Supporting Information

Early-Transition-Metal Complexes of Functionalized Nonagermanide Clusters: Synthesis and Characterization of $[Cp_2(MeCN)Ti(\eta^1\text{-}Ge_9\{Si(TMS)_3\}_3)]$ and $K_3[Cp_2Ti(\eta^1\text{-}Ge_9\{Si(TMS)_3\}_2)_2]$

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Content

Crystallographic Data

Table S1. Crystallographic data of compounds **1** and **2**.

compound	**1**	**2**
fw [g·mol^{-1}]	1686.57	3145.25
space group	*P2$_1$/c*	*P2$_1$/c*
a [Å]	15.458(1)	42.249(1)
b [Å]	22.460(2)	36.427(1)
c [Å]	22.268(2)	18.0896(5)
α [deg]	90	90
β [deg]	95.176(6)	100.638(2)
γ [deg]	90	90
V [Å^3]	7700(11)	27362(1)
Z	4	8
T [K]	100(2)	100(2)
λ [Å]	0.7288	MoK$_\alpha$
ρ_{calcd} [g·cm^{-3}]	1.455	1.527
μ [mm^{-1}]	3.771	4.208
R_{int} / R_δ	0.0771/0.0481	0.0497/0.0449
R_1 [$I > 2\,\sigma(I)$ / all data]	0.0288/0.0426	0.0715/0.0891
wR_2 [$I > 2\,\sigma(I)$ / all data]	0.0568/0.0622	0.1399/0.1455
goodness of fit	1.011	1.215
max./min. diff. el. density [e·Å^{-3}]	0.51/-0.40	2.35/-1.28

Table S2. Selected bond lengths and angles in compound **1**.

bond	distance [Å]
Ge1-Ge2	2.527(1)
Ge1-Ge4	2.527(1)
Ge1-Ge5	2.633(2)
Ge1-Ge8	2.651(2)
Ge2-Ge3	2.557(2)
Ge2-Ge5	2.598(1)
Ge2-Ge6	2.566(1)
Ge3-Ge4	2.567(1)
Ge3-Ge6	2.616(2)
Ge3-Ge7	2.657(2)
Ge4-Ge7	2.568(2)
Ge4-Ge8	2.615(1)
Ge5-Ge8	2.852(2)
Ge5-Ge9	2.514(1)
Ge6-Ge7	2.854(2)
Ge6-Ge9	2.518(2)
Ge7-Ge9	2.525(1)
Ge8-Ge9	2.512(1)
Ge2-Si1	2.405(2)
Ge4-Si2	2.413(2)
Ge9-Si3	2.371(2)
Ge1-Ti	2.767(2)
Ti-Ct1*	2.049(1)
Ti-Ct2*	2.045(1)
Ge7-Ge8 (h_1)	3.053(3)
Ge5-Ge6 (h_2)	3.077(3)
Ge1-Ge3 (h_3)	3.812(3)
atoms	angle [deg]
Ct1-Ti-Ct2*	135.34(5)
Ge1-Ti-N	84.59(3)

*Ct: centroids of Cp rings; Ct1: C1-C5; Ct2: C6-C10

Table S3. Selected bond lengths and angles in **2a-l**.

bond	distance [Å]	bond	distance [Å]
Ge1-Ge2	2.583(1)	Ge10-Ge11	2.584(1)
Ge1-Ge3	2.558(1)	Ge10-Ge12	2.577(1)
Ge1-Ge4	2.561(1)	Ge10-Ge13	2.577(1)
Ge1-Ge5	2.546(1)	Ge10-Ge14	2.583(1)
Ge2-Ge3	2.715(2)	Ge11-Ge12	2.666(1)
Ge2-Ge6	2.595(1)	Ge11-Ge15	2.544(1)
Ge2-Ge7	2.641(1)	Ge11-Ge16	2.591(1)
Ge3-Ge7	2.672(1)	Ge12-Ge16	2.715(1)
Ge3-Ge8	2.553(1)	Ge12-Ge17	2.536(1)
Ge4-Ge7	2.657(2)	Ge13-Ge14	2.673(1)
Ge4-Ge8	2.560(2)	Ge13-Ge17	2.551(1)
Ge4-Ge9	2.638(1)	Ge13-Ge18	2.728(1)
Ge5-Ge6	2.546(1)	Ge14-Ge15	2.545(1)
Ge5-Ge9	2.683(1)	Ge14-Ge18	2.599(1)
Ge6-Ge7	2.531(1)	Ge15-Ge16	2.574(1)
Ge6-Ge9	2.529(1)	Ge15-Ge18	2.542(1)
Ge7-Ge8	2.523(1)	Ge16-Ge17	2.534(2)
Ge8-Ge9	2.539(1)	Ge17-Ge18	2.497(1)
Ge6-Si1	2.387(2)	Ge15-Si9	2.381(2)
Ge8-Si5	2.386(2)	Ge17-Si13 / Ge17-Si17	2.311(6) / 2.486(8)
Ge1-Ti1	2.714(2)	Ge10-Ti1	2.739(2)
Ti1-Ct1*	2.051(2)	Ti1-Ct2*	2.055(1)
Ge2-Ge5 (h_1)	3.018(1)	Ge12-Ge13 (h_1)	2.967(1)
Ge3-Ge4 (h_2)	3.069(1)	Ge11-Ge14 (h_2)	3.468(1)
Ge7-Ge9 (h_3)	3.788(1)	Ge16-Ge18 (h_3)	3.576(1)
atoms	angle [deg]	atoms	angle [deg]
Ct1-Ti1-Ct2*	134.00(2)	Ge1-Ti1-Ge10	83.83(2)

*Ct: centroids of Cp rings; Ct1: C1-C5; Ct2: C6-C10

Table S4. Selected bond lengths and angles in **2a-II**.

bond	distance [Å]	bond	distance [Å]
Ge19-Ge20	2.576(1)	Ge28-Ge29	2.556(1)
Ge19-Ge21	2.585(1)	Ge28-Ge30	2.573(1)
Ge19-Ge22	2.579(1)	Ge28-Ge31	2.547(1)
Ge19-Ge23	2.585(1)	Ge28-Ge32	2.572(1)
Ge20-Ge21	2.670(1)	Ge29-Ge30	2.730(1)
Ge20-Ge24	2.544(1)	Ge29-Ge33	2.559(1)
Ge20-Ge25	2.596(2)	Ge29-Ge34	2.687(1)
Ge21-Ge25	2.709(1)	Ge30-Ge34	2.646(1)
Ge21-Ge26	2.539(1)	Ge30-Ge35	2.586(1)
Ge22-Ge23	2.660(1)	Ge31-Ge32	2.747(1)
Ge22-Ge26	2.554(1)	Ge31-Ge35	2.546(1)
Ge22-Ge27	2.735(1)	Ge31-Ge36	2.673(1)
Ge23-Ge24	2.550(1)	Ge32-Ge33	2.567(1)
Ge23-Ge27	2.592(1)	Ge32-Ge36	2.626(1)
Ge24-Ge25	2.583(1)	Ge33-Ge34	2.521(1)
Ge24-Ge27	2.545(1)	Ge33-Ge36	2.552(1)
Ge25-Ge26	2.539(1)	Ge34-Ge35	2.517(1)
Ge26-Ge27	2.492(1)	Ge35-Ge36	2.540(1)
Ge24-Si21	2.385(3)	Ge33-Si33	2.395(3)
Ge26-Si25 / Ge26-Si29	2.423(8) / 2.358(8)	Ge35-Si37 / Ge35-Si41	2.475(8) / 2.289(9)
Ge19-Ti2	2.732(2)	Ge28-Ti2	2.725(2)
Ti2-Ct3*	2.049(1)	Ti2-Ct4*	2.063(1)
Ge21-Ge22 (h_1)	2.981(1)	Ge30-Ge31 (h_1)	3.020(1)
Ge20-Ge23 (h_2)	3.486(1)	Ge29-Ge32 (h_2)	3.042(1)
Ge25-Ge27 (h_3)	3.558(1)	Ge34-Ge36 (h_3)	3.797(1)
atoms	angle [deg]	atoms	angle [deg]
Ct3-Ti2-Ct4*	133.91(2)	Ge19-Ti2-Ge28	83.52(2)

*Ct: centroids of Cp rings; Ct1: C56-C60; Ct2: C61-C65

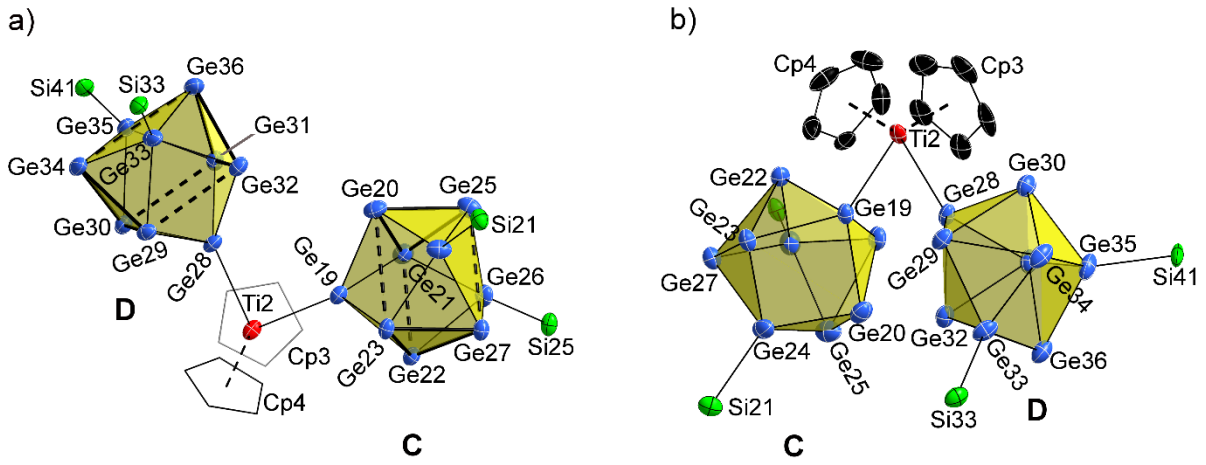

Figure S1. Two perspectives of the labelled molecular structure of **2a-II**. All displacement ellipsoids are shown at a 50 % probability level. a) C_S symmetric shape of the [Ge_9] clusters and coordination of [Ge_9] by the two silyl groups and the [Cp_2Ti]$^+$ moiety via the three capping atoms (Ge19, Ge24, Ge26 or Ge28, Ge33, Ge35) of the trigonal prism. For clarity carbon atoms of the cyclopentadienyl rings are represented as grey or black wire-and-sticks. b) Distorted tetrahedral coordination of Ti(III) by its four ligands. In a) and b) protons, solvent toluene molecules and TMS groups of the hypersilyl ligands are omitted, and only the major species of disordered silyl groups are shown. Selected bond lengths and angles of **2a-II** are summarized in Table 2 in the manuscript and in Table S3 in the Supporting Information. The molecular structure of **2a-I** is presented in the manuscript.

EPR Data

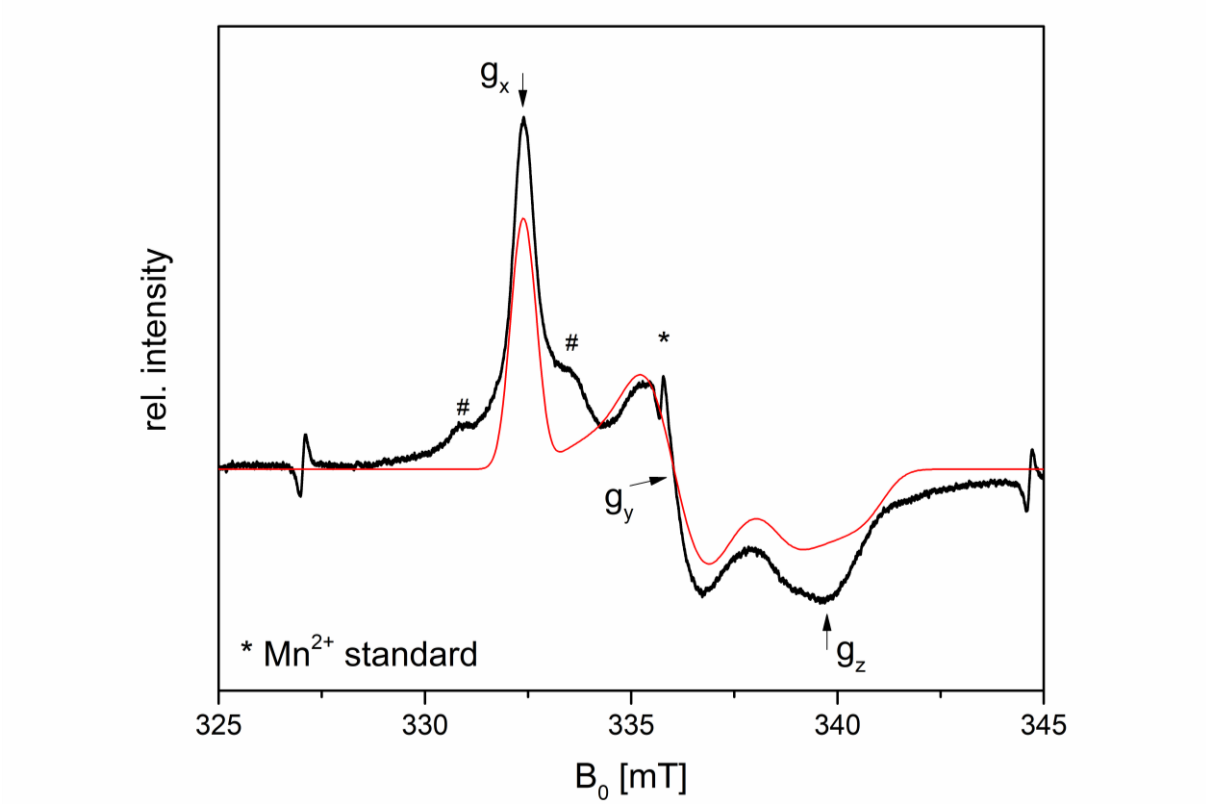

Figure S2. Experimental (black) and simulated (red) X-Band EPR spectrum of compound **2** in frozen thf solution at 130 K. The values for the anisotropic g-factors g_x: 1.992; g_y: 1.970 and g_z: 1.942 were determined relative to an Mn^{2+} standard (phase inverted, labelled with *), and simulated. The average g-factor was calculated to g_{avg} = 1.968. The shoulders labelled with # are probably caused by a minor impurity.

ESI-MS Data

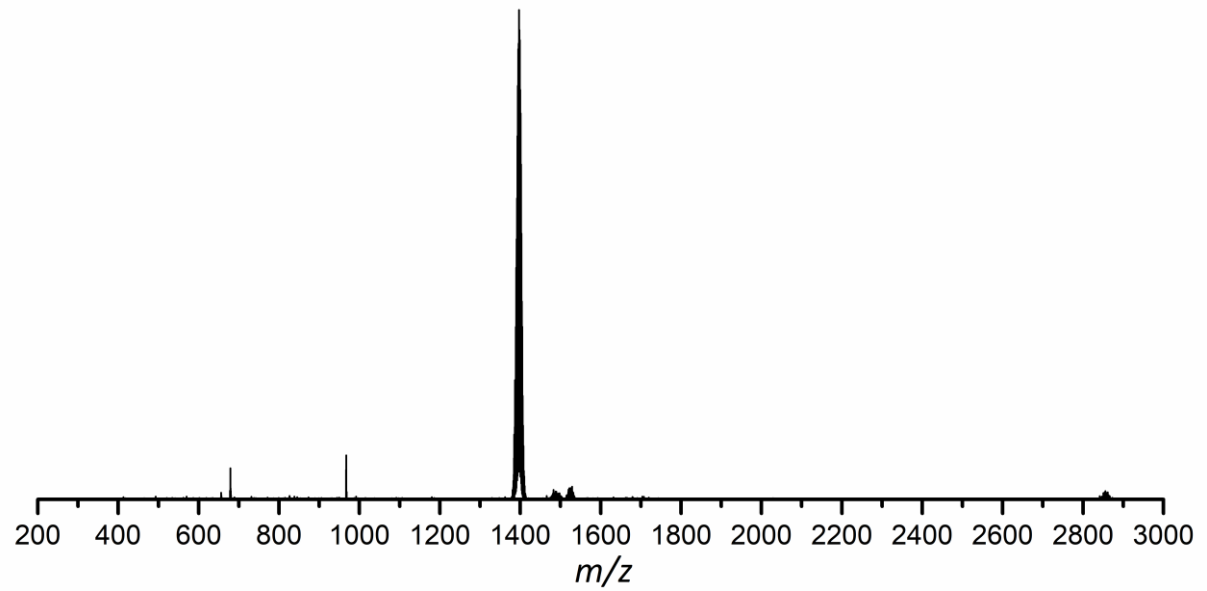

Figure S3. ESI-MS spectrum obtained from an aliquot sample of a thf solution of diluted crystals of **1**. The signal at *m/z* 1396.8 can be assigned to $\{[Ge_9\{Si(TMS)_3\}_3]\}^-$ formed upon cleavage of the $[Cp_2Ti(MeCN)]^+$ moiety from **1** during the ionization process.

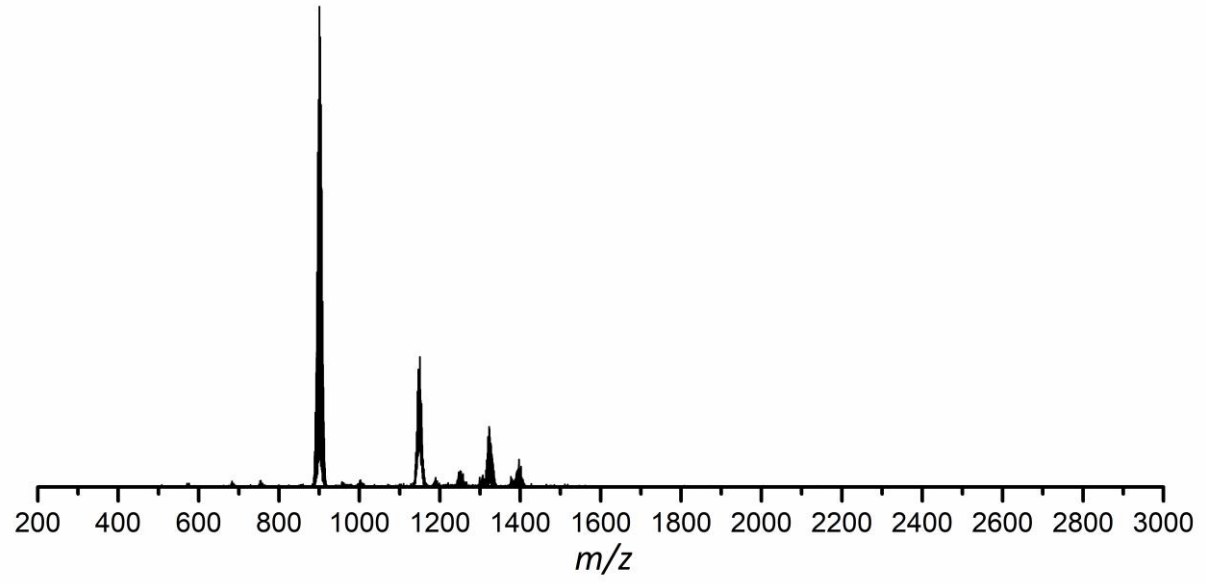

Figure S4. ESI-MS spectrum of an aliquot sample of a thf solution of diluted crystals of compound **2**. The signal at *m/z* 1326.5 can be assigned to $\{[Cp_2Ti(Ge_9\{Si(TMS)_3\}_2)]\}^-$ formed upon cleavage of one bis-silylated $[Ge_9]$ cluster ligand from **2a**. Besides the signal assigned to the Ge_9-Ti compound signals at *m/z* 900.4 and *m/z* 1147.4 appeared which can be assigned to $[Ge_9]$ clusters $\{[Ge_9\{Si(TMS)_3\}_1]\}^-$ or $\{[Ge_9\{Si(TMS)_3\}_2]\}^-$ formed upon further fragmentation of $\{[Cp_2Ti(Ge_9\{Si(TMS)_3\}_2)]\}^-$ during the ionization process.

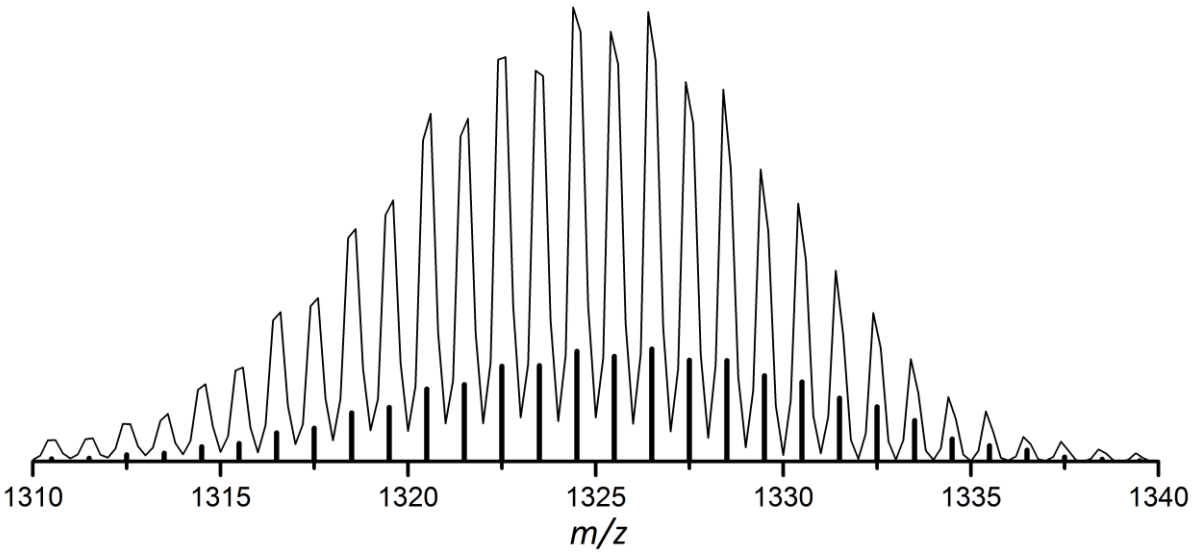

Figure S5. Detail view of the ESI-MS signal at *m/z* 1326.5, which can be assigned to $\{[Cp_2Ti(Ge_9\{Si(TMS)_3\}_2)]\}^-$. The signal was monitored upon measurement of an aliquot sample of a diluted thf solution of crystals of compound **2**. The calculated pattern is shown as black bars.