Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Synthesis, structure and reactivity of an imine-stabilized carboranylphosphorus(I) compound

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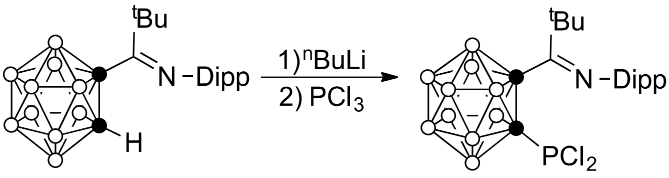
General Procedures. All operations were carried out under a dry argon atmosphere with standard Schlenk and glovebox techniques. ^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400, 100, 128 and 162 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3 \cdot OEt_2$ (0.00 ppm) for boron chemical shifts and to external 85% H_3PO_4 (0.00 ppm) for phosphorus chemical shifts. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Elemental analyses were performed by MEDAC Ltd, U.K., or the Shanghai Institute of Organic Chemistry, CAS, China. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Compounds (Dipp)N=C(^{t}Bu)Cl (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$),[1] 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene,[2] **1**[3] and LiN(TMS)$_2$ were prepared according to literature procedures. All other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified.



1 **2**

○ = BH
● = C

Preparation of 2. To an ether solution (20 mL) of **1** (0.93 g, 2.4 mmol) was slowly added via syringe a hexane solution of n-BuLi (1.6 M, 1.5 mL, 2.4 mmol) at 0 °C under stirring. The reaction mixture was allowed to warm up to room temperature and stirred overnight. PCl_3 (0.25 mL, 2.9 mmol) was then added via syringe at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 4 hours. After removal of precipitate by filtration, the filtrate was concentrated to about 5 mL, to which was added n-hexane (2 mL). Compound **2** was isolated as pale yellow crystals after the solution stood at room temperature overnight (0.94 g, 80 %). ^{1}H NMR (400 MHz, C_6D_6): δ 0.92 (s, 9H; C*Me*$_3$), 1.05 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 1.18 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 2.56 (m, 2H; C*H*Me$_2$), 6.94 (m, 3H; aromatic C*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 23.9, 26.2, 26.4, 28.8, 28.9 (C*Me*$_3$, CH*Me*$_2$), 29.9 (*C*HMe$_2$), 45.5 (*C*Me$_3$), 86.0 (d, J_{PC} = 12.8 Hz, cage *C*), 124.5, 126.5, 136.9, 139.5 (aromatic *C*), 167.9 (*C*N), another cage *C* was not observed. ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -10.0 (4B), -7.55 (4B), -1.70 (1B), 0.22 (1B). ^{31}P NMR (162 MHz, C_6D_6): δ 120.5. Anal. Calcd for $C_{19}H_{36}B_{10}Cl_2NP$ (**2**): C 46.72, H 7.43, N 2.87. Found: C 46.76, H 7.71, N 2.91.

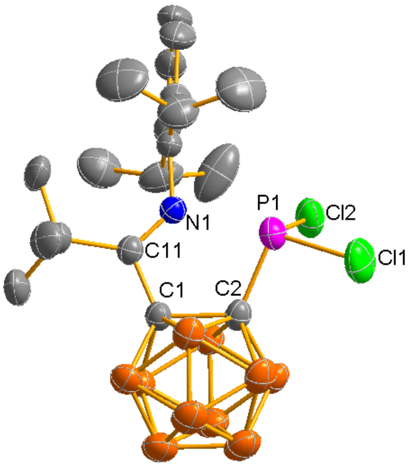
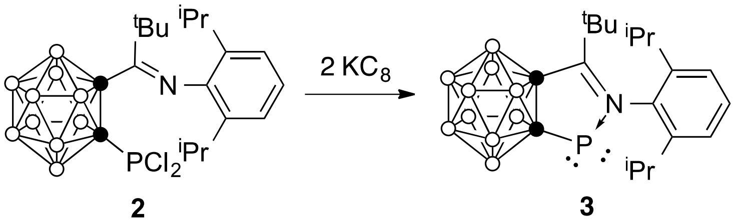


Figure S1. Molecular Structure of **2**.



Preparation of 3. A THF solution (20 mL) of **2** (586 mg, 1.2 mmol) was slowly added to a mixture of KC_8 (324 mg, 2.4 mmol) in THF at room temperature, and the reaction mixture was stirred overnight. The color of the solution was changed to orange yellow. After filtration, the orange yellow filtrate was concentrated to about 5 mL. Compound **3** was isolated as orange yellow crystals after the solution stood at room temperature overnight (400 mg, 80 %). ^{1}H NMR (400 MHz, C_6D_6): δ 1.03 (s, 9H; C*Me*$_3$), 1.08 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 1.18 (d, *J* = 6.4 Hz, 6H; CH*Me*$_2$), 2.66 (m, 2H; C*H*Me$_2$), 6.79 (d, *J* = 7.6 Hz, 2H; aromatic C*H*), 7.00 (t, *J* = 7.6 Hz, 1H; aromatic C*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 23.1, 27.7, 28.3 (C*Me*$_3$, CH*Me*$_2$), 31.0 (*C*HMe$_2$), 45.5 (d, $^4J_{PC}$ = 7.4 Hz, *C*Me$_3$), 86.0 (d, $^1J_{PC}$ = 83.5 Hz, cage *C*), 88.0 (d, $^2J_{PC}$ = 9.7 Hz, cage *C*), 123.1, 124.4, 130.7, 145.1 (aromatic *C*), 161.7 (*C*N). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -12.4 (2B), -10.0 (3B), -8.1 (3B), -6.6 (2B). ^{31}P NMR (162 MHz, C_6D_6): δ 210.5. Anal. Calcd for $C_{19}H_{36}B_{10}NP$ (**3**): C 54.65, H 8.69, N 3.35. Found: 54.46, H 8.39, N 3.05.

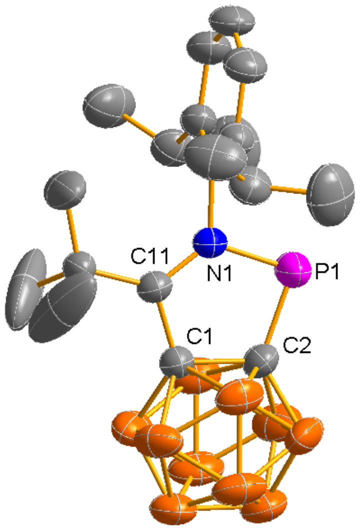
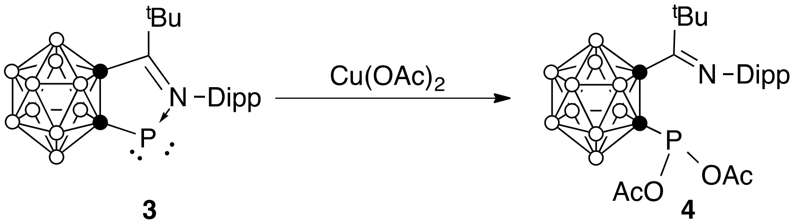


Figure S2. Molecular Structure of **3**.



3 **4**

Preparation of 4. To a THF solution (15 mL) of **3** (41.7 mg, 0.1 mmol) was added Cu(OAc)$_2$ (18.2 mg, 0.1 mmol) at room temperature, and the mixture was stirred at room temperature overnight. The color of solution was changed from orange yellow to deep brown. The ^{31}P NMR spectrum indicated a complete conversion of **3**. After removal of the solvent, the resulting mixture was dissolved in n-hexane (20 mL). After removal of precipitate, the hexane solution was concentrated to about 5 mL. Compound **4** was isolated as colorless crystals after slow evaporation of the solvent at room temperature (37.6 mg, 70 %). ^{1}H NMR (400 MHz, C_6D_6): δ 1.02 (s, 9H; C*Me*$_3$), 1.11 (d, J = 6.4 Hz, 6H; CH*Me*$_2$), 1.36 (d, J = 6.8 Hz, 6H; CH*Me*$_2$), 1.53 (s, 6H; OC*Me*), 2.74 (m, 2H; C*H*Me$_2$), 6.90 (br s, 3H; aromatic C*H*). ^{13}C{^{1}H} (100 MHz, C_6D_6): δ 21.4 (d, $^{3}J_{PC}$ = 3.1 Hz, OC*Me*), 23.7, 26.0, 26.1, 28.7, 28.8 (C*Me*$_3$, CH*Me*$_2$), 29.9 (*C*HMe$_2$), 45.7 (*C*Me$_3$), 83.3 (d, $^{1}J_{PC}$ = 89.3 Hz, cage *C*), 85.0 (d, $^{2}J_{PC}$ = 8.0 Hz, cage *C*), 124.1, 125.3, 129.3, 135.2, 141.3 (aromatic *C*), 165.1 (*C*N), 169.6 (d, $^{2}J_{PC}$ = 10.3 Hz, *C*O). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -10.1 (3B), -7.4 (4B), -0.2 (3B). ^{31}P NMR (162 MHz, C_6D_6): δ 105.8. Anal. Calcd for $C_{23}H_{42}B_{10}NO_4P$ (**4**): C 51.57, H 7.90, N 2.61. Found: 51.78, H 7.90, N 2.61.

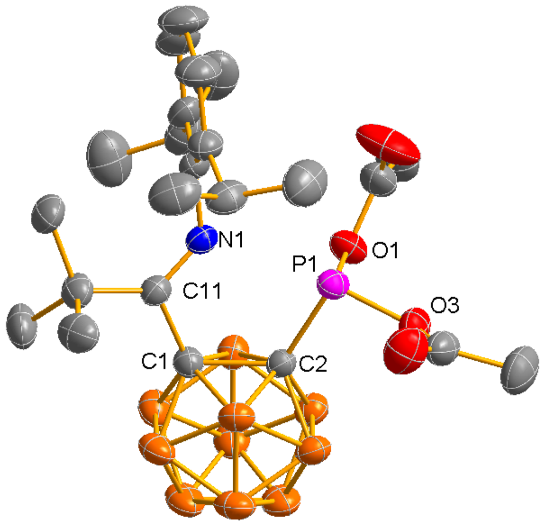
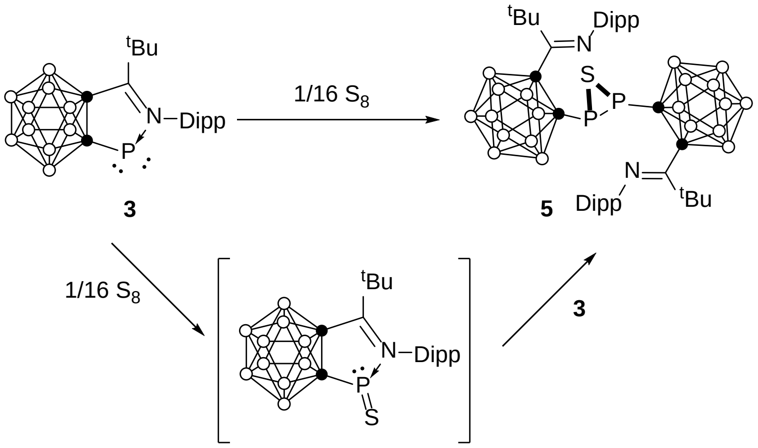


Figure S3. Molecular Structure of **4**.



Preparation of 5. To a THF solution (15 mL) of **3** (83.4 mg, 0.2 mmol) was added S_8 (3.2 mg, 0.0125 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **3**. After removal of solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound **5** was isolated as yellow crystals after slow evaporation of the solvent at room temperature (77.9 mg, 90 %). ^{1}H NMR (400 MHz, C_6D_6): δ 1.03 (s, 18H; C*Me*$_3$), 1.10 (d, *J* = 6.4 Hz, 6H; CH*Me*$_2$), 1.21 (d, *J* = 6.4 Hz, 6H; CH*Me*$_2$), 1.40 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 1.54 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 2.73 (m, 4H; C*H*Me$_2$), 6.95 (m, 4H; aromatic C*H*), 7.00 (m, 2H; aromatic C*H*). ^{13}C{^{1}H} (100 MHz, C_6D_6): δ 23.6, 24.1, 25.7, 27.1, 28.8 (C*Me*$_3$, CH*Me*$_2$), 30.3 (*C*HMe$_2$), 46.0(*C*Me$_3$), 85.8 (cage *C*), 86.2 (cage *C*), 124.0, 124.5, 125.4, 134.2, 134.9, 142.6 (aromatic *C*), 164.9 (*C*N). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -9.8 (8B), -7.9 (8B), -1.7 (4B). ^{31}P NMR (162 MHz, C_6D_6): δ -82.4. Anal. Calcd for $C_{38}H_{72}B_{20}N_2P_2S$ (**5**): C 52.63, H 8.37, N 3.23. Found: C 52.94, H 8.96, N 2.98.

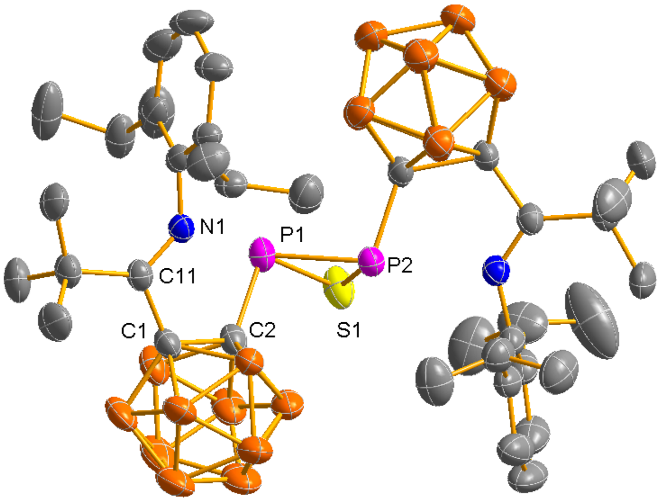
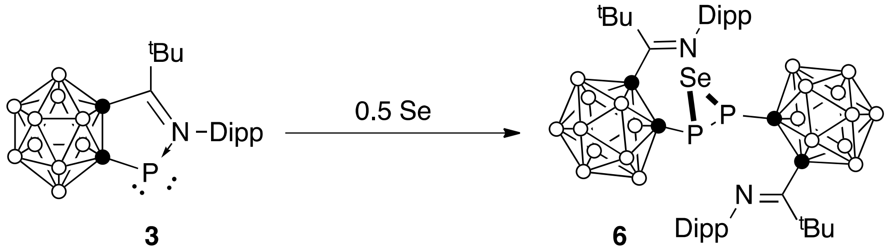


Figure S4. Molecular Structure of **5**.



Preparation of 6. To a THF solution (15 mL) of **3** (41.7 mg, 0.1 mmol) was added Se (4.0 mg, 0.05 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **3**. After removal of the precipitate and solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound **6** was isolated as yellow crystals after slow evaporation of the solvent at room temperature (54.8 mg, 60 %). ^{1}H NMR (400 MHz, C_6D_6): δ 0.99 (s, 18H; CMe_3), 1.04 (d, J = 6.8 Hz, 6H; CHMe_2), 1.16 (d, J = 6.8 Hz, 6H; CHMe_2), 1.31 (d, J = 6.8 Hz, 6H; CHMe_2), 1.48 (d, J = 6.8 Hz, 6H; CHMe_2), 2.67 (m, 2H; CHMe$_2$), 2.73 (m, 2H; CHMe$_2$), 6.89 (d, J = 4.4 Hz, 4H; aromatic CH), 6.95 (t, J = 4.8 Hz, 2H; aromatic CH). ^{13}C{^{1}H} (100 MHz, C_6D_6): δ 23.8, 25.6, 27.2, 28.8, 30.2 (CMe_3, CHMe_2), 30.4 (CHMe$_2$), 46.1(CMe$_3$), 84.6 (d, $^{1}J_{PC}$ = 74.0 Hz, cage C), 87.5 (cage C), 124.0, 124.2, 125.3, 134.3, 134.7, 142.8 (aromatic C), 164.5 (CN). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -9.4 (16B), -2.1 (4B). ^{31}P NMR (162 MHz, C_6D_6): δ -63.8. Anal. Calcd for $C_{38}H_{72}B_{20}N_2P_2Se$ (**6**): C 49.93, H 7.94, N 3.06. Found: C 49.79, H 8.06, N 3.14.

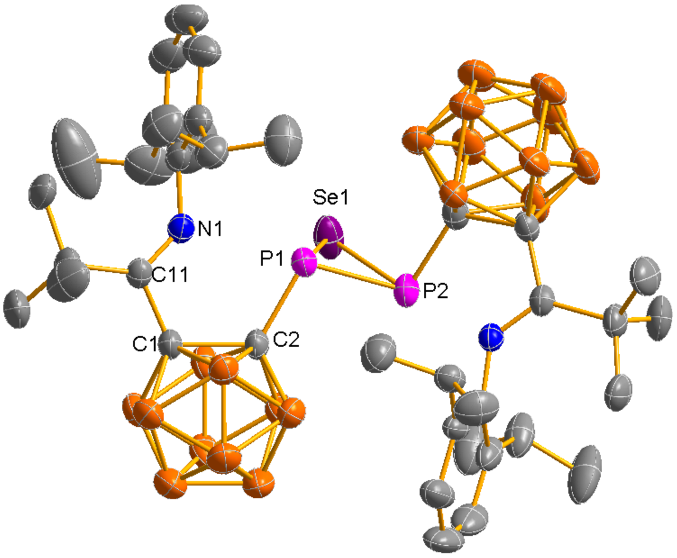
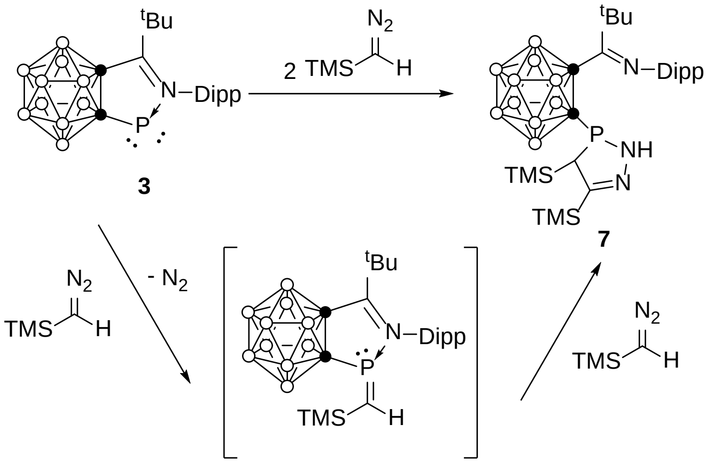


Figure S5. Molecular Structure of **6**.



Preparation of 7. To a THF solution (20 mL) of **3** (41.7 mg, 0.1 mmol) was slowly added a hexane solution of trimethylsilyldiazomethane (2.0 M, 0.1 mL, 0.2 mmol) at room temperature, and the mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **3**. After removal of solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound **7** was isolated as yellow crystals after slow evaporation of the solvent at room temperature (30.8 mg, 50 %). ^{1}H NMR (400 MHz, C_6D_6): δ –0.03 (s, 9H; Si*Me*$_3$), 0.29 (s, 9H; Si*Me*$_3$), 1.10 and 1.12 (s, 12H; C*Me*$_3$ and CH*Me*$_2$), 1.22 (d, *J* = 6.4 Hz, 6H; CH*Me*$_2$), 1.29 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 2.77 (m, 2H; C*H*Me$_2$), 4.44 (s, 1H; C*H*), 6.92 (d, *J* = 3.2 Hz, 2H; aromatic C*H*), 6.97 (d, *J* = 3.6 Hz, 1H; aromatic C*H*). ^{13}C{^{1}H} (100 MHz, C_6D_6): δ -1.84, -1.78, 0.36 (Si*Me*$_3$), 23.2, 23.8, 25.2, 28.1, 28.3 (C*Me*$_3$, CH*Me*$_2$), 30.5 (*C*HMe$_2$), 46.6 (*C*Me$_3$), 60.3 (d, $^{1}J_{PC}$ = 54.0 Hz, *C*H), 87.4 (d, $^{2}J_{PC}$ = 4.0 Hz, cage *C*), 89.7 (d, $^{1}J_{PC}$ = 138.0 Hz, cage *C*), 124.0, 124.3, 124.6 (aromatic *C*H), 133.5 (d, $^{2}J_{PC}$ = 4.0 Hz, TMS*C*=N), 134.2, 134.5, 143.4 (aromatic *C*H), 164.4

(*CN*). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -11.3 (2B), -9.00 (2B), -7.83 (2B), -3.05 (2B), -1.24 (2B). ^{31}P NMR (162 MHz, C_6D_6): δ 14.11. Anal. Calcd for $C_{27}H_{56}B_{10}N_3PSi_2$ (**7**): C 52.47, H 9.13, N 6.80. Found: C 52.79, H 9.06, N 6.64.

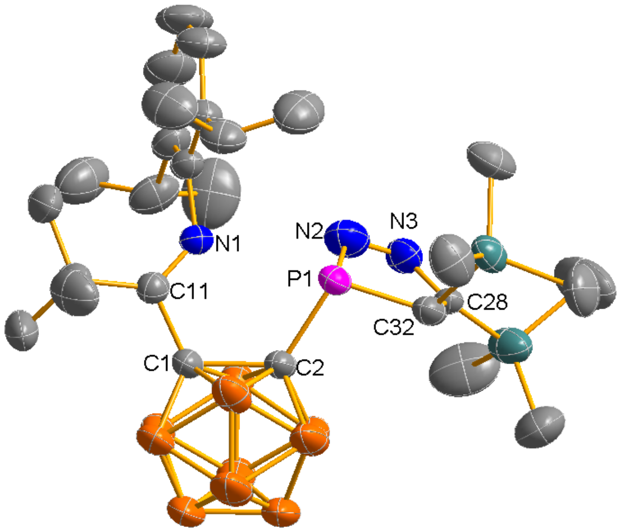
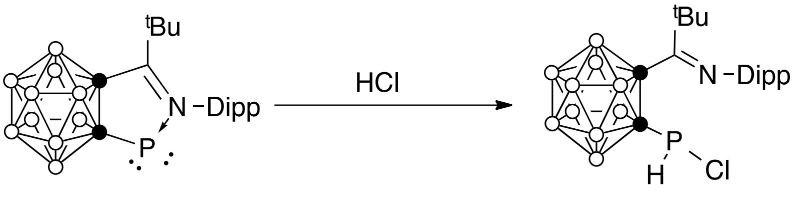


Figure S6. Molecular Structure of **7**.



3 **8**

Preparation of 8. To a THF solution (20 mL) of **3** (83.4 mg, 0.2 mmol) was slowly added via syringe a dioxane solution of HCl (4.0 M, 0.1 mL, 0.4 mmol) at 0 °C under stirring. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The ^{31}P NMR spectrum indicated a complete conversion of **3**. After removal of solvent, the resulting yellow powder was dissolved in toluene (5 mL). Compound **8** was isolated as light yellow crystals after slow evaporation of the solvent at room temperature (38.6 mg, 85 %). ^{1}H NMR (400 MHz, C_6D_6): δ 0.87 (s, 9H; C*Me*$_3$), 0.90 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 0.97 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 1.02 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 1.25 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 2.38 (m, 1H; C*H*Me$_2$), 2.48 (m, 1H; C*H*Me$_2$), 6.23 (d, J_{HP} = 248.4 Hz, 1H; P*H*), 6.76 (d, *J* = 7.2 Hz, 1H; aromatic C*H*), 6.83 (d, *J* = 7.6 Hz, 1H; aromatic C*H*), 6.90 (d, *J* = 7.6 Hz, 1H; aromatic C*H*). ^{13}C{^{1}H} (400 MHz, C_6D_6): δ 22.9, 23.9, 26.0, 26.6, 26.8, 28.2, 29.0 (C*Me*$_3$, CH*Me*$_2$), 29.9 (*C*HMe$_2$), 44.8 (*C*Me$_3$), 78.2 (cage *C*), 83.4 (d, $^{2}J_{PC}$ = 9.3 Hz, cage *C*), 124.2, 125.0, 127.5, 137.5, 138.4 (aromatic *C*), 170.7 (*C*N). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -9.84 (3B), -7.84 (3B), -3.13 (2B), 0.13(2B). ^{31}P NMR (162 MHz, C_6D_6): δ 8.94 (d, J_{PH} = 249.5 Hz). Anal. Calcd for $C_{19}H_{37}B_{10}ClNP$ (**8**): C 50.26, H 8.21, N 3.08. Found: C 49.94, H 8.16, N 2.98.

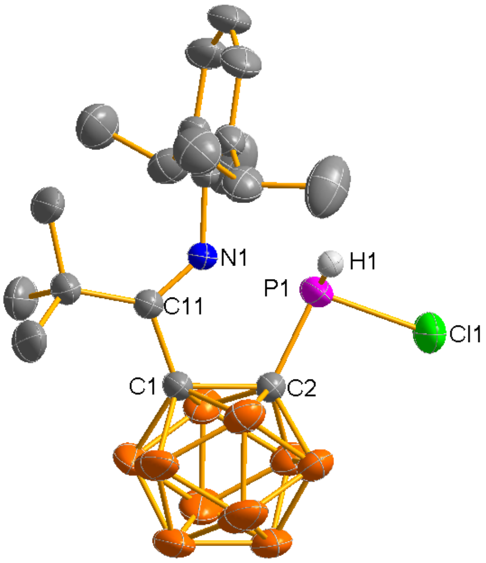
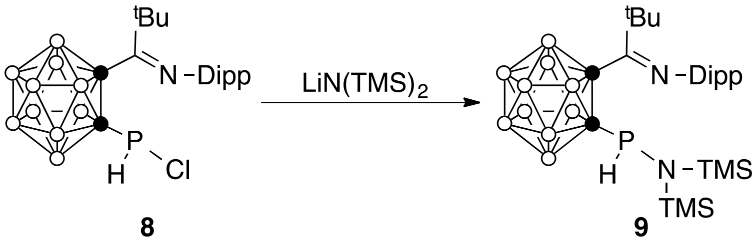


Figure S7. Molecular Structure of **8**.



Preparation of 9. To a toluene solution (15 mL) of **8** (45.4 mg, 0.1 mmol) was added LiN(TMS)$_2$ (16.7 mg, 0.1 mmol) at room temperature, and the mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **8**. After removal of the precipitate and solvent, the resulting pale yellow powder was dissolved in toluene (5 mL). Compound **9** was isolated as pale yellow crystals after slow evaporation of the solvent at room temperature overnight (36.7 mg, 65 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.21 (s, 9H; Si*Me*$_3$), 0.24 (s, 9H; Si*Me*$_3$), 1.15 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 1.22, (s, 9H; C*Me*$_3$), 1.25 (t, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 1.30 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 2.60 (m, 1H; C*H*Me$_2$), 2.72 (m, 1H; C*H*Me$_2$), 5.77 (d, J_{HP} = 255.6 Hz, 1H; P*H*), 7.07 (m, 3H; aromatic C*H*). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 3.5, 3.6, 4.0 (Si*Me*$_3$), 22.6, 24.0, 26.0, 27.8, 27.9, 28.3, 28.4 (C*Me*$_3$, CH*Me*$_2$), 30.5 (*C*HMe$_2$), 46.0 (d, $^{3}J_{PC}$ = 2.1 Hz, *C*Me$_3$), 87.7 (d, $^{1}J_{PC}$ = 119.8 Hz, cage *C*), 89.0 (d, $^{2}J_{PC}$ = 7.2 Hz, cage *C*), 123.4, 124.3, 124.4, 135.0, 135.2, 142.3 (aromatic *C*), 164.6 (*C*N). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ -12.13 (2B), -9.09 (4B); -4.24 (2B), -1.98 (2B). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 37.6 (d, J_{PH} = 255.6 Hz.). Anal. Calcd for $C_{25}H_{55}B_{10}N_2PSi_2$ (**9**): C 60.13, H 7.93, N 4.01. Found: C 59.86, H 7.58, N 3.84.

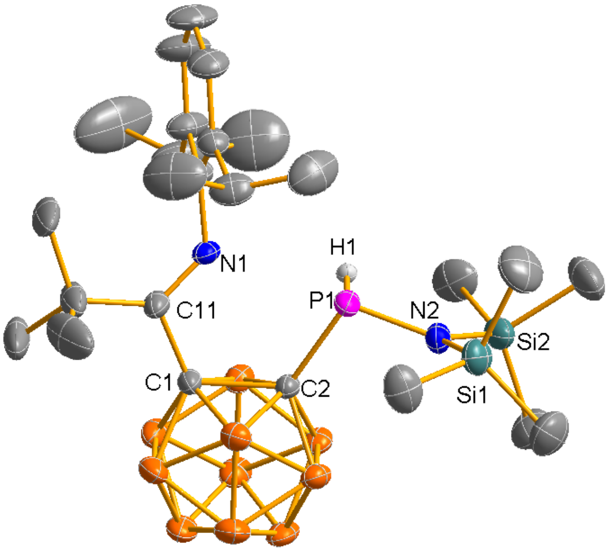
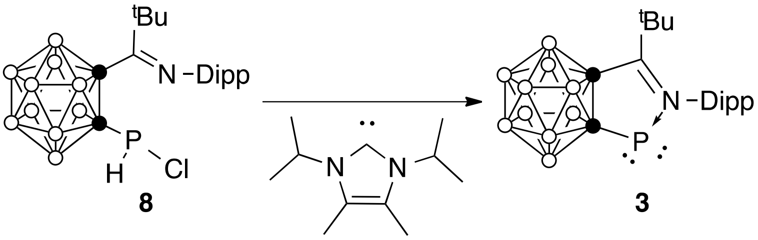


Figure S8. Molecular Structure of **9**.



Reaction of 8 with NHC carbene. To a toluene solution of **8** (45.4 mg, 0.1 mmol) was added 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene (18.0 mg, 0.1 mmol) at room temperature, and the mixture was stirred at room temperature overnight. The ^{31}P NMR spectrum indicated a complete conversion of **8**. After removal of solvent and extraction with n-hexane, the orange solution was concentrated to about 5 mL. Orange crystals (25.1 mg, 60 %) were obtained after the solution stood at room temperature overnight, which was identified as **3** by ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR.

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 K on a Bruker D8 venture diffractometer or a Bruker Kappa ApexII Duo diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[4] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[5] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Table S1. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 1460826-1460833 for **2** - **9**.

Table S1. Crystal Data and Summary of Data Collection and Refinement for **2-9**

Compound	**2**	**3**	**4**	**5**
Formula	$C_{19}H_{36}B_{10}Cl_2NP$	$C_{19}H_{36}B_{10}NP$	$C_{23}H_{42}B_{10}NO_4P$	$C_{38}H_{72}B_{20}N_2P_2S$
MW	488.46	417.56	535.65	867.18
Crystal size (mm^3)	0.40×0.30×0.20	0.50×0.40×0.30	0.50×0.40×0.30	0.50×0.40×0.30
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space Group	$P2_1/c$	*P*nma	*P*-1	*P*-1
a, Å	9.878(1)	17.159(3)	10.309(1)	10.177(1)
b, Å	19.210(1)	13.438(3)	10.919(1)	10.421(1)
c, Å	16.230(1)	11.014(2)	16.065(1)	25.259(2)
α, deg	90	90	80.33(1)	101.48(1)
β, deg	101.76(1)	90	73.80(1)	99.64(1)
γ, deg	90	90	74.73(1)	90.28(1)
V, Å^3	3015.0 (2)	2539.7(9)	1666.4(1)	2586.2(2)
Z	4	4	2	2
D_{calcd} mg/m^3	1.076	1.092	1.068	1.114
Radiation (Å)	0.71073	0.71073	0.71073	0.71073
2θrange, deg	3.32 to 50.50	4.40 to 50.50	2.66 to 50.50	4.62 to 50.50
μ, mm^{-1}	0.278	0.116	0.110	0.155
F(000)	1024	888	568	920
No. of obsd reflns	5450	2405	5994	9363
No. of params refnd	298	157	352	568
Goodness of fit	1.077	1.021	1.089	1.038
R1	0.0378	0.0728	0.0435	0.0440
wR2	0.1040	0.1884	0.1312	0.1208

Compound	**6**	**7**	**8**	**9**
Formula	$C_{38}H_{72}B_{20}N_2P_2Se$	$C_{27}H_{56}B_{10}N_3PSi_2$	$C_{19}H_{37}B_{10}ClNP$	$C_{25}H_{55}B_{10}N_2PSi_2$
MW	914.07	617.99	454.01	578.96
Crystal size (mm^3)	0.50×0.40×0.30	0.50×0.40×0.30	0.50×0.40×0.30	0.40×0.30×0.20
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space Group	P-1	Pbca	Pnma	$P2_1$/c
a, Å	10.214(1)	18.683(1)	17.441(1)	17.440(2)
b, Å	10.414(1)	13.262(1)	13.689(1)	12.404(1)
c, Å	25.274 (2)	31.513(2)	10.898(1)	18.529(2)
α, deg	101.61(2)	90	90	90
β, deg	99.76(2)	90	90	115.89(3)
γ, deg	90.64(2)	90	90	90
V, Å^3	2592.4(2)	7808.2(7)	2601.9(1)	3606.2(5)
Z	2	8	4	4
D_{calcd} mg/m^3	1.171	1.051	1.159	1.066
Radiation (Å)	0.71073	0.71073	0.71073	0.71073
2θ range, deg	4.64 to 50.50	3.38 to 50.50	4.41 to 50.50	2.60 to 50.49
μ, mm^{-1}	0.816	0.154	0.218	0.162
F(000)	956	2656	960	1248
No. of obsd reflns	9397	7065	2447	6528
No. of params refnd	568	396	176	365
Goodness of fit	1.072	1.015	1.030	1.117
R1	0.0396	0.0601	0.0467	0.0758
wR2	0.1170	0.1450	0.1152	0.2035

Computational Details. The geometry optimization of compound **3** was performed using the Gaussian09 program, Revision D.01,[6] at the B3LYP[7] theoretical level using 6-311+g(d,p) basis set. Frequency calculations were made to determine the characteristics of all stationary points as energy minima. Orbital energies of compound **3** were calculated at the B3LYP/6-31g(d) level of theory. NBO analysis at the B3LYP/6-31g(d,p) level of theory was carried out using the NBO program implemented in the Gaussian 09 package. The graphics of the molecular orbitals were produced by using the visualizing software VMD.[8]

Table S2. The Cartesian coordinates of compound **3**

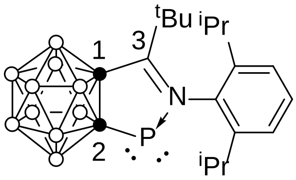
0 1

P	-1.88881300	0.22005300	0.00000000
N	-0.24377100	-0.39303900	0.00000000
C	-1.20789700	1.92512000	0.00000000
C	0.84505400	0.38841200	0.00000000
C	-0.29457200	-1.86240000	0.00000000
C	0.44035100	1.85027900	0.00000000
B	-0.37483400	2.37759500	1.46194200
B	-0.37483400	2.37759500	-1.46194200
B	-1.80507700	3.25284800	0.89421900
B	-1.80507700	3.25284800	-0.89421900
C	2.32574200	-0.06949700	0.00000000
C	-0.38907900	-2.53141500	1.23581200
C	-0.38907900	-2.53141500	-1.23581200
B	1.06548400	3.22393200	0.89527700
B	1.06548400	3.22393200	-0.89527700
H	-0.39717000	1.61382900	2.35773600
B	-0.35981800	4.13079900	1.44230300
H	-0.39717000	1.61382900	-2.35773600
B	-0.35981800	4.13079900	-1.44230300
H	-2.81379900	3.10029100	1.48791000
B	-1.25648800	4.68164000	0.00000000
H	-2.81379900	3.10029100	-1.48791000
C	3.22672822	1.05515256	0.57444371
C	2.78066134	-0.38724291	-1.44868365
C	2.64351393	-1.33261286	0.83047913

C	-0.52499200	-3.92250600	1.20252700
C	-0.37435600	-1.81658600	2.58546500
C	-0.52499200	-3.92250600	-1.20252700
C	-0.37435600	-1.81658600	-2.58546500
H	2.06501300	3.13173700	1.50450300
B	0.53830100	4.65700700	0.00000000
H	2.06501300	3.13173700	-1.50450300
H	-0.34368600	4.70889900	2.47332200
H	-0.34368600	4.70889900	-2.47332200
H	-1.88335400	5.68381400	0.00000000
H	4.25185046	0.68157736	0.64401137
H	2.90767479	1.34929345	1.57727202
H	3.24044517	1.94090404	-0.05300283
H	3.79749939	-0.78760576	-1.41668879
H	2.13810339	-1.13918165	-1.91310366
H	2.79237378	0.49202678	-2.08522166
H	3.71542845	-1.51766156	0.72607041
H	2.43673260	-1.21351830	1.89122361
H	2.12516048	-2.22101347	0.47809449
H	-0.59459500	-4.46982700	2.13502600
C	-0.58337800	-4.61477700	0.00000000
H	-0.17560200	-0.75866100	2.40860200
C	0.72896200	-2.34556900	3.52227900
C	-1.75069000	-1.91212000	3.27316700
H	-0.59459500	-4.46982700	-2.13502600
H	-0.17560200	-0.75866100	-2.40860200
C	0.72896200	-2.34556900	-3.52227900
C	-1.75069000	-1.91212000	-3.27316700
H	1.20645300	5.63250400	0.00000000
H	-0.68921000	-5.69391600	0.00000000
H	1.71995600	-2.28505800	3.06652700
H	0.55527700	-3.38764800	3.80416700
H	0.74776900	-1.75652200	4.44347800
H	-2.53667300	-1.49580300	2.64057300
H	-1.74101300	-1.35502900	4.21442500

H	-2.00705000	-2.95082400	3.50148400
H	1.71995600	-2.28505800	-3.06652700
H	0.55527700	-3.38764800	-3.80416700
H	0.74776900	-1.75652200	-4.44347800
H	-2.53667300	-1.49580300	-2.64057300
H	-1.74101300	-1.35502900	-4.21442500
H	-2.00705000	-2.95082400	-3.50148400

Table S3. Selected experimental and calculated structural parameters of **3** (calculated at the B3LYP/6-311+G(d,p) level of theory)

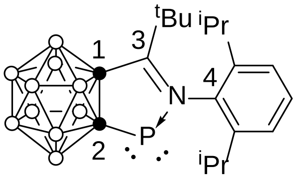


3

Bond length (Å)	Experimental	Calculated
C1-C2	1.637(5)	1.646
C2-P	1.811(4)	1.839
P-N	1.718(3)	1.758
N-C3	1.337(5)	1.341
C3-C1	1.506(6)	1.508

Bond angle (^{o})	Experimental	Calculated
C1-C2-P	108.9(3)	108.7
C2-P-N	89.4(2)	88.8
P-N-C3	123.9(3)	123.4
N-C3-C1	109.8(3)	110.4
C3-C1-C2	108.0(3)	108.6

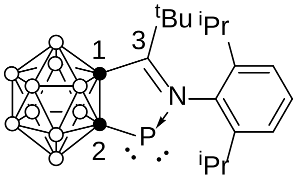
Table S4. Results of the NBO Analyses



3

		Occupancy	Coefficients	
C3-C1	σ	1.97	0.6730* C3	0.7397* C1
C3-C(tBu)	σ	1.97	0.7184* C3	0.6956* C(tBu)
C3-N	σ	1.98	0.6080* C3	0.7939* N
	π	1.95	0.5811* C3	0.8138* N
C4-N	σ	1.98	0.6021* C4	0.7984* N
P-N	σ	1.96	0.4547* P	0.8906* N
P-C2	σ	1.93	0.5211* P	0.8535* C2
C1-C2	σ	1.74	0.7047* C1	0.7095* C2

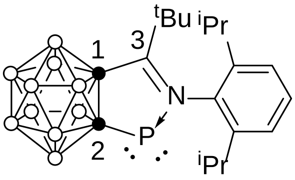
Table S5. Results of the selected Wiberg bonding index



3

Bond	Bonding Index
C1-C2	0.7398
C2-P	0.8151
P-N	0.8603
N-C3	1.4073
C3-C1	1.0245

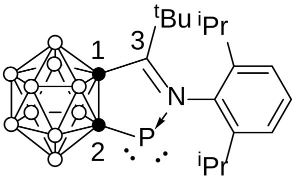
Table S6. Result of the selected Mulliken charges



3

Atom	Mulliken Charge
C1	-0.2709
C2	-0.3492
P	0.2609
N	-0.6247
C3	0.3626

Table S7. Result of the selected NBO charges



3

Atom	NBO Charge
C1	-0.717
C2	-0.363
P	0.628
N	-0.574
C3	0.285

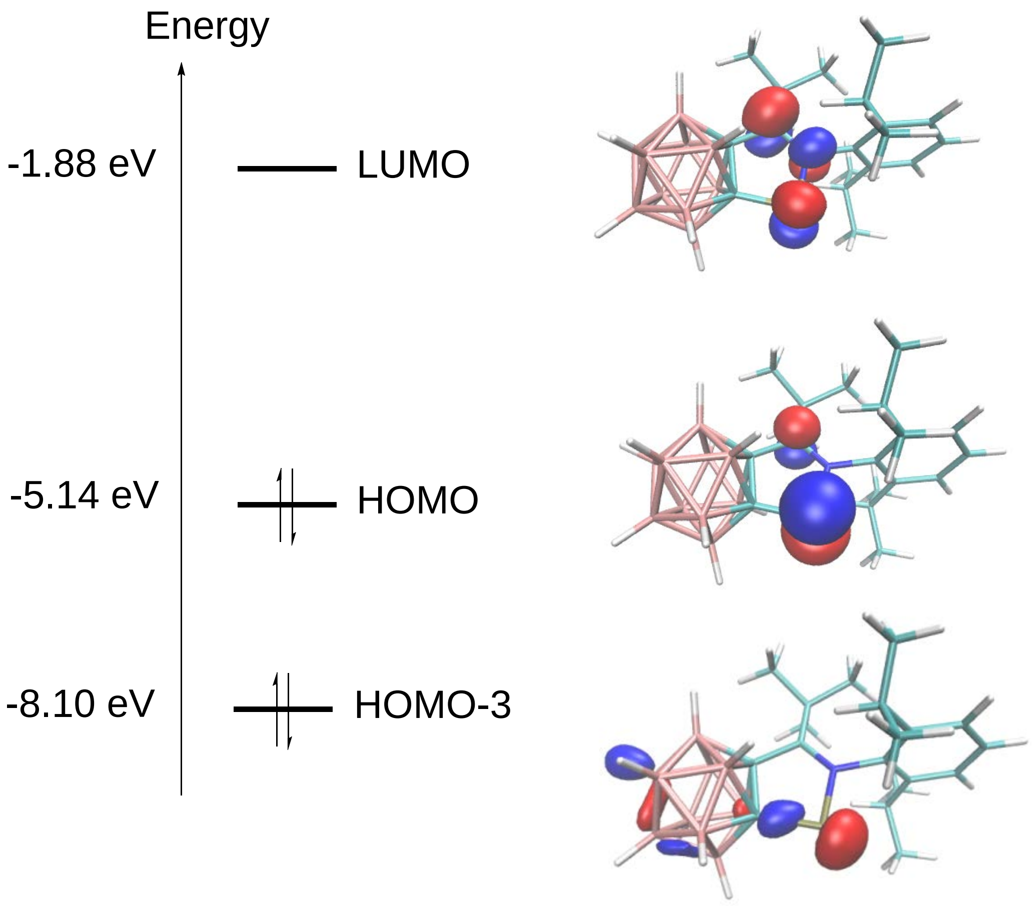


Figure S9. Plots of the HOMO-3, HOMO and LUMO orbitals of **3** calculated at the B3LYP/6-31G(d) level of theory. HOMO-3 and HOMO orbitals display the orbital features of two lone pair orbitals on the phosphorus atom and LUMO orbital shows the orbital features of an allyl-like PNC moiety.

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