Electronic Supplementary Material (ESI) for ChemComm.

Supporting Material

for

Synthesis of Vinyl Germylenes

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Experimental details:

General Remarks: All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen using either Schlenk techniques or a glove box. Solvents were dried using a column solvent purification system.[1]

The following compounds were prepared using published procedures: $(Me_3Si)_3SiK$,[2,3] $GeCl_2 \cdot$dioxane,[4] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (MeIiPr).[5] All other chemicals were bought from different suppliers and were used without further purification.

^1H (299.9 MHz), ^{13}C (75.4 MHz), ^{29}Si (59.3 MHz), and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. All samples were either dissolved in deuterated benzene, or in case of ^{29}Si NMR reaction control experiments measured with a D_2O capillary in order to provide an external lock frequency signal. The INEPT pulse sequence was used to enhance ^{29}Si NMR signals.[6,7]

X-Ray structure determination: For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F^2_o and corrected for absorption effects with SAINT[8] and SADABS[9,10], respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).[11]

If not noted otherwise all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **1a**, **2**, **3**, **4**, **5**, and **6** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 976691 (**1a**), 969564 (**2**), 969563 (**3**), 969566 (**4**), 1008594 (**5**), and 969567 (**6**). Copies of the data can be obtained free of charge at: http://www.ccdc.cam.ac.uk/products/csd/request/.

Bis[tris(trimethylsilyl)silyl]germylene·[:C{N(*i*Pr)C(Me)}$_2$] (1a)

A solution of tris(trimethylsilyl)silyl potassium (1.56 mmol) in THF (40 mL) was slowly added dropwise to a vigorously stirred solution of $GeCl_2$·dioxane (180 mg; 0.78 mmol) and 1,3-diisopropylo-4,5-dimethylimidazol-2-ylidene (140 mg, 0.78 mmol) in THF (20 mL) at -30 °C. Stirring of the reaction mixture was continued for 14 h at rt. The solvent was removed under reduced pressure and the product was extracted with pentane (3 x 20 mL). The solvent was removed to yield **1a** as an orange solid (469 mg; 80 %). Crystallization from toluene at -35 °C gave orange crystals suitable for X-ray study. Mp = 108-110 °C. ^{1}H NMR (δ in ppm): 6.56 (br, 1H, C*H*(CH$_3$)), 5.73 (br, 1H, C*H*(CH$_3$)), 1.55 (s, 6H, NHC-C*H*$_3$), 1.30 (br, 12H, CH(C*H*$_3$)), 0.41 (s, 54H, Si*Me*$_3$). ^{1}H NMR (δ in ppm, toluene-d$_8$, -20 °C): 6.55 (m, 1H, C*H*(CH$_3$)), 5.58 (m, 1H, C*H*(CH$_3$)), 1.55 (s, 3H, NHC-C*H*$_3$), 1.49 (s, 3H, NHC-C*H*$_3$), 1.24 (d, 6H, CH(C*H*$_3$), ^3J=7.0 Hz), 1.05 (d, 6H, CH(C*H*$_3$), ^3J=6.9 Hz), 0.37 (s, 54H, Si*Me*$_3$). ^{13}C NMR (δ in ppm): 173.2 (N-C-N), 126.5 (Me*C*=*C*Me), 54.8 (*C*H(CH$_3$)), 52.3 (*C*H(CH$_3$)), 22.7 (CH(*C*H$_3$)), 21.7 (CH(*C*H$_3$)), 10.0 (NHC-*C*H$_3$), 4.7 (Si*Me*$_3$). ^{29}Si NMR (δ in ppm): -8.8 (*Si*Me$_3$), -122.9 (*Si*(SiMe$_3$)$_3$). Anal. calcd for $C_{29}H_{74}GeN_2Si_8$ (748.23): C 46.55, H 9.97, N 3.74. Found: C 46.84, H 9.65, N 3.89.

Bis[tris(trimethylsilyl)silyl]germylene·PMe$_3$ (1b)

A solution of tris(trimethylsilyl)silyl potassium (0.62 mmol) in THF (2 mL) was slowly added dropwise to a vigorously stirred solution of $GeCl_2$·dioxane (72 mg, 0.31 mmol) and trimetylphosphine (23 mg, 0.31 mmol) in THF (2 mL) at -30°C. Full conversion was detected by ^{29}Si NMR after 15 minutes. Compound **1b** was used without further purification. An approximate yield of 60 % was estimated by comparing the SiMe$_3$ ^{1}H signal of **1b** to the SiMe$_3$ ^{1}H signal of Me$_3$SiOtBu which is present in the solution from the formation of tris(trimethylsilyl)silyl potassium. ^{1}H NMR (δ in ppm, D$_2$O capillary): 1.37 (s, 9H, P*Me*$_3$), 0.43 (s, 54H, Si*Me*$_3$). ^{29}Si NMR (δ in ppm, D$_2$O capillary): -8.7 (d, *Si*Me$_3$, $^3J_{Si\text{-}P}$ = 11 Hz), -119.9 (*Si*(SiMe$_3$)$_3$, $^2J_{Si\text{-}P}$ = 15 Hz). ^{31}P NMR (δ in ppm, D$_2$O capillary): -20.1 (*P*Me$_3$).

1,1-Bis[tris(trimethylsilyl)silyl]-2,3-diphenyl-1-germacyclopropene (2)

Diphenylacetylene (138 mg, 0.76 mmol) was added to the solution of **1b** (0.78 mmol) in THF (10 mL) at rt and stirred for 12 h. The solvent was removed under reduced pressure and product was extracted with pentane (3 x 5 mL). The solvent was removed to yield **2** as an orange solid (248 mg, 44%). Crystallization from pentane gives orange crystals suitable for X-ray measurement. Mp = 104-106 °C. ^{1}H NMR (δ in ppm): 7.92 (d, 4H, *o*-H), 7.23 (t, 4H, *m*-H), 7.02 (t, 2H, *p*-H), 0.26 (s, 54H, Si*Me*$_3$). ^{13}C

NMR (δ in ppm): 145.4, 134.4, 131.6, 130.0, 128.2, 2.9 (Si*Me*$_3$). ^{29}Si NMR (δ in ppm): -9.2 (*Si*Me$_3$), -92.6 (*Si*(SiMe$_3$)$_3$). Anal. calcd for $C_{32}H_{64}GeSi_8$ (746.17): C 51.51, H 8.65. Found: C 50.54, H 8.38.

[(Z)-1-Phenyl-2-(tris(trimethylsilyl)silyl)vinyl)]tris(trimethylsilyl)silylgermylene·PMe$_3$ (3)

Phenylacetylene (79 mg, 0.78 mmol) was added to a stirred solution of **1b** (0.78 mmol) in THF (10 mL) at rt. After 1 h the solvent was evaporated under reduced pressure and the orange residue was extracted with pentane (3 x 5 ml). After concentration to 1.5 mL and storage at -35 °C orange crystals of **3** (108 mg, 19 %) were obtained. Mp = 119-130 °C. ^{1}H NMR (δ in ppm): 7.52 (d, 2H, *o*-H), 7.15 (t, 2H, *m*-H), 6.94 (t, 1H, *p*-H), 6.86 (s, 1H, C*H*), 0.87 (d, 9H, P*Me*$_3$, $^2J_{H\text{-}P}$ = 9.6 Hz), 0.40 (s, 27H, CSi(Si*Me*$_3$)$_3$), 0.39 (s, 27H, GeSi(Si*Me*$_3$)$_3$). ^{13}C NMR (δ in ppm): 173.0 (d, *C*=CH, $^2J_{P\text{-}C}$ = 7 Hz), 153.2 (d, *Ph*-Ge, $^3J_{P\text{-}C}$ = 3 Hz), 142.0 (d, C=*C*H, $^3J_{P\text{-}C}$ = 16 Hz), 127.7 (2 signals), 125.5, 2.2 (Si*Me*$_3$), 15.1 (d, P*Me*$_3$, $^1J_{P\text{-}C}$ = 20 Hz), 3.9 (Si*Me*$_3$). ^{29}Si NMR (δ in ppm):-8.9 (d, GeSi(*Si*Me$_3$)$_3$, $^3J_{P\text{-}Si}$ = 12 Hz), -12.9 (d, CSi(*Si*Me$_3$)$_3$, $^5J_{P\text{-}Si}$ = 2 Hz), -83.4 (C*Si*(SiMe$_3$)$_3$), -126.9 (d, Ge*Si*(SiMe$_3$)$_3$, $^4J_{P\text{-}Si}$ = 15 Hz). ^{31}P NMR (δ in ppm): -24.6. Anal. calcd for $C_{29}H_{69}GePSi_8$ (746.15): C 46.68, H 9.32. Found: C 46.25, H 9.14.

Bis[(Z)-1-phenyl-2-(tris(trimethylsilyl)silyl)vinyl)germylene·PMe$_3$ (4)

Phenylacetylene (60 mg, 0.59 mmol) was added to the stirred solution of **1b** (0.29 mmol) in THF (10 mL) at rt. After 1 h the solvent was removed under reduced pressure and the product was extracted with pentane (3 x 5 mL). The solvent was removed to yield **4** as an orange solid (232 mg, 93%). Slow evaporation of pentane gave orange crystal suitable for X-ray study. ^{1}H NMR (δ in ppm): 7.02 (m, 4H, *m*-H), 6.83 (m, 6H, *o*-H, *p*-H), 6.66 (s, 2H, C*H*), 0.87 (d, 9H, P*Me*$_3$, $^2J_{H\text{-}P}$ = 8.7 Hz), 0.40 (s, 54H, Si*Me*$_3$). ^{13}C NMR (δ in ppm): 177.6 (C=*C*-Ph), 156.1 (*Ph*-Ge), 138.7 (*C*H), 126.2 (1 signal overlapping with C_6D_6), 124.7, 15.1 (d, P*Me*$_3$, $^1J_{P\text{-}C}$ = 21 Hz), 2.1 (Si*Me*$_3$). ^{29}Si NMR (δ in ppm):-12.9 (*Si*Me$_3$), -86.2 (*Si*(SiMe$_3$)$_3$). ^{31}P NMR (δ in ppm): -24.6.

2-[Tris(trimethylsilyl)silyl]-3-phenyl-1,1,2-tris(trimethylsilyl)-1,2-dihydro-1,2-silagermete (5)

B(C_6F_5)$_3$ (66 mg, 0.13 mmol) in pentane (3 mL) was added dropwise to the stirred solution of **3** (100 mg, 0.13 mmol) in pentane (2 mL). During reaction white precipitate was formed. The suspension was filtrated through the glass wool and celite. The solvent was evaporated to give **5** as a pale yellow solid (72 mg, 83%). Mp = 108-110 °C. ^{1}H NMR (δ in ppm):, 7.44 (s, 1H, C-*H*), 7.44 (d, 2H, *o-H*,), 7.17 (t, 2H, *m-H*), 7.03 (t, 1H, *p-H*), 0.42 (s, 9H, Si*Me*$_3$), 0.41 (s, 9H, Si*Me*$_3$), 0.38 (s, 9H, Si*Me*$_3$), 0.35 (s, 27H,

Si*Me*$_3$).^{13}C NMR (δ in ppm): 169.0 (C_{ipso}), 140.8 (*C*-Ph), 140.0 (*C*-H), one signal missing, 127.8, 126.5, 3.5 (Si*Me*$_3$), 2.5 (Si*Me*$_3$), 2.1 (Si*Me*$_3$). ^{29}Si NMR (δ in ppm): -3.7 (*Si*Me$_3$), -8.4 (*Si*Me$_3$), -9.0 (*Si*Me$_3$), -14.6 (*Si*Me$_3$), -50.9 (C-*Si*-Ge), -116.6 (Ge*Si*(SiMe$_3$)$_3$). Anal. calcd for $C_{26}H_{60}GeSi_8$ (670.08): C 46.60, H 9.03. Found: C 44.38, H 5.39.

(Z)-2-(2-(tris(trimethylsilyl)silyl)-1-phenylvinyl)-3-phenyl-1,1,2-tris(trimethylsilyl)-1,2-dihydro-1,2-silagermete (6)

Method A: A solution of B(C_6F_5)$_3$ (45 mg, 0.088 mmol) in pentane (3 mL) was added dropwise to a stirred solution of **4** (75 mg, 0.088 mmol) in pentane (2 mL). During the reaction a white precipitate was formed. The suspension was filtrated through plugs of glass wool and celite. After evaporation of the solvent **6** (42 mg, 62%) was obtained as a yellowish solid. **Method B:** Storage of **4** in pentane for 1 week at -35 °C led to formation of **6**. Mp = 131-132 °C. ^{1}H NMR (δ in ppm): 7.46 (s, 1H, C-*H*), 7.41 (m, 1H, *p*-*H*), 7.27 (d, 2H, *o*-*H*), 6.85 (m, 4H), 6.79 (m, 2H), 6.67 (m, 2H), 0.49 (s, 9H, Si*Me*$_3$), 0.40 (s, 9H, Si*Me*$_3$), 0.33 (s, 9H, Si*Me*$_3$), 0.30 (s, 27H, Si*Me*$_3$). ^{13}C NMR (δ in ppm): 173.1, 163.4, 153.2, 141.1, 140.8, 138.9, 138.2, 128.5, 127.5, 126.9, 126.2, 126.1, 29.8 (Si*Me*$_3$), 2.1 (Si*Me*$_3$), 1.7 (Si*Me*$_3$), 1.1 (Si*Me*$_3$). ^{29}Si NMR (δ in ppm): -4.6 (*Si*Me$_3$), -10.0 (*Si*Me$_3$), -12.5 (*Si*Me$_3$), -13.1 (CSi(*Si*Me$_3$)$_3$), -45.0 (*Si*-Ge), -86.5 (C*Si*(SiMe$_3$)$_3$). Anal. calcd for $C_{34}H_{66}GeSi_8$ (772.21): C 52.88, H 8.62. Found: C 52.99, H 8.31.

Table S-1. Crystallographic data for compounds **1a**, **2**, and **3**.

	1a	**2**	**3**
Empirical formula	$Ge_2C_{62}H_{144}Si_{16}N_4$	$GeC_{32}H_{64}Si_8$	$GeC_{29}H_{69}Si_8P$
M_w	1540.43	746.14	746.12
Temperature [K]	100(2)	100(2)	100(2)
Size [mm]	0.38×0.22×0.22	0.30×0.18×0.12	0.36×0.24×0.08
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	Pca2(1)	P2(1)/c	Pbca
a [Å]	31.634(6)	13.326(3)	25.174(5)
b [Å]	16.787(3)	18.718(4)	14.054(3)
c [Å]	17.540(4)	18.391(4)	25.198(5)
α [°]	90	90	90
β [°]	90	102.16(3)	90
γ [°]	90	90	90
V [Å ^{3}]	9314(3)	4484(2)	8915(3)
Z	4	4	8
ρ_{calc} [gcm^{-3}]	1.099	1.105	1.112
Absorption coefficient [mm^{-1}]	0.885	0.916	0.955
F(000)	3328	1600	3216
θ range	1.29<θ<26.37	1.56<θ<26.36	1.62<θ<26.35
Reflections collected/unique	72640/18943	35111/9152	65992/9077
Completeness to θ [%]	99.9	99.8	99.8
Data/restraints/parameters	18943/1/802	9152/0/388	9077/0/373
Goodness of fit on F^2	1.10	1.04	1.07
Final R indices [I>2σ(I)]	R1=0.048, *w*R2=0.098	R1=0.034, *w*R2=0.079	R1=0.040, *w*R2=0.097
R indices (all data)	R1=0.055, *w*R2=0.101	R1=0.043, *w*R2=0.082	R1=0.048, *w*R2=0.100
Largest diff. Peak/hole [e^-/ $Å^3$]	1.02/-0.30	0.67/-0.24	1.19/-0.96

Table S-2. Crystallographic data for compounds **4**, **5**, and **6**.

	4	**5**	**6**
Empirical formula	$GeC_{37}H_{75}Si_8P$	$GeC_{26}H_{60}Si_8$	$GeC_{34}H_{66}Si_8$
M_w	848.25	670.05	772.18
Temperature [K]	100(2)	150(2)	100(2)
Size [mm]	0.45×0.34×0.24	0.38×0.32×0.12	0.40×0.22×0.14
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2(1)/n	P2(1)/n
a [Å]	9.809(2)	9.642(2)	13.204(3)
b [Å]	14.698(3)	18.886(4)	19.641(4)
c [Å]	20.257(4)	22.043(4)	18.411(4)
α [°]	105.37(3)	90	90
β [°]	97.24(3)	98.58(3)	109.70(3)
γ [°]	109.32(3)	90	90
V [Å ^{3}]	2583(2)	3969(2)	4495(2)
Z	2	4	4
ρ_{calc} [gcm^{-3}]	1.090	1.121	1.141
Absorption coefficient [mm^{-1}]	0.832	1.028	0.916
F(000)	912	1440	1656
θ range	1.55<θ<26.37	1.87<θ<26.34	1.57<θ<26.38
Reflections collected/unique	20672/10411	31171/8067	34964/9187
Completeness to θ [%]	98.4	99.8	99.8
Data/restraints/parameters	10411/0/445	8067/0/334	9187/0/406
Goodness of fit on F^2	1.04	1.05	1.10
Final R indices [I>2σ(I)]	R1=0.038, *w*R2=0.091	R1=0.029, *w*R2=0.074	R1=0.043, *w*R2=0.092
R indices (all data)	R1=0.046, *w*R2=0.094	R1=0.033, *w*R2=0.076	R1=0.052, *w*R2=0.095
Largest diff. Peak/hole [e^-/ $Å^3$]	0.77/-0.30	0.46/-0.22	0.80/-0.37

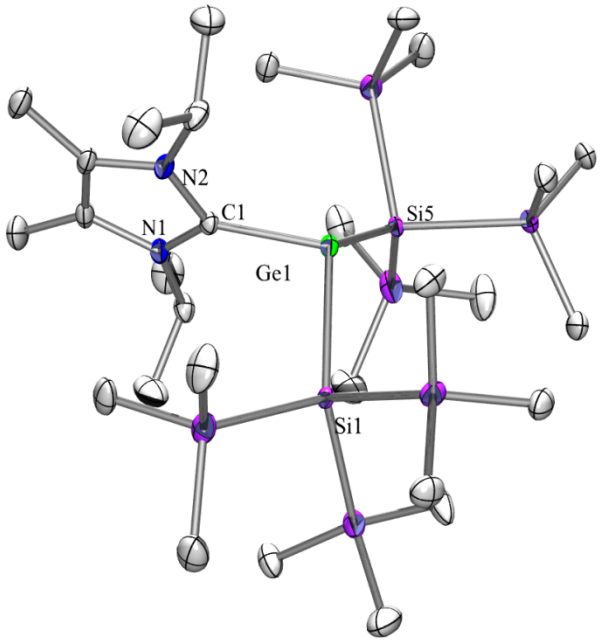

Figure S-1. Crystal structure of **1a**. Thermal ellipsoids are represented at the 30% level and hydrogen atoms have been omitted for clarity (bond lengths in Å, angles in deg). C(1)-N(1) 1.357(3), C(1)-N(2) 1.365(3), C(1)-Ge(1) 2.089(2), Ge(1)-Si(5) 2.4834(8), Ge(1)-Si(1) 2.5023(9), Si(1)-Si(4) 2.3647(10), N(1)-C(1)-N(2) 104.7(2), N(1)-C(1)-Ge(1) 135.66(17), N(2)-C(1)-Ge(1) 119.63(17), C(1)-Ge(1)-Si(5) 104.69(7), C(1)-Ge(1)-Si(1) 102.36(7), Si(5)-Ge(1)-Si(1) 117.39(2).

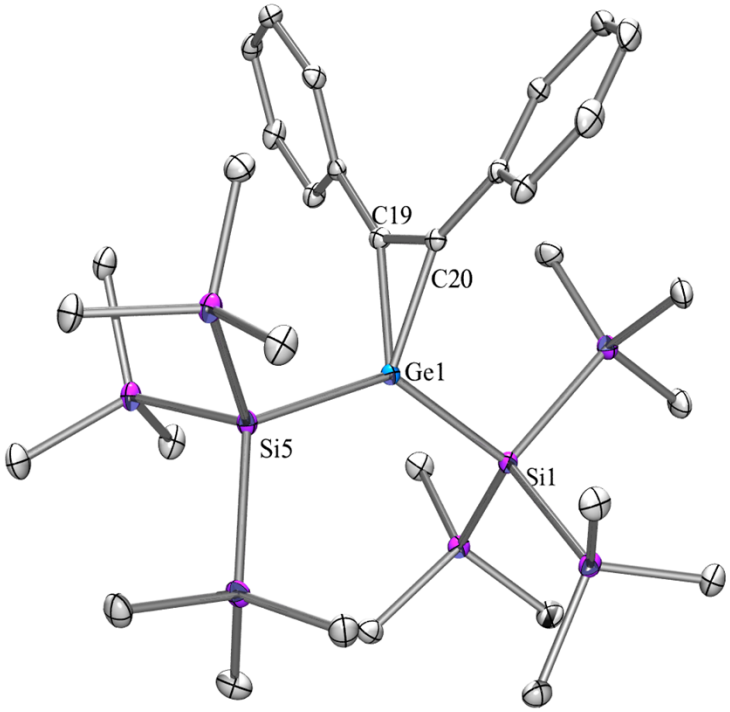

Figure S-2. Crystal structure of **2**. Thermal ellipsoids are represented at the 30% level and hydrogen atoms have been omitted for clarity (bond lengths in Å, angles in deg). C(1)-Si(2) 1.870(2), C(19)-C(20) 1.322(3), C(19)-Ge(1) 1.9684(19), C(20)-Ge(1) 1.9695(18), Ge(1)-Si(1) 2.4049(7), Ge(1)-Si(5) 2.4102(7), C(20)-C(19)-Ge(1) 70.43(11), C(19)-C(20)-Ge(1) 70.34(11), C(19)-Ge(1)-C(20) 39.24(8), C(19)-Ge(1)-Si(1) 113.88(6), C(20)-Ge(1)-Si(1) 109.73(6), C(19)-Ge(1)-Si(5) 109.34(6), C(20)-Ge(1)-Si(5) 113.73(6), Si(1)-Ge(1)-Si(5) 133.88(2).

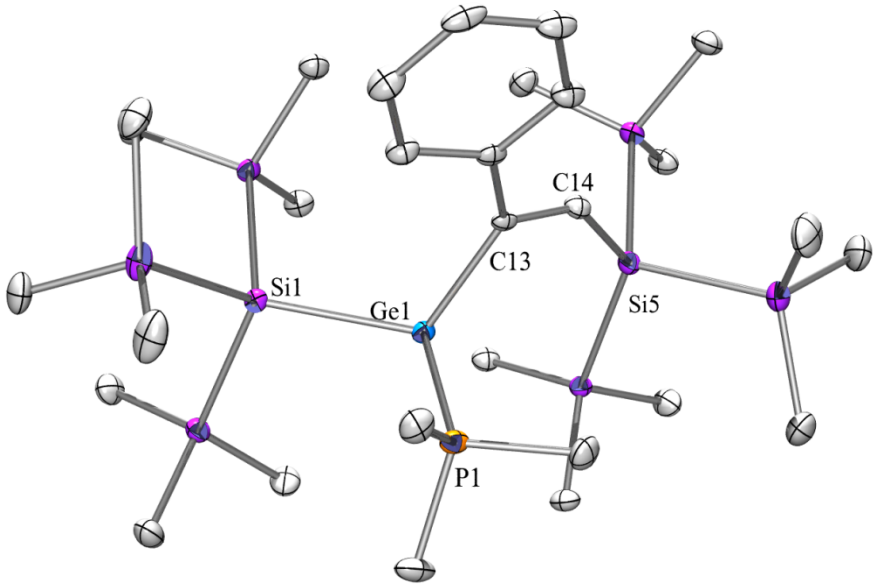

Figure S-3. Crystal structure of **3**. Thermal ellipsoids are represented at the 30% level and hydrogen atoms have been omitted for clarity (bond lengths in Å, angles in deg). C(10)-P(1) 1.810(3), C(13)-C(14) 1.347(3), C(13)-Ge(1) 2.031(2), C(14)-Si(5) 1.893(2), Ge(1)-P(1) 2.3900(7), Ge(1)-Si(1) 2.4816(8), Si(1)-Si(4) 2.3566(9), C(14)-C(13)-Ge(1) 112.85(15), C(13)-C(14)-Si(5) 138.84(17), C(13)-Ge(1)-P(1) 93.22(6), C(13)-Ge(1)-Si(1) 114.36(6), P(1)-Ge(1)-Si(1) 103.53(2).

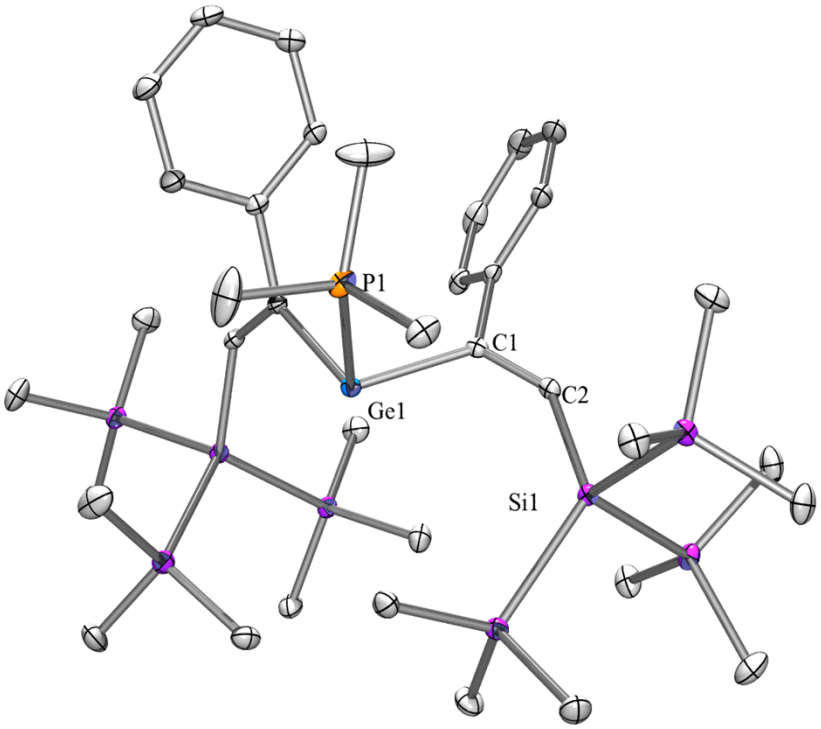

Figure S-4. Crystal structure of **4**. Thermal ellipsoids are represented at the 30% level and hydrogen atoms have been omitted for clarity (bond lengths in Å, angles in deg). Ge(1)-C(1) 2.043(2), Ge(1)-P(1) 2.4261(9), P(1)-C(36) 1.799(2), Si(1)-C(2) 1.896(2), Si(1)-Si(2) 2.3557(16), C(1)-C(2) 1.347(3), C(1)-Ge(1)-P(1) 91.84(6), C(2)-Si(1)-Si(2) 127.15(8), C(2)-Si(1)-Si(3) 98.03(7), C(2)-Si(1)-Si(4) 106.81(8), C(1)-C(2)-Si(1) 141.72(17).

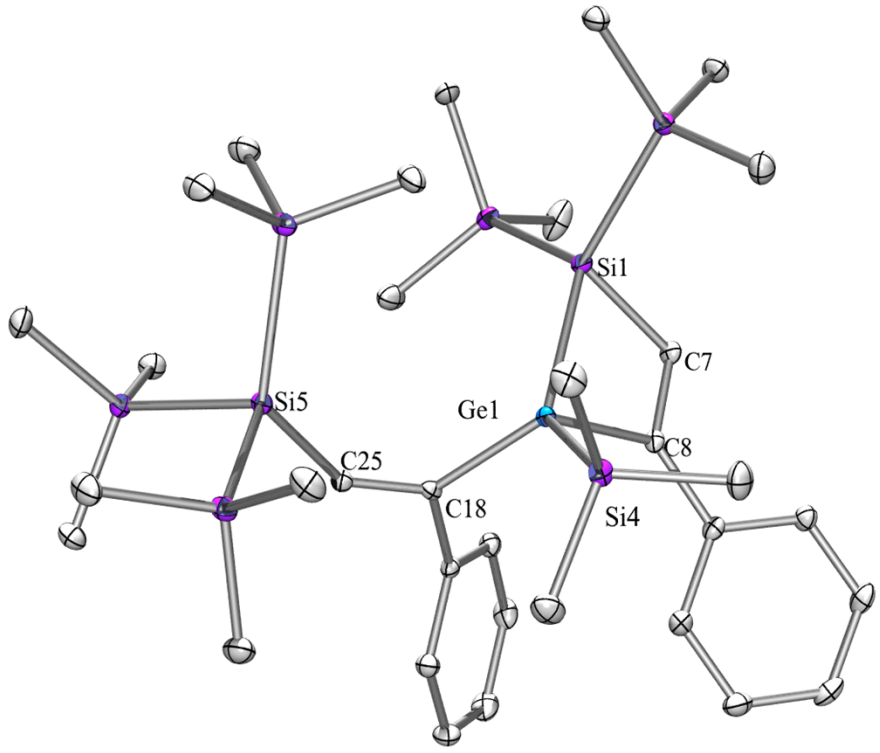

Figure S-5. Crystal structure of **6**. Thermal ellipsoids are represented at the 30% level and hydrogen atoms have been omitted for clarity (bond lengths in Å, angles in deg). Ge(1)-C(18) 1.997(2), Ge(1)-C(8) 2.008(2), Ge(1)-Si(4) 2.3959(8), Ge(1)-Si(1) 2.4132(8), Si(1)-C(7) 1.887(2), Si(4)-C(15) 1.869(3), Si(5)-C(25) 1.899(2), C(7)-C(8) 1.349(3), C(18)-C(25) 1.347(3), C(18)-Ge(1)-C(8) 113.89(9), C(18)-Ge(1)-Si(4) 110.71(7), C(8)-Ge(1)-Si(4) 104.08(7), C(18)-Ge(1)-Si(1) 118.99(7), C(8)-Ge(1)-Si(1) 72.78(7), Si(4)-Ge(1)-Si(1) 126.80(3), C(7)-Si(1)-Ge(1) 75.44(8), C(7)-C(8)-Ge(1) 103.27(16), C(25)-C(18)-Ge(1) 128.29(18), C(18)-C(25)-Si(5) 141.77(19).

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