Electronic Supplementary Material (ESI) for Dalton Transactions
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Supplemental Information for

$[Si(SiMe_3)_3]_3Ge_9M(CO)_3^-$ (M = Cr, Mo, W): Coordination Chemistry with metalloid Clusters.

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Figure TS1: Molecular structure of $[(CO)_3MGe_9R_3]^-$; M = Cr, Mo, W; R = $Si(SiMe_3)_3$. Numeration of the atoms as used in table S1; ligand bound germanium atoms: Ge1, Ge2 and Ge3.

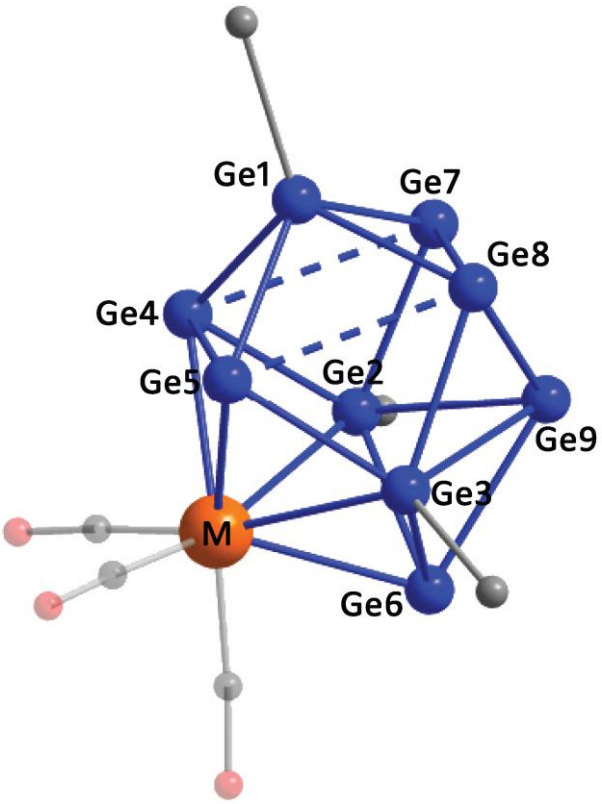

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Table S1: Ge-Ge and Ge-M distances (pm) in the metalloid cluster compounds $[(CO)_3MGe_9R_3]^-$; M = Cr, Mo, W; R = $Si(SiMe_3)_3$. Numeration of the germanium atoms is performed according to Figure TS1.

	$[(CO)_3CrGe_9R_3]^-$ **2** $[Li(THF)_2]^+$	$[(CO)_3CrGe_9R_3]^-$ **2**$[Li(TMEDA)_2]^+$	$[(CO)_3MoGe_9R_3]^-$ **4** $[Li(THF)_3]^+$	$[(CO)_3MoGe_9R_3]^-$ **4**$[Li(TMEDA)_2]^+$	$[(CO)_3WGe_9R_3]^-$ **5**$[Li(TMEDA)_2]^+$
d(M-Ge2)	268.60(14)	267.43(51)	280.92(10)	284.07(31)	280.52(9)
d(M-Ge3)	269.57(14)	270.41(45)	281.92(8)	280.52(24)	282.41(12)
d(M-Ge4)	266.06(13)	262.33(47)	273.61(9)	273.16(23)	273.37(11)
d(M-Ge5)	264.62(13)	265.27(49)	271.37(10)	273.91(27)	272.67(11)
d(M-Ge6)	267.85(16)	265.15(49)	274.13(7)	276.92(29)	275.06(12)
d(Ge1-Ge4)	254.43(11)	253.74(41)	251.81(9)	253.20(27)	252.95(16)
d(Ge1-Ge5)	253.87(11)	253.72(45)	253.79(10)	252.40(33)	253.40(15)
d(Ge1-Ge7)	250.16(12)	250.16(50)	251.57(9)	252.63(41)	250.99(15)
d(Ge1-Ge8)	250.11(13)	250.81(42)	249.37(8)	250.67(29)	250.79(19)
d(Ge2-Ge4)	254.43(12)	253.10(38)	256.15(8)	257.27(31)	259.00(14)
d(Ge2-Ge6)	253.55(12)	253.44(38)	253.65(8)	255.16(25)	254.36(14)
d(Ge2-Ge7)	260.75(11)	260.518(40)	257.53(9)	259.10(24)	259.50(14)
d(Ge2-Ge9)	273.98(11)	272.50(38)	271.47(8)	270.67(26)	272.90(16)
d(Ge3-Ge5)	254.61(12)	253.99(36)	256.28(8)	257.93(31)	257.25(15)
d(Ge3-Ge6)	252.90(11)	254.41(40)	252.42(9)	254.62(32)	255.57(14)
d(Ge3-Ge8)	259.65(11)	259.20(39)	258.14(9)	259.35(26)	259.36(14)
d(Ge3-Ge9)	275.29(12)	269.76(40)	273.64(10)	273.29(37)	270.31(15)
d(Ge4-Ge5)	274.02(11)	277.47(38)	282.22(10)	282.44(32)	281.86(15)
d(Ge4-Ge7)	317.6(3)	317.2(4)	313.50(9)	316.91(32)	316.81(15)
d(Ge5-Ge8)	318.7(2)	317.72(40)	316.58(9)	316.29(32)	317.60(16)
d(Ge6-Ge9)	272.77(11)	273.91(39)	271.2(1)	271.87(27)	273.30(15)
d(Ge7-Ge8)	281.85(12)	279.96(43)	282.29(9)	281.06(34)	279.97(16)
d(Ge7-Ge9)	258.43(12)	258.90(38)	258.85(8)	259.40(27)	259.27(15)
d(Ge8-Ge9)	258.48(11)	258.3(4)	256.95(9)	259.12(33)	258.81(15)

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Table S2: Results of an Ahlrichs-Heinzmann-population analysis of $H_3Ge_9M(CO)_3^-$ (M = Cr(**3a**), Mo(**4a**) and W(**5a**); SEN = shared electron numbers; numeration of atoms as emphasized in the last row.

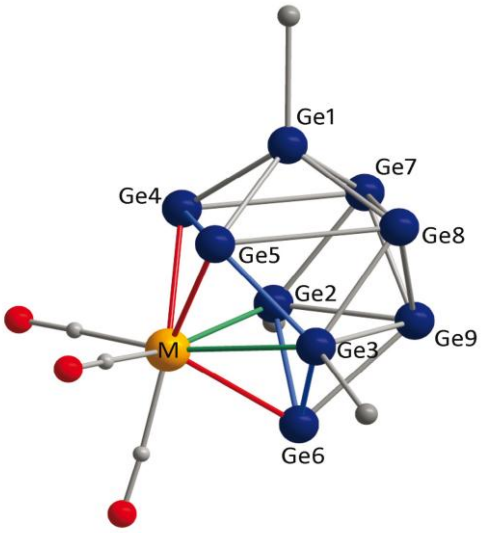
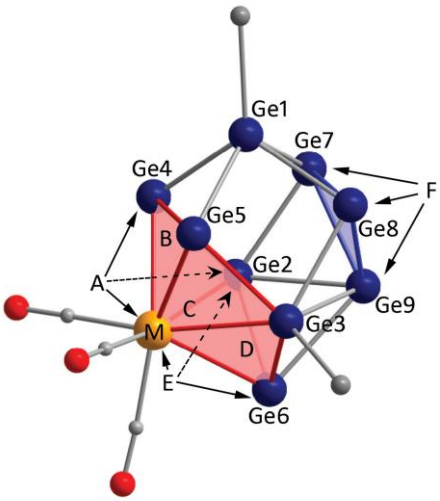
	3a	**4a**	**5a**
2c-SEN			
Ge4-M (red)	1.1322	0.6204	0.6981
Ge5-M (red)	1.1319	0.6207	0.6980
Ge6-M (red)	1.0867	0.5683	0.6880
Ge2-M (green)	0.9273	0.3907	0.4771
Ge3-M (green)	0.9234	0.3921	0.4798
Ge2-Ge4 (blue)	0.9706	0.9731	0.9839
Ge4-Ge5 (blue)	0.7514	0.6713	0.6505
Ge5-Ge3 (blue)	0.9747	0.9729	0.9839
Ge3-Ge6 (blue)	1.0513	1.0478	1.0667
Ge6-Ge2 (blue)	1.0496	1.0482	1.0684
3c-SEN			
Ge2-M-Ge4 A	0.2777	0.1587	0.1904
Ge4-M-Ge5 B	0.2994	0.1354	0.1375
Ge5-M-Ge3 C	0.2785	0.1590	0.1908
Ge3-M-Ge6 D	0.2807	0.1438	0.1867
Ge6-M-Ge2 E	0.2811	0.1436	0.1868
(red faces)			
Ge7-Ge8-Ge9 F (blue face)	0.2994	0.2963	0.2967
Charge M	-2.3270	-1.4015	-1.3009
			

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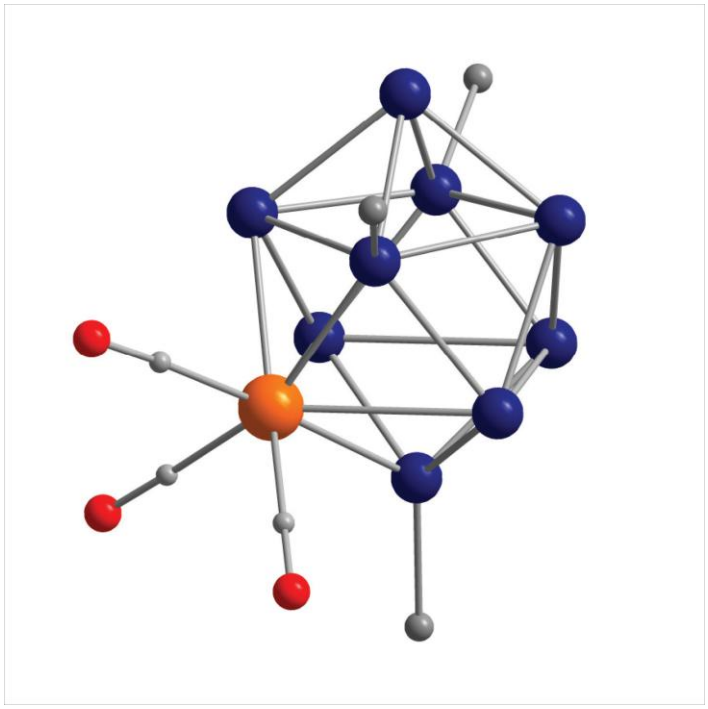
Figure S1: **Top:** Calculated molecular Structure of a second η^5 isomer of $[Ge_9R_3M(CO)_3]^-$ (M = Cr, Mo, W). Energetic difference to the observed η^5 isomer in **3**, **4** and **5** is +21.3 kJ/mol, +18.9 kJ/mol and -5.7 kJ/mol respectively. **Bottom:** Possible formation of the second η^5 isomer starting from the η^3 isomer **1c**; movement of the different atoms is emphasized by arrows.



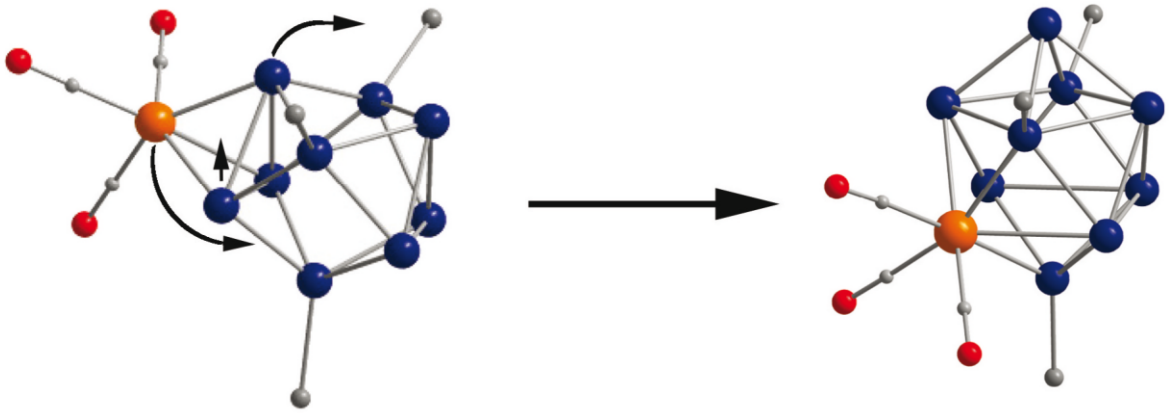


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Figure S2: Possible reaction sequence for the formation of **3** from a reaction of **1** and $Cr(CO)_3(CH_3CN)_3$ also considering reaction intermediates where CH_3CN ligands are substituted by THF ligands. The molecular structures of the intermediates **1a**, **1b** and **1c** are calculated minimumstructures obtained by DFT calculations. The given energies are also obtained by DFT calculations only taking the enthalpy into account.