Main-Group Chemistry

DOI: 10.1002/anie.201407288

Origin and Location of Electrons and Protons during the Formation of Intermetalloid Clusters $[Sm@Ga_{3-x}H_{3-2x}Bi_{10+x}]^{3-}$ ($x = 0, 1$)**

*Bastian Weinert, Fabian Müller, Klaus Harms, Rodolphe Clérac, and Stefanie Dehnen**

In memory of John D. Corbett

Abstract: *Reaction of $[GaBi_3]^{2-}$ with $[Sm(C_5Me_4H)_3]$ yielded the first protonated ternary intermetalloid clusters $[Sm@Ga_{3-x}H_{3-2x}Bi_{10+x}]^{3-}$ (**1**; $x = 0,1$). The presence of the Ga–H bonds and the transfer of electrons and protons during the formation of **1** were elucidated by a combination of experimental and quantum chemical methods, thereby rationalizing the role of the solvent ethane-1,2-diamine as a Brønsted acid. As an organic by-product, we observed the previously unknown octamethylfulvene (**2**) upon C–C coupling of $(C_5Me_4H)^-$.*

The chemistry of intermetalloid clusters—main-group (semi-)metal cages that accommodate one to three interstitial transition-metal atoms[1]—has become a multifaceted field. Besides derivatization by organic or element–organic ligands,[2] recent developments include non-classical, non-deltahedral species,[3] ternary anions including lanthanide-centered cages,[4] and multi-metal containers.[5] Not only the structural aesthetics and the uncommon bonding situations continue to inspire research, but also the potential application of the salt-like compounds, as well as the still unanswered questions concerning the formation processes.[6]

In the course of our recent work using the highly soluble binary $[Tt_2Pn_2]^{2-}$ ions (Tt = tetrel, Pn = pentel) of atoms of Groups 14 and 15 as reactants, we found reaction conditions that allow for a vivid re-arrangement of the precursor cages into even more complex architectures. By provision of atoms of two different main-group elements that enable the adjustment of electron numbers for a suitable total charge, a large variety of ternary anions, such as $[Zn@Zn_5Tt_3Bi_3@Bi_5]^{4-}$, $[Ni_2@Tt_7Bi_5]^{3-}$ (Tt = Sn, Pb),[5a–c] $[Eu@Sn_6Bi_8]^{4-}$,[4a] $[Pd_3@Sn_8Bi_6]^{4-}$,[5d] $[Pd@Pd_2Pb_{10}Bi_6]^{4-}$,[5e] or $[Sn_2Sb_5(ZnPh)_2]^{3-}$[5f] were obtained from $[K([2.2.2]crypt)]^+$ salts of these precursors in ethane-1,2-diamine (en) solutions (Figure 1).

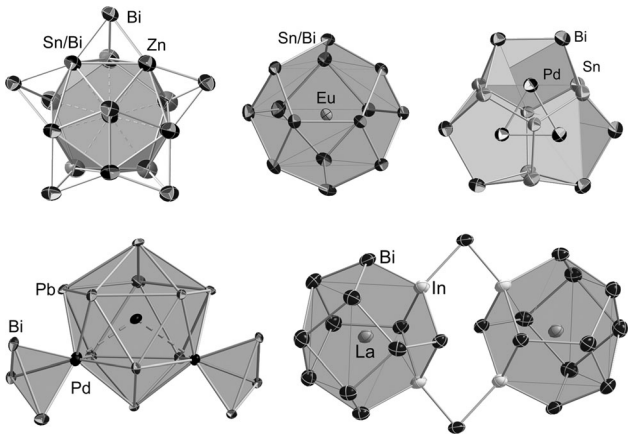

Figure 1. Selected examples of ternary intermetalloid cluster anions. From left: top row: $[Zn@Zn_5Sn_3Bi_3@Bi_5]^{4-}$,[5a] $[Eu@Sn_6Bi_8]^{4-}$,[4a] $[Pd_3@Sn_8Bi_6]^{4-}$;[5d] bottom row: $[Pd@Pd_2Pb_{10}Bi_6]^{4-}$,[5e] $[(La@In_2Bi_{11})(\mu\text{-}Bi)_2(La@In_2Bi_{11})]^{6-}$.[8]

Most recently, we have transferred the synthetic approach to an isoelectronic Group 13/15 analogue, $[InBi_3]^{2-}$. Accordingly, by reaction of $[K([2.2.2]crypt)]_2[InBi_3]\cdot en$[7] with $[La(C_5Me_4H)_3]$ we obtained a La-centered 13-atom cage "$[La@In_2Bi_{11}]^{4-}$", which is isoelectronic to $[Ln@Sn_4Bi_9]^{4-}$.[4b] However, involving triel atoms (Tr) instead of tetrel atoms, with a formal 2– instead of formal 1– charge per atom, lead to the formation of a "dimeric" anion $[(La@In_2Bi_{11})(\mu\text{-}Bi)_2(La@In_2Bi_{11})]^{6-}$ (Figure 1).[8] Comprehensive quantum chemical investigations demonstrated that this reaction was driven by the necessity to reduce the large charge-overload at the Lewis basic "In^{2-}" sites by Lewis acid–base interactions of the type $In^{2-} \rightarrow \mu\text{-}Bi^{+} \leftarrow In^{2-}$.

To even enhance this basicity, we tested the behavior of the lighter homologue, $[K([2.2.2]crypt)]_2[GaBi_3]\cdot en$,[7] in reactions with $[Sm(C_5Me_4H)_3]$. The studies showed that a Sm^{3+} ion can be included in the corresponding 13-atom cage, however with uncommon composition, which also shed new light on the cluster formation processes.

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (GRK 1782), the Fonds der Chemischen Industrie (Chemiefonds-Stipendium for B.W.), the CNRS, the University of Bordeaux, and the Aquitaine Région. We thank Prof. Dr. Rhett Kempe for valuable discussion.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201407288.

By single-crystal X-ray analyses,[9] we determined the presence of three $[K([2.2.2]crypt)]^+$ counterions per cluster unit in the product, clearly indicating a 3− total charge of the anion. Owing to rotational disorder, which is typical for these near-spherical intermetalloid clusters, the crystallographic determination of the atomic ratio of the two main-group elements was not trivial. Combination of sophisticated structure refinement and energy dispersive X-ray (EDX) spectroscopy finally indicated a situation between the established 2:11 ratio (92%) and a so far unknown 3:10 ratio (8%) of the Tr:Pn atoms. However, assignment of the typical formal charges for this type of 13-atom cage, namely Ga^{2-} and Bi^0 and a "capping" $(Bi_5)^{3-}$ unit (according to quantum chemical calculations, see Refs. [4b, 8, 10] and Figures S25 and S26) and Sm^{3+} (as confirmed by magnetic measurements, see Figure S30 in the Supporting Information), would not give the 3− charge indicated above, but would rather result in the apparently wrong formulae "$[Sm@Ga_2Bi_{11}]^{4-}$" or "$[Sm@Ga_3Bi_{10}]^{6-}$".

Electrospray ionization mass spectrometry (ESI-MS) helped to explain the situation as being the result of a Brønsted acid–base reaction. Hence, the title compound contains predominately the mono-protonated intermetalloid cluster $[Sm@Ga_2HBi_{11}]^{3-}$ and small amount of the triple-protonated intermetalloid cluster $[Sm@Ga_3H_3Bi_{10}]^{3-}$ and can be formulated as: $[K([2.2.2]crypt)]_3[Sm@Ga_2HBi_{11}]_{0.9}$-$[Sm@Ga_3H_3Bi_{10}]_{0.1}$·en·tol (**1**; stoichiometric numbers are rounded to one decimal digit for clarity; tol = toluene; Figure 2). As outlined below, we found that electrons and protons come from "Ga^{2-}" atoms and the solvent ethane-1,2-diamine, respectively.

The overall Ga/Bi architecture, which has crystallographic C_s symmetry in **1**, corresponds to the structure of the 13-atom cage found in $[Ln@Sn_4Bi_9]^{4-}$ (Ln = La, Ce)[4b] or in $[(La@In_2Bi_{11})(\mu\text{-}Bi)_2(La@In_2Bi_{11})]^{6-}$.[8] Selected interatomic distances are Bi9–Bi 3.3225(4)–3.3313(4) Å, Bi7,8–Ga/Bi 2.9876(4)–3.0178(5) Å, Ga/Bi–Ga/Bi 2.750(4)–3.0100(4) Å, Bi9–Sm1 3.0464(6) Å, Bi7,8–Sm1 3.4050(5)–3.4306(4) Å, and Bi/Ga–Sm1 3.2370(3)–3.4134(6) Å.

Structure refinement with the use of second free variables and quantum chemical investigations agree on the placement of the two or three Ga atoms in the cluster anions, as shown in Figure 2. According to both methods, the two Ga atoms that are present in both anionic species are disordered over the four positions of the basal 4-atom face (Ga1/Bi1-Ga3/Bi3), with site occupation factors (s.o.f.) of approximately 0.5:0.5 each. The third Ga atom, which is only present in 10% of the anionic species, is disordered over two adjacent positions (Ga5/Bi5, Ga6/Bi6, s.o.f. 0.03:0.97 each), while the two remaining neighboring atom positions are only occupied by Bi (Bi4). The anion's "cap" of the is formed, for energetic reasons, by five Bi atoms without any Ga contribution (for details see the Supporting Information, Tables S7–S9, Figure S20). Since the protons attached to the disordered Ga atoms could not be localized on the X-ray diffraction difference Fourier map, they were calculated to be on idealized positions at the respective Ga atoms with the respective site occupation factors set to result in an average number of 1.2 H atoms. To confirm the presence of the H atoms, the nature of the anion and its formation were explored and confirmed by further analytical methods, namely ESI-MS, electron ionization MS (EI-MS), gas chromatography MS (GC-MS), Fourier-transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and density functional theory (DFT) calculations.

ESI mass spectra of a solution of **1** in *N*,*N*-dimethylformamide (DMF; Figure 3) show signals of about equal intensity from the two cluster species. This situation differs from the observation of a majority of $[Sm@Ga_2HBi_{11}]^{3-}$ ions in the single-crystal structure, which is not untypical for ternary intermetalloid anions.[4,5,8] This is most probably due to a different composition of single-crystalline versus microcrystalline or powder sample, the first of which was exclusively used for X-ray diffraction, whereas a combination of all the samples is present in the bulk analyses.

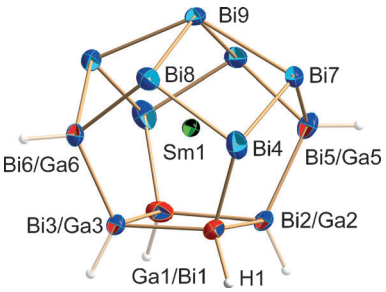


Figure 2. Thermal ellipsoid plot (set at 50% probability) of the anion in **1**, averaged as $[Sm@Ga_{2.1}H_{1.2}Bi_{10.9}]^{3-}$. A total of 1.2 protons were calculated at idealized positions at six sites (two-colored) that are occupied by a total number of 3.9 Bi and 2.1 Ga atoms (Table S2). As an example, the majority structure of $[Sm@Ga_2H_1Bi_{10}]^{3-}$ is emphasized by red-blue Ga, non-transparent H1 atom and blue-red Bi atoms. Full occupation of positions Bi4 and Bi7–Bi9 with Bi atoms (blue) is in accordance with quantum chemical investigations (Tables S7–S9).

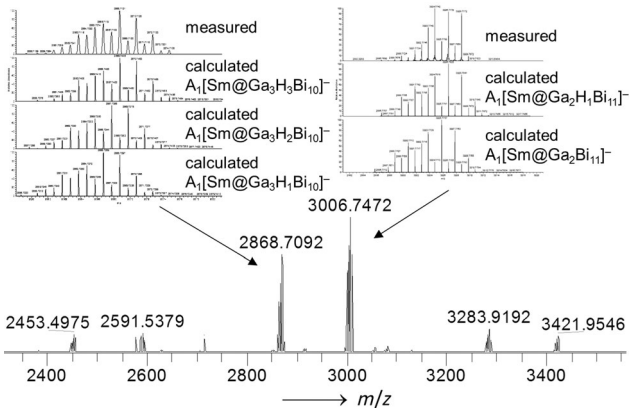


Figure 3. ESI mass spectrum of a fresh solution of **1** in DMF (m/z 2400–3500), recorded in negative ion mode. The expansions of the two dominant peaks indicate the signals as representing mixtures of the species given in the formula of **1** with traces of further species with lower degrees of protonation. Note that all species abundant in the spectrum exhibit charge 1− under ESI-MS conditions, regardless of their original charge, which is typical for corresponding experiments on intermetalloid clusters; thus, species with originally different charges can be detected side by side, as long as they are anionic in nature. The overview mass spectra and expansions of all assignable peaks are provided in Figures S8–S11.

The ESI-MS signals arise as three pairs of peaks, each representing the two clusters with a 3:10 or 2:11 ratio of Ga:Bi atoms, with different numbers of $[K([2.2.2]crypt)]^+$ complexes attached: no-counterion complexes (Figure 3, left), one-counterion complexes (predominant; Figure 3, center), or two-counterion complexes (Figure 3, right). The molecule signals are in excellent agreement with the simulation of anionic clusters with three protons or one proton, respectively (insets in Figure 3; very small amounts of (partially) deprotonated clusters were additionally considered in both cases to meet the exact relative abundances within the measured isotope patterns). The ESI mass spectra thus confirm the co-existence of two protonated clusters, being retained in solution and in the gas phase.

The H atoms bonded to the Ga atoms were detected by means of ^{1}H NMR spectroscopy of a fresh solution of **1** in $[D_7]$DMF (Figure 4). Besides sharp signals of [2.2.2]crypt and

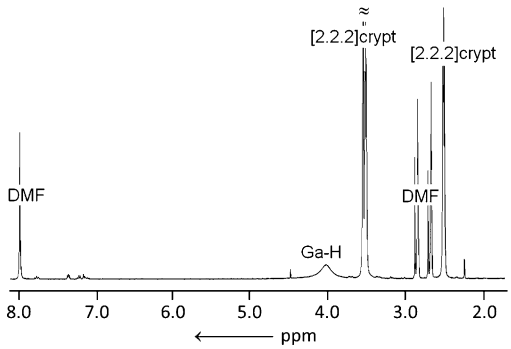


Figure 4. ^{1}H NMR spectrum of a fresh solution of **1** in $[D_7]$DMF. Further details, including temperature–dependent NMR spectra, are provided in the Supporting Information (Figures S2–S7). Owing to evaporation and mild drying of the crystals prior to dissolution for the measurement, signals of the crystal solvents are absent.

DMF molecules, a broad signal is observed at a chemical shift of $\delta = 4.03$ ppm, which narrows with decreasing temperature (Figure S3). Since Sm^{3+} is known not to affect the ^{1}H proton resonance, because of its weak paramagnetism and therefore low influence on signal shift and peak broadening,[11a–c] the signal broadening in the spectrum of **1** is ascribed to the coupling with ^{69}Ga and ^{71}Ga (both $I = {}^3/_2$)[11d] and the chemical exchange of the proton position—in agreement with the proposed structural properties and the temperature dependency of the NMR signal.

The FT-IR spectrum of a solid suspension of hand-selected single crystals of **1** in dry KBr has a relatively broad band between 1560 cm^{-1} and 1685 cm^{-1}, centered around 1633.29 cm^{-1} (Figure S19). This can be assigned to the Ga–H stretching mode, as suggested by quantum chemical investigations (using DFT methods implemented within the program system TURBOMOLE[12–19]) on $[Sm@Ga_2HBi_{11}]^{3-}$ (1672 cm^{-1}) and $[Sm@Ga_3H_3Bi_{10}]^{3-}$ (1655 cm^{-1}, 1682 cm^{-1}, 1694 cm^{-1} (isomer 1 H) or 1664 cm^{-1}, 1694 cm^{-1}, 1701 cm^{-1} (isomer 2 H)). As confirmed by ^{1}H NMR spectroscopy of the same crystal sample it can be excluded that the observed signal derives from scissoring modes of ethane-1,2-diamine (NH_2 group) and/or bending modes of toluene (ring and methyl group), both of which are situated in the same wavenumber range (en: 1600 cm^{-1}, toluene: 1605 cm^{-1}).[20]

The observed protonation represents the second possible way to overcome the high basicity of the negatively charged triel atoms in intermetalloid $M/E^{13}/E^{15}$ cluster anions. For the (less basic) "In^{2-}" sites in the La/In/Bi cluster mentioned above, a "Bi^+" bridge served to stabilize the charge overload in the solid state. However, (partial) protonation, suggested previously as a potential alternative,[8] was shown to be possible by the present work. The necessity of charge decrease is furthermore shown by the quantum chemical structure optimizations of the unprotonated clusters "$[Sm@Ga_2Bi_{11}]^{4-}$" and "$[Sm@Ga_3Bi_{10}]^{6-}$": both converge into species with distinctly elongated Bi7/8–Bi9 edges (located in the Bi_5 "cap"), whereas for calculations of the protonated clusters $[Sm@Ga_2HBi_{11}]^{3-}$ and $[Sm@Ga_3H_3Bi_{10}]^{3-}$, this effect is reduced (Table S9).

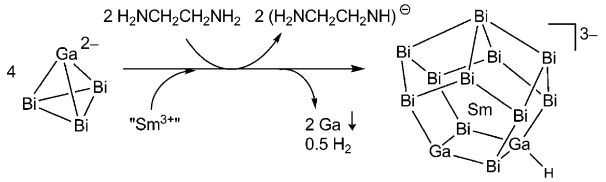
Clearly, the match between a 13-atom cage of this particular Ga/Bi elemental combination and the size of a lanthanide (3+) ion is at the border of being possible. The 13-atom cages $[La@Sn_4Bi_9]^{4-}$, $[Ce@Sn_4Bi_9]^{4-}$, and "$[La@In_2Bi_{11}]^{4-}$" (as a fragment of $[(La@In_2Bi_{11})(\mu\text{-}Bi)_2\text{-}(La@In_2Bi_{11})]^{6-}$) have diameters of 5.74–5.86 Å (measured from the apical Bi atom to the center of the basal tetrahedral face). In **1** this diameter amounts to only 5.66 Å, indicating tight fit around the inner atom. As one consequence, the electron density of the main-group metal cage is strongly polarized towards the central Sm^{3+} ion (see Figures S25 and S26), which has not been observed to that extent in the In/Bi or Sn/Bi clusters. As a second consequence, it seems to be crucial to delocalize the electron density onto terminal ligands, such as H atoms. Hence, we will explore the possibility of introducing further Lewis acidic ligands instead of protons.

Having confirmed the presence of protons at the cluster anions of the title compound, a possible source needs to be identified. In recent reports on the generation of the only other intermetalloid clusters with H atoms on their surface, $[M@Sn_9H]^{3-}$ (M = Ni, Pt),[21a,b] and on alkenylation reactions of Zintl anions,[22c] deprotonation of the solvent en was discussed, which could not be fully verified.[22] Yet, our findings confirm this assumption. We have checked whether the $(C_5Me_4H)^-$ ligand released from the initially used Sm^{3+} complex might have (additionally) acted as Brønsted acid, but deuteration experiments served to rule this out (see Supporting Information). Still, we detected the previously unknown species 2,2′,3,3′,4,4′,5,5′-octamethyl-[1,1′-bi(cyclopentylidene)]-2,2′,4,4′-tetraene (octamethylfulvene, **2**) as a C–C coupling product of $(C_5Me_4H)^-$ in the mother liquor of the title compound. This gives an indication that the clusters in **1** have some C–H bond activation capability, and/or a catalytic activity for C–C coupling reactions. Details on the experimental and quantum chemical characterization of **2** are provided in the Supporting Information.[23] Hence, en indeed remains the only reasonable proton donor.

As modeled by quantum chemical calculations, the Brønsted basicity of the protonated anions is similar to that of $[H_2SiO_4]^{2-}$ or $[HSiO_4]^{3-}$ (see Figure S21). As the acidity is

also high enough to principally allow for protonation of ethane-1,2-diamine, as well, the cluster should be viewed as ampholytes in ethane-1,2-diamine, thus co-existing in different degrees of protonation in certain ranges of their concentration (in agreement with the ESI-MS findings), but they clearly prefer the species with 3− charges for crystallization.

Comparison of the formal charges of the atoms within the binary anion $[(Ga^{2-})_1(Bi^0)_3]^{2-}$ with those of the ternary ones, $[(Sm^{3+})@(Ga^{2-})_2(H^+)_1(Bi^0)_6(Bi^-)_4(Bi^+)_1]^{3-}$ or $[(Sm^{3+})@(Ga^{2-})_3(H^+)_3(Bi^0)_5(Bi^-)_4(Bi^+)_1]^{3-}$, indicates the additional necessity of a source of electrons: all the 13-atom cages have three more electrons than the number of electrons provided by the reactant.[10] Another unbalanced situation is found in the relative number of Ga and Bi, which is 1:3 in the reactant but 2:11 or 3:10 in the product. Consequently, Ga atoms need to be set free during the reaction, which was confirmed by precipitation of Ga metal. This is in accordance with our findings in the formation of $[Bi_{11}]^{3-}$ from $[GaBi_3]^{2-}$ in pyridine.[24] An remaining excess of electrons is used for reductive production of H_2, which was also observed as side-product in all the corresponding reactions.[4,5,24] Scheme 1 summarizes these findings in an stoichiometric reaction scheme for the formation of the dominant cluster species $[Sm@Ga_2HBi_{11}]^{3-}$.



Scheme 1. Stoichiometric reaction scheme for the formation of the major anion in **1**, $[Sm@Ga_2HBi_{11}]^{3-}$, under electron transfer from the "Ga^{2-}" atoms of the precursor anion and proton transfer from the solvent en.

Scheme 1 illustrates idealized stoichiometry and quantitative processes, which deviates from the observed low (crystalline) yields, the occurrence of a minor second cluster species, and the generation of Bi polyanions, such as the known $[Bi_2]^{2-}$,[25] which was observed in the ESI mass spectrum of the reaction solution (see Figures S8 and S9). However, it indicates all of the involved reactants and observed by-products regarding the cluster formation under the given conditions.

In summary, compound **1** contains the first ternary intermetalloid anions involving highly basic "Ga^{2-}" atoms and, at the same time, the first protonated ternary intermetalloid clusters. This result indicates, first, the large synthetic potential of heterometallic, highly basic Group 13/15 precursor anions, which will now be extended towards derivatization of ternary cluster anions with (element)organic groups. Second, the studies rationalized and more deeply explored the role of the solvent ethane-1,2-diamine (en) as a Brønsted acid and, third, the findings indicated further potential reactivity of the cluster anions, which clearly trigger C–H bond activation and C–C coupling reactions of $(C_5Me_4H)^-$ and the formation of previously unknown octamethylfulvene (**2**) as an organic byproduct.

Experimental Section

All manipulations and reactions were performed under an Ar atmosphere using standard Schlenk or glovebox techniques. [K-([2.2.2]crypt)]$_2$[$GaBi_3$]·en was prepared according to the literature procedure.[7] All solvents were dried, freshly distilled and stored under Ar prior to use. [2.2.2]crypt[7] (Merck) and [$Sm(C_5Me_4H)_3$] (Aldrich) were dried in vacuum for 13 h.

Data collection for single-crystal X-ray diffraction was performed using a STOE IPDS2T diffractometer at 100 K with $Mo_{K\alpha}$ radiation and graphite monochromatization ($\lambda = 0.71073$ Å). Structure solution was realized by direct methods, refinement with full-matrix-least-squares against F^2 using SHELXS-97 and SHELXL-2013 software.[9] For details see the Supporting Information. CCDC 969954 (**1**) contains 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.

Details on the synthesis of **1**, on NMR, IR, and EDX spectroscopy, magnetic measurements, high-resolution ESI-MS, high-resolution EI-MS, and GC-MS measurements are provided in the Supporting Information.

DFT calculations were done with the program system TURBOMOLE[12] employing the Becke–Perdew 86 (BP86) functional[13,14] with def2-TZVP bases[15] and respective fitting bases[16] for the evaluation of the Coulomb matrix. Effective core potentials (ECPs) were used for Sm (ECP-46)[17] and Bi atoms (ECP-60).[19] Counter ions were modeled by the COSMO model with default parameters.[19]

Received: July 17, 2014
Published online: September 11, 2014

Keywords: intermetalloid clusters · mass spectrometry · NMR spectroscopy · structure elucidation · Zintl anions

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[22] Owing to the much higher intensity of the relatively broad solvent en CH_2 signals in the ^1H and ^{13}C NMR spectra of the reaction solution (see Figures S4 and S5), and to the protolytic exchange, which is likely to be too rapid for the NMR time scale, it has not been possible so far to detect any additional signals for the corresponding anion $(H_2NCH_2CH_2NH)^-$. See also Ref. [21].

[23] Fulvene itself was synthesized under related conditions, by using strong bases, such as BuLi—replaced by "Ga^{2-}" in this work—and oxygen or metal Lewis acids/oxidants such as Cu^{2+}—corresponding to the presence of Sm^{3+}/Bi herein; a) A. Escher, W. Rutsch, M. Neuenschwander, *Helv. Chim. Acta* **1986**, *69*, 1644 – 1654; b) W. von E. Doering, *Kekulé Symposium, London, 1958*, Butterworth, London, **1959**, p. 35.

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