

Supporting Information

Phosphaalkenyl germylenes and their gold, tungsten and molybdenum complexes

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General procedure

All manipulations with air-sensitive materials were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line and glove-box techniques. Solvents were purified with the MBRAUN SBS-800 purification system except THF which was distilled upon Na/benzophenone. NMR spectra were recorded with a Bruker Avance II 300: ^1H (300.13MHz), ^{13}C (74.48 MHz), ^{31}P (121.50 MHz) at 298 K in C_6D_6 or in CD_2Cl_2 . Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^1H and $^{13}\text{C}\{^1\text{H}\}$) or with an external reference (H_3PO_4 for ^{31}P). NMR assignments were confirmed by COSY (^1H), HSQC (^1H - ^{13}C), and HMBC (^1H - ^{13}C) experiments. Melting points were measured with a sealed capillary using the Stuart automatic melting point SMP40 apparatus. The compounds $(\text{NHC})\text{GeCl}_2^1$ and $\text{Mes}^*\text{P}=\text{CCl}_2^2$ were prepared according to literature procedures.

Synthesis of bis(phosphaalkenyl) germylene 1:

To a solution of $\text{Mes}^*\text{P}=\text{C}(\text{Li})\text{Cl}$ (1.64 mmol) in THF (6 mL) freshly prepared and cooled at $-90\text{ }^\circ\text{C}$ was added a suspension of $(\text{NHC})\text{GeCl}_2$ (0.27 g, 0.82 mmol) in THF (3 mL). After 1h the solution was warmed to room temperature and stirred for a further 1h. The volatiles were removed under reduced pressure and the solid residue was extracted with toluene (12 mL). After filtration through a glass-fritted celite layer, the filtrate was evaporated under vacuum to yield **1** as a brown powder (0.62 g, 84%). Crystallization from a saturated toluene solution at $-24\text{ }^\circ\text{C}$ gave crystals (M.p.: $118\text{ }^\circ\text{C}$, dec) suitable for an X-ray study. ^1H NMR (C_6D_6): $\delta = 1.25$ (d, $^3J_{\text{HH}}$ = 6.8 Hz, 12H, CHMe_2); 1.35 (s, 18H, C_pCMe_3); 1.53 (s, 6H, $=\text{CMe}$); 1.75 (s, 18H, C_oCMe_3); 1.78 (s, 18H, C_oCMe_3); 5.20-6.60 (m, 2H, CHMe_2); 7.64 (s, 4H, CH of Mes^*). ^{13}C NMR (C_6D_6): $\delta = 10.11$ ($=\text{CMe}$); 22.19 (CHMe_2); 31.53 (C_pCMe_3); 33.16 and 33.21 (C_oCMe_3); 35.03 (C_pC);

38.18 and 38.52 (C_oC); 52.17 (CHMe₂); 121.26 and 122.03 (C_m); 126.18 (C=); 140.53 (dd, ¹J_{CP} = 82.0 Hz, ⁵J_{CP} = 11.6 Hz, C_i); 149.33 (C_p); 153.34 and 153.57 (C_o); 168.33 (t, ³J_{CP} = 16.9 Hz, C:); 197.08 (d, ¹J_{CP} = 86.3 Hz, C=P). ³¹P NMR (C₆D₆): δ = 265.7.

Synthesis of tungsten[bis(phosphaalkenyl) germylene] **3**:

To a solution of **1** (0.30 g, 0.33 mmol in THF (3 mL) was added at -78 °C a solution of (cod)W(CO)₄ (0.13 g, 0.33 mmol) in THF (3 mL). The solution was heated at 60 °C for 3h. The volatiles were removed under reduced pressure and the residue was washed with pentane. The precipitate was dried under reduced pressure to yield **3** as a brown powder (0.29 g, 73%). Crystallization from dichloromethane at -24 °C gave crystals (M.p.: 232 °C, dec) suitable for an X-ray study. ¹H NMR (C₆D₆): δ = 1.04 (d, ³J_{HH} = 6.9 Hz, 3H, CHMeMe'); 1.18 (d, ³J_{HH} = 6.9 Hz, 3H, CHMeMe'); 1.27 (d, ³J_{HH} = 6.9 Hz, 3H, CHMeMe'); 1.29 and 1.30 (2s, 2 x 9H, C_pCMe₃); 1.37 and 1.44 (2s, 2 x 3H, =CMe); 1.59 and 1.65 (2s, 2 x 9H, C_oCMe₃); 1.65 (d, ³J_{HH} = 6.8 Hz, 3H, CHMeMe'); 1.81 and 1.87 (2s, 2 x 9H, C_oCMe₃); 5.25 (sept, ³J_{HH} = 6.9 Hz, 1H, CHMeMe'); 6.52 (sept, ³J_{HH} = 6.8 Hz, 1H, CHMeMe'); 7.58 (s, 2H, CH of Mes*); 7.59-7.62 (m, 2H, CH of Mes*). ¹³C NMR (C₆D₆): δ = 9.83 and 10.14 (=CMe); 21.43, 22.06, 22.39 and 22.48 (CHMeMe'); 31.20 and 31.37 (C_pCMe₃); 32.68, 32.72, 32.76, 32.81 and 33.85 (C_oCMe₃); 35.04 and 35.15 (C_pC); 37.97, 38.01, 38.55 and 38.80 (C_oC); 53.31 and 53.36 (CHMeMe'); 121.94, 122.12, 122.19, 122.30 and 122.37 (C_m); 126.47 and 128.57 (C=); 131.99 (d, ¹J_{CP} = 31.8 Hz, C_i); 137.65 (d, ¹J_{CP} = 65.8 Hz, C_i); 150.50 and 151.96 (C_p); 153.28, 153.66, 154.73 and 156.31 (C_o); 157.11 (dd, ³J_{CP} = 11.9 and 19.7 Hz C:); 182.09 (dd, ¹J_{CP} = 90.9 Hz, ³J_{CP} = 19.6 Hz, C=P); 187.87 (d, ³J_{CP} = 12.5 Hz, C=PW); 206.26 (d, ²J_{CP} = 11.5 Hz, CO); 208.84 (d, ²J_{CP} = 10.1 Hz, CO); 211.38 (d, ²J_{CP} = 7.9 Hz, CO); 214.16 (d, ²J_{CP} = 36.8 Hz, CO). ³¹P NMR (C₆D₆): δ = 267.2 (¹J_{PW} = 214.7 Hz, PW); 281.9 (P).

¹H NMR (CD₂Cl₂): δ = 1.34 and 1.36 (2s, 2 x 9H, C_pCMe₃); 1.38 (d, ³J_{HH} = 7.1 Hz, 3H, CHMeMe'); 1.44 and 1.46 (2s, 2 x 9H, C_oCMe₃); 1.57 (d, ³J_{HH} = 7.0 Hz, 3H, CHMeMe'); 1.62 (s, 9H, C_oCMe₃); 1.64 (d, ³J_{HH} = 7.1 Hz, 3H, CHMeMe'); 1.68 (s, 9H, C_oCMe₃); 1.74 (d, ³J_{HH} = 6.8 Hz, 3H, CHMeMe'); 2.35 and 2.37 (2s, 2 x 3H, =CMe); 5.22 (sept, ³J_{HH} = 6.9 Hz, 1H, CHMeMe'); 6.21 (sept, ³J_{HH} = 6.9 Hz, 1H, CHMeMe'); 7.40 (s, 2H, CH of Mes*); 7.44-7.47 (m, 2H, CH of Mes*). ¹³C NMR (CD₂Cl₂): δ = 11.39 and 11.61 (=CMe); 22.56, 22.67, 23.35 and 23.45 (CHMeMe'); 31.72, and 31.87 (C_pCMe₃); 33.01, 33.05, 33.10, 33.14, 34.17, 34.19, 34.24

and 34.27 (C_0CMe_3); 35.74 and 35.89 (C_pC); 38.44, 38.54, 39.05 and 39.17 (C_0C); 54.01 and 54.38 (CH); 122.53, 122.80, 122.87 and 122.94 (C_m); 128.05 and 129.81 (C=); 131.51 (d, $^1J_{CP} = 31.7$ Hz, C_i); 131.93 (d, $^1J_{CP} = 66.9$ Hz, C_i); 151.10 and 152.76 (C_p); 153.66, 154.08, 155.24 and 156.24 (C_0); 156.96 (dd, $^3J_{CP} = 10.7$ and 20.2 Hz, C:); 182.38 (dd, $^1J_{CP} = 90.5$ Hz, $^3J_{CP} = 21.2$ Hz, C=P); 189.40 (dd, $^1J_{CP} = 12.6$ Hz, $^3J_{CP} = 12.2$ Hz, C=PW); 206.76 (d, $^2J_{CP} = 11.7$ Hz, CO); 208.57 (d, $^2J_{CP} = 10.1$ Hz, CO); 212.44 (d, $^2J_{CP} = 7.9$ Hz, CO); 214.68 (d, $^2J_{CP} = 36.6$ Hz, CO). ^{31}P NMR (CD_2Cl_2): $\delta = 264.7$ ($^1J_{PW} = 210.8$ Hz, PW); 280.37 (P). IR (nujol): ν_{CO} (1853, 1883, 1900 and 2000 cm^{-1}). HR-MS (CI CH_4): ($C_{53}H_{78}Cl_2GeN_2O_4P_2W$): $[M]^+$ Calcd: 1196.3550, found: 1196.3545

Synthesis of molybdenum[bis(phosphaalkenyl) germylene] 4:

To a solution of (nbd)Mo(CO)₄ (0.03 g, 0.11 mmol) in THF (2 mL) was added a solution of **1** (0.10 g, 0.11 mmol) in THF (3 mL) at $-78\text{ }^\circ\text{C}$. The solution was heated at $60\text{ }^\circ\text{C}$ for 3h. The volatiles were removed under reduced pressure and the crude precipitate was washed with pentane. After drying under reduced pressure, a yellow powder of **4** was obtained (0.08 g, 67%). (M.p.: $198\text{ }^\circ\text{C}$, dec). 1H NMR (C_6D_6): $\delta = 1.04$ (d, $^3J_{HH} = 6.9$ Hz, 3H, CHMeMe'); 1.20 (d, $^3J_{HH} = 7.0$ Hz, 3H, CHMeMe'); 1.29 and 1.30 (2s, 2 x 9H, C_pCMe_3); 1.41 (d, $^3J_{HH} = 7.0$ Hz, 3H, CHMeMe'); 1.41 and 1.45 (2s, 2 x 3H, =CMe); 1.59 and 1.65 (2s, 2 x 9H, C_0CMe_3); 1.65 (d, $^3J_{HH} = 6.9$ Hz, 3H, CHMeMe'); 1.79 and 1.85 (2s, 2 x 9H, C_0CMe_3); 5.28 (sept, $^3J_{HH} = 6.9$ Hz, 1H, CHMeMe'); 6.66 (sept, $^3J_{HH} = 6.9$ Hz, 1H, CHMeMe'); 7.58 (s, 2H, CH of Mes*); 7.59-7.61 (m, 2H, CH of Mes*). ^{31}P NMR (C_6D_6): $\delta = 280.2$ (PMo); 296.2 (P).

1H NMR (CD_2Cl_2): $\delta = 1.33$ and 1.35 (2s, 2 x 9H, C_pCMe_3); 1.36 (d, $^3J_{HH} = 7.7$ Hz, 3H, CHMeMe'); 1.44 and 1.45 (2s, 2 x 9H, C_0CMe_3); 1.56 (d, $^3J_{HH} = 7.0$ Hz, 3H, CHMeMe'); 1.61 (s, 9H, C_0CMe_3); 1.63 (d, $^3J_{HH} = 7.2$ Hz, 3H, CHMeMe'); 1.66 (s, 9H, C_0CMe_3); 1.74 (d, $^3J_{HH} = 6.9$ Hz, 3H, CHMeMe'); 2.33 and 2.36 (2s, 2 x 3H, =CMe); 5.23 (sept, $^3J_{HH} = 6.9$ Hz, 1H, CHMeMe'); 6.36 (sept, $^3J_{HH} = 7.0$ Hz, 1H, CHMeMe'); 7.39 (s, 2H, CH of Mes*); 7.42-7.45 (m, 2H, CH of Mes*). ^{13}C NMR (CD_2Cl_2): $\delta = 11.40$ and 11.62 (=CMe); 22.59, 22.64, 23.36 and 23.47 ($CHMe_2$); 31.73, and 31.86 (C_pCMe_3); 32.98, 33.01, 33.07, 33.09, 34.07, 34.10, 34.13 and 34.17 (C_0CMe_3); 35.72, and 35.84 (C_pC); 38.42, 38.52, 38.96 and 39.09 (C_0C); 51.84 and 53.17 (CHMeMe'); 122.47, 122.69, 122.76 and 122.84 (C_m); 128.00 and 129.61 (C=); 133.27 (d, $^1J_{CP} = 38.5$ Hz, C_i); 138.16 (d, $^1J_{CP} = 66.6$ Hz, C_i); 150.98 and 152.52 (C_p); 153.59, 154.04, 155.08

and 155.98 (C_o); 158.79 (dd, ³J_{CP} = 10.7 and 18.4 Hz, C:); 182.57 (dd, ¹J_{CP} = 12.6 Hz, ³J_{CP} = 10.3 Hz, C=PW); 185.87 (dd, ¹J_{CP} = 91.7 Hz, ³J_{CP} = 18.8 Hz, C=P); 213.47 (d, ²J_{CP} = 12.3 Hz, CO); 215.38 (d, ²J_{CP} = 11.5 Hz, CO); 221.22 (d, ²J_{CP} = 9.4 Hz, CO); 224.04 (d, ²J_{CP} = 9.4 Hz, CO). ³¹P (CD₂Cl₂): δ = 278.7 (PMo); 293.3 (P). IR (nujol): ν_{CO} (1858, 1892, 1908 and 2005 cm⁻¹). HR-MS (CI, CH₄): (C₅₃H₇₈MoCl₂GeN₂O₄P₂): [M]⁺ Calcd: 1108.3094, found: 1108.3123.

Synthesis of chlorogold[bis(phosphaalkenyl) germylene] 5:

To a solution of **1** (0.10 g, 0.11 mmol) in toluene (1 mL) was added a solution of ClAuS(Me)₂ (0.03 g, 0.11 mmol) in toluene (1 mL). After 5 minutes under magnetic stirring in the absence of light, the solution was filtrated and the volatiles removed under reduced pressure to yield **5** as a brown powder (0.13 g, 100%). Crystallization from dichloromethane at room temperature gave crystals (M.p.: 127 °C) suitable for an X-ray study. ¹H NMR (C₆D₆): δ = 1.18 (d, ³J_{HH} = 6.9 Hz, 12H, CHMe₂); 1.30 (s, 18H, C_pCMe₃); 1.50 (s, 6H, =CMe); 1.66 (s, 18H, C_oCMe₃); 1.67 (s, 18H, C_oCMe₃); 5.87-6.25 (m, 2H, CHMe₂); 7.60 (s, 4H, CH of Mes*). ¹³C NMR (C₆D₆): δ = 10.69 (=CMe); 22.11 (CHMe₂); 31.38 (C_pCMe₃); 33.24 and 33.40 (C_oCMe₃); 35.03 (C_pC); 38.03 and 38.51 (C_oC); 52.86 (CHMe₂); 121.77 and 122.54 (C_m); 129.19 (C=); 136.70 (dd, ¹J_{CP} = 75.6 Hz, ⁵J_{CP} = 8.4 Hz, C_i); 150.56 (C_p); 153.60 (t, ³J_{CP} = 14.7 Hz, C:); 153.73 and 154.25 (C_o); 175.14 (dd, ¹J_{CP} = 95.9 Hz, ³J_{CP} = 15.4 Hz, C=P). ³¹P NMR (C₆D₆): δ = 293.0. HR-MS (CI, CH₄): (C₄₉H₇₈AuCl₃GeN₂P₂): [M]⁺ Calcd: 1132.3584, found: 1132.3538.

Synthesis of iodogold[bis(phosphaalkenyl) germylene] 6:

A solution of AuI (0.04 g, 0.11 mmol) in toluene (1 mL) was added to a solution of **1** (0.10 g, 0.11 mmol) in toluene (2 mL). After 5 minutes under magnetic stirring in the absence of light, the solution was filtrated and the volatiles removed under reduced pressure to yield **6** as an orange powder (0.13 g, 97%). Crystallization from benzene at room temperature gave crystals (M.p.: 121 °C) suitable for an X-ray study. ¹H NMR (C₆D₆): δ = 1.22 (d, ³J_{HH} = 7.0 Hz, 12H, CHMe₂); 1.30 (s, 18H, C_pCMe₃); 1.58 (s, 6H, =CMe); 1.65 (s, 18H, C_oCMe₃); 1.67 (s, 18H, C_oCMe₃); 5.85-6.32 (m, 2H, CHMe₂); 7.59 (s, 4H, CH of Mes*). ¹³C NMR (C₆D₆): δ = 10.68 (=CMe); 22.23 (CHMe₂); 31.37 (C_pCMe₃); 33.22 and 33.58 (C_oCMe₃); 35.01 (C_pC); 38.00 and 38.46 (C_oC); 52.62 (CHMe₂); 121.72 and 122.57 (C_m); 128.54 (C=); 136.71 (dd, ¹J_{CP} = 77.8 Hz, ⁵J_{CP} = 11.1 Hz, C_i); 150.54 (C_p); 153.67 and 154.39 (C_o); 155.29 (t, ³J_{CP} = 15.7 Hz, C:); 175.45

(dd, $^1J_{CP} = 97.0$ Hz, $^3J_{CP} = 16.7$ Hz, C=P). ^{31}P NMR (C_6D_6): $\delta = 292.6$. HR-MS (CI, CH_4): ($\text{C}_{49}\text{H}_{78}\text{AuCl}_2\text{GeIN}_2\text{P}_2$): $[\text{M}]^+$ Calcd: 1224.2944, found: 1224.2842.

X-ray Structure Determinations

X-ray data were collected at low temperature (193(2) K) using an oil-coated shock-cooled crystal on a Bruker Kappa APEX II Quazar diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) with graphite-monochromated Mo $\text{K}\alpha$ radiation (wavelength = 0.71073 Å) by using phi- and omega-scans. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.³ The structures were solved by direct methods, using SHELXS-97⁴ and refined using the least-squares method on F^2 .⁵ All non-H atoms were treated anisotropically. The H atoms were located by difference Fourier maps and refined with a riding model. Structural data are summarized in Table 1.

	1	3	5	6
Empirical formula	C ₄₉ H ₇₈ Cl ₂ GeN ₂ P ₂ , 2 (C ₇ H ₈)	C ₅₃ H ₇₈ Cl ₂ GeN ₂ O ₄ P ₂ W, 3 (CH ₂ Cl ₂)	C ₄₉ H ₇₈ AuCl ₃ GeN ₂ P ₂ , 2.5 (CH ₂ Cl ₂)	C ₄₉ H ₇₈ AuCl ₂ GeIN ₂ P ₂ , 1.5 (C ₆ H ₆)
Formula weight (g/mol)	1084.83	1451.23	1345.30	1341.59
Temperature (K)	193(2)	193(2)	193(2)	193(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
a (Å)	13.9844(4)	12.0774(6)	11.3212(6)	12.1895(9)
b (Å)	14.0830(4)	14.8952(8)	15.4945(7)	37.193(3)
c (Å)	18.5657(6)	21.9932(16)	18.5887(10)	27.7641(18)
α (deg.)	79.5190(10)	100.256(3)	79.533(2)	90
β (deg.)	75.8570(10)	96.379(3)	87.667(2)	95.446(3)
γ (deg.)	63.2850(10)	113.219(2)	77.006(2)	90
Volume (Å ³)	3156.09(16)	3505.3(4)	3124.4(3)	12530.3(16)
Z	2	2	2	8
Density calculated (g/cm ³)	1.142	1.375	1.430	1.422
Absorption coefficient (mm ⁻¹)	0.658	2.459	3.252	3.483
F(000)	1164	1476	1366	5416
Crystal size (mm)	0.30 x 0.12 x 0.10	0.38 x 0.18 x 0.08	0.34 x 0.10 x 0.08	0.10 x 0.05 x 0.02
θ range (deg.)	5.10 - 26.37	5.11 - 26.37	5.16 - 28.28	5.15 - 26.37
Index range h k l	-17 ≤ h ≤ 14 -17 ≤ k ≤ 17 -23 ≤ l ≤ 22	-15 ≤ h ≤ 15 -18 ≤ k ≤ 18 -27 ≤ l ≤ 27	-15 ≤ h ≤ 15 -20 ≤ k ≤ 20 -24 ≤ l ≤ 24	-15 ≤ h ≤ 15 -44 ≤ k ≤ 46 -34 ≤ l ≤ 33
Reflections collected / Unique	48874 / 12787 R(int) = 0.0490	63975 / 14094 R(int) = 0.0361	65805 / 15160 R(int) = 0.0365	124173 / 12726 R(int) = 0.0988
Completeness to θ (%)	98.8	98.2	97.7	99.2
Data/Restraints/Parameters	12787 / 241 / 720	14094 / 103 / 748	15160 / 230 / 706	12726 / 244 / 708
Goodness-of-fit	1.019	1.055	1.022	1.047
R1, wR2 (<i>I</i> > 2(σ) <i>I</i>)	0.0458, 0.1114	0.0347, 0.0877	0.0325, 0.0723	0.0452, 0.0805
R1, wR2 (all data)	0.0730, 0.1262	0.0445, 0.0930	0.0490, 0.0790	0.0875, 0.0917
Largest diff. peak and hole (eÅ ⁻³)	1.060, -0.387	1.226, -0.817	0.906, -0.909	0.598, -0.814

Table 1. Crystallographic data

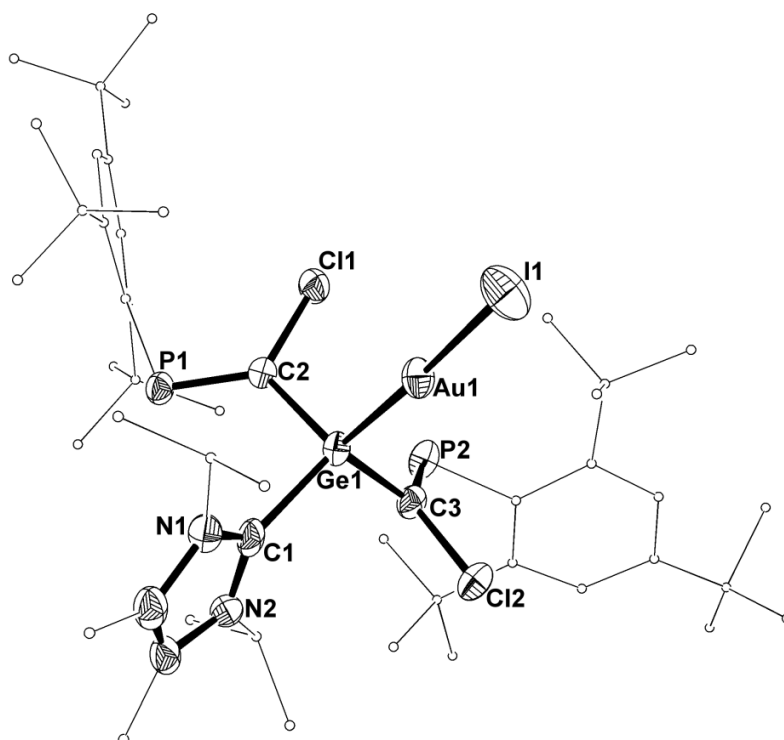


Fig. 3. Molecular structure of compound **6** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and crystallization solvent (benzene) are omitted. Me, *i*Pr and Mes* groups are simplified. Selected bond distances [Å] and bond angles [°]: Ge1–C1 2.030(6), Ge1–C2 1.979(5), Ge1–C3 1.981(5), Au1–Ge1 2.3641(6), Au1–I1 2.5783(5), P1–C2 1.671(5), P2–C3 1.671(6), Cl1–C2 1.740(5), Cl2–C3 1.752(5) ; I1–Au1–Ge 176.75(2), C2–Ge1–C3 107.1(2), C1–Ge1–C2 108.9(2), C1–Ge1–C3 101.2(2), C1–Ge1–Au1 114.08(17), C2–Ge1–Au1 111.01(15), C3–Ge1–Au1 113.88(9).

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- 2 S. J. Goede and F. Bickelhaupt, *Chem. Ber.*, 1991, **124**, 2677.
- 3 (a) Madison, SAINT-NT; Bruker AXS Inc.; Wisconsin 2000.(b) SADABS; Program for data correction; Bruker-AXS M.
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- 5 SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick; University of Göttingen, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.