orbitals of the compound 4. Hydrogen atoms in 3D structures are omitted for clarity. The isosurface 0.050 au is plotted.

Cartesian Coordinates

**Compound 2**

TPSS-D3BJ/Def2-SVP~ma-TZVP

\[ E = -2937.629024 \text{ a.u.} \]

| Element | X      | Y      | Z      |
|---------|--------|--------|--------|
| Si      | 1.37194300 | 1.15187600 | 0.26464600 |
| Si      | -1.37182500 | 1.15194800 | -0.26531000 |
| P       | 0.80045600  | 3.11144000  | 0.81150800  |
| P       | -0.80089200 | 3.11131600  | -0.81327900 |
| N       | 2.61852500  | 0.18260900  | 1.19851600  |
| N       | 0.00004100  | 0.09424900  | -0.00030600 |
| N       | 2.75332500  | 0.68312600  | -0.89930500 |
| N       | -2.61845600 | 0.18191000  | -1.19852300 |
| N       | -2.75309200 | 0.68373900  | 0.89900000  |
| C       | -0.00003300 | -1.31407500 | 0.00024100  |
| C       | 4.80257800  | -0.44852900 | 0.07067300  |
| C       | 3.42894500  | 0.11599000  | 0.12030000  |
| C       | -0.91027100 | -2.03947200 | 0.80383500  |
| H       | -1.60685800 | -1.48193100 | 1.43588300  |
| C       | 3.23297400  | 1.26789000  | -2.17557000 |
| C       | 2.72634800  | -0.41671100 | 2.54725800  |
| C       | 0.91012800  | -2.03971400 | -0.80419100 |
| H       | 1.60685100  | -1.48236700 | -1.43625700 |
| C       | -0.00022300 | -4.15249400 | -0.00033300 |
| C       | -0.00032200 | -5.24710800 | -0.00026000 |
| C       | -3.42879300 | 0.11602100  | -0.11997600 |
| C       | -0.90930000 | -3.43986100 | 0.79822600  |
|   | X        | Y        | Z        |   |
|---|----------|----------|----------|---|
| H | -1.61954900 | -3.98084400 | 1.43422700 |   |
| C | 1.40067600  | -0.08514200 | 3.25458700  |   |
| H | 1.22317400  | 1.00389500  | 3.26103100  |   |
| H | 1.42476200  | -0.45401200 | 4.29391700  |   |
| H | 0.55964200  | -0.56601400 | 2.72919700  |   |
| C | 3.90943000  | 2.62283700  | -1.87815600 |   |
| H | 3.20973800  | 3.27702400  | -1.32989900 |   |
| H | 4.20862300  | 3.11606400  | -2.81963600 |   |
| H | 4.81451800  | 2.47727600  | -1.26282000 |   |
| C | -4.80237300 | -0.44861000 | -0.07001900 |   |
| C | 1.97140100  | 1.48360900  | -3.02910700 |   |
| H | 1.52141600  | 0.51409800  | -3.30097000 |   |
| H | 2.23000200  | 0.20219200  | -3.95691900 |   |
| H | 1.21447500  | 2.07362500  | -2.47967800 |   |
| C | 0.90896700  | -3.44009800 | -0.79838100 |   |
| H | 1.61917100  | -3.98126000 | -1.43428000 |   |
| C | 5.91215700  | 0.33905100  | 0.43103800  |   |
| H | 5.75806500  | 1.36741600  | 0.77145100  |   |
| C | 3.90148000  | 0.21840700  | 3.31763800  |   |
| H | 4.86821500  | -0.03343300 | 2.85182400  |   |
| H | 3.91488300  | -0.15657400 | 4.35575900  |   |
| H | 3.79274400  | 1.31608900  | 3.34223000  |   |
| C | 4.19071700  | 0.32367800  | -2.91358300 |   |
| H | 5.16848700  | 0.22677000  | -2.39871300 |   |
| H | 4.39094100  | 0.72957800  | -3.92187600 |   |
| H | 3.75866100  | -0.68215700 | -3.02570800 |   |
| C | 4.99676000  | -1.77303900 | -0.36593300 |   |
| H | 4.12968800  | 2.37970100  | -0.64445600 |   |
| C | 2.89223600  | -1.94677600 | 2.45250600  |   |
| H | 2.07873300  | -2.38579600 | 1.85120100  |   |
| H | 2.85768000  | -2.38503800 | 3.46519900  |   |
| H | 3.85855800  | -2.21974000 | 1.99795700  |   |
| C | -2.72685400 | -0.41733300 | -2.54723600 |   |
| C | -3.23254400 | 1.26887600  | 2.17514800  |   |
| C | 7.20522100  | -0.19415900 | 0.34658800  |   |
| H | 8.06554900  | 0.42396600  | 0.62295100  |   |
| C | 6.29084100  | -2.30210200 | -0.44206400 |   |
| H | 6.43676900  | -3.32380500 | -0.78122200 |   |
| C | -5.91225400 | 0.33883500  | -0.42973800 |   |
| H | -5.75850100 | 1.36723300  | -0.77020100 |   |
| C | 7.39649900  | -1.51347200 | -0.08942300 |   |
| H | 8.40794000  | -1.92761000 | -0.15422500 |   |
| C | -1.40122700 | -0.08628200 | -3.25491100 |   |
| H | -1.22314500 | 1.00266700  | -3.26109100 |   |
| H | -1.42589700 | -0.45424000 | -4.29434100 |   |
| H | -0.56028300 | -0.56780300 | -2.72996600 |   |
| C | -4.19957300 | 0.32502700  | 2.91351000  |   |
| H | -5.16820300 | 0.22804800  | 2.39871400  |   |
| H | -4.39053500 | 0.73132400  | 3.92165800  |   |
| H | -3.75844500 | -0.68081300 | 3.02957600  |   |
| C | -4.99615400 | -1.77314700 | 0.36669200  |   |
| H | -4.12883500 | -2.37970500 | 0.64472700  |   |
| C | -6.29012900 | -2.30235600 | 0.44358300  |   |
| C | -6.43573900 | -3.33036400 | 0.78285800  |   |
| C | -1.97092000 | 1.48457300  | 0.302862200 |   |
| H | -1.52123900 | 0.51504100  | 3.30091300  |   |
| H | -2.22938000 | 2.02292600  | 3.95620300  |   |
| H | -1.21383100 | 2.07416500  | 2.47626200  |   |
| C | -3.90879400 | 2.62386600  | 1.87746600  |   |
| H | -3.20908300 | 3.27778100  | 1.32891700  |   |
| H | -4.20779900 | 3.11741700  | 2.81884000  |   |
| H | -4.81397500 | 2.47829600  | 1.26226800  |   |
C  -7.20520400  -0.19453700  -0.34457300
H  -8.06576000  0.42348200  -0.62046600
C  -7.39608300  -1.51387000  0.09156100
H  -8.40743700  -1.92819800  0.15693600
C  -2.89328900  -1.94734600  -2.45253000
H  -2.07984400  -2.38666500  -1.85135200
H  -2.85912100  -2.38556300  -3.46517200
C  -3.85963800  -2.21998800  -1.99785900
C  -2.89328900  -1.94734600  -2.45253000
H  -2.07984400  -2.38666500  -1.85135200
H  -2.85912100  -2.38556300  -3.46517200
C  -3.85963800  -2.21998800  -1.99785900
H  -3.91608100  -0.15706700  -4.35527100
H  -3.90190600  0.21829900  -3.34233500
H  -3.91608100  -0.15706700  -4.35527100
H  -3.85963800  -2.21998800  -1.99785900
H  -3.79243700  1.31590000  -3.34233500

Compound 3
TPSS-D3BJ/Def2-SVP~ma-TZVP
E = -6558.177786 a.u.

P                  1.43870100  -0.92291900  1.58229800
Si                 1.86021400  1.25715100  0.81619100
P                  3.18449400  -2.19853800  1.19800400
P                  0.16226700  -1.09046900  -0.24905300
Si                 3.86096600  -0.73099700  -0.18110900
P                  0.16261500  1.08998200  -0.24890100
P                  1.43890000  0.92232100  1.58256900
Si                 3.86108100  0.73084500  -0.18105900
N                  3.38801000  0.94054800  -0.02927300
N                  2.00031300  2.26527800  2.33150500
N                  1.77373000  3.29253900  0.43073700
N                  5.65895100  0.79073600  -0.55601200
N                  4.08999000  -1.12653000  -2.00147000
N                  3.38829900  -0.94077500  -0.02935500
N                  1.77412500  3.29311700  0.43019800
N                  4.08983300  1.12674100  -2.00135400
N                  2.00034400  -2.26600000  2.33111300
N                  -5.65902100  0.79095000  -0.55615300
C                  4.31393900  1.95094900  -0.42212900
C                  4.81877400  2.02369300  -1.73718300
H                  4.45067200  1.31547100  -2.48206700
C                  1.67558600  3.45380000  1.74005400
C                  5.41654300  -2.26527800  2.33150500
C                  4.78277000  2.89790900  0.52361400
C                  4.39805000  2.83404500  1.54466800
C                  1.67570000  -3.45448400  1.73945700
C                  4.31430100  -1.95106800  -0.42232200
C                  6.88267200  -0.84462600  0.27785600
C                  1.08880700  4.60516500  2.48023200
C                  5.76828400  2.99219300  -2.09018600
H                  6.14042600  3.03043000  -3.12057100
C                  -0.22304700  4.44414400  2.97178000
H                  -0.75251700  3.50244800  2.78748000
C                  -5.41637100  1.21446900  -1.81612900
C                  1.35989900  4.22357800  -0.65042500
C                  2.37319200  1.96926700  3.74134800
C                  6.23070900  3.91649600  -1.14180800
H                  6.97036700  4.67449000  -1.41897500
C                  5.72627500  3.85832800  0.16719800
H                  6.07380300  4.57290400  0.92172800
C                  1.77325300  5.81400100  2.69768600
H                  2.80129200  5.92788900  2.34131500
C                  3.53269400  0.95317200  3.69104100
| Atom | X            | Y            | Z            |
|------|--------------|--------------|--------------|
| C    | -2.60560700  | -0.68071600  | -3.42979700  |
| C    | 0.84623300   | -5.49348000  | 3.65734800   |
| H    | 1.87111600   | -5.36481900  | 4.02015400   |
| C    | -7.29447300  | 2.31320500   | 0.51297600   |
| H    | -6.45602300  | 2.87183400   | 0.96374600   |
| H    | -8.15794800  | 2.35910200   | 1.19952300   |
| H    | -7.58286500  | 2.80175200   | -0.43284200  |
| C    | -8.02291700  | 0.03935000   | -0.37277600  |
| H    | -8.40000000  | 0.52612300   | -1.28614500  |
| H    | -8.86310400  | -0.04365200  | 0.33833900   |
| H    | -7.67360700  | -0.97660300  | -0.62445000  |
| C    | 7.52177600   | -3.59287800  | -3.88073000  |
| H    | 7.65004600   | -4.67255300  | -4.00911200  |
| C    | -2.52421500  | 2.77437300   | -2.89756800  |
| H    | -3.27826700  | 3.57948300   | -2.85788500  |
| H    | -1.80488600  | 3.00017100   | -3.70419800  |
| H    | -1.98437900  | 2.75103400   | -1.93793800  |
| C    | 0.16181100   | -6.69965400  | 3.87341800   |
| H    | 0.64864800   | -7.51786700  | 4.41462600   |
| C    | -2.87604200  | -3.22482800  | 4.48146300   |
| H    | -3.64849700  | -3.75337100  | 3.89464600   |
| H    | -3.33187700  | -2.90430300  | 5.43415500   |
| H    | -2.06645700  | -3.93217500  | 4.71470700   |
| C    | -1.14842800  | -6.85623300  | 3.39647700   |
| H    | -1.68863800  | -7.79267200  | 3.57109400   |

**Cartesian Coordinates**

**Compound 4**

TPSS-D3BJ/Def2-SVP~ma-TZVP

E = -5192.458127 a.u.

P
-1.76750500 -0.46810600 -0.14755700
Si
2.03109100 -0.58065500 0.17198000
Si
-0.71889700 1.39419800 0.02839000
P
1.46398600 1.46672400 0.17424100
Si
-3.84314400 0.14462900 -0.11074100
Si
4.61215500 0.78821700 0.88195300
N
1.27288600 -1.91848300 1.20414300
N
-4.89113500 -1.00362600 0.95591400
N
1.46321300 -1.92669200 -0.94501600
N
5.80882200 1.29407000 -0.51948700
N
3.76755100 -0.66638900 0.21426200
N
6.33469900 0.05321300 1.15742300
N
-1.23412900 2.80236600 -1.06466400
N
-4.79688700 -1.07618200 -1.20237400
N
-1.35959500 2.76984300 1.08538000
N
-4.40739800 1.68676400 -0.02729000
C
0.97679000 -2.62618100 0.09822000
C
0.28863600 -3.94427000 0.04530000
C
-5.38432500 -1.62511000 -0.12420600
C
4.46719400 -1.80764800 -0.25673300
C
1.00588500 -2.15007700 2.64309000
C
6.85801000 0.79429300 0.16309600
C
8.29991300 1.08866200 -0.07307600
C
5.36497300 -1.71542700 -1.34459000
H
5.50128500 -0.74416300 -1.82380800
C
-1.61459700 3.52426100 0.00161300
C
-5.74332400 2.01618500 0.06201900
C
1.43797900 -2.17518900 -2.40624000
C
1.05362700 -5.12409200 -0.03510600
H
2.14510500 -5.05952700 -0.06314400
C
-5.34052600 -1.01044800 2.36435500
C  -1.11580600  -4.01630400  0.08896200
H  -1.68976300  -3.08434100  0.14124200
C  -2.24209500  4.87136100  -0.01286900
C  2.09331000  -0.93318500  -3.03402800
H  1.55093900  -0.02032300  -2.74048300
H  2.09081100  -1.01800600  -4.13341500
H  3.13640500  -0.84034000  -2.69053800
C  -6.43077300  -2.68278600  -0.14132100
C  5.72698500  2.33216100  -1.56749000
H  4.29414400  -3.06918900  0.35510100
H  3.60649600  -3.14798700  1.19992900
C  -1.30516400  3.12115300  2.51783900
C  6.98398900  -0.71493300  2.23628900
C  -4.67545800  -1.58191300  -2.58479000
C  -1.74655600  -5.26639300  0.04376600
H  -2.83982100  -5.31899500  0.06696300
C  0.41329900  -6.36919300  -0.07201500
H  1.01142200  -7.28432000  -0.13186900
C  -0.98746600  -6.44288200  -0.03478400
H  -1.48579200  -7.41739100  -0.06806000
C  6.06428700  -2.84264400  -1.79426300
H  6.75220700  -2.74501100  -2.64195500
C  1.81266900  -1.06371300  3.37867700
H  2.89051300  -1.18199800  3.18120900
H  1.64144400  -1.13304600  4.46569900
H  1.51511600  -0.06010900  3.03204800
C  2.26421400  -3.42709800  -2.76390400
H  3.28199700  -3.35907600  -2.34779600
H  2.33844300  -3.51125900  -3.86231800
H  1.78334000  -4.34403700  -2.38746900
C  -0.49655100  -1.99934300  2.94937200
C  -0.88578000  -1.06403800  2.51995400
C  -0.65662500  -2.00424400  4.04180000
H  -1.07264600  -2.83092800  2.51140200
C  8.89655900  2.24549400  0.46400300
H  8.30097500  2.91934000  1.08774400
C  -1.38945800  3.04714600  -2.51264700
C  -3.76997500  -2.83149700  -2.58667400
H  -2.80427200  -2.58951200  -2.11495300
H  -3.58460100  -3.17788800  -3.61886200
H  -4.24365100  -3.65694200  -2.02812000
C  -3.64679000  4.94262900  -0.05756800
H  -4.21911700  4.00676600  -0.08786100
C  -6.21262600  2.87881300  1.10011800
C  -5.48396600  3.25806400  1.82377100
C  -0.01018400  -2.32096100  -2.90505300
H  -0.46936900  -3.24629500  -2.52011400
H  -0.02099300  -2.36765300  -4.00793400
H  -0.61930300  -1.46723700  -2.56532600
C  -6.10280800  -4.03437200  0.06920700
H  -5.06362900  -4.31232700  0.26884200
C  4.98877700  -4.19638700  -0.10305900
H  4.83789800  -5.16177100  0.39373200
C  9.06878300  0.21546300  -0.86519100
H  8.59850300  -0.67848100  -1.28709000
C  -1.03035800  1.80095100  3.25597400
H  -1.84461200  1.08410600  3.07444900
H  -0.94251000  1.98008300  4.34075000
H  -0.08812400  1.35936600  2.89015200
C  -7.76957600  -2.31829900  -0.38651200
H  -8.01587700  -1.26366600  -0.54520300
C  5.84044500  -1.22804300  3.13062100

44
C References

1. Fink, W. Beitraege zur Chemie der Si-N-Bindung, VII. N,N'-alkylierte und -arylierte cyclodisilazane. *Helvetica Chimica Acta*. 1964, 47, Fasciculus 2, 58.

2. Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; and Stalke, D. High Yield Access to Silylene RSiCl(R = PhC(NtBu)2) and Its Reactivity toward Alkyne: Synthesis of Stable Disilacyclobutene. *J. Am. Chem. Soc*. 2010, 132, 1123-1126.

3. Sheldrick, G. M. *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen, Germany (1997).

4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, K.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. G.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 16, Revision A.03; Gaussian, Inc., Wallingford CT, 2016.
5. Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.

6. Weigend F.; Ahlrichs. R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-305.

7. Zheng, J.; Xu, X.; Truhlar, D. G. Minimally augmented Karlsruhe basis sets. *Theor. Chem. Acc.* **2010**, *128*, 295-305.

8. Papajak, E.; Zheng, J.; Xu, X.; Leverentz, H. R.; Truhlar, D. G. Perspectives on Basis Sets Beautiful: Seasonal Plantings of Diffuse Basis Functions. *J. Chem. Theory. Comput.* **2011**, *7*, 3027-3034.

9. Wilson, P. J.; Bradley, T. J.; Tozer, D. J. Hybrid exchange-correlation functional determined from thermochemical data and ab initio potentials. *J. Chem. Phys.* **2001**, *115*, 9233-9242

10. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

11. Jameson, C. J.; De Dios, A.; Keith Jameson, A. Absolute shielding scale for $^{31}$P from gas-phase NMR studies. *Chem. Phys. Lett.* **1990**, *167*, 575-582.

12. Legault, C. Y.; CYL view, 1.0b ed.; Université de Sherbrooke: Sherbrooke, Québec, Canada, 2009; [http://www.cylview.org](http://www.cylview.org).

13. Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14*, 33-38.

14. Lu, T.; Chen, F.; Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580-592.

15. Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta R.; Schleyer, P. v. R. Which NICS aromaticity index for planar p rings is best? *Org. Lett.* **2006**, *8*, 863-866.

16. Simeth, N. A.; Bellisario, A.; Crespi, S.; Fagnoni, M.; König, B. Substituent Effects on 3-Arylazoindole Photoswitches. *J. Org. Chem.* **2019**, *84*, 6565−6575.