Supporting Information

$[\text{Ge}_9\{\text{M(CO)}_5\}_3]^{4-}$: Electrophilic Addition of $\text{M(CO)}_5$ and $[\text{E}_9]^{4-}$ Zintl ions ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)

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Additional experimental details

All manipulations were carried out under argon using standard Schlenk-line and glovebox techniques. Ethylenediamine (Acros, 99%) was distilled over sodium metal and stored in a gastight Schlenk under argon in the glovebox. 18-crown-6 (1, 4, 7, 10, 13, 16-hexaoxa - cyclooctadecane, Alfa-Aesar, 99 %) was dried by refluxing over sodium metal in diethyl ether and recrystallized from dry n-hexanes. Toluene were dried with potassium-sodium alloy and then stored in the glovebox. Cr(CO)(ACROS, 99%), Mo(CO) 5 (Alfa-Aesar, 98%), W(CO) 6 (Alfa-Aesar, 97%) was used as received. Precursors with nominal compositions $\text{K}_4\text{Ge}_9$ was synthesized by heating the corresponding mixtures of elements (K: 99 %; Ge: 99.999 %, all from Strem) at 900 °C for two days in sealed niobium containers that were jacketed in evacuated fused-silica ampoules. IR data were recorded as KBr pellets in Nujol mulls on a Magna 750 FT-IR spectrometer photometer. Electrospray mass spectra were recorded from DMF solutions of 1 with nitrogen as sheath gas flow on a Finnigan LCQ-Ion Trap Mass Spectrometer (LCQ DECAX-30000 LCQ Deca XP) in negative-ion mode (spray voltage 4.5 kV, capillary temperature 275 °C, capillary voltage 15 V). The samples were made up inside a glovebox under an inert atmosphere and rapidly transferred to the spectrometer in an air-tight syringe by direct infusion with a Harvard syringe pump at 15 mLmin⁻¹.

**Synthesis and Crystallization of $[\text{K}(18\text{-crown-6})]_2[\text{Ge}_9\{\text{Cr(CO)}_5\}_3]$**

$\text{K}_4\text{Ge}_9$ (114 mg, 0.141 mmol) and 18-crown-6 (151 mg, 0.571 mmol) were dissolved in 2 mL ethylenediamine and stirred for 10 minutes at room temperature resulting in a dark red solution. Cr(CO) 5 (18.1 mg, 0.0821 mmol) was then added, and the mixture is stirred for another 30 minutes to an hour at room temperature, upon which it turns brownish-green. The temperature is then raised to 60 °C and kept for 2 hours. The resulting dark brownish solution is centrifuged and filtered via a glass fiber pipette. Aliquots of this solution are used for crystallization by layering with toluene (8 mL) solutions. The solution afforded long black needle-like crystals $[\text{K}(18\text{-crown-6})]_2[\text{Ge}_9\{\text{Cr(CO)}_5\}_3]$ (yield of 20-30% based on the crown ether) after several days to a week. The IR spectrum (KBr) of 1 shows the characteristic CO stretching vibrations: 1990 cm⁻¹ (vs, sh), 1910 cm⁻¹ (vs, sh).

**Synthesis and Crystallization of $[\text{K}(18\text{-crown-6})]_2[\text{Ge}_9\{\text{Mo(CO)}_5\}_3]$**

$\text{K}_4\text{Ge}_9$ (114 mg, 0.141 mmol) and 18-crown-6 (151 mg, 0.571 mmol) were dissolved in 2 mL ethylenediamine and stirred for 10 minutes at room temperature resulting in a dark red solution. Mo(CO) 5 (21.7 mg, 0.0821 mmol) was then added, and the mixture is stirred for another 30 minutes to an hour at room temperature, upon which it turns brownish-green. The temperature is then raised to 60 °C and kept for 2 hours. The resulting dark brownish solution is centrifuged and filtered via a glass fiber pipette. Aliquots of this solution are used for crystallization by layering with toluene (8 mL) solutions. The solution afforded long black needle-like crystals $[\text{K}(18\text{-crown-6})]_2[\text{Ge}_9\{\text{Mo(CO)}_5\}_3]$ (yield of 20-30% based on the crown ether) after several days to a week. The IR spectrum (KBr) of 1 shows the characteristic CO stretching vibrations: 2046 cm⁻¹ (s, sh), 1921 cm⁻¹ (vs, sh).
Structure Determination Data sets were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 173 K. The crystals were selected under mixed Araldite resin, mounted on fibers. The structure was solved by direct methods and refined on $F^2$ using the SHELXTL V6.21 package.¹

DFT Calculation Computational studies on the discrete clusters $\text{[Ge}_9\text{W}($CO$)_5\text{]}_3^{4-}$ were carried out using the GAUSSIAN 09 program package (Revision A.02).² Hybrid DFT calculations were performed with the B3LYP functional.³,⁴ GAUSSVIEW⁵ was used to visualize molecular orbitals. In these calculations, the solvent effects were taken into account by the Polarizable Continuum Model (PCM)⁶.

Fig. S1. Structural comparisons of 22e-[Ge$_9$] in (A) $D_{3h}-3a$, (B) distorted $D_{3h}$-[Ge$_9$Si(SiMe$_3$)$_3$]$_3$ $^{10a}$, (C) $C_{4v}$-Cs$_3$Ge$_9$(en) $^{16}$ and (D) $C_{2v}$-[K-(2,2)diaza-18-crown-6]K$_3$Ge$_9$(en)$_2$ $^{19}$

Fig. S2. Side-directed arrangement of [K(18-crown-6)]$^+$ counterions toward the [Ge$_9$]$^{4+}$ core cluster of 3.
**Fig. S3.** The observed (top) and theoretical (bottom) electrospray mass spectra in negative ion mode of the crystalline 3 in DMF solution (all species are monoanions). The dianion [Ge₃(W(CO)₅)₃]²⁻ coupled with K⁺ or [K(18-crown-6)]⁺ is clearly visible.

**Fig. S4.** IR spectrum of 3 in Nujol mulls.
**Fig. S5.** PXRD of the precursor with a nominal composition "K₄Ge₉".

**References**