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Formation of $[Bi_{11}]^{3-}$, A Homoatomic, Polycyclic Bismuth Polyanion, by Pyridine-Assisted Decomposition of $[GaBi_3]^{2-}$**

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Dedicated to Professor Reinhard Nesper on the occasion of his 65th birthday

Abstract: *Until now, polycyclic bismuth polyanions have not been known—thus discriminating bismuth from its lighter congeners. However, the synthesis of* $[K([2.2.2]crypt)]_3(Bi_{11})\cdot 2py\cdot tol$, *allows us to present the first structurally characterized homoatomic, polycyclic bismuth polyanion, which exhibits the* $[P_{11}]^{3-}$ *"ufosan" structure. It was obtained upon treatment of* $[K([2.2.2]crypt)]_2(GaBi_3)\cdot en$ *with the solvent pyridine. The binary Zintl anion* $[GaBi_3]^{2-}$ *decomposes under oxidative coupling of pyridine molecules and release of* H_2 *to form the title compound. The unprecedented reaction, its products and by-products were investigated by means of spectroscopy, spectrometry, and DFT studies. All findings reveal the specific reaction conditions to be crucial for the formation of the* $[Bi_{11}]^{3-}$ *ion—and indicate the possibility of the generation and isolation of further, large bismuth polyanions.*

The activation of P_4, as the most prominent 20 valence-electron cage, and its homologue As_4 by transition-metal complexes or carbenes has been studied extensively over the past four decades, and has resulted in a large variety of fascinating products. Depending on the reaction conditions and the reactants, the cages were either E_4 ligands, or they underwent complex bond-opening and fragmentation steps. In some cases, also salts of polyarsenide or polyphosphide anions emerged from the experiments without traces of the activating species.[1–5]

Our recent work has focused on the synthesis of ternary intermetalloid clusters by reactions of binary tetrahedral anions $[E^{14}{}_2E^{15}{}_2]^{2-}$ ($E^{14}=Sn$, Pb; $E^{15}=Sb$, Bi)[6] or $[E^{13}Bi_3]^{2-}$(E^{13}=Ga, In),[7] which are iso(valence)electronic with P_4 or As_4, with complexes of electron-rich transition-metal or lanthanide atoms.[6b,d,8] In addition to the organic functionalization of Zintl ions,[9a–c] or their employment as precursors to novel solid-state phases,[9d,e] a highly topical development in Zintl ion chemistry and physics is the intermetalloid clusters,[9f,g] which show novel aspects in structure and bonding, dynamics, and potential applications.

To date, most of the syntheses have been realized using $[K([2.2.2]crypt)]^+$ salts of the anions in ethane-1,2-diamine (en), whereas the behavior of the precursors in different chemical environments were only fragmentarily explored.[10] We therefore intended to transfer our previous investigations to other solvents, thereby starting out with an examination of the solubility and chemical behavior of $[K([2.2.2]crypt)]_2(GaBi_3)\cdot en$[7] in pyridine (py). However, in contrast to all other studies it was not the precursor that re-crystallized. After three hours of stirring, the solution was separated from a greyish-black residue by filtration and then layered by toluene. Black needles of $[K([2.2.2]crypt)]_3(Bi_{11})\cdot 2py\cdot tol$ (**1**, tol = toluene), suitable for single-crystal X-ray diffraction,[11] appeared within three days in 15% yield, along with black blocks of $[K([2.2.2]crypt)]_2(Bi_4)$ (4%).[12]

The $[Bi_{11}]^{3-}$ ion in **1** (Figure 1) is the first polycyclic bismuth polyanion known to date, the structure and formation of which we discuss herein.

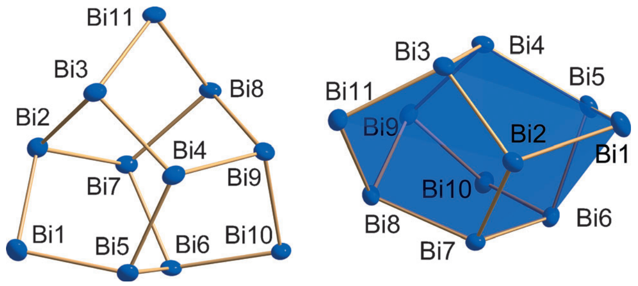

Figure 1. Thermal ellipsoid plot (ellipsoids set at 50% probability; two different views) of the $[Bi_{11}]^{3-}$ ion in **1**. Structural parameters are listed in Table 1.

In addition to linear or monocyclic polyanions, which are known for most of the main-group elements, the most prominent polyhedral/polycyclic species are certainly $[E^{14}{}_5]^{2-}$, $[E^{14}{}_9]^{x-}$, $[E^{15}{}_7]^{3-}$, and $[E^{15}{}_{11}]^{3-}$.[9,13–16] Although in some cases, a species within one main group has been missing for a long time, such as $[Si_9]^{4-}$ within the $[E^{14}{}_9]^{4-}$ family,[17] most species have been realized by all elements of the respective main group, and have been used in a variety of consecutive investigations, such as mentioned above.[9]

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However, one "rule" has not been broken over the years: bismuth has an extremely low tendency to form polyanions in general, with $[Bi_2]^{2-}$[18] and $[Bi_4]^{2-}$[12] being the only fully characterized polybismuthide anions to date. A long debate has taken place on the existence of unsubstituted bismuth polyanions, beginning with the first indication of larger bismuth clusters in Zintl's historical potentiometric titration experiments, which were erroneously assigned as "$[Bi_7]^{3-}$",[19] and continuing through the stabilization of previously unidentified species by metal carbonyl complexes or interstitial transition-metal atoms.[20] Compound **1** thus serves to finally close this debate, at least by application of the very uncommon synthetic approach outlined above.

Aside from being the first homoatomic polybismuthide anion with more than four Bi atoms, the anion in **1** is the previously missing, heaviest homologue of the $[E^{15}{}_{11}]^{3-}$ series, introduced by von Schnering and co-workers with the polyphosphide anion $[P_{11}]^{3-}$ in Na_3P_{11},[14a] which was called "ufosan" for its extraordinary architecture. Derivatives R_3P_{11} were also described with R = H, *i*Pr, or $SiMe_3$.[21]

The structure of the anion in **1** is topologically identical with that of the lighter homologues—with the expected changes in bond lengths. It is worth noting that the Bi–Bi bond lengths (2.9164(14)–3.0292(15) Å) are in agreement with values reported for Bi–Bi single bonds, such as found in Bi_2Ph_4 (2.990 Å) or $C_{36}H_{42}Bi_2N_2$ (3.0648 Å),[22] whereas some of the Bi-Bi-Bi angles (94.08(4)–108.25(4)°) differ significantly from the value of 90° that would be expected for (dominant) 6p–6p orbital interactions within according 2-center-2-electron (2c2e) bonds. Table 1 summarizes the structural parameters of the four homologous anions.

To get some deeper insight, we have investigated the $[E^{15}{}_{11}]^{3-}$ series using DFT methods implemented in the program system TURBOMOLE.[23–28] Structural parameters are well reproduced (Table S3 in the Supporting Information), and localized molecular orbitals (LMOs, Figure S12)[29a,b] correlate well with a description according to the simple pseudo-element concept, including 2c2e bonds and lone pairs; thus the unexpected angles are clearly due to restrictions of the uncommon topology. However, a closer look indicates some deformation of the LMOs, and an inspection of the delocalized molecular orbitals (MOs) of all four congeners also indicates that the simple picture requires a slight extension in this case: all $[E^{15}{}_{11}]^{3-}$ ions show typical cluster orbitals, formed by atomic orbitals (s and p AOs), under delocalization of the electron density over several or all atoms, and also within the cage. Three representative MOs of these anions are shown in Figure 2.

Table 1: Structural parameters in the isostructural anions $[E^{15}{}_{11}]^{3-}$.[a]

$[E^{15}{}_{11}]^{3-}$	Counterions	Distances [Å] and angles [°]	Ref.
$[P_{11}]^{3-}$	Li^+, Na^+, K^+, Rb^+, Cs^+, Ba^{2+}, $[NMeEt_3]^+$, $[NEt_4]^+$, $[K(18\text{-crown-}6)]^+$[b]	P-P⁻: 2.141–2.196 P-P: 2.189–2.269 P-P⁻-P: 94.04–99.11 P-P-P⁽⁻⁾: 96.64–106.86	[14]
$[As_{11}]^{3-}$	Li^+, Na^+, K^+, Rb^+, Cs^+, $[K([2.2.2]crypt]^+$, $[Cs(18\text{-crown-}6)]^+$[b]	As-As⁻: 2.356–2.409 As-As: 2.420–2.489 As-As⁻-As: 94.32–97.90 As-As-As⁽⁻⁾: 98.55–106.86	[15]
$[Sb_{11}]^{3-}$	$[Na([2.2.2]crypt]^+$, $[K([2.2.2]crypt]^+$, $[K(18\text{-crown-}6)]^+$,[b] $[Li(12\text{-crown-}4)]^+$[b]	Sb-Sb⁻: 2.760–2.776 Sb-Sb: 2.799–2.855 Sb-Sb⁻-Sb: 95.82–96.48 Sb-Sb-Sb⁽⁻⁾: 98.17–106.77	[16]
$[Bi_{11}]^{3-}$	$[K([2.2.2]crypt]^+$	Bi-Bi⁻: 2.9164(14)–2.9489(17) Bi-Bi: 2.9659(15)–3.0292(15) Bi-Bi⁻-Bi: 94.08(4)–96.47(4) Bi-Bi-Bi⁽⁻⁾: 96.99(4)–108.25(4)	[c]

[a] Values of $[E^{15}{}_{11}]^{3-}$ species that exhibit direct coordination to alkali-metal ions[15b] are not included, because this dramatically affects the adjacent bond lengths and angles within the $[E^{15}{}_{11}]^{3-}$ cage. [b] 18-crown-6: 1,4,7,10,13,16-hexaoxacyclooctadecane. 12-crown-4: 1,4,7,10-tetraoxacyclododecane. [c] This work.

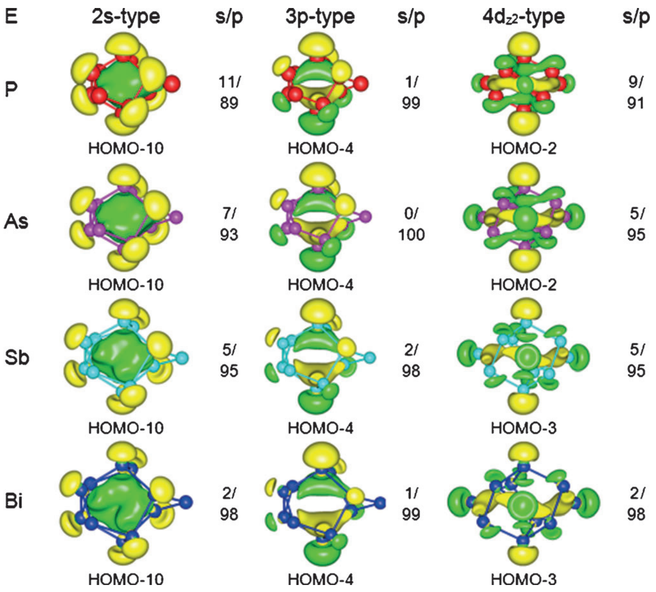


Figure 2. Visualization of three cluster orbitals (s, p, d_{z^2}) calculated for $[E^{15}{}_{11}]^{3-}$ ions (DFT methods),[23–28] and s versus p AO contributions to the MOs (Mulliken population analyses).[29c] Further MOs of $[Bi_{11}]^{3-}$ are shown in Figure S11. Amplitudes are plotted at 0.033 a.u., using the program gOpenMole.[30]

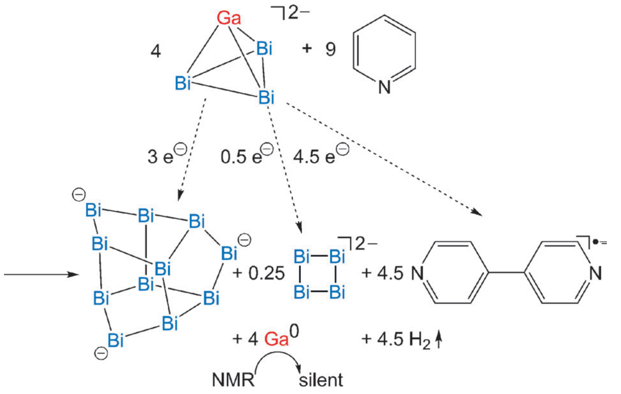
The reason why homoatomic bismuth polyanions larger than $[Bi_4]^{2-}$,[12] or any polyhedral/polycyclic ones, have not been known to date, is not really understood so far. Neither the position of bismuth in the periodic table, nor its electronegativity give a clear answer to this question; thus its non-existence is due to the absence of suitable synthetic approaches so far, which has been overcome by our Lewis base induced degradation of the pseudo-P_4 anion $[GaBi_3]^{2-}$. A comparison of the HOMO–LUMO gaps of the $[E^{15}{}_{11}]^{3-}$ series may help to understand this. It is clear that this gap is decreasing notably from $E^{15} = P$ (2.33 eV), through As (2.00 eV) and Sb (1.63 eV) to Bi (1.41 eV). Although the energy gap may well be systematically underestimated by DFT methods, this trend is still an indication of easier oxidation and thus lower stability of the heaviest $[E_{11}]^{3-}$ species during the syntheses.

Furthermore the extension of the electron density within the cluster orbitals decreases along the series P to Bi, with increasing size of the cage; in turn, along the series P to Bi the electron density is concentrated more onto E^{15}–E^{15} contacts and onto lone pairs. This can be seen, for instance, in the example of the $4d_{z^2}$ type cluster orbital in Figure 2, that when going from P to Bi, the electron density is withdrawn from both the eight E^{15} atoms that have three bonds and the intracluster bonds moved towards the p AOs of the atoms that have two bonds. A comparison of the electronic situation in other pentel polyanions—including the $[E^{15}{}_7]^{3-}$ series, which was unknown for E^{15} = Bi until now—underlines the findings above: the situation is similar for all congeners, with a decreasing tendency for electron delocalization with increasing atomic number; thus, we assume that also further Bi polyanions, such as "$[Bi_7]^{3-}$" and structurally related oligomers, might in principle be generated and crystallized upon development of suitable synthesis methods or conditions.

Hence, in the present case, two preconditions were apparently helpful for the formation and isolation of the $[Bi_{11}]^{3-}$ ion. First, the presence of a mild oxidizing agent, and second, the presence of a cation such as $[K([2.2.2]crypt]^+$, which supports crystallization. The formation of the product still needed further examination to explain the whereabouts of the Ga atoms from the starting material and the role of all reactants during the reaction.

The ^{71}Ga NMR spectrum of a fresh [D$_5$]pyridine solution of $[K([2.2.2]crypt)]_2(GaBi_3)\cdot en$[7] shows one signal at $\delta = -662.04$ ppm, indicating maintenance of the starting material (Figure S4). After 3 h, and upon filtration of the mixture, the signal has vanished, indicating that elemental Ga has been removed by filtration along with the insoluble residue (see Experimental Section). Thus, with an average oxidation state of $-(^3/_{11})$ for the Bi atoms in the product, that were formally uncharged in the starting material, and product Ga(0) atoms that carried the formal negative charges in $[GaBi_3]^{2-}$, an intramolecular redox process has taken place during formation of the $[Bi_{11}]^{3-}$ ion.

The number of electrons that were transferred from Ga atoms to Bi atoms indicates a stoichiometric reaction scheme. The formation of one $[Bi_{11}]^{3-}$ ion, requires a minimum of four $[GaBi_3]^{2-}$ molecules that would donate a total of eight electrons—five more than needed for the anion in **1**. Therefore, further species must have been involved, one of which was determined to be the $[Bi_4]^{2-}$ ion by means of single crystal X-ray diffraction of the by-product $[K([2.2.2]crypt)]_2(Bi_4)$.[12] Assuming, that $^1/_4$ of an equivalent of this species was formed along with one equivalent of $[Bi_{11}]^{3-}$ in agreement with the observed yields, the whereabouts of 3.5 of the eight electrons is clarified. For the remaining 4.5 electrons per formula unit to be consumed, the most likely explanation seems to be a reaction with the solvent pyridine, or—more precisely—with 4,4′-bipyridine, the formation of which under release of H$_2$ was demonstrated by means of GC-MS studies of the mother liquor after crystallization of **1** (Figure S13–S15). The reduction of bipyridine has been demonstrated electrochemically,[31] and the dimerization of pyridine and its subsequent reduction under formation of a bipyridine radical anion and dihydrogen was recently suggested by Sevov and co-workers to occur during the formation of the heterometallic cluster anion $[Bi_4Ni_4(CO)_6]^{2-}$ from $[Bi_3Ni_4(CO)_6]^{3-}$ in pyridine.[20a] Although it has not been possible to date to detect the bipyridine anion in reaction solutions, diverse salts of this radical anion have been crystallized, demonstrating its existence.[20a] Since the radical is not likely to be stable under GC-MS conditions, direct evidence is also lacking in the present study. However, the proposed reaction scheme correlates with the necessity of pyridine to be present for the formation of **1** (see below), which can be best understood in terms of its (electro-neutral) reaction to 4,4′-bipyridine plus H$_2$, and the role of the organic product as an electron acceptor. A summary of the findings is given in Scheme 1, which is meant to suggest a plausible reaction scheme for the formation of the unprecedented polycyclic bismuth polyanion.



Scheme 1. A possible reaction scheme to form the anion of compound **1** by electron transfer from the reactant to Bi clusters and pyridine; the role of 4,4′-bipyridine as an electron acceptor and the reduction of Bi atoms still lacks an analytical proof, but seems to be the most plausible explanation for the necessity of the solvent pyridine, as indicated previously.[20a]

To explore whether the redox processes giving the $[Bi_{11}]^{3-}$ ion are indeed specific for the binary anion and the solvent used, a series of reactions were carried out under slightly varied conditions. We performed reactions starting out from a) $[K([2.2.2]crypt)]_2(Bi_2)$[18] or $[K([2.2.2]crypt)]_2(Bi_4)$,[12] thus using $[Bi_2]^{2-}$ or $[Bi_4]^{2-}$ ions instead of $[GaBi_3]^{2-}$, b) $[K([2.2.2]crypt)]_2(InBi_3)\cdot en$, thus using $[InBi_3]^{2-}$ instead of $[GaBi_3]^{2-}$, c) $[K([2.2.2]crypt)]_2(Sn_2Bi_2)\cdot en$, thus using $[Sn_2Bi_2]^{2-}$ instead of $[GaBi_3]^{2-}$, and we performed d) reactions in dimethylformamide (DMF) instead of pyridine. Whereas from reaction (d) in DMF, the known phase $[K([2.2.2]crypt)]_2(Bi_4)$[12] formed as a single-crystalline product, all the other reactions only led to re-crystallization of the starting material (a) or yielded black powders containing mixtures of non-crystalline K_2Bi_x phases ($x \leq 4$) and elemental In (b) or Sn (c) according to EDX analyses. All of the reactions failed in producing a crystalline solid with $[Bi_{11}]^{3-}$ ions, such as **1**, hence supporting the statement above.

Being interested in learning whether the leaving Ga might be captured by a donor ligand, we added the N-heterocyclic carbene (NHC) 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene (TMPI) to the reaction mixture. The first observation was that the ^{71}Ga-NMR spectroscopy signal of the precursor also disappears, and that both **1** and the by-product are formed as single-crystals. Both the ^{1}H and ^{13}C NMR spectra of the reaction mixture after 2 h stirring and filtration (Figure S5 and S6) point towards the same result in that second sets of signals are observed, with distinctly shifted signals of the carbene C atoms (new signals at $\delta = 147.0$ ppm and $\delta = 183.5$ ppm in addition to the signal of free TMPI at $\delta = 242.1$ ppm). Second, an ESI mass spectrum of the reaction solution (Figure S7) contains several organogallium species, one of which accords with the Na$^+$ adduct of [Ga=TMPI]$^-$ (Figure S8).

To find out whether the observed NMR signals indeed arise from an interaction of a Ga atom with the carbene C atom, we optimized the geometric and electronic structures of several possible minimum structures, $[(Bi_3Ga){-}TMPI]^{2-}$ (**A**), $[Ga{=}TMPI]^-$ (**B**), $[py{\rightarrow}Ga{-}TMPI]^-$ (**C**), $[TMPI{=}Ga{=}TMPI]^-$ (**D**), $[H_2Ga{-}TMPI]^-$ (**E**), and $[H_3Ga{\leftarrow}TMPI]$ (**F**), by means of DFT calculations, and calculated their ^{1}H and ^{13}C NMR chemical shifts (Figure S9 and Table S4, Supporting Information); the values calculated for **C** and **D** show reasonable agreement with the experimentally observed ones.

Interestingly, Krossing et al. determined the crystal structure of a salt of the related stable cation $[Ga(IPr)_2]^+$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), a twofold oxidized analogue of **D** (disregarding the different NHCs).[32] The question whether the species with two electrons more would also be stable might be positively answered in the light of comprehensive quantum chemical investigations by Frenking et al., who suggested the isoelectronic carbo-dicarbene family with formal carbon(0) atoms to be stable,[33] which was indeed confirmed shortly after by first syntheses by Bertrand and co-workers.[34] In the meantime, both the theoretical[35] and the experimental[36] work has been extended to the heavier tetrel(0) homologues—with the same qualitative result—and the theoretical treatment was also extended to the negatively charged analogues of Group 13, however with imidazolium-based NHCs. Our results above indicate these species might be experimentally available.

In summary, herein, we did not only present the unexpected compound **1**, but we also contributed to the discussion on the applicability of reaction methods along an isolobal series of precursors. Based on the findings, future work will be dedicated to reactions of the diverse binary anions with further (element)organic compounds, including N-heterocyclic carbenes and phosphines with distinct donor/acceptor characteristics in order to systematically study activation and degradation of the tetrahedral P_4 or As_4 analogues.

Experimental Section

General: All manipulations and reactions were performed under an Ar atmosphere and the absence of light, using standard Schlenk or glove box techniques. All solvents were dried, freshly distilled, and stored under Ar prior to use. [2.2.2]crypt[10] (Merck), sodium hydride (60 % dispersion in mineral oil; washed several times with hexane prior to use) and 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (Sigma Aldrich, 95 %) were dried in vacuum for 13 h. $[K([2.2.2]crypt)]_2(GaBi_3){\cdot}en$ was prepared according to the literature procedure.[10]

1: A solution of $[K([2.2.2]crypt)]_2(GaBi_3){\cdot}en$ (153 mg, 0.1 mmol) in pyridine (4 mL) was stirred vigorously for 3 h, before the reactions mixture was filtered through a standard glass frit and carefully layered with toluene (4 mL). The alternative synthesis of **1** in the presence of 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (TMPI-Cl) was performed by dissolving TMPI-Cl (34.2 mg, 0.1 mmol) and sodium hydride (2.9 mg, 0.12 mmol) in pyridine (4 mL) under vigorous stirring. Upon completion of the hydrogen formation (ca. 1 h), the reaction solution was filtered through a standard glass frit onto $[K([2.2.2]crypt)]_2(GaBi_3){\cdot}en$ (153 mg, 0.1 mmol), and the mixture was stirred vigorously again. After 3 h, the reactions mixture was filtered again and carefully layered with toluene (4 mL). In both cases, black needles of $[K([2.2.2]crypt)]_3(Bi_{11}){\cdot}2py{\cdot}tol$ (**1**) formed at the wall of the Schlenk tube in 14–15 % yield (5.7 mg, 1.50×10^{-6} mol) within three days. The product contains a small fraction of lower quality crystals of a second polymorph with the same composition, denoted as **1a** in the Supporting Information. Semiquantitative energy-dispersive X-ray spectroscopy (EDX) analyses of several crystals confirmed the composition of **1** and **1a**. For details and further analyses see the Supporting Information.

Single-Crystal X-ray Diffraction: Single crystal X-ray diffraction experiments for **1** and **1a** were performed using a Bruker D8 Quest diffractometer or a STOE IPDS 2T diffractometer, respectively, at 100 K with $Mo_{K\alpha}$ radiation and graphite monochromatization ($\lambda = 0.71073$ nm). For details see Table S1 in the Supporting Information. Structure solutions were realized by direct methods, refinements with full-matrix-least-squares against F^2 using SHELXS-97 and SHELXL-2013 software.[11] CCDC-972755 (**1**) and 937466 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical methods: DFT calculations were performed with the program system TURBOMOLE[23] employing the Becke–Perdew 86 (BP86) functional[24] with def2-TZVP bases[25] and respective fitting bases[26] for the evaluation of the Coulomb matrix. Effective core potentials (ECPs) were used for Sb and Bi atoms (ECP-28 and ECP-60, respectively).[27] Counterions were modeled by application of COSMO with default parameters.[28]

Gas chromatography mass spectrometry: The gas chromatography electron ionization mass spectrum (GC-MS) was acquired with an Agilent 5973N system.

Gas chromatography: The gas chromatography for H_2 detection was performed at the Max-Planck-Institute for Terrestrial Microbiology with a Shimadzu gas chromatograph GC-8A (injection temp. 180 °C, column temp. 80 °C, flow 150 kPa). The gas chromatograph was calibrated with standard gases (Messer Griesheim, 2.0 ppm H_2).

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