The access to molecules comprising direct Zn-Zn bonds has become very topical in recent years for various reasons. Low-valent organozinc compounds show remarkable reactivities, and larger Zn-Zn-bonded gas-phase species exhibit a very unusual coexistence of insulating and metallic properties. However, as Zn atoms do not show a high tendency to form clusters in condensed phases, synthetic approaches for generating purely inorganic metalloid Zn$_x$ units under ambient conditions have been lacking so far. Here we show that the reaction of a highly reductive solid with the nominal composition K$_5$Ga$_2$Bi$_4$ with ZnPh$_2$ at room temperature yields the heterometallic cluster anion [K$_2$Zn$_{20}$Bi$_{16}$]$^{6-}$. A 24-atom polymetallide ring embeds a metalloid {Zn$_{12}$} unit. Density functional theory calculations reveal multicenter bonding, an essentially zero-valent situation in the cluster center, and weak aromaticity. The heterometallic character, the notable electron-delocalization, and the uncommon nano-architecture points at a high potential for nano-heterocatalysis.
The use of nontoxic elements for applications in chemical synthesis, as well as for innovative and harmless materials, is highly desirable. Zinc and bismuth are such nontoxic metals, hence enjoying high reputation in this context. However, especially zinc is predominantly found in the +II oxidation state in its compounds, owing to the inherently high stability of the corresponding 3d10 electronic configuration. For this, one branch of contemporary zinc chemistry is dedicated to the formation of low-valent zinc compounds for enhancing its chemical reactivity.

A straightforward strategy toward low-valent metal compounds is the using of the cluster shell. In the second, they show some segregation, with the Zn atoms being found in a triangle and two dumbbells in the cluster, respectively benign metals in the periodic table of the elements have been known to the metallic state eventually, yet in molecular compounds. Most an experimental access was actually found.

The quoted clusters were obtained by reactions of K5Bi4 or K5Ga2Bi4 (ref. 2) in contrast (with five negative charges per six metal atoms instead of two negative charges per four atoms), seemed to be reductive enough: indeed, the precursor is able to reduce ZnPh2 to form the heterometallic cluster [K2Zn20Bi16]6−, with an essentially zero-valent situation at the Zn atoms in the cluster center and distinct electron delocalization within its extraordinary molecular architecture.

Here, we report an approach to molecular Zn clusters via heterometallic cluster synthesis that was developed by systematic investigations of potential elemental combinations in corresponding reactions in solution.

Results

Synthesis and characterization of [K(crypt-222)][K2Zn20Bi16] (1). The reaction of a solid with the nominal composition K2Ga2Bi4 with ZnPh2 in a 1:2.5 molar ratio in en/crypt-222 at room temperature, subsequent filtration and layering of the solution with toluene affords thin, black crystals of the most probable composition [K(crypt-222)]16[K2Zn20Bi16]16− (1; Supplementary Fig. 1). An X-ray structure analysis reveals the presence of the cluster anion [K2Zn20Bi16]16− (1a), comprising a homoatomic subunit of 12 directly bonded Zn atoms. Despite being obtained from solution, 1a represents a ligand-free nanocluster comprising 36 metal atoms, hence exceeding the number of metal atoms reported recently for [Rh3@Sn12]3− (ref. 31).

The cluster anion 1a is shown in Fig. 1. It possesses an idealized point group symmetry of D4h, which is reduced to C2v in the crystal structure due to slight distortions. The C4 axis runs through two K+ cations that are coordinated above and beneath a bimetallic, crown-like [Zn20Bi16]18− cluster; besides K1 and K2, the two vertical mirror planes include Bi2, Bi4, Zn5 and Bi5, Bi6, Zn6, respectively. The outer dimensions of the nanocluster 1a are 12.60 Å (Bi2···Bi2c), 12.55 Å (Bi5···Bi5c), 11.36 Å (Bi1···Bi1c), and 6.86 Å (K1···K2). During the reaction, all Zn atoms released their Ph groups to be ligand-free atoms within the cluster. Unusually high, yet reasonable, displacement parameters in the structure of 1a point to orientational disorder of the metal atoms over close positions. Obviously, this also involves disorder of the cations, which in the presence of the heavy atoms of the anions hampers the localization of the atomic positions of the light atoms of the cryptate ligands from the Fourier map. Yet, the spatial demand around the K atoms (Supplementary Fig. 2 and Supplementary Discussion) and the features of the electron density distribution in the Fourier maps agrees with the assumption of [K(crypt-222)]16− cations. To reduce the impairment of the refinement of the anionic cluster by an incomplete model, the influence of these parts was detracted from the data by the back Fourier transform method. The crystal data and experimental parameters of the structure determination of 1 (CCDC 1969162) are collected in Supplementary Table 1. Figure 1c, d, illustrates the packing of cations and anionic clusters. The latter are arranged in two types...
of pillars along the crystallographic c axis, with inverse orientations of the clusters with respect to the (idealized) S₄ axis, and with the clusters shifted by c/2 relative to each other.

The most intriguing feature within the [Zn₁₂Bi₁₆]⁶⁻ cluster structure is the assembly of 12 Zn atoms ([Zn₃–Zn₆] and symmetry equivalents) in the cluster center. These atoms are arranged in four corner-sharing tetrahedra that form a nearly undistorted inner Zn₄ square (angle Zn₆–Zn₅–Zn₆ 90.48(14)°). The tetrahedra are not regular, with a short inner Zn₅–Zn₆ edge (2.544(3) Å), somewhat longer contacts to the outer edges (2.664(3)–2.682(3) Å) and an elongated outer Zn₃–Zn₄ edge (2.812(4) Å). However, the Zn–Zn angles differ only slightly from ideal values (56.72(9)–63.48(8)°). As Ga and Zn atoms cannot be easily distinguished by means of common X-ray diffraction, the question whether Ga atoms might be involved in the structure instead of or in addition to Zn atoms was clarified by energy-dispersive X-ray spectroscopy (EDS) on single crystals of 1 (Supplementary Figs. 3, 4, and Supplementary Table 2), and by DFT calculations (vide infra). Both clearly rule out the presence of any Ga atoms in the cluster anion 1a.

The inner [Zn₁₂] unit is embedded in a macrocycle consisting of the eight remaining Zn atoms (Zn₁, Zn₂, and symmetry equivalents) and 16 Bi atoms (Bi¹–Bi⁷ and symmetry equivalents), to which it is bonded by Zn–Bi contacts (2.798(2)–2.893(3) Å). The atoms of the [Zn₁₂Bi₁₆] moiety are connected by different metal–metal bonds: Zn–Zn (2.756(5), 2.831(5) Å), Bi–Bi (3.053(2), 3.041(2) Å) and Zn–Bi (2.683(3)–2.930(3) Å). The nature of the interatomic interactions were studied in detail by means of quantum chemical calculations.

Quantum chemical investigation of the bonding in [K₂Zn₂₀Bi₁₆]⁶⁻ (1a). We optimized the geometric structure at DFT level (TPSS/dhf-TZVP/grid m3). The calculated molecular

![Crystal structure of [K₂(crypt-222)]₆[K₂Zn₂₀Bi₁₆] (1).](https://doi.org/10.1038/s41467-020-18799-6)
The HOMO–LUMO gap is significant at 1.4 eV, but no further significant gaps are present in the region of frontier orbitals, indicating that the total electron number and thus the assumed composition are correct (an isoelectronic alternative, including Ga atoms in the cluster center would require a lower overall charge, hence $[\text{K}_2\text{Zn}_{16}\text{Ga}_4\text{Bi}_{16}]^2^-$, which is clearly ruled out by the detection of six additional K$^+$ counterions in the crystal structure of $[\text{K}_2\text{Zn}_{16}\text{Bi}_{16}]^6^-$).

For a plausible assignment of bonds in $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^6^-$, we carried out a Boys localization procedure\(^{35}\) for the 164 valence orbitals and calculated the atomic Mulliken contributions\(^{36,37}\) to each localized molecular orbital (LMO). The results are illustrated in Fig. 2. For each of the LMOs, one representative is shown in Fig. 2c. When neglecting atomic contributions <20%, this reveals the following picture.

A total of 116 LMOs represent one-center contributions: 20 × 5 LMOs for the Zn($d$) orbitals and 16 LMOs A–D, representing one lone pair for each of the 16 Bi atoms. A total of 32 LMOs E–H represent Zn–Bi two-electron-two-center bonds (straight lines): eight Zn–Bi bonds within the upper inner ring (E), another eight within the lower inner ring (F), and 16 within the outer ring (G, H). All of these bonds are polarized, which is evident from the Mulliken contributions to the LMOs, which amount to 52–66% for Bi and to 22–41% for Zn (for a more refined picture we note that the two-center bonds in the outer ring show contributions from the Zn atoms in the inner rings (typically 10%) and vice versa, in particular LMO H). Among the remaining 16 LMOs, 12 connect the outer ring with the two inner rings: 4 Bi–Bi bonds (I), 4 three-center bonds (blue triangles, K), and four more bonds (blue triangles, J), which also may best be viewed as three-center bonds (the shown representative as well as two of its equivalents binds mainly to the lower inner ring, whereas the fourth binds mainly to the upper inner ring. This is an unphysical break of symmetry from the localization procedure, and a less
strict interpretation as three-center bonds appears more reasonable. The inner four Zn atoms are involved exclusively in the finally remaining four LMOs (gray tetrahedra, I) representing four-center bonds that connect the unique Zn13 unit within 1a.

A natural population analysis (NPA)38 performed on the optimized structure of 1a (Fig. 2b) yields charges of +0.05 for the inner four Zn atoms and +0.71 for the other eight Zn atoms. The latter is a typical value for an oxidation state of +I (compare, for instance, ZnCl: +0.71, ZnBr: +0.67), so this unit as a whole is clearly low valent. We note in passing that this [Zn13] unit as an isolated species is stable even as a neutral species. Structure optimizations carried out for charges \( q = 0, +2, +6 \) (Supplementary Fig. 5) show that the structure of the [Zn13] moiety persists in an isolated form, for \( q = 0 \) even with a reasonable HOMO–LUMO gap of 1.6 eV, indicating the general stability of this cluster unit. However, a second local minimum was found that is less stable for \([Zn13]^{2+} (\approx +57 \text{kJ/mol})\) and \([Zn13]^{3+} (\approx +9 \text{kJ/mol})\), but is favorable for \([Zn13]^{\text{6+}} (\approx -138 \text{kJ/mol})\). In summary, the calculations confirm 1a as being a cluster with a low valent subunit of group ten metals known to date. Efforts to experimentally probe the atomic charges by means of X-ray photoelectron spectroscopy (XPS) failed so far owing to the high sensitivity of the very thin crystals, which spontaneously oxidized during sample preparation and thereupon produced XPS signals of Zn2+ and Bi3+ only. Further studies are underway to first of all increase the crystal size.

**Relationship of the \([Zn8Bi16]^{9−}\) unit in 1a to porphine.** Remarkably, the \([Zn8Bi16]^{9−}\) unit \((q = 8...14\) embedding \([Zn13]^{20...6+}\) exhibits a certain relationship with the organic macrocycle porphine, \(C_{20}N_{4}H_{14}\): both rings possess 24 ring valence electrons, and \(s \) and \(p \) valence electrons (104 for \([Zn8Bi16]^{8−}\) or 110 for \([Zn8Bi16]^{14−}\), vs. 114 for \(C_{20}N_{4}H_{14}\)). In both cases, five-atomic units \((Zn8Bi vs. C\text{N})\) are connected by a one-atom bridge \((\text{Bi vs. C})\), with lone pairs in \(1\text{a}\) replacing the \(H\) substituents of porphine. In contrast to porphine, the \([Zn8Bi16]^{9−}\) metallacycle is not known as a separate entity, but both macrocycles are capable of accommodating metal atoms or ions. Of course, owing to the very different nature of the involved elements, the detailed behavior of both macrocycles differs. Very obviously, owing to the larger atomic sizes, the \([Zn8Bi16]^{9−}\) unit in \(1\text{a}\) is planar. It represents a nearly planar \(Zn_{8}Bi_{2}\) diamond that is inclined with respect to the molecule’s equatorial plane, with Bi3 and Bi6 (and symmetry equivalents) being further exposed by binding exclusively to Bi2 and Bi5, respectively (and symmetry equivalents) as being a cluster with a low valent subunit of group ten metals known to date. Efforts to experimentally probe the atomic charges by means of X-ray photoelectron spectroscopy (XPS) failed so far owing to the high sensitivity of the very thin crystals, which spontaneously oxidized during sample preparation and thereupon produced XPS signals of Zn2+ and Bi3+ only. Further studies are underway to first of all increase the crystal size.

**Coordination properties of the \([Zn20Bi16]^{8−}\) polyanion in 1a.** Another point worth mentioning is the fact that the oblate polyanion \([Zn20Bi16]^{8−}\) in the trimetallic cluster \(1\text{a}\) coordinates two K+ ions, in an inverse-sandwich-type manner, at Bi–K distances of 3.528(2) or 3.533(2) Å (Bi(3,6)–K), and 3.741(3) or 3.725(3) Å (Bi(4,7)–K). Figure 3 illustrates the calculated electrostatic potential with and without coordination of K+. The polyanion \([Zn20Bi16]^{8−}\) bears a relatively even (negative) electrostatic potential, and the four Bi atoms that are exposed in the inner ring of the cluster (Bi3, Bi4, Bi6, and Bi7) are attractive enough to trap the K+ cations, which polarize these Bi atoms upon coordination.

Notably, the K+ ions prefer this site although an excess of the cation-sequestering agent crypt-222 was present during the formation and crystallization of the title compound. This is a rare observation, which was reported for heterometallic clusters in a few cases only, \([\text{NbAs}3]^{3−}\) \((\text{ref. 49})\), \([\text{MesCu})\text{Ge}4]^{4−}\) \((\text{ref. 50})\), \([\text{M}_{10}e_{@}\text{Sn}4]^{4−}\), \((M/x = Ni/0 \text{ (ref. 51)}\), Co = 0.32 \((\text{ref. 52})\)), and \([\text{Au}_{4}\text{Ge}4]^{9−}\) \((\text{ref. 53})\). Calculated energies of exchange reactions of \(1\text{a}\) with crypt-222 or 18-crown-6 (18c6), according to Eqs. (1)/(2) and (3)/(4), clearly indicate that the cluster would lose its K+ cations to the cation-sequestering agents, if considered as an isolated species (in kJ/mol): \(-182 \text{ [Eq. (1)]}, \rightleftharpoons \text{ -132 [Eq. (2)]}, \rightleftharpoons \text{ -126 [Eq. (3)]}, \rightleftharpoons \text{ and -76 [Eq. (4)].} \)

\[
\begin{align*}
\text{[K}_2\text{Zn}_{20}\text{Bi}_{16}^{8−} & +\text{ crypt-222} \rightarrow \text{[KZn}_{20}\text{Bi}_{16}^{7−} + \text{[K(cryp-222)]^2]}, \\
\text{[K}_2\text{Zn}_{20}\text{Bi}_{16}^{7−} & +\text{ crypt-222} \rightarrow \text{[Zn}_{20}\text{Bi}_{16}^{6−} + \text{[K(cryp-222)]^2]}, \\
\text{[K}_2\text{Zn}_{20}\text{Bi}_{16}^{6−} & + 18c6 \rightarrow \text{[KZn}_{20}\text{Bi}_{16}^{5−} + \text{[K(18c6)]^2]}, \\
\text{[KZn}_{20}\text{Bi}_{16}^{5−} & + 18c6 \rightarrow \text{[Zn}_{20}\text{Bi}_{16}^{4−} + \text{[K(18c6)]^2]}. 
\end{align*}
\]

The same holds for many other cations that were tested this way, also with Sb or As atoms replacing Bi atoms in \(1\text{a}\) (Supplementary Tables 3–8 and Supplementary Equations (1)–(7). However, in the crystalline state, the two K+ cations remain

coordinated—most probably to reduce the overall charge and allow for the formation of single crystals along with six (instead of eight) \([\text{K(crypt-222)}]^{+}\) counterions.

**Discussion**

We report on the targeted synthesis of a salt of the heterometallic cluster anion \([\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6–}\) (1a), comprising a homoatomic subunit of 12 Zn atoms, and at the same time a large molecular architecture, involving 20 Zn and 16 Bi atoms. As shown by quantum chemical investigations, an inner \([\text{Zn}_{12}]^{q}\) unit represents a really metalloid zinc cluster, which is held together by four-center bonding exclusively. This unit is embedded in a polymetallide \([\text{Zn}_8\text{Bi}_{16}]^{q–}\) ring \((q = 8...14)\), to which it is connected by three-center and two-center bonds. In striking contrast to the large number of metalloid clusters of other electron-rich elements, like the coinage metals Ag and Au, only a few low-valent organozinc clusters were reported to date. In example of a purely inorganic metalloid group 12 cluster within a block metals, thermore, the disc-shaped anion coordinates two \(\text{K}\) atoms. Notably, the cluster also shows weak aromaticity, indicated by the occurrence of a global ring current that was calculated to be about a fifth of the value calculated for porphine. Weak aromaticity is also suggested by the NICS approach. Furthermore, the disc-shaped anion coordinates two \(\text{K}^+\) cations in an inverse-sandwich-type manner to reduce the overall charge of the cluster anion, and finally crystallizes as \([\text{K(crypt-222)}]_6[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]\) (1). We envisage using this monodisperse metal nano-cluster, with its heterometallic architecture and its uncommon electronic features in reactivity studies, and eventually nano-heterocatalysis.

**Methods**

**General synthesis details.** All manipulations and reactions were performed under dry Ar atmosphere using standard Schlenk or glovebox techniques, as all Zintl compounds are sensitive to air and moisture. Elements were used as received: K lumps, Acros Organics, 98%; Ga pellets, Alfa Aesar, 99,9999% (metals basis); Bi powder, ChemPur Karlsruhe, 99%; Diphenyl zinc (ZnPh2) was prepared according to a modified literature procedure\(^\text{56}\): a 1/2 mixture of \(\text{ZnCl}_2\) (0.2 mol/l in THF) and \(\text{Ph}_2\text{MgBr}\) (1.3 mol/l in THF) in dry THF was stirred for 3 h at ambient temperature, before the solvent volume was doubled by addition of dioxane for precipitation of ZnPh2 as colorless crystalline powder. The en and \(\text{N},\text{N}\)-dimethylformamide (DMF; Aldrich, 99.8%) were distilled from CaH2 and stored over 3 Å molecular sieves. Toluene (Acros Organics, 99%) was distilled from sodium–potassium alloy and stored over 4 Å molecular sieves. Kryptofax\(^\text{\texttrademark}\) 222 (crypt-222, Merck) was dried under vacuum overnight. A solid with the nominal composition \(\text{K}_2\text{Ga}_2\text{Bi}_4\) was prepared by stoichiometric fusion of the elements in a heterogeneous temperature chamber oven. The elements were weighed into a niobium tube that was sealed within an evacuated silica amouple. The mixture was heated to 550 °C, kept at this temperature for 24 h, and then cooled down to room temperature at a cooling rate of 5 K/h, and grinded prior to use.

**Synthesis of \([\text{K(crypt-222)}]_6[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]\) (1).** The starting material with the nominal composition \(\text{K}_2\text{Ga}_2\text{Bi}_4\) (176 mg, 150 µmol) was dissolved in THF (4.5 ml) with slight stirring. After stirring for 2 h, an intense green solution, indicating the formation of biologic-green \(\text{Bi}_6^{2–}\) (ref. \(\text{55}\)), was filtered through densely packed glass wool. The solution was stored at room temperature for one night and layered with 5 ml of toluene the next day. Crystals of 1 suitable for SC-XRD (Supplementary Fig. 1) formed on the wall of the tube after 10 days. Although the yield per batch is systematically not high (<50%), the compound is the only one to crystallize from the reaction mixture besides biologic-green crystals of the known by-product \([\text{K(crypt-222)}]_6\text{Bi}_6\) and thus can be obtained in decent amounts by multiple reactions. While the exact processes during the formation of 1 are not yet clarified and subject to current in-depth studies, we suggest that it takes place under precipitation of elemental Ga and Bi upon the redox process, and under release of \(\text{Ph}^-\), which may then undergo a potential follow-up reaction with the solvent en to form benzene and \((\text{H}_2\text{NCH}_2\text{CH}_2\text{NH})^{–}\); such processes have been known for reactions of Zintl anions with metal phenyl compounds\(^\text{56}\). Compound 1 is soluble in dry en and DMF. Although the integrity of the highly charged anion in solution could not be confirmed by means of electrospray ionization mass spectrometry (ESI-MS; which may be a consequence of the corresponding measurement conditions), room temperature solution \(\text{H NMR of }\text{[K(crypt-222)]}^{1+}\) (Supplementary Fig. 10), hence corroborating the solubility as such.

**Single-crystal X-ray diffraction.** Several data sets for the X-ray structural analyses were collected at \(T = 100(2)\) K on different crystals with different sizes and on different diffractometers with \(\text{Mo-K} α\) radiation and \(\text{Cu-K} α\) radiation, as it was difficult to obtain sufficient data, especially at higher angles. In spite of high absorption, best results were gained from data measured with \(\text{Cu radiation (λ} = 1.54186\text{ Å on an area detector system Stoe StadiVario at a GenIX 3D microfocus source. The structure was solved by direct methods (SHELXTL)}\(^\text{37}\)). The refinement was done by full-matrix least-squares methods against \(\text{P}^2_{1}\) with the program SHELXL\(^\text{38}\). It clearly revealed the \([\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6–}\) anion and the \(\text{K}\) centers of the \([\text{K(crypt-222)}]^{+}\) cations (Fig. 1). The large displacement parameters are not the result of an inappropriate absorption correction: in several refinements with different data sets, with different absorption corrections, and even with the uncorrected original data, their size shows only small variations (<20%). As this disorder likely influences the atomic positions of adjacent cations, it is comprehensible that the light atoms of the cryptate ligands could not be localized from the Fourier map. In addition, this explains the intensity decay at higher angles in the data.

**Energy-dispersive X-ray spectroscopy.** The EDS analysis on 1 was performed using the EDS device Bruker XFlash 5010 attached to a JEOL JIB-4801F SEM (implemented in a SEM/focused ion beam dual beam system) operating at 15 kV. Data acquisition was performed with at least 100 s accumulation time. For the analyses, multiple single crystals were tested (Supplementary Figs. 3 and 4, and Supplementary Table 2).
Quantum chemical calculations. Structure parameters were optimized with the functional TPS56 using basis sets of type dhf-SVP60 together with corresponding effective core potentials57 and Coulomb fitting basis sets57. The negative charge was compensated with the conductor-like screening model (COSMO)58, employed with default parameters, except for the cavity radius of Zn. This was set to 2.223 Å, the default value for both neighboring elements Cu and Ga, as well as for K. The induced current density was studied with basis sets of type dhf-TZVP56. Scalar-relativistic all-electron calculations were carried out with the diagonal local approximation to the unitary decoiling transformation of the exact two-component (DLU-X2C) Hamiltonian46–48 and basis sets of type x2c-TZVP49–57. For details, see the Supplementary Discussion. Calculations of [Hg4Te(C6H5)7]2+ were performed with the same settings as above, but employed the same basis set as in ref. 39.

Powder X-ray diffraction. Powder X-ray diffraction data were collected on a Stoe StadiMP diffractometer system equipped with a Mythen 1 K silicon strip detector and Cu–Kα radiation (λ = 1.54056 Å). A sample of the starting material with the nominal composition K5Ga2Bi4 was filled into a glass capillary (0.3 mm in diameter), which was sealed air-tightly with soft wax. The tube was then mounted onto the goniometer head using wax (horizontal setup) and rotated throughout the measurement.

Electrospray ionization mass spectrometry. ESI mass spectra (Supplementary Figs. 8 and 9) were recorded with a Thermo Fisher Scientific Finnigan LTQ-FT spectrometer in the negative ion mode. All samples were prepared inside of a glovebox, where they were dissolved in anhydrous DMF and filtered through a 0.45 m syringe filters with a pore size of 0.45 μm. The solutions were injected into the spectrometer with gastight 250 μl Hamilton syringes by syringe pump infusion. All capillaries within the system were washed with dry DMF for 30 min before, and at least 10 min in between measurements to avoid decomposition reactions and consequent clogging.

Data availability
All data generated or analyzed during this study are included in this published article and its Supplementary information files. The X-ray crystallographic coordinates for the structure reported in this study have been deposited at the Cambridge Crystallographic Data Center (CCDC), under the deposition number 1969162. These data can be obtained free of charge from The CCDC via www.ccdc.cam.ac.uk/data_request/cif. Input files or sets of all input parameters for TURBOMOLE and GIMIC are available from the corresponding authors upon request. See also the Supplementary Discussion for details on the computational methods noting all non-default parameters for TURBOMOLE. Cartesian coordinates of the optimized structures are listed in the Supplementary Information.

Code availability
The TURBOMOLE quantum program suite is available from https://www.turbomole.org (Accessed 29 August 2020), and the GIMIC code can be obtained from the GitHub repository also includes a sample input for GIMIC. The TURBOMOLE quantum program suite is available from https://www.turbomole.org. All data generated or analyzed during this study are included in this published article and its Supplementary information files. The X-ray crystallographic coordinates for the structure reported in this study have been deposited at the Cambridge Crystallographic Data Center (CCDC), under the deposition number 1969162. These data can be obtained free of charge from The CCDC via www.ccdc.cam.ac.uk/data_request/cif. Input files or sets of all input parameters for TURBOMOLE and GIMIC are available from the corresponding authors upon request. See also the Supplementary Discussion for details on the computational methods noting all non-default parameters for TURBOMOLE. Cartesian coordinates of the optimized structures are listed in the Supplementary Information.
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Author contributions

A.R.E conceived and performed the synthetic experiments, collected single-crystal X-ray crystallographic data, solved and refined the structure for the first time, performed ESI mass spectrometry, and prepared samples for further analyses. W.M. performed sophisticated structure solution and refinement of different data sets, and finalized the structure analysis. Y.J.F., P.B., and F.W. carried out and documented the quantum chemical calculations. Y.J.F. is grateful to Fonds der Chemischen Industrie (FCI) for general support of his Ph.D. studies (Kekulé fellowship) and the German Academic Exchange Service (Deutscher Akademischer Austauschdienst, DAAD) for a fellowship (grant no. 57348025), and Prof. F. Furche for hosting.

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Competing interests

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