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Supporting Information

(Ge₂P₂)²⁻: A Binary Analogue of P₄ as a Precursor to the Ternary Cluster Anion [Cd₃(Ge₃P)₃]³⁻

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1. Synthesis details

1.1. General

All manipulations and reactions were performed under dry Ar atmosphere by using standard Schlenk or glovebox techniques. Ethane-1,2-diamine (ethylenediamine, *en*) was distilled over CaH₂ and stored over molecular sieves. Toluene and tetrahydrofurane (THF) were distilled over Na/K alloy and stored over molecular sieves. crypt-222^[1] (Merck) was dried *in vacuo* for at least 18 h. Ge and P (red) of a purity of 99.99% or higher was used.

The solid mixture with a nominal composition "K₂Ge₂P₂" was accessed by combining K, Ge and P (red) in equimolar amounts in a niobium ampoule. The ampoule was sealed by arc-welding, and then stored in silica glass ampoule, which was sealed under vacuum, before heating in an oven at 950°C for 2 d. The resulting solid was pulverized in a mortar thoroughly prior to further use.

1.2. Syntheses

1.2.1. Synthesis of [K([crypt-222]2(Ge2P2)·en (1) and [K([crypt-222]2(Ge7P2) (2)

0.2 mmol of "K₂Ge₂P₂" and 0.2 mmol of crypt-222 were weighed out into a Schlenk tube. Then *en* (ethane-1,2-diamine, 6 mL) was added. The reaction mixture was allowed to stir at room temperature for 3 h. The liquid was filtered through a standard glass frit (D3), yielding a yellow solution that was carefully layered with *tol* (toluene, 12 mL). After 3 days, clear yellow tabular prisms of [K(crypt-222)]₂(Ge₂P₂)·en (**1**) crystallized. Yield: approx. 21%.



Figure S1. Crystals of $[K(crypt-222)]_2(Ge_2P_2) \cdot en(1)$.

If the Schlenk tube is left undisturbed for a longer time (>7 days), dark orange cubes of [K(crypt-222)]₂(Ge₇P₂) (**2**) crystallize beside the clear yellow tabular prisms of **1** in approx. 10% yield.

After several weeks, all crystals of **1** have disappeared, and the only visible crystals are dark red cubes of **2**. Yield: approx. 20%.



Figure S2. Crystals of [K([crypt-222]₂(Ge₇P₂) (**2**).

To obtain **1** in high purity and yield the extraction process is stopped after 3 h. After filtration through a standard glass frit (D3) a large volume of dry THF is added. **1** precipitates and is separated by filtration. The filtrate is cooled at 5°C over night. After a second filtration, the combined precipitates are dried *in vacuo*. A bright yellow solid is obtained at 70% yield.

1.2.2. Synthesis of [K(crypt-222)]2[(Ge₃P)₃Cd₃] (3)

0.05 mmol of **1** are dissolved in 3 ml of *en*. Then 0.05 mmol of Ph₂Cd (or small excess) were added. After 3 h of stirring at room temperature the solution is filtered through a standard glass frit (D3) and layered with *tol*. After one week elongated red square prisms that dendritically agglomerate into a leaf-like morphology crystallized. They had to be broken down to single crystalline fragments for SCXD. Yield: approx. 24%. The synthesis of **3** can also be addressed directly from "K₂Ge₂P₂" and Ph₂Cd in the presence of crypt-222 in *en*.



Figure S3. Crystal agglomerates of [K(crypt-222)]₃[(Ge₃P)₃Cd₃]·tol (**3**).

2. Single crystal X-ray crystallography

The data for the X-ray structural analyses were collected at T = 100(2) K with Mo-K_αradiation ($\lambda_{Mo-K\alpha}$ = 0.71073 Å) on an area detector system Stoe IPDS2 or Stoe IPDS2T or with a CCD detector system on a Bruker QUEST. The structures were solved by direct methods (SHELXS-97^[2]), and refined by full-matrix-least-squares methods against *F*² with program SHELXL-2013.^[2] Crystallographic data for the three structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications No. CCDC 1579583 (**1**), CCDC 1579584 (**2**) and CCDC 1579585 (**3**). The crystal data and experimental parameters of the structure determinations are collected in Table S1. Supplementary Figures are provided in Figures S4-S10 and selected structural parameters are listed in Tables S2-S4.
 Table S1. Crystal data and details of the structure determinations of 1 - 3.

Compound	1	2	3
empirical formula	$C_{38}H_{82}Ge_2K_2N_6O_{12}P_2$	C ₃₆ H ₇₂ Ge ₇ K ₂ N ₄ O ₁₂ P ₂	$C_{61}H_{116}Cd_3Ge_9K_3N_6O_{18}P_3$
formula weight [g mol ⁻¹]	1100.41	1401.24	2422.53
crystal color, shape	Yellow tabular prism	Dark red cube	Dark red block
crystal size [mm ³]	0.59 × 0.34 × 0.30	0.075 × 0.097 × 0.116	0.054 × 0.171 × 0.189
crystal system	triclinic	trigonal	hexagonal
space group	<i>P</i> 1	<i>P</i> –3c1	P6522
<i>a</i> [Å]	10.932(2)	11.8967(17)	15.237(2)
b[Å]	11.924(2)	11.8967(17)	15.237(2)
<i>c</i> [Å]	12.549(3)	22.394(5)	68.672(14)
α [°]	118.03(3)	90	90
β [°]	108.44(3)	90	90
γ [°]	96.10(3)	120	120
V [ų]	1304.7(6)	2744.8(10)	13807(5)
Z, $ ho_{calc}$ [g cm ⁻³]	1, 1.390	2, 1.695	6, 1.748
μ (Mo _{Kα}) [mm ⁻¹]	1.431	4.045	3.816
Absorption correction type	numerical	numerical	multi-scan
20 range [°]	4.00 to 53.60	5.36 to 52.00	4.80 to 51.40
total reflections	34245	3628	132693
unique reflections [R _{int}]	10561	3313	8698
obs. reflections [I> 2σ (I)]	8825	1787	7688
parameters	548	119	489
R1 [I>2σ(I)] / <i>w</i> R2 (all data)	0.0452 / 0.1210	0.0652 / 0.1674	0.0733 / 0.1796
GooF (all data)	0.9730	0.8770	1.123
max peak/hole [e ų]	0.80 / -0.69	1.5500 / -0.9300	1.1800 / -1.0700
Flack parameter	0.102(5)	-	-

2.1. Details of the structure determination of [K(crypt-222)]₂(Ge₂P₂) (1)

A numerical absorption correction has been applied based on crystal faces optimized by the XSHAPE procedure in X-AREA (Stoe 2013).

Cluster anion: The anionic cluster component is a tetrahedral $(Ge_2P_2)^{2-}$. Due to rotational disorder two germanium atoms and one phosphorous atom are equally distributed over three cluster positions leading to site occupation factors of 2/3 for Ge and 1/3 for P for these positions, while the second phosphorous atom is clearly localized. The disordered *en* molecule breaks the *P*–1 symmetry resulting in the space group *P*1, as already observed for the heavier binary tetrahedral group 14/15 Zintl anion species.

Cations: The two [K(crypt-222)]⁺ cations are well localized. All cations were refined using geometrical restraints on the bond lengths and 1,3-distances but leaving conformational freedom (SAME option of SHELXL). This explains the large number of restraints.

Solvent: One *en* molecule was found in the unit cell, the atoms of which were refined using anisotropic displacement parameters.

Atom numbers	Bond length
1–2	2.387(2) Å
1–3	2.388(2) Å
1–4	2.349(2) Å
2–3	2.521(1) Å
2–4	2.635(2) Å
3–4	2.598(2) Å
Average	2.479 Å

 Table S2. Bond lengths of the anionic cluster in 1.



Figure S4. $(Ge_2P_2)^{2-}$ anion in 1 with one of the disorder models shown. Ellipsoids shown at 50% probability.

2.2. Details of the structure determination of [K(crypt-222)]₂(Ge₇P₂) (2)

A numerical absorption correction has been applied based on crystal faces optimized by the XSHAPE procedure in XAREA (Stoe 2013).

Cluster anion: The $(Ge_7P_2)^{2-}$ anion itself has the site symmetry 32. (D₃). Around the Wyckoff position 2a, the 3-fold symmetry axis creates 24 atom positions which can be assigned to three anion orientations, in which two atoms in each anion orientation are shared with one other orientation. Ge1 and Ge2 occupy a .2. site (Wyckoff position 6f), whereas Ge3, Ge4 and P1 occupy a 12g Wyckoff position. The crystal structure is closely related to the one of [K([crypt-222]₂(Ge₇As₂),^[3] featuring the same crystallographic disorder.

Cations: The structure of 2 crystallizes in space group P–3c1 with the [K(crypt-222)]⁺ cation on a 3-fold axis which runs through atoms K1, N1 and N2 with 3.. site symmetry (Wyckoff position 4d). C1-C6 as well as O1 and O2 occupy a 12g Wyckoff position. All cations were refined using enhanced rigid bond restraints (RIGU option) on the bond lengths and 1,3-distances.

Solvent: There is no solvent present.

Atom numbers	Bond length
Ge1–Ge2	2.502(3) Å
Ge2–Ge4	2.630(5) Å
Ge1–Ge3	2.461(2) Å
Ge3–Ge4	2.470(5) Å
P1–Ge3	2.447(8) Å
P1–Ge4	2.578(7) Å

 Table S3. Selected bond lengths of the anionic cluster in 2.



Figure S5. Three anion orientations in 2 overlaid.



Figure S6. Separated anion orientations in 2. Shared sites are indicated by mixed color.



Figure S7. $(Ge_7P_2)^{2-}$ anion in 2 with only one of the disorder models shown. Ellipsoids shown at 50% probability.

2.3. Details of the structure determination of [K(crypt-222)]₃[(Ge₃P)₃Cd₃]·tol (3)

MULTISCAN absorption correction was applied within the APEX3 software suite (Bruker 2016). The compound crystallizes in the space group $P6_522$ with a very long *c* axis of 68.672(14) Å.



Figure S8. View of the unit cell of 3 along the *a* axis.

Cluster anion: The cluster anion consists of three [(Ge₃P)Cd]⁻ units. The Cd atoms are coordinated and interconnected by Ge atoms of the Ge₃P unit, while the P atoms do not bind to the Cd atoms. The disk-like cluster anion has two orientations that crystallize with a 0.5:0.5 ratio on the same position. Cd1 occupies the Wyckoff position 6b with ..2 site symmetry. Cd2A and Cd2B occupy a 12c Wyckoff position with an occupancy of 0.5 each. All Ge and P atoms occupy a 12c Wyckoff position, and also possess a 0.5 occupancy.



Figure S9. Overlaid image of the two anion orientations in **3**, illustrated by drawing one of them in solid mode and the other one in transparent mode. Dashed lines that connect Cd atoms do not indicate bonds but serve as a guide to the eye. Ellipsoids shown at 50% probability.

Cations: 18 [K(crypt-222)]⁺ units are present within one unit cell. C–C distances in the cation have been fixed with DFIX at 1.49 Å or using enhanced rigid bond restraints (RIGU option) on the bond lengths and 1,3-distances.

Solvent: Six toluene molecules are present within the unit cell. To model the solvent molecule with anisotropic displacement parameters, DELU, SIMU and RIGU commands were used.

Atom numbers	Bond length
Cd2A–Ge2	2.793(3) Å
Cd2A–Ge3	2.723(3) Å
Cd2B–Ge1	2.685(4) Å
Cd2B–Ge4	2.791(4) Å
Cd2B–Ge5	2.752(4) Å
P1–Ge1	2.352(7) Å
P1–Ge2	2.305(9) Å

 Table S4. Selected bond lengths of the anionic cluster in 3.

3. Energy dispersive X-ray spectroscopy (EDX) analysis

EDX analyses were performed to support the elemental composition that was suggested based on the XRD experiments. These were carried out using an EDX-device Voyager 4.0 of Noran Instruments coupled with an electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 20 kV and 100 s accumulation time. The radiation emitted by the atoms was analyzed: K-K, Ge-K, P-K. Results are summarized in Table S5.

Element	k-ratio	ZAF	Atom%	Atomic ratio	Element wt %	wt % Err.
				observed (calc)		(1-sigma)
[K(crypt-2	22)]2(Ge2P	₂) <i>∙en</i> (1)				
P-K	0.1075	1.838	30.92	1.83 (2)	19.77	+/- 0.31
K-K	0.2242	1.211	33.65	2 (2)	27.15	+/- 0.36
Ge-K	0.4798	1.106	35.43	2.11 (2)	53.08	+/- 1.93
Total			100	5.94 (6)	100	
[K(crypt-2	22)]2(Ge7P	2) (2)				
P-K	0.0488	2.171	19.78	2.02 (2)	10.60	+/- 0.81
K-K	0.1096	1.212	19.62	2 (2)	13.28	+/- 1.34
Ge-K	0.7222	1.054	60.60	6.12 (7)	76.12	+/- 8.67
Total			100	10.14 (11)	100	
[K(crypt-222)]₃(Ge₃P₃Cd₃) <i>·tol</i> (3)						
P-K	0.0421	1.882	17.20	3.07 (3)	7.92	+/- 1.09
K-K	0.0873	1.118	16.79	3 (3)	9.76	+/- 0.72
Ge-K	0.4994	1.024	47.36	8.46 (9)	51.12	+/- 4.15
Cd-L	0.2535	1.230	18.66	3.33 (3)	31.19	+/-1.96
Total			100	17.86 (18)	100	

Table S5. EDX analysis of 1 - 3 (K, Ge, P).

The results of the EDX investigations confirm the Ge:P ratios of the investigated substances within the expected accuracy. The Ge values show largest deviations from the calculated values, in accordance with the large error indicated in the rightmost column.

4. Electrospray Ionization Mass Spectrometry (ESI-MS) Investigations

ESI(-) mass spectrometry has been performed on Micromass Q-Tof *micro* or a Finnigan LTQ-FT spectrometer by Thermo Fischer Scientific in the negative ion mode: Spray voltage 3.90 kV, capillary temperature 300°C, capillary voltage -11 V, tube lens voltage -140 V, sheath gas flow rate 25 arb, sweep gas flow rate 0 arb. For the measurements, the filtered solutions were dried *in vacuo* and re-dissolved in dry DMF or *en*. Additional peaks observed in the ESI(-) spectrum are believed to belong to decomposition products and fragments formed by a dynamic re-organization of the cluster anions and their fragments in solution under ESI-MS conditions. As it is common for Zintl anions and intermetallic cluster anions, the observed fragments have been detected as oxidized, singly charged species. Despite multiple measurements with varied ionization conditions and solvents a high-resolution mass spectrum of (1) could not be obtained on the Finnigan LTQ-FT spectrometer, whereas it was easily obtained in low resolution on a Micromass Q-Tof *micro*. Figures S10-S14 show spectra of the observed peaks, with measured (top) and calculated (bottom) isotope patterns each.

We thank Rhonda Stoddard and Dr. Eric Janusson (University of Victoria, BC, Canada), as well as Jan Bamberger (Philipps-Universität Marburg) for their help in collecting the ESI-MS data.



Figure S10. ESI-MS(–) spectrum of the (Ge₂P₂H)⁻ anion.



Figure S11. ESI-MS(-) spectrum of the (Ge₇P₂K(crypt-222))⁻ anion.



Figure S12. ESI-MS(–) spectrum of $(Cd_3Ge_9P_3K(crypt-222)H)^-$ anion.

A time-dependent ESI-MS(–) study has been performed on a suspension of "K₂Ge₂P₂" in *en*, utilizing pressure-sample-infusion (PSI) at 2 bar of Ar pressure. Immediately after start of the extraction the mass peak of the $(Ge_2P_2H)^-$ anion was detected. No other species have been observed within the first minutes of the extraction (see Figure S13, sum of 277 scans). This indicates the presence of the $(Ge_2P_2)^{2-}$ in the solid phase or its rapid formation upon extraction. As no evidence of the larger cluster $(Ge_7P_2)^{2-}$ was detected in the fresh extraction suspension, this study aligns with the conclusion from NMR spectroscopy, which indicates the latter to be formed in solution over time.



Figure S13. ESI-MS(–) spectrum of a fresh "K₂Ge₂P₂" suspension in *en*, showing $(Ge_2P_2H)^-$ as only peak present (sum of 277 scans, top).

In an ESI(–)-MS measurement of "K₂Ge₂P₂"/crypt-222 in *en* (with/without addition of pyridine), we found various peaks that can be assigned to a "GeP₃" moiety (see Figure S14). Due to the low resolution in this measurement a detailed assignment of the solvent fragments accompanying the "GeP₃" moiety a precise assignment was not possible, however, the isotopic distribution of the mass peak reveals unambiguously the presence of only one Ge atom in the isotopic pattern. This may hint at a complex reorganization process in *en* that yields "Ge₃P" moieties, as present in the crystal structure of **3**, and "GeP₃" moieties.



Figure S14. ESI(-)-MS spectrum of a "GeP3" species – here (GeP3C10N2H14)⁻

5. Nuclear magnetic resonance (NMR) spectroscopy

NMR measurements of **1** and **2** have been performed a Bruker 400 MHz AV-III HD FT-NMR spectrometer equipped with H/FX Bruker SmartProbe with Automated Tuning and Matching (ATM). NMR measurements of **3** have been performed on a Bruker 500 MHz AV-III spectrometer with a Progidy cryo probe with forward observation for the broadband channel (BBO). Bruker standard single pulse sequences were used. ³¹P-NMR and ¹¹³Cd-NMR spectra were recorded at 25°C at 202.5 and 111.0 MHz, respectively.

For the ¹¹³Cd-NMR experiment, in order to define the resonance signal, several spectra with a spectral width of 800 ppm were recorded to cover the whole chemical shift range (+2000 to –2000 ppm). The final spectrum was acquired with a spectral width of 200 ppm and a relaxation delay of 0.5 s with a number of 8192 scans. Chemical shift of ¹¹³Cd was referenced to 1.0 M Cd(ClO₄)₂ in D₂O (δ = –641.0 ppm) and the spectra were processed with Bruker Topspin 3.2.

5.1. ³¹P-NMR spectroscopy on compounds 1 and 2

Table S6 summarizes the ³¹P-NMR data for compounds **1** and **2** observed in DMF-d₇ and *en*. respectively.

Table S6. ³¹P-NMR chemical shift data (ppm) for the anions in **1** and **2** in different solvents.

	[K(crypt-222)] ₂ (Ge ₂ P ₂)· <i>en</i> (1)	[K(crypt-222)] ₂₂ (Ge ₇ P ₂) (2)
DMF-d ₇ , 400 MHz	-432.38 (s)	-252.21 (s)
en/C ₆ D ₆ , 400 MHz	-459.75 (s)	–255.70 (s)

In a flame-sealed NMR-tube, a complete conversion from **1** into **2** was observed over the course of two weeks (see Figure S15). A red precipitate was found after complete conversion that was identified as red phosphorus by EDX measurement.



Figure S15. Time-dependent ³¹P-NMR spectra of a solution of [K(crypt-222)]₂(Ge₂P₂) in DMF-d₇ (0, 7,14 days).

Upon extraction of the "K₂Ge₂P₂" phase and crypt-222 in *en*, a doubly protonated species was detected alongside the two anions indicated above in a proton coupled ³¹P-NMR (see Figures S16-S17), producing a triplet at δ = -269.38 (*J* = 138.6 Hz). Upon addition of small amounts of pyridine, the triplet vanished, indicating deprotonation by the base pyridine. Notably, the signal is not present in the NMR spectrum of the extraction liquid in the aprotic solvent DMF, and it is also absent in a DMF solution of [K(crypt-222)]₂(Ge₂P₂) (**1**), in agreements with the assumption that *en* acts as an acid here. The chemical shift is in the range of the values known for phosphanes (PH₃: -244.3 ppm; P₂H₄: -214 ppm), yet we cannot exclude it to be (Ge₃PH₂)⁻. The exact nature of the species is subject to an ongoing study.





Figure S17. ³¹P-NMR (¹H-coupled) spectrum of the filtered extraction liquor upon extraction of "K₂Ge₂P₂"/crypt-222 in *en* for 4d.

5.2. ¹¹³Cd-NMR and ³¹P-NMR spectroscopy on compound 3

In the ¹¹³Cd-NMR spectrum (see Figure S18, left), a triplet was observed at 636.6 ppm, with a coupling constant of 72 Hz under the experimental condition. The observed splitting pattern of the ¹¹³Cd signal is due to its coupling with the phosphorus atoms in the cluster and is in the expected range of a ${}^{2}J_{Cd-P}$ coupling (see below).



Figure S18. Detail of the ¹¹³Cd (left) and the ³¹P (right) NMR spectrum of **3** in DMF-*d*⁷ at room temperature.

The ³¹P-NMR spectrum consists of a central peak at –129.4 ppm, surrounded by two satellites with a separation of 72 Hz. A close inspection of the signal revealed two additional weak shoulders distributed symmetrically on either side of the central signal, with a distance of 72 Hz to the central signal. A distribution of the integral area is shown in Figure 1 (right). This complex distribution can be explained by the various isotopes of Cadmium: ¹⁰⁶Cd, ¹⁰⁸Cd, ¹¹⁰Cd, ¹¹¹Cd, ¹¹²Cd, ¹¹³Cd, and ¹¹⁴Cd. Among these isotopes, only ¹¹¹Cd and ¹¹³Cd possess a non-zero spin quantum number (S = ½) and account for a natural abundance of 25%. Therefore, on the basis of the molecular structure of the anionic cluster in the crystal (see Figure S9), assuming a uniform coupling constant between all P and Cd atoms and a negligible coupling constant for all long-range couplings, a distribution for the integral area of the ³¹P signal was calculated. After various combinations of the positioning of the different Cd isotopes within the cluster, the central peak was predicted and verified to account for 58% of the intensity. The remaining integral area is distributed over a pair of satellites with 19 % each, and two additional shoulders with 2% each.

The observed coupling constant of 72 Hz is in the range of ${}^{2}J_{Cd-P}$ couplings (e.g. 30 Hz for Cd-enriched enzyme phosphate complexes, see Ref. [4]). Literature reports values for a ${}^{1}J_{Cd-P}$ coupling to be more than one order of magnitude larger than the coupling constant observed in here (1123–2960 Hz, see Refs. [5] and [6]).

The NMR data confirms that the near C_3 -symmetric structure observed in the solid state is also present in solution, as no additional ¹¹³Cd signals were detected that would be expected upon opening into a chain or upon fragmentation. The presence of a ${}^2J_{Cd-P}$ coupling also verifies the assignment of the P atom in the crystal structure as pointing outwards instead of coordinating the Cd atoms.

6. Quantum Chemical Investigations

6.1. Methods

Quantum chemical calculations were carried out with TURBOMOLE^[7] employing the B3LYP^[8] functional with basis sets of type def2-TZVP^[9] together with respective auxiliary basis sets^[10] and an effective core potential for Cd^[11] modelling the inner 28 electrons. The negative charge was compensated by the conductor-like solvation model (COSMO)^[12] with default settings. Transition pathways were optimized with the method proposed by Plessow,^[13] which is available in TURBOMOLE. Cartesian coordinates are provided in Tables S7-S10.

6.2. Relative stabilities of isomers of [Cd₃(Ge₃P)₃]³⁻

The optimization of structure parameters was started from the X-ray structure. It yielded isomer B shown in Figure S19, center (Cartesian coordinates in Table S8), for which the original connectivity of the (Ge₃P)³⁻ unit is maintained only in one of the three cases. This structure is a local minimum (with a very weak mode of 4 cm⁻¹). Enforcing C_3 symmetry during the optimization yields isomer D (for Cartesian coordinates see Table S10), which shows three imaginary modes (11,13 and 25 cm⁻¹, and is higher in energy than isomer B by 15 kJ/mol. Isomers with energies lower than that of isomer B were obtained by disturbing isomer B along the weakest vibrational mode. One ends up either in a (virtually) C_{3v} symmetric case (isomer A, see Figure S19, left hand side, and Table S7), where all P atoms are above the plane spanned by the three Cd atoms, or in a C_s symmetric case (isomer C, see Figure S19, right hand side, and Table S9), where one of the P atoms is situated below this plane. Isomers A and C are favored over B by 8 and 14 kJ/mol, respectively, and thus over the C_3 -symmetric structure by 23 and 29 kJ/mol, respectively. For both isomers, A and C, the wavenumber of the weakest vibrational mode is 8 cm⁻¹. Finally, the reaction pathway A-B-C was optimized. The result is also shown in Figure S19. It is evident that the rotation of a $(Ge_3P)^{3-}$ unit is feasible with low energy (~10 kJ/mol) and not hindered by a significant barrier (< 1 kJ/mol).



Figure S19. Relative energies of isomers of $[Cd_3(Ge_3P)_3]^{3-}$, being interlinked by two 90° rotations of one of the $(Ge_3P)^{3-}$ units about the (virtual) Cd2…P3 axis. Note that the labeling scheme of the Cd atoms is not identical to that in Figure 2 in the main document, as the calculations were done without symmetry restrictions (C1) and do naturally not account for any disorder.

Cd	0.0106616	0.0064862	-0.0140049
Ge	1.6079153	-1.8717357	-1.2899844
Ge	0.2992342	-2.5278476	1.1403701
Ge	0.3714045	-4.0821403	-1.2289160
Р	2.1882707	-3.6047699	0.2943055
Cd	-4.1306441	0.0047284	-0.0003718
Cd	-2.0465121	-3.5828471	0.0314239
Ge	-3.3265223	2.3370170	-1.2662270
Ge	-4.4623234	-4.0544356	-1.2455091
Ge	-2.0565838	1.5082106	1.1343302
Ge	-4.3926096	-2.5345138	1.1482672
Ge	-0.7926548	2.3469651	-1.2639035
Ge	-5.7480070	-1.8718296	-1.2511684
Р	-2.0665504	3.6859118	0.2965473
Р	-6.2666706	-3.6441050	0.3113954

Table S7. Cartesian coordinates (in Å) for isomer A.

Table S8. Cartesian coordinates (in Å) for isomer B.

Cd	0.0003216	-0.0050127	-0.0018330
Ge	1.1269667	-2.1638944	-1.4584744
Ge	1.0663767	-2.1679886	1.4966064
Ge	1.2751420	-4.4044713	-0.0005389
Р	2.8842471	-2.6286966	0.0623094
Cd	-3.8747209	0.0045927	-0.0000666
Cd	-1.2550723	-3.2829845	0.0042240
Ge	-3.2207765	2.3276738	-1.3574016
Ge	-3.6007712	-3.9926690	-1.2964026
Ge	-1.9490249	1.6933798	1.1185225
Ge	-3.7106670	-2.5424147	1.1533135
Ge	-0.6812998	2.3405065	-1.3333244
Ge	-5.2528538	-2.0841802	-1.1737124
Р	-1.9748441	3.7912629	0.1070931
Р	-5.3774648	-3.9647628	0.3497360

Cd	0.0000000	0.000000	0.000000
Ge	0.2776194	-2.5489324	-1.1111404
Ge	1.5961034	-1.8490899	1.2907968
Ge	0.3454653	-4.0403451	1.2904645
Р	2.1623603	-3.6239061	-0.2572257
Cd	-4.1691700	-0.0000000	0.000000
Cd	-2.0597939	-3.5932058	0.0000000
Ge	-3.3619661	2.3255271	-1.2798606
Ge	-4.4648056	-4.0188959	-1.2865939
Ge	-2.0857038	1.5011568	1.1127449
Ge	-4.3936906	-2.5461853	1.1357015
Ge	-0.8375521	2.2817695	-1.3055128
Ge	-5.8038313	-1.8767937	-1.2281519
Р	-2.0532271	3.6706511	0.2550860
Р	-6.2493906	-3.6954227	0.3109239

Table S9. Cartesian coordinates (in Å) for isomer C.

Table S10. Cartesian coordinates (in Å) for isomer D.

Cd	-1.4812411	-1.2714871	0.0012022
Ge	0.6806557	-2.7814824	1.4838009
Ge	-1.1678159	-4.0247915	-0.0028197
Ge	-2.7494102	0.8064784	1.4838347
Р	1.1869750	-4.5478579	0.0018016
Cd	1.8445015	-0.6489905	-0.0004363
Cd	-0.3628153	1.9240459	0.0029126
Ge	4.0689281	0.9942918	-0.0030599
Ge	-2.9039140	3.0287102	-0.0043126
Ge	2.0693479	1.9768886	1.4850814
Ge	0.6838991	-2.7831945	-1.4839497
Ge	2.0661791	1.9801936	-1.4830666
Ge	-2.7514897	0.8032603	-1.4835799
Р	3.3481943	3.2953925	0.0012506
Р	-4.5319944	1.2485424	0.0013407

7. References for the supplementary information

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