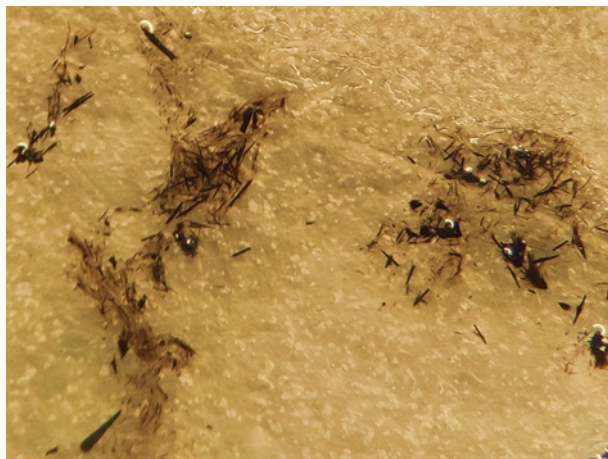


Supplementary Information

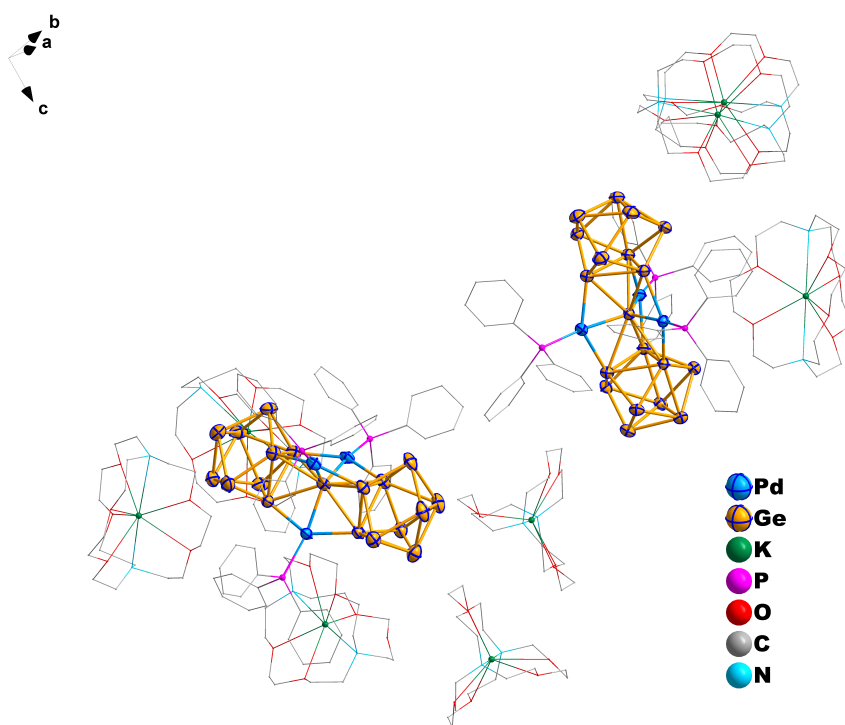
A Sandwich-Type Cluster Containing Ge@Pd₃ Planar Fragment Flanked by Aromatic Nonagermanide Caps

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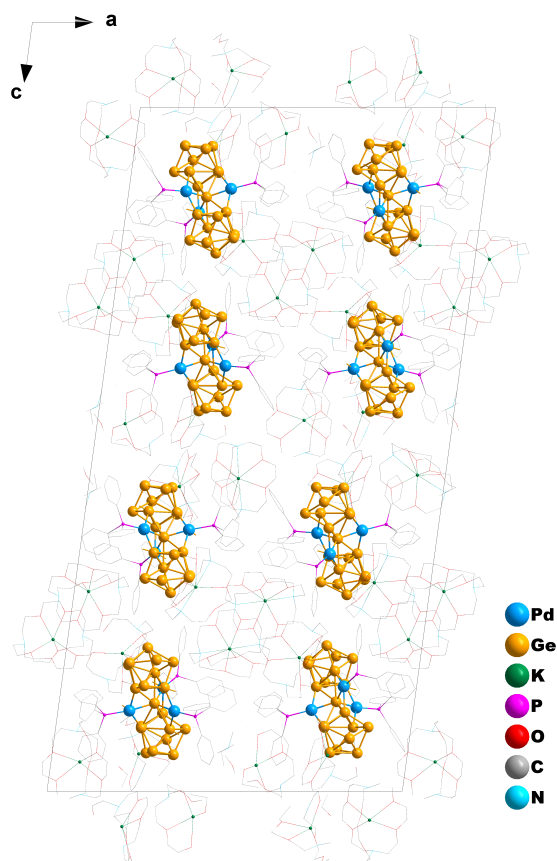
Supplementary Figures



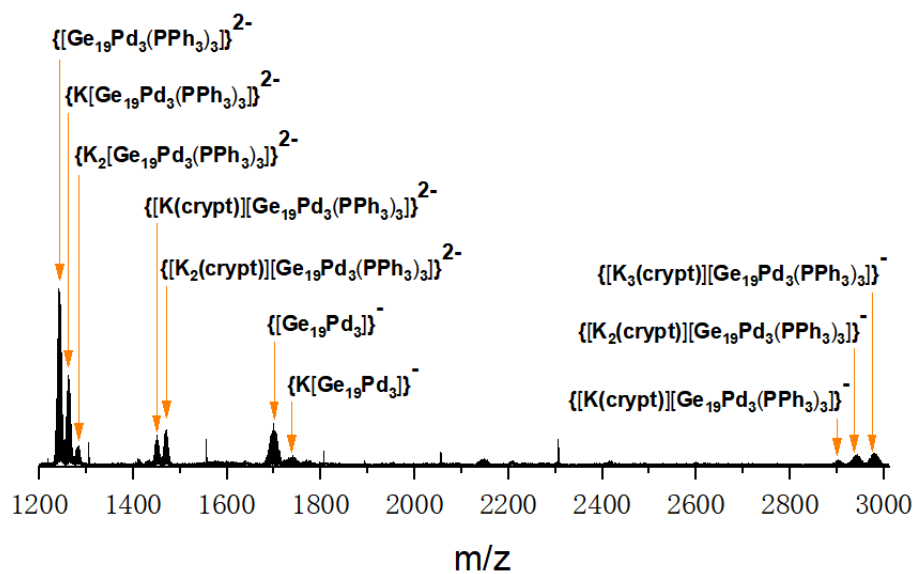
Supplementary Figure 1. Crystals of $[K(2,2,2\text{-crypt})]_4\{((Ge_9)_2[\eta^6\text{-Ge(PdPPh}_3)_3])\}$ dispersed in silicon oil.



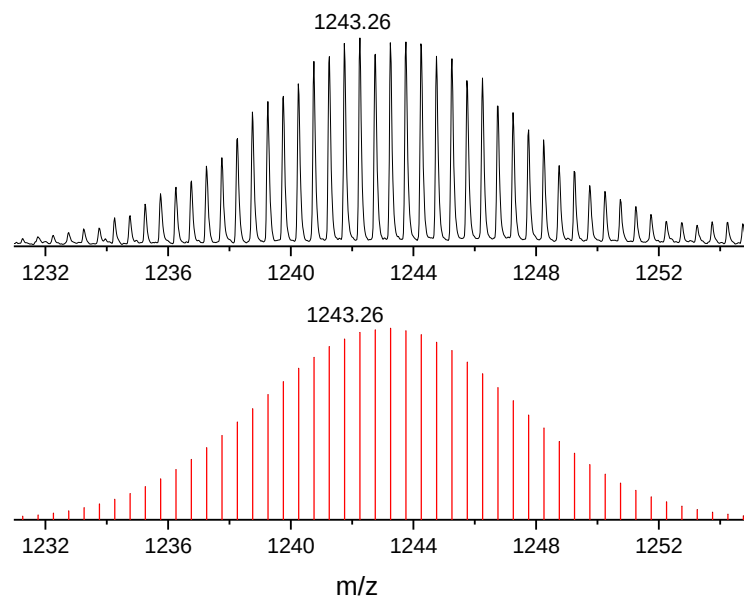
Supplementary Figure 2. Asymmetric unit of $[K(2,2,2\text{-crypt})]_4\{((Ge_9)_2[\eta^6\text{-Ge(PdPPh}_3)_3])\}$ with the cluster fragment. Thermal ellipsoids are drawn at 50% probability. The minor components are omitted for clarity.



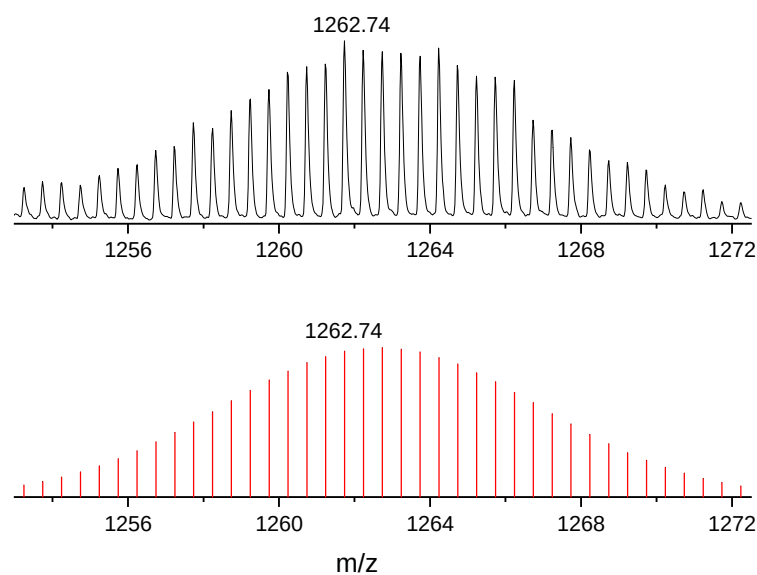
Supplementary Figure 3. Unit cell of $[\text{K}(2,2,2\text{-crypt})]_4\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPPh}_3)_3]\}$. Minor component in the cluster site are omitted for clarity.



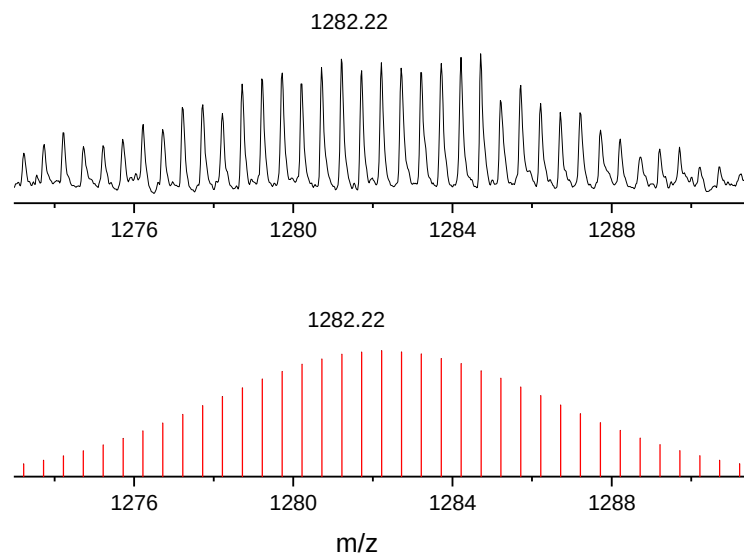
Supplementary Figure 4. Overview ESI mass spectrum in negative ion mode of a freshly dissolved crystalline sample of $[\text{K}(2,2,2\text{-crypt})]_4\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPPh}_3)_3]\}$ in DMF.



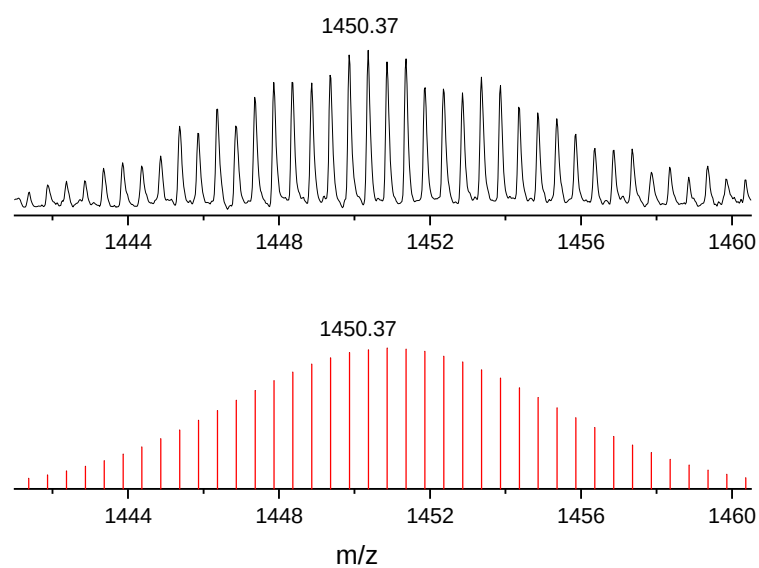
Supplementary Figure 5. Measured (top) and simulated (bottom) spectrum of the fragment $\{[\text{Ge}_{19}\text{Pd}_3(\text{PPh}_3)_3]\}^{2-}$.



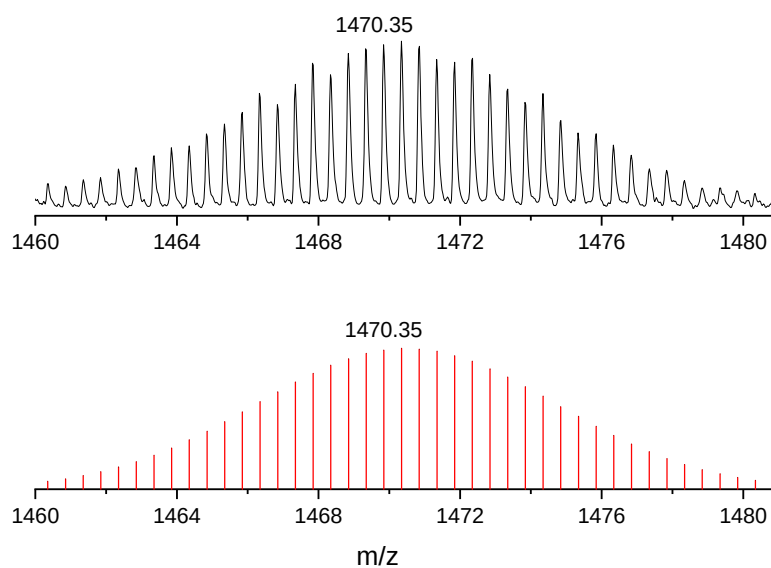
Supplementary Figure 6. Measured (top) and simulated (bottom) spectrum of the fragment $\{\text{K}[\text{Ge}_{19}\text{Pd}_3(\text{PPh}_3)_3]\}^{2-}$.



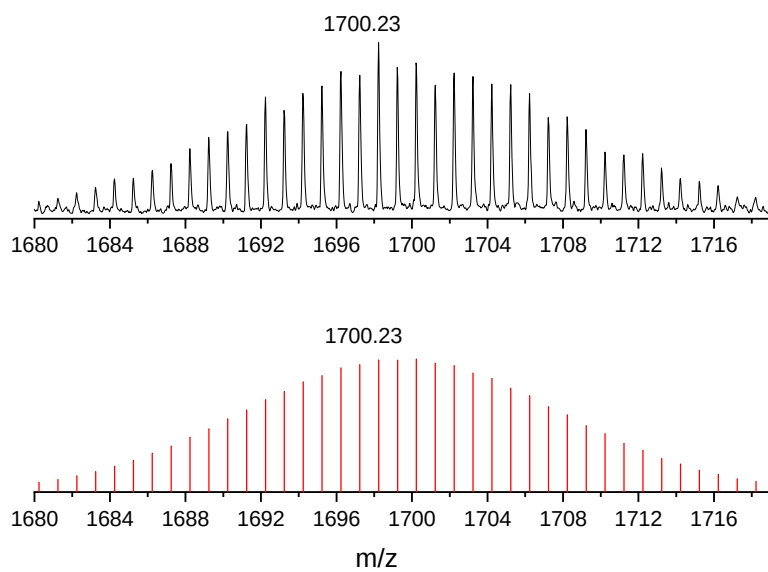
Supplementary Figure 7. Measured (top) and simulated (bottom) spectrum of the fragment $\{K_2[Ge_{19}Pd_3(PPh_3)_3]\}^{2-}$.



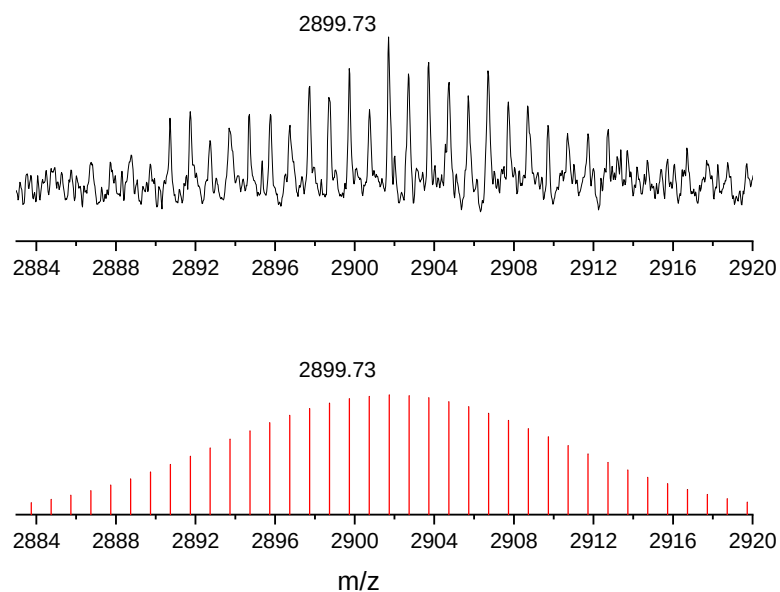
Supplementary Figure 8. Measured (top) and simulated (bottom) spectrum of the fragment $\{[K(2,2,2\text{-crypt})][Ge_{19}Pd_3(PPh_3)_3]\}^{2-}$.



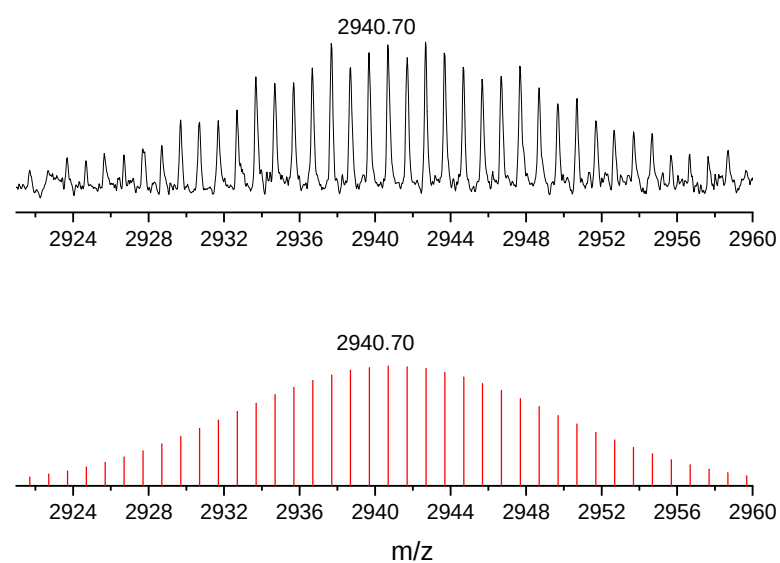
Supplementary Figure 9. Measured (top) and simulated (bottom) spectrum of the fragment $\{[K_2(2,2,2\text{-crypt})][Ge_{19}Pd_3(PPh_3)_3]\}^{2-}$.



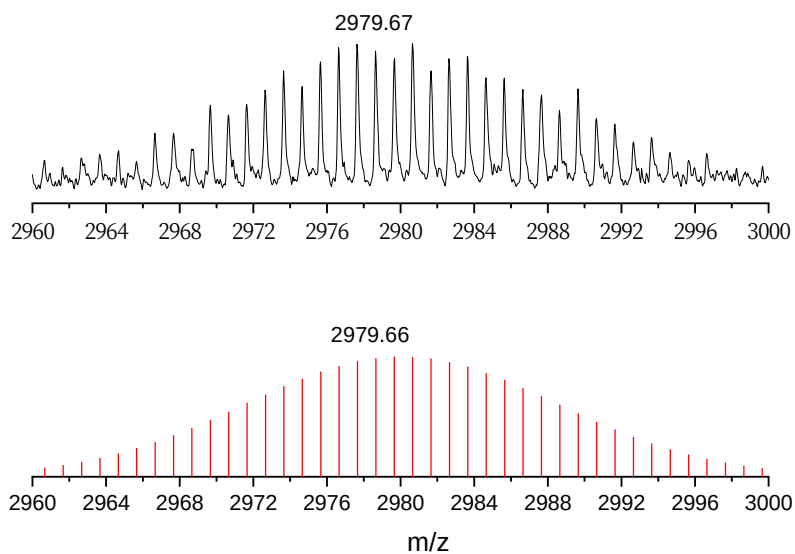
Supplementary Figure 10. Measured (top) and simulated (bottom) spectrum of the fragment $\{[Ge_{19}Pd_3]\}^-$.



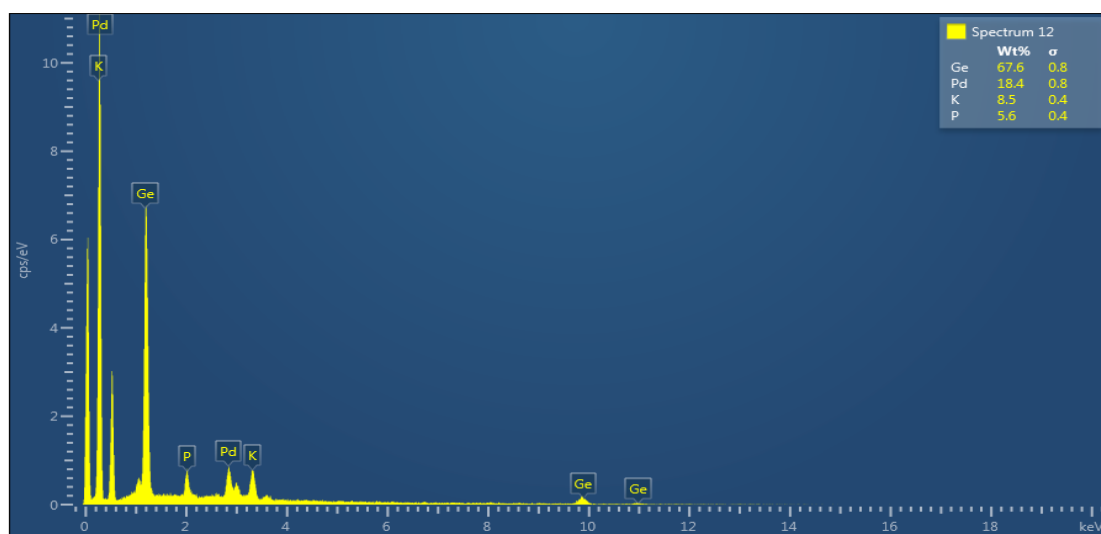
Supplementary Figure 11. Measured (top) and simulated (bottom) spectrum of the fragment $\{[K(2,2,2\text{-crypt})][Ge_{19}Pd_3(PPh_3)_3]\}^-$.



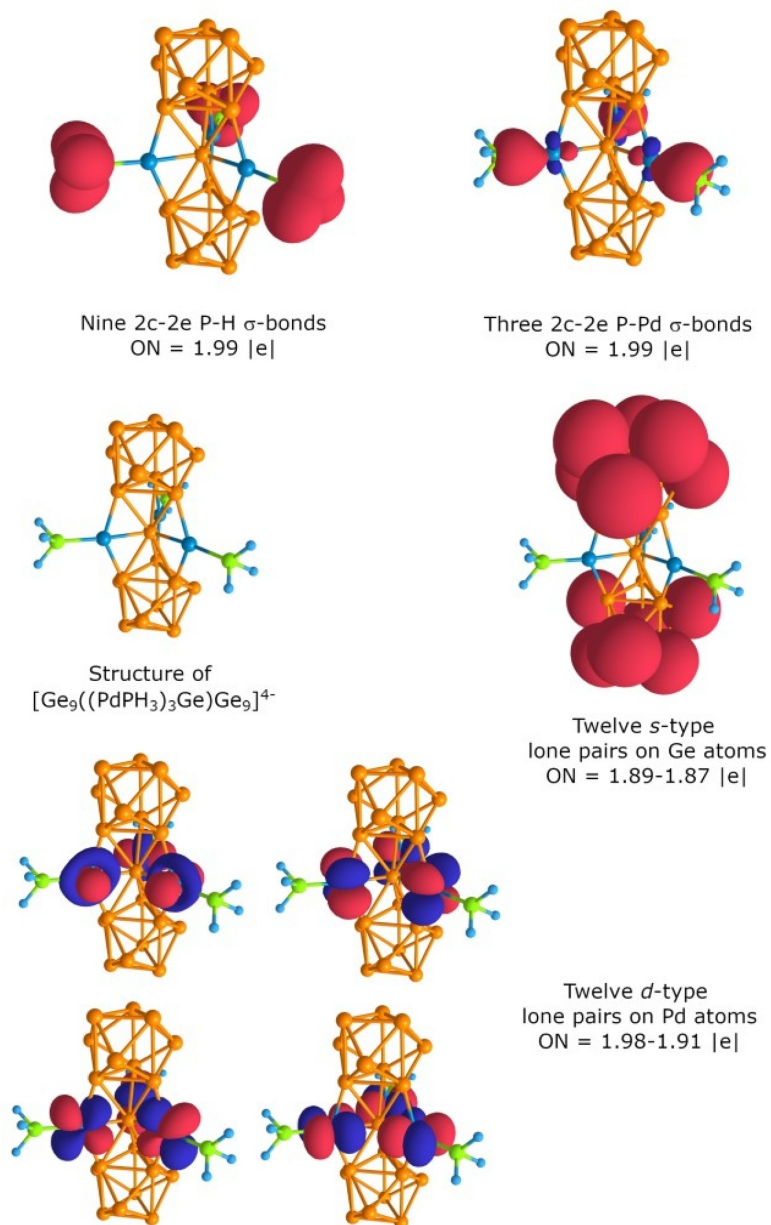
Supplementary Figure 12. Measured (top) and simulated (bottom) spectrum of the fragment $\{[K_2(2,2,2\text{-crypt})][Ge_{19}Pd_3(PPh_3)_3]\}^-$.



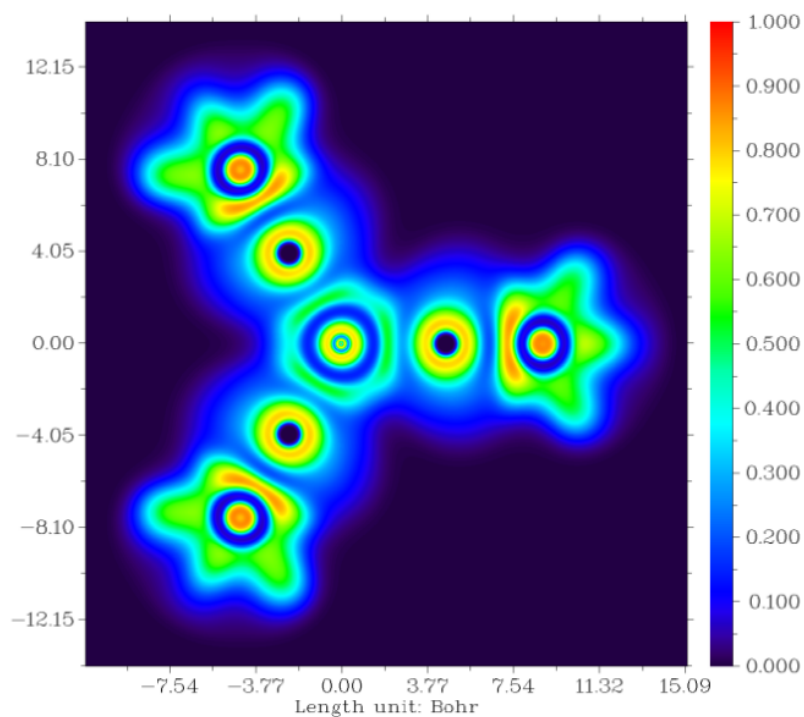
Supplementary Figure 13. Measured (top) and simulated (bottom) spectrum of the fragment $\{[K_3(2,2,2\text{-crypt})][Ge_{19}Pd_3(PPh_3)_3]\}^+$.



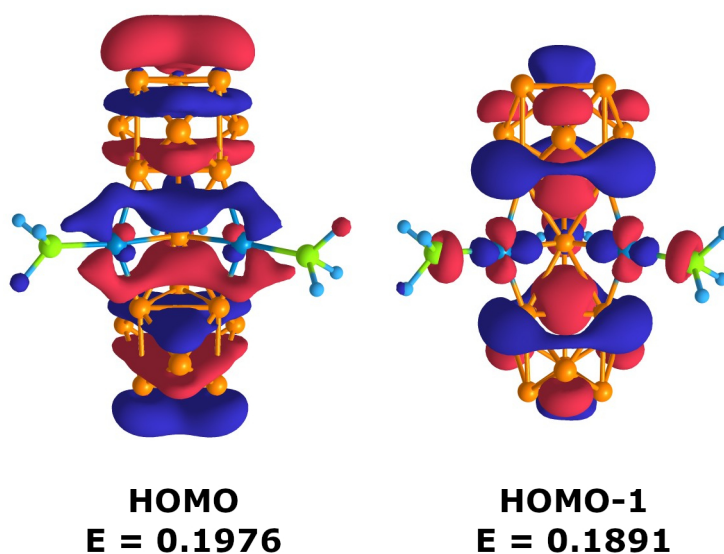
Supplementary Figure 14. EDX analysis of title compound (K, Ge, Pd, P).



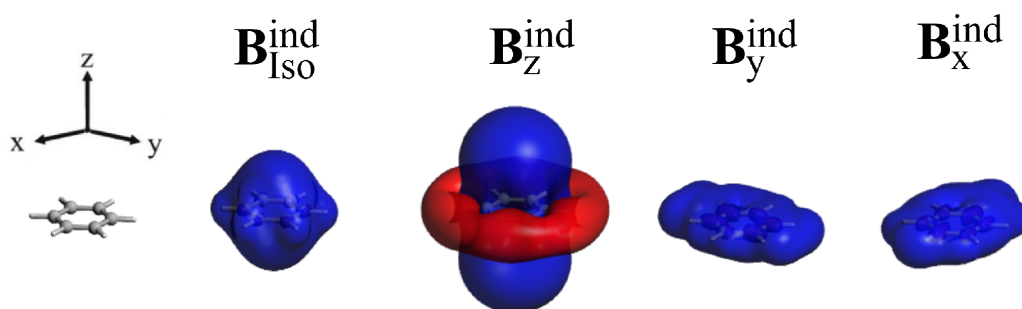
Supplementary Figure 15. Localized 2c-2e bonds and lone pairs of $\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPH}_3)_3]\}^{4-}$.



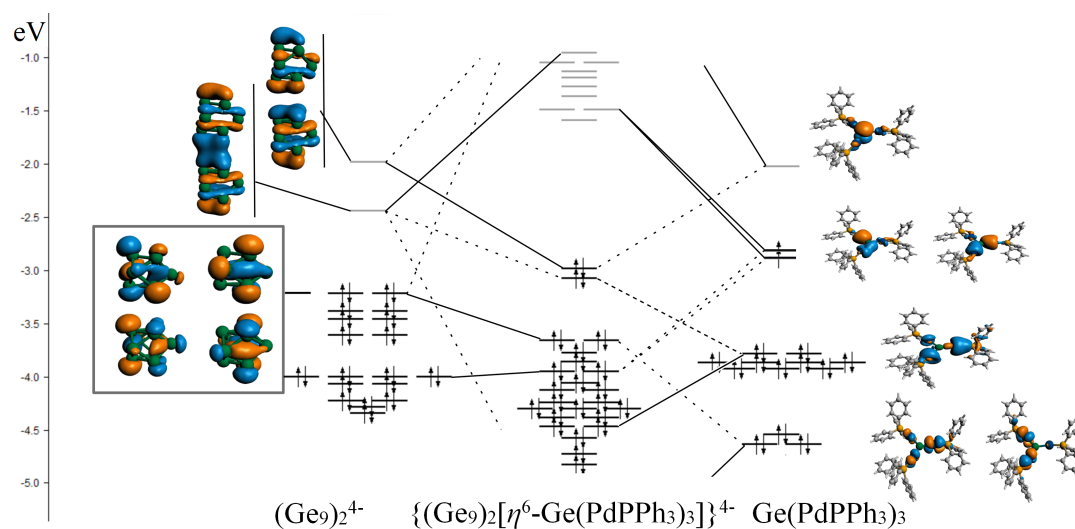
Supplementary Figure 16. ELF-plot of planar GePd_3 fragment. Different values of ELF are shown with different colors according to the color scale on the right side of the figure.



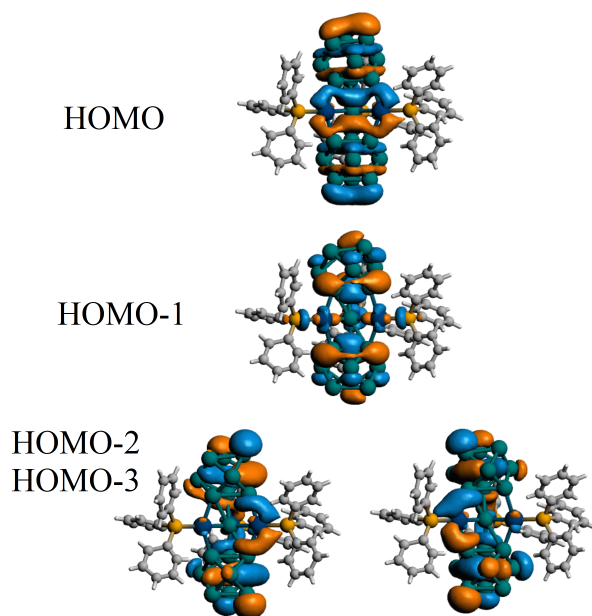
Supplementary Figure 17. Plots of HOMO and HOMO-1 molecular orbitals and their energies (Hartree) for $\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPH}_3)_3]\}^4$ cluster.



Supplementary Figure 18. The induced magnetic field for benzene.



Supplementary Figure 19. Molecular orbital diagram denoting the $(\text{Ge}_9)_2^{4-}$ - $\text{Ge}(\text{PdPPh}_3)_3$ interaction. See Supplementary Figure 20 for HOMO-2 and HOMO-3 orbitals of the overall cluster.



Supplementary Figure 20. Molecular orbitals for $\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPPh}_3)_3]\}^{4+}$ cluster. Note resemblance to $\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPH}_3)_3]\}^{4+}$ cluster (Supplementary Figure 17).

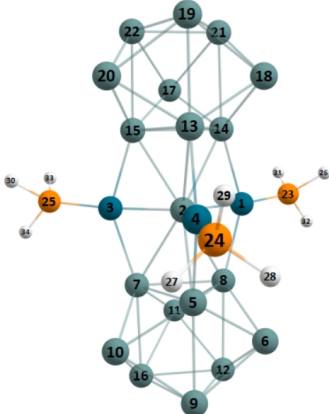
Supplementary Tables

Supplementary Table 1. Crystal data and structure refinement.

Identification code	$[\text{K}(2,2,2\text{-crypt})]_4\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPPh}_3)_3]\}$
Empirical formula	$\text{C}_{126}\text{H}_{189}\text{Ge}_{19}\text{K}_4\text{N}_8\text{O}_{24}\text{P}_3\text{Pd}_3$
Formula weight	4148.46
Temperature/K	100.00(2)
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	32.6511(4)
$b/\text{\AA}$	16.94251(18)
$c/\text{\AA}$	63.3300(8)
$\alpha/^\circ$	90
$\beta/^\circ$	97.7775(12)
$\gamma/^\circ$	90
Volume/ \AA^3	34711.3(7)
Z	8

$P_{\text{calc.}}/\text{g cm}^{-3}$	1.585
μ/mm^{-1}	7.618
$F(000)$	16456.0
2θ range for data collection/ $^{\circ}$	4.71 to 132.2
Reflections collected	171092
Data/restraints/parameters	60441/9473/3358
Goodness-of-fit on F^2	1.033
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0957$, $wR_2 = 0.2334$
Final R indexes [all data]	$R_1 = 0.1133$, $wR_2 = 0.2431$
Largest diff. peak/hole / e \AA^{-3}	2.36/-1.66
CCDC	1997656

Supplementary Table 2. The calculated natural charges of the selected atoms.

		
Atom	No	Charge
Pd	1	-0.39034
Ge	2	0.13383
Pd	3	-0.39034
Pd	4	-0.39075
Ge	5	-0.13035
Ge	6	-0.21708
Ge	7	-0.11487
Ge	8	-0.11487
Ge	9	-0.21029
Ge	10	-0.21708
Ge	11	-0.21608
Ge	12	-0.20795
Ge	13	-0.11177
Ge	14	-0.12743
Ge	15	-0.12743

Ge	16	-0.20795
Ge	17	-0.21804
Ge	18	-0.2169
Ge	19	-0.20663
Ge	20	-0.2169
Ge	21	-0.20934
Ge	22	-0.20934
P	23	0.21237
P	24	0.21223
P	25	0.21237
H	26	-0.02598
H	27	-0.02564
H	28	-0.02564
H	29	-0.05492
H	30	-0.02598
H	31	-0.02588
H	32	-0.05457
H	33	-0.02588
H	34	-0.05457

Supplementary Methods

ESI-MS Studies

Negative ion mode ESI-MS of a DMF solution of crystals of $[\text{K}(2,2,2\text{-crypt})]_4\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPPh}_3)_3]\}$ was measured on an LTQ linear ion trap spectrometer by Agilent Technologies ESI-TOF-MS (6230). The spray voltage was 5.48 kV, the capillary temperature was kept at 300 °C and the capillary voltage was 30 V. The sample was prepared inside a glovebox and very rapidly transferred to the spectrometer in an airtight syringe by direct infusion with a Harvard syringe pump at 0.1 mL min⁻¹.

Energy Dispersive X-ray (EDX) Spectroscopic Analysis

EDX analysis on $[\text{K}(2,2,2\text{-crypt})]_4\{(\text{Ge}_9)_2[\eta^6\text{-Ge}(\text{PdPPh}_3)_3]\}$ (Supplementary Figure 14) was performed by a scanning electron microscope (FE-SEM, JEOL JSM-7800F, Japan). Data acquisition was performed with an acceleration voltage of 15 kV and an accumulation time of 60 s. The atomic ratio of K/Ge/Pd/P is 4.2:18.3:3.3:3.4.