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Distinct different reactivity of bis(silylenyl)- versus phosphanyl-silylenyl- substituted *o*-dicarborane towards O_2, N_2O and CO_2

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Table of Content

A. Experimental Section

A1. General Considerations

All experiments and manipulations were carried out under dry nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified N_2. Solvents were deoxygenated and dried by standard methods, saturated with purified N_2 and freshly distilled prior to use. The precursor compounds $[CH_2N(t\text{Bu})]_2PCl$ [1] and $[PhC(N(t\text{Bu}))_2]SiCl$, [2] **1** [3] and **3** [4] were prepared according to literature procedure. The ^{1}H, ^{13}C, ^{31}P, ^{11}B, ^{29}Si-NMR spectra were recorded on Brucker ARX200, AV 400, AV500 spectrometers referenced to residual solvent signals as internal standards (^{1}H and $^{13}C\{^{1}H\}$) or with an external reference ($SiMe_4$ for ^{29}Si, 85% H_3PO_4 for ^{31}P, and $BF_3{\cdot}OEt_2$ for ^{11}B). Abbreviations: *s* = singlet; *d* = doublet; *t* = triplet; *sept* = septet; *m* = multiplet; *br* = broad. IR spectra were measured with a Nicolet iS5 FT-IR Spectrometer from the company of Thermo Scientific. Elemental analyses and ESI-MS were performed by the analytical labor and MS-Service in the Institute of Chemistry, Technical University of Berlin, Germany. Melting points were measured on a Stuart SMP30 melting point apparatus.

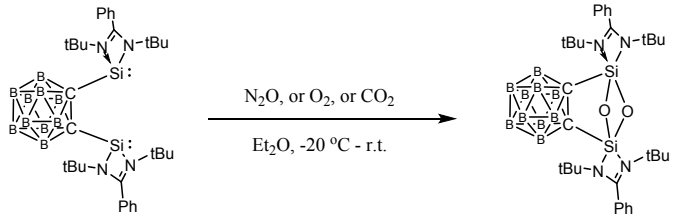
A2. Single-Crystal X-ray Structure Determinations

Crystals were each mounted on a glass capillary in per-fluorinated oil and measured in a cold N_2 flow. The data of **2**, **4** - **7** 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 [5] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 2075598 (compound **2**), 2075596 (compound **4**), 2075600 (compound **5**), 2075599 (compound **6**), and 2075597 (compound **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

A3. Synthesis and Characterization

Compound CB-**Si_2O_2** **(2)**: A solution of CB-**SiSi** (**1**) (0.35, 0.44 mmol) in Et_2O was cooled to -20 °C. The N_2 atmosphere in the flask was exchanged to O_2. The reaction mixture was slowly warmed to room temperature, after 16h the volatiles were removed under vacuum and the residue was washed with *n*-hexane and extracted with toluene. From toluene at -20 ^{0}C colorless crystals of **2** were formed. The crystals were isolated via filtration and dried under vacuum (0.30 g, 0.37 mmol, 85%). Under same reaction conditions, the reactions of **1** with N_2O or CO_2 yielded also **2** as the exclusive product. M. p. 253 °C (decomp.). ^{1}H NMR (500.25 MHz, THF-d_8, 298 K): δ (ppm) = 1.22, 1.23 (*s*, 18 H; Si-NC(CH_3)$_3$), 7.12 – 7.63 (*m*, 5 H; *Ph*); $^{13}C\{^{1}H\}$ NMR (125.79 MHz, THF-d_8, 298 K): δ (ppm) = 33.1 (*s*, Si-NC(CH_3)$_3$), 56.2 (*s*, Si-NCMe_3), 80.6 (cage-C), 129.5, 129.6, 130.4, 131.3 (*Ph*), 131.9, 134.0 (quaternary *Ph*), 181.5 (NCN); $^{29}Si\{^{1}H\}$ NMR (99.39 MHz, THF-d_8, 298 K): δ (ppm) = -98.6 (*br*); $^{11}B\{^{1}H\}$ NMR (64.21 MHz, THF-d_8, 298 K): δ (ppm) = -17.7 – 0.7 (*br*); ESI-MS: m/z: 693.50059 (calc. 693.50177 $[M]^+$); Elemental analysis calcd (%) for $C_{32}H_{56}N_4B_{10}Si_2O_2{\cdot}C_7H_8$ (785.23 g/mol): C 59.65, H 8.21, N 7.14, found: C 59.03, H 8.29, N 7.00. IR (KBr, cm^{-1}): 2970(w), 2547(m), 1528(w), 1480(w), 1445(m), 1420(s),

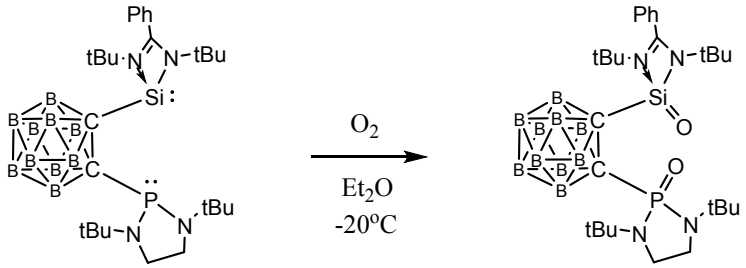
1394(s), 1362(s), 1193(s), 1086(m), 1069(m), 1024(w), 976(w), 923(w), 848(w), 780(vs), 728(vs), 704(vs), 693(s), 638(m), 578(m), 560(m).



1 **2**

Scheme S1 Reactions of **1** with N_2O, O_2, or CO_2 affording **2**.

Compound CB-**PSi**O_2 **(4)**: A solution of CB-**PSi** (**3**) (0.39 g, 0.65 mmol) in diethyl ether (15 ml) was cooled to -20 °C. The N_2 atmosphere in the flask was exchanged to O_2. The reaction mixture was stored at refrigerator (-20 °C). After 16 h colorless crystals of **4** were formed. The collected crystals of **4** amounted to 0.28 g (0.44 mmol, 68%). M.p. 153°C (decomp.). ^{1}H NMR (500.25 MHz, THF-d_8, 253 K): δ (ppm) = 1.32 (*s*, 18 H; Si-NC(C*H*$_3$)$_3$), 1.45 (*s*, 18 H; P-NC(C*H*$_3$)$_3$), 1.95 – 3.13 (*br*, 10 H; B*H*), 3.27 – 3.33 (*m*, 2 H; C*H*$_2$), 3.56 – 3.62 (*m*, 2 H; C*H*$_2$), 7.45 – 7.80 (*m*, 5 H; *Ph*); ^{31}P{^{1}H} NMR (202.50 MHz, THF-d_8, 253 K): δ (ppm) = 26.4; ^{13}C{^{1}H} NMR (125.78 MHz, THF-d_8, 253 K): δ (ppm) = 28.6 (*d*, $^3J_{(P,C)}$ = 2.3 Hz; P-NC(*C*H$_3$)$_3$), 30.6 (*s*, Si-NC(*C*H$_3$)$_3$), 41.0 (*d*, $^2J_{(P,C)}$ = 14.1 Hz; P-N-*C*H$_2$), 55.5 (*s*, Si-N(*C*Me$_3$)$_3$), 56.2 (*d*, $^2J_{(P,C)}$ = 4.9 Hz; P-N(*C*Me$_3$), 75.9 (*d*, $^1J_{(P,C)}$ = 7.6 Hz; cage C), 88.5 (*d*, $^2J_{(P,C)}$= 121.9 Hz; cage C), 128.1 (*Ph*), 128.2 (*Ph*), 128.6 (*Ph*), 128.6 (*Ph*), 129.1 (quaternary *Ph*), 131.3 (*Ph*), 181.4 (N*C*N); ^{29}Si{^{1}H} NMR (99.38 MHz, THF-d_8, 253 K): δ (ppm) = -52.8 (*br*); ^{11}B{^{1}H} NMR (64.21 MHz, THF-d_8, 298 K): δ (ppm) = -14.2 - 1.2 (*br*) Elemental analysis calcd (%) for $C_{27}H_{55}N_4SiPB_{10}O_2$ (634.92): C 51.08, H 8.73, N 8.82, found: C 50.83, H 8.30, N 8.94. IR (KBr, cm^{-1}): 2970(m), 2569(m), 1477(w), 1445(w), 1394(s), 1366(s), 1267(m), 1193(vs), 1022(vs), 799(m), 770(m), 735(m), 704(s), 651(s).

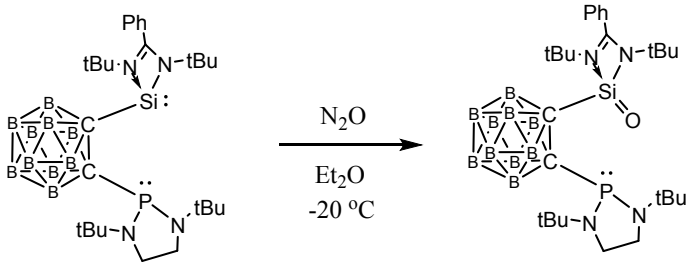


3 **4**

Scheme S2 Reaction of **3** with O_2 to give **4**.

Compound CB-**PSi**O **(5)**: A solution of CB-**PSi** (**3**) (0.38 g, 0.63 mmol) in Et_2O was cooled to -20 °C. The N_2 atmosphere in the flask was exchanged to N_2O. The reaction solution was stored at -20 °C. After 20 min

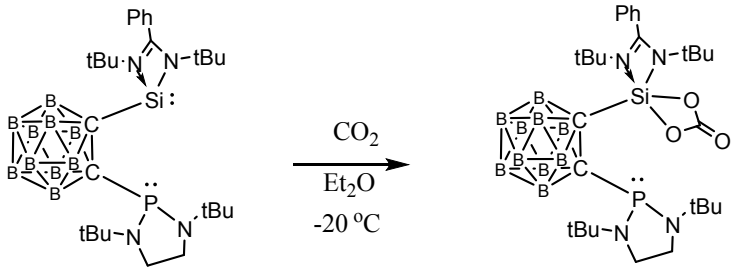
colorless crystals of **5** were formed. At -20 °C the crystals were isolated via filtration and dried under vacuum (0.20 g, 0.32 mmol, 51%). M. p. 176 °C (decomp.). ^{1}H NMR (500.25 MHz, THF- d_8, 243 K): δ (ppm) = 1.29 (s, 18 H; Si-NC(CH_3)$_3$), 1.35 (*br*, 18 H; P-NC(CH_3)$_3$), 1.87 – 3.08 (*br*, 10 H, B*H*), 3.25 – 3.30 (*m*, 2 H; CH_2), 3.36 – 3.39 (*m*, 2 H; CH_2), 7.43 – 7.85 (*m*, 5 H; *Ph*); ^{31}P {^{1}H} NMR (202.50 MHz, THF-d_8, 243 K): δ (ppm) = 114.2; ^{13}C{^{1}H} NMR (125.79 MHz, THF-d_8, 243 K): δ (ppm) = 29.9 (*d*, $^{3}J_{(P,C)}$ = 9.3 Hz; P-NC(*C*H$_3$)$_3$), 30.4 (*s*, Si-NC(*C*H$_3$)$_3$), 47.6 (*d*, $^{2}J_{(P,C)}$ = 7.3 Hz; P-N-*C*H$_2$), 54.8 (*d*, $^{2}J_{(P,C)}$ = 27.3 Hz; P-N*C*Me$_3$), 55.3 (*s*, Si-N*C*Me$_3$), 75.8 (*d*, $^{2}J_{(P,C)}$ = 8.0 Hz; cage C), 96.9 (*d*, $^{1}J_{(P,C)}$= 140.9 Hz; cage C), 128.1 (*br*, *Ph*), 128.3 (*Ph*), 128.6 (*Ph*), 129.2 (quaternary *Ph*), 131.2 (*Ph*), 181.0 (NCN); ^{29}Si{^{1}H} NMR (99.39 MHz, THF-d_8, 243 K): δ (ppm) = -51.9 (*br*.); ^{11}B{^{1}H} NMR (64.21 MHz, THF-d_8, 298 K): δ (ppm) = -15.9 - -1.4 (*br*); Elemental analysis calcd (%) for $C_{27}H_{55}N_4SiPB_{10}O$ (618.92 g/mol): C 52.40, H 8.96, N 9.05, found: C 52.01, H, 8.53, N 8.89 IR (KBr, cm^{-1}): 2970(m), 2565(m), 1391(vs), 1363(s), 1187(vs), 1154(m), 1095(m), 1070(m), 962(m), 798(m), 772(s), 766(s), 734(m), 7145(s), 645(m), 635(s), 614(w).



3 **5**

Scheme S3 Reaction of **3** with N_2O to form **5**.

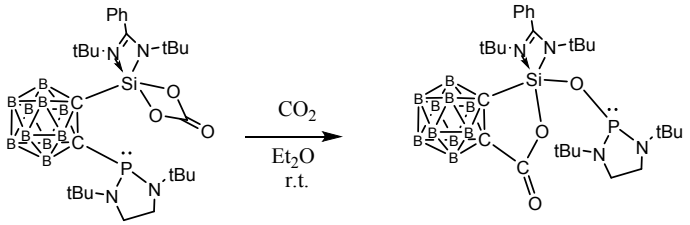
Compound CB-**PSi**(O_2C=O) **(6)**: A solution of **3** (0.47 g, 0.78 mmol) in diethyl ether (15 ml) was cooled to -20 °C. The N_2 atmosphere in the flask was exchanged to CO_2. After 30 min colorless crystals of **6** were formed from the resulted solution and rapidly isolated via filtration. The collected crystals of **6** amounted to 0.39 g (0.60 mmol, 77 %). M.p. 263 °C (decomp.). ^{1}H NMR (500.25 MHz, THF-d_8, 273 K): δ (ppm) = 1.21 (*s*, 18 H; Si-NC(CH_3)$_3$), 1.34 (*br*, 18 H; P-NC(CH_3)$_3$), 1.86 – 3.17 (*br*, 10 H; B*H*), 3.27 – 3.33 (*m*, 2 H; CH_2), 3.42 – 3.46 (*m*, 2 H; CH_2), 7.40 – 7.76 (*m*, 5 H; *Ph*); ^{31}P{^{1}H} NMR (200.13 MHz, THF-d_8, 273 K): δ (ppm) = 115.5; ^{13}C{^{1}H} NMR (125.79 MHz, THF-d_8, 263 K): δ (ppm) = 31.5 (*d*, $^{3}J_{(P,C)}$ = 8.2 Hz; P-NC(*C*H$_3$)$_3$), 32.1 (*s*, Si-NC(*C*H$_3$)$_3$), 49.2 (*d*, $^{2}J_{(P,C)}$ = 8.6 Hz; P-N-*C*H$_2$), 56.7 (*d*, $^{2}J_{(P,C)}$ = 25.8 Hz; P-N*C*Me$_3$), 57.4 (*s*, Si-N*C*Me$_3$), 77.8 (*d*, $^{2}J_{(P,C)}$ = 14.7 Hz; cage C), 99.6 (*d*, $^{1}J_{(P,C)}$= 127.7 Hz; cage C), 127.1, 128.3, 128.5, 128.9, 130.2 (quaternary *Ph*), 131.1 (*Ph*), 149.8 (*C*O$_3$), 181.1 (N*C*N); ^{29}Si{^{1}H} NMR (99.38 MHz, THF-d_8, 273 K): δ (ppm) = -93.1; ^{11}B{^{1}H} NMR (64.21 MHz, THF-d_8, 298 K): δ (ppm) = -15.2 – 2.0 (*br*); Elemental analysis calcd (%) for $C_{28}H_{55}N_4SiPO_3B_{10}$ (662.93): C 50.73, H 8.36, N 8.45, found: C 50.05, H 8.56, N 8.62. IR (KBr, cm^{-1}): 2971(w), 2611(w), 2577(w), 1813(vs, ν_{CO}), 1409(s), 1399(s), 1368(s), 1360(m), 1196(vs), 1092(m), 1072(w), 1004(m), 866(s), 787(vs), 775(m), 748(m), 740(m), 705(s), 678(m), 660(s), 632(w), 577(m), 561(w).



3 **6**

Scheme S4 Reaction of **3** with CO_2 affording **6**.

Compound **7**: A solution of **6** in diethyl ether was allowed to stand at room temperature. After 24 h compound **6** isomerized to **7** completely, the latter crystallized as colorless crystals. M.p. 274 °C (decomp.). ^{1}H NMR (200.13 MHz, THF-d_8, 298K): δ (ppm) = 1.20 (*s*, 9 H; Si-NC(CH_3)$_3$), 1.23 (*s*, 9 H; Si-NC(CH_3)$_3$), 1.34 (*d*, $^{3}J_{(H,P)}$ = 1.0 Hz, 9 H; P-NC(CH_3)$_3$), 1.38 (*d*, $^{3}J_{(H,P)}$ = 1.1 Hz, 9 H; P-NC(CH_3)$_3$), 3.22 – 3.38 (*m*, 4 H; CH_2), 7.51 – 7.65 (*m*, 5 H; *Ph*); ^{31}P {^{1}H} NMR (81.01 MHz, THF-d_8, 298 K): δ (ppm) = 119.6; ^{13}C{^{1}H} NMR (50.32 MHz, THF-d_8, 298 K): δ (ppm) = 31.3 (*d*, $^{3}J_{(P,C)}$ = 7.5 Hz; P-NC(*C*H$_3$)$_3$), 31.5 (*d*, $^{3}J_{(P,C)}$ = 7.5 Hz; P-NC(*C*H$_3$)$_3$), 33.0, 33.8 (*s*, Si-NC(*C*H$_3$)$_3$), 46.8 (*d*, $^{2}J_{(P,C)}$ = 8.0 Hz; P-N-*C*H$_2$), 47.4 (*d*, $^{2}J_{(P,C)}$ = 8.0 Hz; P-N-*C*H$_2$), 54.6 (*d*, $^{2}J_{(P,C)}$ = 10.3 Hz; P-N*C*Me$_3$), 54.9 (*d*, $^{2}J_{(P,C)}$ = 13.6 Hz; P-N*C*Me$_3$), 57.3, 57.4 (*s*, Si-N*C*Me$_3$), 71.8, 76.3 (*s*, cage C), 129.4, 129.9, 130.2, 132.0, 132.5 (*Ph*), 133.4 (quaternary *Ph*), 159.4 (*C*O$_2$), 180.6 (N*C*N); ^{29}Si{^{1}H} NMR (79.49 MHz, THF-d_8, 298 K): δ (ppm) = -110.4 (*d*, $^{2}J_{(Si,P)}$ = 9.4 Hz); ^{11}B{^{1}H} NMR (64.21 MHz, THF-d_8, 298 K): δ (ppm) = -14.7 – 2.2 (*br*); Elemental analysis calcd (%) for $C_{28}H_{55}N_4SiPO_3B_{10}$ (662.93): C 50.73, H 8.36, N 8.45, found: C 50.35, H 8.25, N 8.46. IR (KBr, cm^{-1}): 2966(m), 2594(m), 2580(m), 2552(m), 1740(s, CO), 1545(m), 1488(w), 1367(vs), 1280(m), 1249(m), 1219(m), 1188(s), 1130(w), 1075(m), 931(vs), 875(w), 845(w), 814(m), 800(s), 773(s), 742(s), 708(s), 679(w), 642(s), 606(s).



6 **7**

Scheme S5 Isomerization of **6** to **7**.

A4. Single-Crystal X-ray Structure Determinations

Compound **2** (CCDC 2075598)

Table S1 Crystal data and structure refinement for **2**.

Empirical formula	C39 H64 B10 N4 O2 Si2	
Formula weight	785.22	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 15.4300(2) Å	α= 90°.
	b = 20.2433(2) Å	β= 96.0730(10)°.
	c = 14.5257(2) Å	γ = 90°.
Volume	4511.70(10) Å^3	
Z	4	
Density (calculated)	1.156 Mg/m^3	
Absorption coefficient	0.993 mm^{-1}	
F(000)	1680	
Crystal size	0.300 x 0.230 x 0.170 mm^3	
Theta range for data collection	3.615 to 67.497°.	
Index ranges	-17<=h<=18, -13<=k<=24, -17<=l<=17	
Reflections collected	14505	
Independent reflections	4072 [R(int) = 0.0203]	
Completeness to theta = 67.497°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.65064	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4072 / 120 / 296	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1232	
R indices (all data)	R1 = 0.0466, wR2 = 0.1257	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.585 and -0.325 e.Å^{-3}	

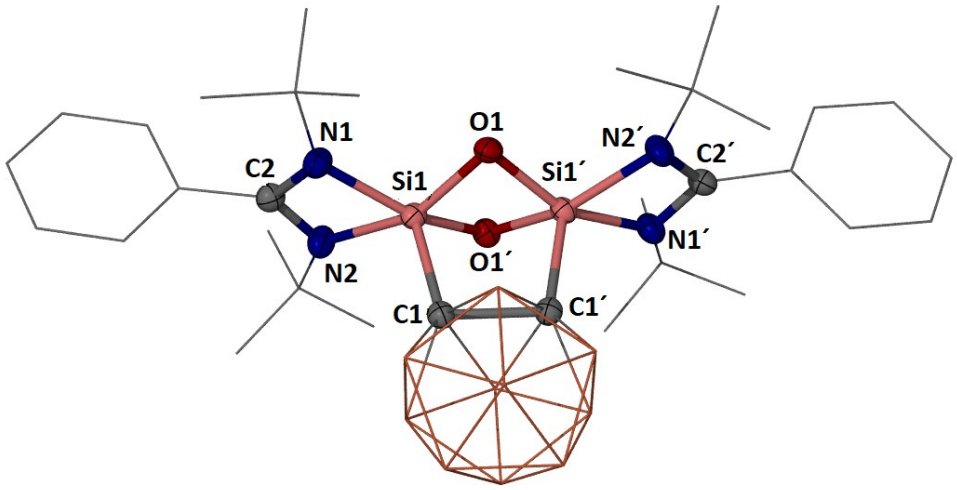


Fig. S1. Molecular Structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S2 Bond lengths [Å] and angles [°] for **2**.

Si1-O1	1.695(1)
Si1-O1´	1.708(1)
Si1-N1	1.861(1)
Si1-N2	1.884(1)
Si1-C1	1.961(2)
Si1-C2	2.332(2)
Si1-Si1´	2.403(1)
O1-Si1´	1.708(1)
N1-C2	1.332(2)
C1-C1´	1.687(3)
N2-C2	1.335(2)
O1-Si1-O1´	83.4(1)
O1-Si1-N1	154.4(1)
O1´-Si1-N1	98.3(1)
O1-Si1-N2	98.3(1)
O1´-Si1-N2	155.0(1)
N1-Si1-N2	69.7(1)
O1-Si1-C1	96.6(1)
O1´-Si1-C1	96.1(1)
N1-Si1-C1	108.6(1)
N2-Si1-C1	108.4(1)
O1-Si1-C2	130.0(1)

O1-Si1-C2	130.1(1)
N1-Si1-C2	34.8(1)
N2-Si1-C2	34.9 (1)
C1-Si1-C2	112.0(1)
O1-Si1-Si1´	45.3(1)
O1´-Si1-Si1´	44.9(1)
N1-Si1-Si1´	143.1(1)
N2-Si1-Si1´	143.6(1)
C1-Si1-Si1´	79.5(1)
C2-Si1-Si1´	168.6(1)
Si1-O1-Si1´	89.8(1)
C2-N1-Si1	92.3(1)
C1´-C1-Si1	100.5(1)
C2-N2-Si1	91.2(1)
N1-C2-N2	106.8(1)
N1-C2-Si1	52.9(1)
N2-C2-Si1	53.9(1)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

Compound **4** (CCDC 2075596)

Table S3 Crystal data and structure refinement for **4**.

Empirical formula	C29 H60 B10 N4 O2.50 P Si	
Formula weight	671.97	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 33.1770(9) Å	α= 90°.
	b = 10.4724(3) Å	β= 100.412(3)°.
	c = 22.8239(6) Å	γ = 90°.
Volume	7799.4(4) $Å^3$	
Z	8	
Density (calculated)	1.145 Mg/m^3	
Absorption coefficient	1.166 mm^{-1}	
F(000)	2888	
Crystal size	0.160 x 0.090 x 0.060 mm^3	

Theta range for data collection	2.708 to 67.499°.
Index ranges	-31<=h<=39, -12<=k<=12, -27<=l<=27
Reflections collected	53977
Independent reflections	14060 [R(int) = 0.1289]
Completeness to theta = 67.499°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.57714
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14060 / 0 / 882
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.1418
R indices (all data)	R1 = 0.1325, wR2 = 0.1823
Extinction coefficient	n/a
Largest diff. peak and hole	0.506 and -0.340 e.Å^{-3}

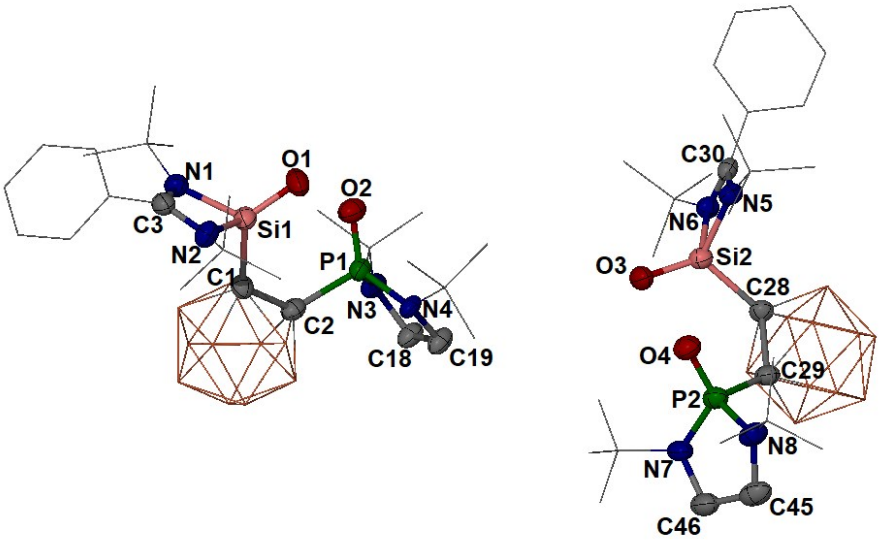


Fig. S2 Molecular Structure of **4**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Bond lengths [Å] and angles [°] for **4**.

Table S4 Crystal data and structure refinement for **4**.

P1-O2	1.456(3)
P1-N3	1.638(3)
P1-N4	1.656(3)
P1-C2	1.899(4)
Si1-O1	1.524(3)
Si1-N2	1.814(3)
Si1-N1	1.820(3)

Si1-C1	1.943(4)
N4-C19	1.474(5)
N1-C3	1.339(5)
N2-C3	1.335(5)
N3-C18	1.476(5)
C1-C2	1.768(5)
C3-C4	1.487(6)
C18-C19	1.544(5)
C4-C5	1.388(6)
Si2-O3	1.524(3)
Si2-N6	1.807(3)
Si2-N5	1.828(3)
Si2-C28	1.937(4)
P2-O4	1.463(3)
P2-N8	1.634(4)
P2-N7	1.673(3)
P2-C29	1.893(4)
N5-C30	1.335(5)
N6-C30	1.334(5)
N7-C46	1.469(5)
N8-C45	1.481(5)
C28-C29	1.733(5)

O2-P1-N3	117.3(2)
O2-P1-N4	121.5(2)
N3-P1-N4	98.0(2)
O2-P1-C2	109.2(2)
N3-P1-C2	104.4(2)
N4-P1-C2	104.5(2)
O1-Si1-N2	118.5(2)
O1-Si1-N1	120.2(2)
N2-Si1-N1	72.5(2)
O1-Si1-C1	122.5(2)
N2-Si1-C1	104.9(2)
N1-Si1-C1	107.1(2)
C19-N4-P1	111.0(3)
C3-N1-Si1	90.0(3)
C3-N2-Si1	90.4(3)
C18-N3-P1	111.2(3)

C2-C1-Si1	126.0(2)
N2-C3-N1	107.0(4)
N2-C3-C4	126.1(4)
N1-C3-C4	126.6(4)
C1-C2-P1	124.3(2)
N3-C18-C19	107.2(3)
N4-C19-C18	108.9(3)
C5-C4-C3	124.2(4)
O3-Si2-N6	116.2(2)
O3-Si2-N5	123.0(2)
N6-Si2-N5	72.0(1)
O3-Si2-C28	121.4(2)
N6-Si2-C28	105.2(2)
N5-Si2-C28	107.8(2)
O4-P2-N8	117.7(2)
O4-P2-N7	121.9(2)
N8-P2-N7	98.7(2)
O4-P2-C29	108.0(2)
N8-P2-C29	104.3(2)
N7-P2-C29	104.2(2)
C30-N5-Si2	90.4(2)
C30-N6-Si2	91.3(2)
N6-C30-N5	106.3(3)
N6-C30-C31	127.5(4)
N5-C30-C31	126.0(3)
C46-N7-C51	115.6(3)
C46-N7-P2	109.2(3)
C45-N8-P2	109.4(3)
C29-C28-Si2	124.6(3)
C28-C29-P2	121.7(3)
N8-C45-C46	107.9(4)
N7-C46-C45	109.9(4)

Symmetry transformations used to generate equivalent atoms:

Compound **5** (CCDC 2075600)

Table S5 Crystal data and structure refinement for **5**.

Empirical formula	C27 H55 B10 N4 O P Si	
Formula weight	618.91	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 19.7759(5) Å	α= 90°.
	b = 9.9587(2) Å	β= 98.741(2)°.
	c = 37.0968(11) Å	γ = 90°.
Volume	7221.1(3) $Å^3$	
Z	8	
Density (calculated)	1.139 Mg/m^3	
Absorption coefficient	1.188 mm^{-1}	
F(000)	2656	
Crystal size	0.260 x 0.180 x 0.100 mm^3	
Theta range for data collection	2.410 to 67.500°.	
Index ranges	-23<=h<=22, -9<=k<=11, -29<=l<=44	
Reflections collected	13276	
Independent reflections	6495 [R(int) = 0.0356]	
Completeness to theta = 67.500°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63761	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6495 / 0 / 409	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1135	
R indices (all data)	R1 = 0.0620, wR2 = 0.1277	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.300 and -0.348 $e.Å^{-3}$	

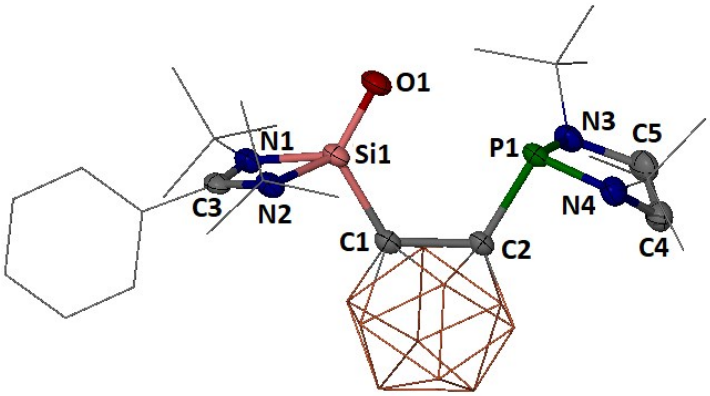


Fig. S3 Molecular Structure of **5**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table S6 Bond lengths [Å] and angles [°] for **5**.

P1-N4	1.677(2)
P1-N3	1.717(2)
P1-C2	1.949(2)
Si1-O1	1.524(1)
Si1-N2	1.814(2)
Si1-N1	1.827(2)
Si1-C1	1.930(2)
N1-C3	1.339(3)
N3-C5	1.481(3)
N4-C4	1.468(3)
C3-N2	1.341(3)
C2-C1	1.739(3)
C4-C5	1.515(3)

N4-P1-N3	94.5(1)
N4-P1-C2	100.0(1)
N3-P1-C2	98.9(1)
O1-Si1-N2	122.1(1)
O1-Si1-N1	121.2(1)
N2-Si1-N1	72.5(1)
O1-Si1-C1	120.2(1)
N2-Si1-C1	105.3(1)
N1-Si1-C1	105.5(1)

C5-N3-P1	110.7(1)
C4-N4-P1	111.1(2)
N1-C3-N2	106.9(2)
C3-N2-Si1	90.6(1)
C1-C2-P1	117.8(1)
N3-C5-C4	108.2(2)

Symmetry transformations used to generate equivalent atoms:

Compound **6** (CCDC 2075599)

Table S7 Crystal data and structure refinement for **6**.

Empirical formula	C28 H55 B10 N4 O3 P Si	
Formula weight	662.92	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.7706(2) Å	α= 90°.
	b = 22.3265(4) Å	β= 103.718(2)°.
	c = 17.6158(4) Å	γ = 90°.
Volume	3733.15(14) $Å^3$	
Z	4	
Density (calculated)	1.179 Mg/m^3	
Absorption coefficient	1.224 mm^{-1}	
F(000)	1416	
Crystal size	0.260 x 0.210 x 0.130 mm^3	
Theta range for data collection	3.254 to 67.495°.	
Index ranges	-11<=h<=9, -25<=k<=26, -21<=l<=21	
Reflections collected	14627	
Independent reflections	6729 [R(int) = 0.0377]	
Completeness to theta = 67.496°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92297	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6729 / 0 / 436	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1013	
R indices (all data)	R1 = 0.0601, wR2 = 0.1147	

Extinction coefficient	n/a
Largest diff. peak and hole	0.369 and -0.276 e.Å^{-3}

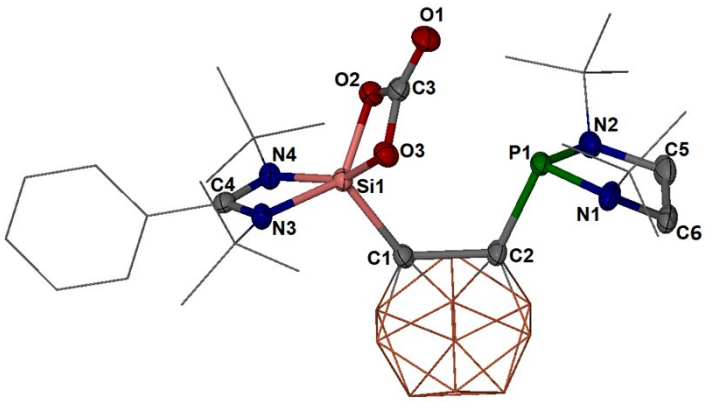


Fig. S4 Molecular Structure of **6**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Bond lengths [Å] and angles [°] for **6**.

Table S8 Bond lengths [Å] and angles [°] for **6**.

P1-N1	1.684(2)
P1-N2	1.708(2)
P1-C2	1.932(2)
Si1-O2	1.718(1)
Si1-O3	1.770(1)
Si1-N3	1.811(2)
Si1-N4	1.874(2)
Si1-C1	1.939(2)
Si1-C3	2.217(2)
Si1-C4	2.288(2)
O1-C3	1.194(2)
O2-C3	1.362(2)
O3-C3	1.340(2)
N3-C4	1.348(3)
N1-C6	1.472(3)
C4-N4	1.325(3)
N2-C5	1.483(3)
C5-C6	1.516(4)
C1-C2	1.738(3)

N1-P1-N2	95.4(1)
N1-P1-C2	98.8(1)

N2-P1-C2	101.2(1)
O2-Si1-O3	75.0(1)
O2-Si1-N3	132.7(1)
O3-Si1-N3	98.2(1)
O2-Si1-N4	94.8(1)
O3-Si1-N4	154.7(1)
N3-Si1-N4	71.4(1)
O2-Si1-C1	117.5(1)
O3-Si1-C1	102.1(1)
N3-Si1-C1	109.8(1)
N4-Si1-C1	103.2(1)
O2-Si1-C3	37.9(1)
O3-Si1-C3	37.2(1)
N3-Si1-C3	120.2(1)
N4-Si1-C3	128.3(1)
C1-Si1-C3	115.8(1)
O2-Si1-C4	116.6(1)
O3-Si1-C4	129.7(1)
N3-Si1-C4	36.1(1)
N4-Si1-C4	35.4(1)
C1-Si1-C4	111.8(1)
C3-Si1-C4	132.4(1)
C3-O2-Si1	91.3(1)
C3-O3-Si1	89.9(1)
C4-N3-Si1	91.6(1)
C6-N1-P1	109.4(2)
N4-C4-N3	107.2(2)
N4-C4-Si1	55.0(1)
N3-C4-Si1	52.3(1)
C4-N4-Si1	89.6(1)
O1-C3-O3	129.3(2)
O1-C3-O2	126.9(2)
O3-C3-O2	103.7(2)
O1-C3-Si1	176.8(2)
O3-C3-Si1	53.0(1)
O2-C3-Si1	50.8(1)
C5-N2-P1	110.8(2)
C2-C1-Si1	123.9(1)
C1-C2-P1	117.0(1)

N2-C5-C6	107.9(2)
N1-C6-C5	107.6(2)

Symmetry transformations used to generate equivalent atoms:

Compound **7** (CCDC 2075597)

Table S9 Crystal data and structure refinement for **7**.

Empirical formula	C28 H55 B10 N4 O3 P Si	
Formula weight	662.92	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.6462(7) Å	α= 90°.
	b = 15.4729(5) Å	β= 117.670(6)°.
	c = 16.1445(7) Å	γ = 90°.
Volume	3682.7(3) $Å^3$	
Z	4	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	1.241 mm^{-1}	
F(000)	1416	
Crystal size	0.230 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.998 to 67.500°.	
Index ranges	-15<=h<=19, -18<=k<=15, -19<=l<=19	
Reflections collected	18908	
Independent reflections	6629 [R(int) = 0.0619]	
Completeness to theta = 67.500°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.47626	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6629 / 15 / 467	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1333	
R indices (all data)	R1 = 0.0746, wR2 = 0.1546	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.481 and -0.358 $e.Å^{-3}$	

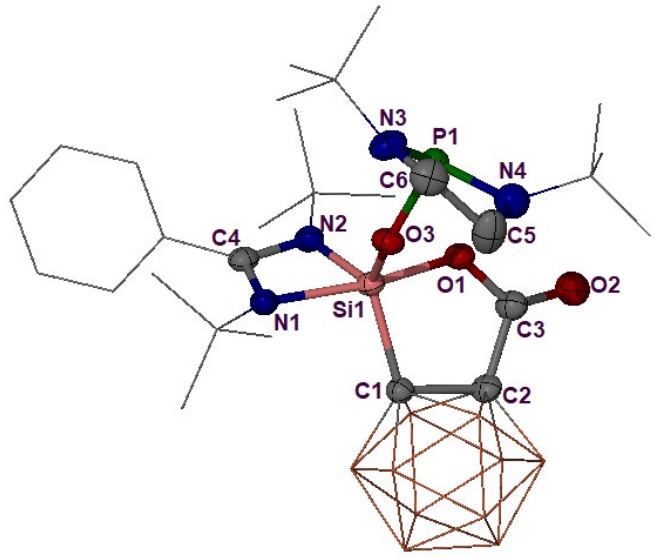


Fig. S5 Molecular Structure of **7**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Bond lengths [Å] and angles [°] for **7**.

Table S10 Bond lengths [Å] and angles [°] for **7**.

P1-O3	1.666(2)
P1-N4	1.679(2)
P1-N3	1.697(2)
Si1-O3	1.624(1)
Si1-O1	1.773(2)
Si1-N2	1.796(2)
Si1-C1	1.937(3)
Si1-N1	1.944(2)
O1-C3	1.314(3)
O2-C3	1.200(3)
N1-C4	1.314(3)
C1-C2	1.652(3)
N2-C4	1.371(3)
C3-C2	1.515(4)
N3-C6	1.470(3)
C6-C5	1.516(4)
N4-C5	1.469(4)
O3-P1-N4	99.8(1)
O3-P1-N3	97.9(1)

N4-P1-N3	94.1(1)
O3-Si1-O1	94.2(1)
O3-Si1-N2	120.2(1)
O1-Si1-N2	97.4(1)
O3-Si1-C1	120.6(1)
O1-Si1-C1	88.2(1)
N2-Si1-C1	118.3(1)
O3-Si1-N1	92.2(1)
O1-Si1-N1	167.8(1)
N2-Si1-N1	70.5(1)
C1-Si1-N1	97.5(1)
C3-O1-Si1	123.9(2)
Si1-O3-P1	134.7(1)
C4-N1-Si1	88.8(2)
C2-C1-Si1	106.2(2)
C4-N2-Si1	93.4(2)
O2-C3-O1	125.5(2)
O2-C3-C2	122.4(2)
O1-C3-C2	112.1(2)
C6-N3-P1	112.5(2)
N1-C4-N2	107.1(2)
C3-C2-C1	109.5(2)
N3-C6-C5	105.9(2)
C5-N4-P1	109.0(2)
N4-C5-C6	107.3(2)

Symmetry transformations used to generate equivalent atoms:

B. References

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