Video Article

The Synthesis of $[Sn_{10}(Si(SiMe_3)_3)_4]^{2-}$ Using a Metastable Sn(I) Halide Solution Synthesized via a Co-condensation Technique

Mareike Binder[1], Claudio Schrenk[1], Andreas Schnepf[1]

[1]Chemistry Department, Institute of Inorganic Chemistry, University of Tübingen

Correspondence to: Andreas Schnepf at andreas.schnepf@uni-tuebingen.de

URL: https://www.jove.com/video/54498
DOI: doi:10.3791/54498

Keywords: Chemistry, Issue 117, Co-condensation, cryochemistry, disproportionation, group 14, metalloid cluster, metathesis, metal subhalide, tin

Date Published: 11/28/2016

Citation: Binder, M., Schrenk, C., Schnepf, A. The Synthesis of $[Sn_{10}(Si(SiMe_3)_3)_4]^{2-}$ Using a Metastable Sn(I) Halide Solution Synthesized via a Co-condensation Technique. *J. Vis. Exp.* (117), e54498, doi:10.3791/54498 (2016).

Abstract

The number of well-characterized metalloid tin clusters, synthesized by applying the disproportionation of a metastable Sn(I) halide in the presence of a sterically demanding ligand, has increased in recent years. The metastable Sn(I) halide is synthesized at "outer space conditions" via the preparative co-condensation technique. Thereby, the subhalide is synthesized in an oven at high temperatures, around 1,300 °C, and at reduced pressure by the reaction of elemental tin with hydrogen halide gas (*e.g.,* HCl). The subhalide (*e.g.,* SnCl) is trapped within a matrix of an inert solvent, like toluene at -196 °C. Heating the solid matrix to -78 °C gives a metastable solution of the subhalide. The metastable subhalide solution is highly reactive but can be stored at -78 °C for several weeks. On heating the solution to room temperature, a disproportionation reaction occurs, leading to elemental tin and the corresponding dihalide. By applying bulky ligands like $Si(SiMe_3)_3$, the intermediate metalloid cluster compounds can be trapped before complete disproportionation to elemental tin. Hence, the reaction of a metastable Sn(I)Cl solution with $Li\text{-}Si(SiMe_3)_3$ gives $[Sn_{10}(Si(SiMe_3)_3)_4]^{2-}$ **1** as black crystals in high yield. **1** is formed via a complex reaction sequence including salt metathesis, disproportionation, and degradation of larger clusters. Further, **1** can be analyzed by various methods like NMR or single crystal X-ray structure analysis.

Video Link

The video component of this article can be found at https://www.jove.com/video/54498/

Introduction

Due to recent progress in the field of nanotechnology, the nanoscale size range between molecules and the solid state became more and more important and is the focus of various research efforts[1]. Research with nanoscaled compounds is especially of interest for metals or semimetals, as drastic changes take place during the transformation from small molecular species (*e.g.,* oxides, halides: non-conducting; *e.g.,* $AlCl_3$, $AuCl_3$, GeO_2, *etc.*) to metalloid clusters[2] of the general formulae M_nR_m (n>m; M = metal such as Al, Au, Sn, *etc.*; R = ligand such as $S\text{-}C_6H_4\text{-}COOH$, $N(SiMe_3)_2$, *etc.*), to the final bulk elemental phase (metal: conducting; semimetal: semiconducting; *e.g.,* elemental Al, Au, or Ge)[3].

The synthesis of a definite molecular nanoscaled compound is challenging due to its metastable character. Many synthetic procedures give metal nanoparticles with a certain size distribution[4], meaning a mixture of metalloid cluster compounds of different sizes. Consequently, to establish a basis for a structure-property relationship of nanoscaled materials, synthetic procedures must be developed to access definite nanoscaled molecular compounds. These definite molecular compounds (metalloid clusters in the case of metals[5,6,7,8]) will shed light on the complexity and the fundamental principles of deceptively simple chemistry, such as the dissolution and the formation of metals[9].

One synthetic route to access metalloid clusters of various metals starts from the reduction of stable precursors that are reduced to form a metalloid cluster, mostly in low yield (*e.g.,* metalloid group 14 clusters like $Sn_{15}(DippNSiMe_3)_6$ (Dipp = $2,6\text{-}iPr_2\text{-}C_6H_3$)[10], $Pb_{10}(Hyp)_6$ (Hyp = $Si(SiMe_3)_3$)[11], or $Ge_5(CH(SiMe_3)_2)_4$[12]). Additionally, an increasing number of metalloid clusters of coinage metals are synthesized via the reduction of precursors in the presence of a trapping ligand like $[Ag_{44}(p\text{-}MBA)_{30}]^{4-}$ (p-MBA = p-mercaptobenzoic acid)[13] and $Au_{102}(p\text{-}MBA)_{44}$[14]. Beside the synthetic route of applying the reductive dehalogenation, Schnöckel *et al*. introduced a synthetic route to metalloid group 13 clusters by applying the disproportionation reaction of highly reactive metastable monohalides of the corresponding element (*e.g.,* $3AlCl \rightarrow 2Al + AlCl_3$).

The synthesis of the needed monohalides is thereby performed via a preparative co-condensation technique, where at high temperatures, gas-phase molecules of AlX and GaX (X = Cl, Br, I) are synthesized and afterwards trapped in a matrix of frozen solvents (**Figure 1**)[15]. This technique thus gives access to novel reagents, opening the way to novel areas of chemistry (*e.g.,* starting from the metastable monohalides, metalloid clusters with diameters in the nanometer range like $[Al_{77}(N(SiMe_3)_2)_{20}]^{2-}$ or $[Ga_{84}(N(SiMe_3)_2)_{20}]^{4-}$ could be obtained)[16,17].

The synthetic route via the disproportionation reaction is thus the most productive, leading to clusters with diameters in the nanometer range. However, this synthetic route is only possible if a metastable subhalide is at hand that disproportionates at low temperatures (normally far below 0 °C). Again, in the case of group 14, monohalides are needed, as the subvalent dihalides MX_2 (M = Ge, Sn, Pb) are too stable and disproportionate at temperatures well above 100 °C. The synthesis of metastable group 14 monohalide solutions is possible via the preparative co-condensation technique. However, group 14 monohalides are obtained at much higher temperatures with respect to the group 13 monohalides, which are readily available as gas phase species at 1,000 °C. Hence, SnBr is obtained in maximum yield at 1,250 °C[18], whereas GeBr[19], as well as $SiCl_2$[20], are obtained at even higher temperatures, up to 1,600 °C. The monohalides are "trapped" via a preparative co-condensation technique (**Figure 1**), leading to metastable monohalide solutions. Starting from these metastable solutions, we were recently able to synthesize a variety of novel metalloid group 14 cluster compounds of germanium and tin, namely $[Li(thf)_2]_3[Ge_{14}(Hyp)_5]$ (Hyp = $Si(SiMe)_3)$)[21], $Sn_{10}(Hyp)_6$[22], and $\{[Li([12]crown\text{-}4)_2]\}_2\,[Sn_{10}(Hyp)_4]$[23]. Here, we present the synthesis of a metastable Sn(I)Cl solution within a homemade co-condensation apparatus and describe its reactivity with LiHyp to give the metalloid cluster $[Sn_{10}(Hyp)_4]^{2-}$ **1** in high yield.

Protocol

CAUTION! Please consult all relevant material safety data sheets (MSDS) before use. Several of the chemicals used in these syntheses are acutely toxic, pyrophoric, and carcinogenic. Nanomaterials may have additional hazards compared to their bulk counterpart. Please use all appropriate safety practices when performing a reaction, including the use of engineering controls (fume hood and glovebox) and personal protective equipment (safety glasses, gloves, lab coat, full length pants, and closed-toe shoes). Portions of the following procedures involve standard air-free Schlenk techniques. The co-condensation apparatus applied contains a 20 kW high-frequency generator. People with a cardiac pacemaker can have strictly no admittance. Gaseous HCl is highly corrosive. Store in a well-ventilated place or in a fume hood. Liquid nitrogen and dry ice are extremely cold substances; special gloves must be used to prevent frostbite.

1. Preliminary Work

1. **Setup of the graphite reactor**
    1. Take five reaction chambers, one terminal ring, one hollow graphite tube topped with a quartz glass tube, and two 0.7 mm graphite rods. Fill all five reaction chambers with elemental tin (pieces), in total 6 g. Stack the reaction chambers over the terminal ring, each of them twisted by 30°, and fix the stack with the graphite rod. Ensure that the rod is not longer than the stack.
    2. Insert the stack into the graphite tube so that the holes of the terminal ring fit with the holes in the graphite tube. Fix the setup with a second graphite rod. Ensure that the rod is not longer than the diameter of the tube. Weigh the whole setup with a scale and note the value to determine the amount of tin consumed during the reaction.

2. **Preparing the solvent mixture**
    NOTE: Toluene must be pre-dried over sodium/benzophenone and distilled. Tributylphosphine must be vacuum-distilled prior to use.
    1. Attach a 200 ml Schlenk tube with a glassy stopcock to a lab Schlenk-line. Evacuate and purge the system with inert gas three times. Flame heat the evacuated Schlenk tube after the first evacuation cycle.
    NOTE: Use either dry nitrogen or dry argon as inert gas.
    2. Fill with 180 ml of toluene and 20 ml of tributylphosphine. Mix the solvents by manually shaking the flask.
    NOTE: Tributylphosphine reacts with paper towels. Do not wipe drops of tributylphosphine with paper.
    3. Cool the mixture with dry ice for at least 20 min and degas the mixture by slightly evaporating and shaking the cold flask. Close the valve under vacuum and let the mixture heat to room temperature.
    NOTE: The mixture can evaporate violently, which can be avoided by continuously shaking the flask.

2. Set up the Co-condensation Apparatus

1. **Reaction**
    1. Place the graphite reactor inside the copper induction coil and pass the quartz tube through the central hole of the top copper sheet, placed above the induction coil. Fix the quartz tube to the gas supply with a gasket and a screw nut. Check the position of the reactor inside the coil. Ensure that the reactor protrudes from the coil by 5 ± 0.5 mm.
    NOTE: The copper induction coil is the central portion of the co-condensation apparatus. The coil is flush with cooling water and is connected to a high-frequency generator. Thus, the graphite tube will be heated inductively. To get reproducible conditions, the position of the graphite tube inside the coil is crucial. It should be located in the center of the coil's cavity, with 5 ± 0.5 mm protruding out the bottom.
    2. Connect the cooling shield to the water pins of the connector with the screw nuts. Fix the cooling shield at the other side with a screw. Test the water-tightness of the cooling cycle by opening the water tap for 30 sec.
    NOTE: Due to the high voltage inside, there must be no direct metal-metal contact to prevent bypasses or electric arcs, especially at the top copper sheet. If there are contacts, change the position of the copper sheet with a stick. If this is not possible, remove all the components and restart from 2.1.1.
    3. Fix the fiber optics of the pyrometer (temperature control) to the holder at the copper shield with a screw. Put a quartz glass in the holder at the optics to prevent contamination of the optical system by chemicals like SnCl.
    4. Fix the solvent vapor diffuser with a screw nut. Be sure that the diffuser is centered under the cavity of the copper shield. Re-check that the graphite reactor is still in the center of the induction coil, and that there is no contact of the coil to the top copper sheet.
    5. Mount the Schlenk vessel, for solvent evaporation, onto the valve, which is connected via a steel tube to the vapor diffuser. Attach the prepared solvent mixture flask to the Schlenk vessel. Add a hemispherical heating mantle to the evaporating Schlenk vessel.
    6. Connect the long steel cannula to the apparatus with a screw nut. Close the outer tail with a small round-bottom flask. Place a magnetic stir bar (10 cm) inside the big stainless steel vessel, put the gasket into the cavity of the plane flange, and connect the vessel to the co-condensation apparatus.

2. **Gas supply**
    1. Connect an HCl-containing glass vessel to a small steel tube and then to a four-point adapter.
    NOTE: The HCl pressure inside the glass vessel must be below 1 atm so that the differential pressure manometer can work.

2. Close the rear exit of the four-point adaptor with a blind flange. Connect the differential pressure manometer to the front exit and set up a valve at the top exit. Connect a fine-needle valve to the valve at the top exit of the four-point adapter. Then, use a long steel tube to connect the gas supply part to the co-condensation apparatus.
   NOTE: Instead of a fine-needle valve, a mass flow controller can be used.

3. **Further preparatory work**
   1. Connect the double-walled steel dewar bucket to the vacuum pump and evacuate the double-walled space for at least 30 min.
      NOTE: This step can also be done during the setup of the reaction part of the co-condensation apparatus.
   2. Evacuate the whole co-condensation apparatus with a rotary vane pump to a final pressure of 10^{-2} mbar, which takes 60 min.
   3. After reaching the final pressure, preheat the oil diffusion pump. Switch on the cooling water cycle and evacuate the oil diffusion pump with the rotary vane pump during heating.
      NOTE: During this time the apparatus stays under static vacuum until the diffusion pump is heated. This takes at least 45 min.
   4. Evacuate the apparatus with the pre-heated diffusion pump overnight to reach the final pressure of about 8×10^{-6} mbar the next morning.

3. Co-condensation Reaction

1. **Setting up the reaction**
   1. Fill the cooling trap of the diffusion pump with 4 L of liquid nitrogen. Switch on the cooling water cycle of the high-frequency generator by opening the water tap. Then, switch on the high-frequency generator.
   2. Slowly pre-heat the graphite reactor by increasing the output power of the high-frequency generator manually, in incremental steps of 0.1 to 0.5 kW, until the reaction temperature is around 1,300 °C.
      NOTE: The temperature is monitored with the optical pyrometer and should not be higher than 1,300 °C. In normal cases, this procedure needs approximately 30 min, and the final temperature is achieved at 3.5 kV. During the process, the stainless steel vessel also gets warm.
   3. Adjust the value of the generator to 1.0 kV to cool down the reactor. Fill the steel dewar with about 30 L liquid nitrogen. Lift the dewar with a lifting platform so that the reaction vessel is placed within the dewar. Add more liquid nitrogen to the steel dewar to reach the final level of liquid nitrogen.
      NOTE: In the following steps, the level of liquid nitrogen should always be at the upper third of the stainless steel vessel.

2. **Performing the reaction**
   1. Evaporate the solvent dropwise. Fix the drop rate so that all solvent is used during the reaction (4 hr). Switch on the hemispherical heating mantle on the lowest level to maintain evaporation.
   2. Close the fine-needle and the gas valve. Open the HCl vessel. Ensure that the displayed voltage at the differential pressure manometer is higher than 1,600 mV. If this is not the case, apply low pressure at the second connection of the manometer by connecting an evacuated vessel to the outer connection of the manometer. Write down the displayed starting value.
   3. Heat the graphite reactor to the final temperature of 1,300 °C by adjusting the value of the generator to 3.5 kV. Open the gas valve. Slowly open the fine-needle valve to let in the reaction gas (HCl) with a constant rate of 8 mV/min. Check the rate at least every 10 min and write down the measured values.
      NOTE: The control of a constant gas flow rate is absolutely necessary for a reproducible reaction. If a mass flow controller is used, the flow rate can be controlled via a computer program. Otherwise, the control can be done by noting the decreasing values of the differential pressure manometer during the gas inlet. The rate should be within 7-8 mV/min, and the reaction is finished when the displayed value is decreased by 1,600 mV, which is equal to 40 mmol of HCl consumed.
      NOTE: When the reaction is running, hydrogen gas is produced, which can be monitored by the increase in pressure inside the apparatus from about 8×10^{-6} mbar to around 4×10^{-5} mbar.
   4. Put 2 L of liquid nitrogen in the dewar approximately every 10 min so that the level of liquid nitrogen is always at the upper third of the stainless steel vessel. This process will take 4 hr.
   5. After the value of the differential manometer is decreased by 1,600 mV, close the gas valve. Then, introduce the remaining HCl gas that is within the gas supply part by slowly opening the fine-needle valve. Wait until the pressure in the apparatus gets lower than 4×10^{-5} mbar and then switch off the high-frequency generator and let in the remaining solvent mixture if necessary.
   6. Change the liquid nitrogen-filled steel dewar to an insulated bucket placed on a magnetic stirrer. Disconnect the oil diffusion pump by closing the main valve and flush the apparatus with dry nitrogen (5.0) to a pressure around 1 atm (rough barometer). Add ~5 kg of fine, powdered dry ice into the bucket so that the stainless steel vessel will be cooled from outside and switch on the magnetic stirrer.
   7. Wait until the magnetic stirrer rotates freely. This indicates that the reaction mixture is molten. Let the solution stir for at least 45 min.
      NOTE: During the heating process, the pressure increases and might get higher than 1.2 atm, which can be seen at the rough barometer. The overpressure can be released via the valve in the round-bottom flask at the long press cannula.
   8. Switch off the stirrer. Change the round bottom flask at the press cannula to a double valve Schlenk tube while still cooling with dry ice under constant flow of nitrogen. Fix the height of the press cannula so that it touches the bottom of the stainless steel vessel.
   9. Push out the Sn(I)Cl solution with slight overpressure by opening the valves at the double valve Schlenk tube.
      NOTE: The solution should be deep red, dark brown to black, when concentrated.

3. **Determine the quality of the solution**
   1. Halide titration
      Take 2 ml of the solution and dissolve it in 20 ml of diluted nitric acid. Add 1 ml of 30% H_2O_2 and stir for 10 min. Perform a potentiometric titration of $AgNO_3$ against the calomel electrode.
      NOTE: The concentration of the halide should be ~0.2 M.
   2. Take the graphite tube and weigh it to determine the amount of consumed tin, which should be in between 4 g and 4.8 g.
      NOTE: In normal cases, the amount of reacted tin is lower than the amount of the halide inside the solution, due to the side reaction:
      $Sn + 2\,HCl \rightarrow SnCl_2$

NOTE: This reaction takes place in small amounts, but it will not decrease the quality of the solution and the ability of the disproportionation reaction to form tin cluster species. A tin:c ratio of 1:1.2 is in the normal range.

4. Synthesis of $Sn_{10}(Hyp)_4^{2-}$

1. **Preliminary work**
    1. Place 2 g (4.4 mmol) of LiHyp • 3 THF, prepared according to the literature[24] and a small magnetic stir bar into a Schlenk tube in a glovebox.
    2. Prepare a 2-propanol/dry ice cooling bath at -78 °C. Do not use a cryostat.
    3. Place the Schlenk vessel inside the cooling bath and place both on a magnetic stirrer.

2. **Reaction**
    1. Add 20 ml of a 0.2 M SnCl solution to the cooled Schlenk vessel containing 2 g (4.4 mmol) of LiHyp • 3 THF via a steel or Teflon cannula. Switch on the magnetic stirrer. Let the reaction run and slowly warm it up to room temperature within 3 hr. Observe the color of the reaction solution change to dark brown.
    NOTE: If the concentration of the solution is not 0.2 M, adjust the added volume so that 4 mmol of halide are applied (*e.g.,* 40 ml of a 0.1 M solution).

3. **Work-up procedure**
    1. Stop the stirrer and allow all insoluble precipitate inside the Schlenk tube to settle. Decant the black solution into another Schlenk vessel.
    NOTE: In most cases, during the decantation process, it is useful to check the precipitate with a lamp to ensure complete transformation of the supernatant. The non-soluble precipitate LiCl can be identified as a grey solid at the bottom.
    2. Add 0.2 ml of TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) to the mixture and allow it to stand overnight. Black, tetrahedral crystals grow in the solution. Upon isolation, identify the crystals via proton NMR as $Li_2(tmeda)_4Sn_{10}Hyp_4$[23].
    NOTE: Over time, the mother liquor produces more crystals of the product. Hence, storing the mother liquor for at least one month is recommended to increase the yield. Concentration of the mother liquor also might be helpful to initiate further crystallization.
    3. To obtain crystals for X-ray crystal structure analysis, recrystallize the cluster in the following way: Dissolve 150 mg of $Li_2(tmeda)_4Sn_{10}Hyp_4$ at -40 °C in 15 ml of absolute THF. Add in 1 ml of 12-crown-4 (5 g in 25 ml toluene) to the mixture. The solution should be dark green and must be stored at -30 °C, as the cluster is not stable in THF at room temperature.
    4. After one day, obtain large blocks of $Li_2(12\text{-crown-}4)_4Sn_{10}Hyp_4$(140 mg). Use one of the single crystals for structural analysis (**Figure 9**) using X-ray crystallography[23].

Representative Results

The principle of the matrix isolation technique in conjugation with the preparative co-condensation technique is shown (**Figure 1**), as well as the setup of the co-condensation apparatus (**Figure 2**) and the graphite reactor (**Figure 3**). **Figures 4** and **5** show photos of the assembly of the co-condensation apparatus. In **Figure 6**, the gas supply components with the mass flow controller are shown. **Figure 7** shows the main apparatus shortly before the steel vessel is fixed to the main flange to close the co-condensation apparatus. The principle of the synthetic route to the metalloid cluster compound **1** by applying the disproportionation reaction of the metastable subhalide SnCl is shown in **Figure 8**. In **Figure 9 (a)-(c)**, the NMR spectra of dissolved crystals of $Li_2(tmeda)_4Sn_{10}Hyp_4$ are shown (a: ^{1}H-, b: ^{13}C, and c: ^{29}Si-NMR) and (d) shows the molecular structure of **1** as determined by X-ray crystallographic analysis.

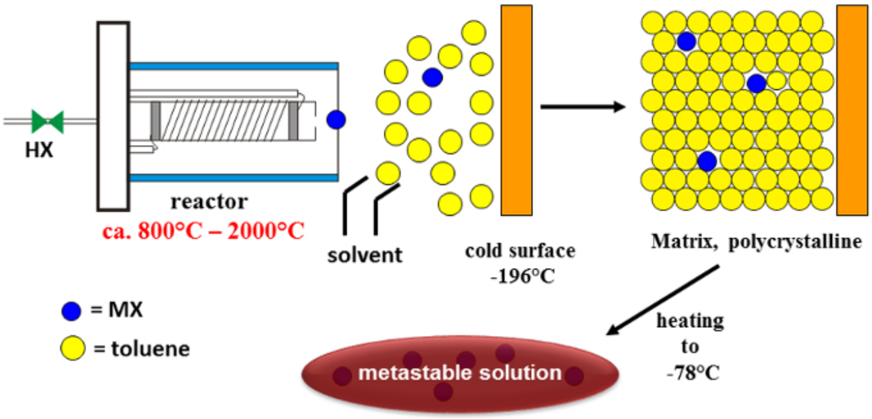

Figure 1. Principle of the preparative co-condensation technique. Left: Within a reactor, a molecule is synthesized at a high temperature and is condensed together with an inert solvent on a cold surface (middle) forming the matrix (right). The solvent is used in large excess so that the MX molecules are completely separated in the solid matrix. Heating of the matrix above the melting temperature of the solvent gives a metastable solution of MX at a low temperature that can be used for further applications (M = Al, Ga, Si, Ge, Sn; X = Cl, Br, I). Please click here to view a larger version of this figure.

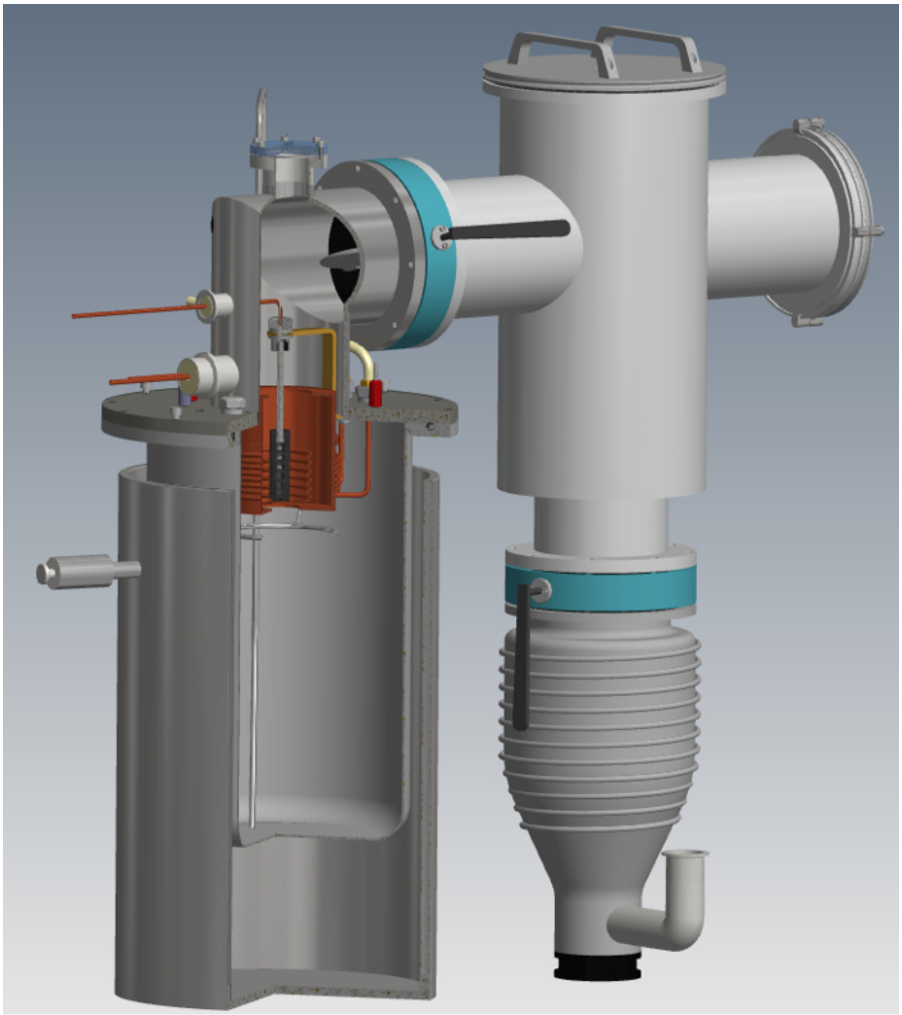

Figure 2. 3D-Model of the co-condensation apparatus without the gas-supplying part. To show the interior setup inside the apparatus (graphite reactor, induction coil, copper cooling shield, *etc.*), the apparatus is sliced on the left side.

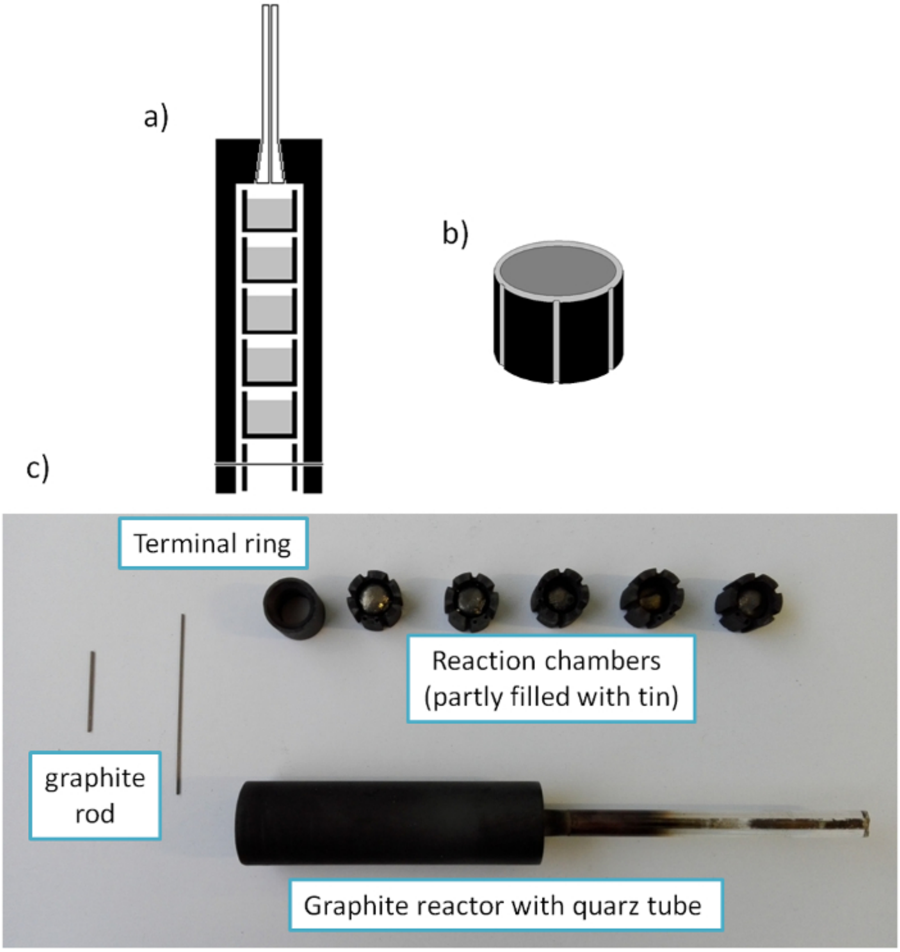

Figure 3. Graphite reactor. (**a**) General setup of the graphite reactor with the stack of reaction chambers. (**b**) Example of a reaction chamber, which should be filled with the metal (in the present case, elemental tin) prior to use. (**c**) Photo of the necessary pieces of the graphite reactor. Please click here to view a larger version of this figure.

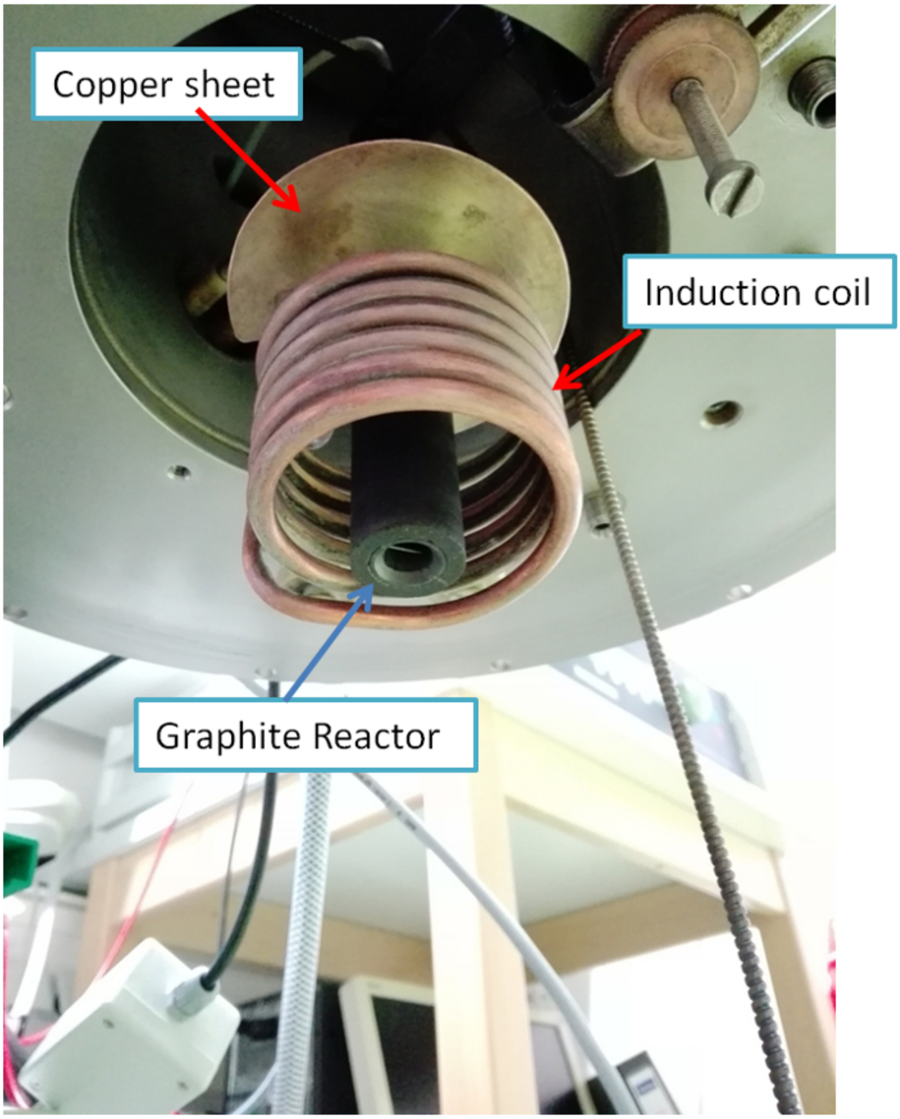

Figure 4. Mounted graphite reactor. Photo of the graphite reactor mounted inside the induction coil, together with the top copper sheet.

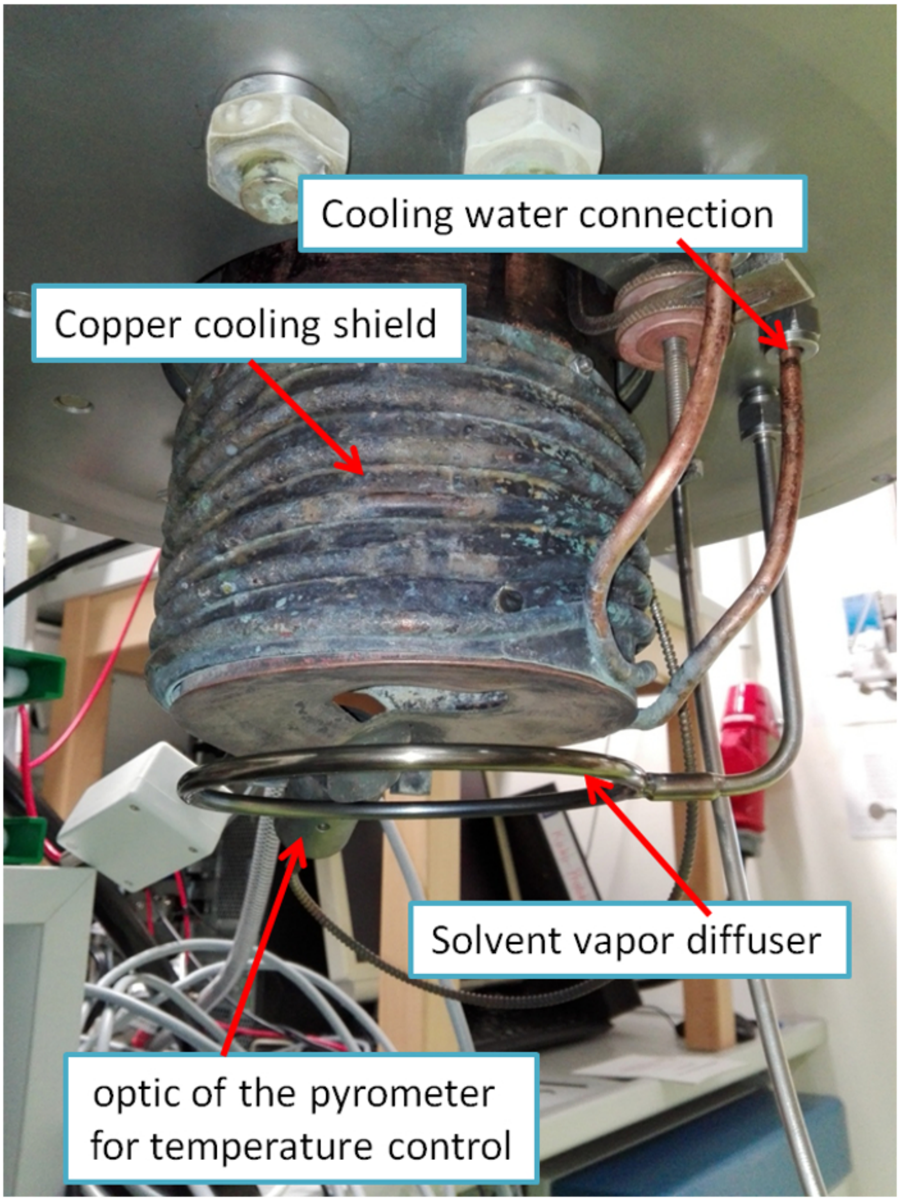

Figure 5. Mounted reaction chamber. Photo of the copper cooling shield during assembly, together with the solvent vapor diffuser placed below the copper cooling shield.

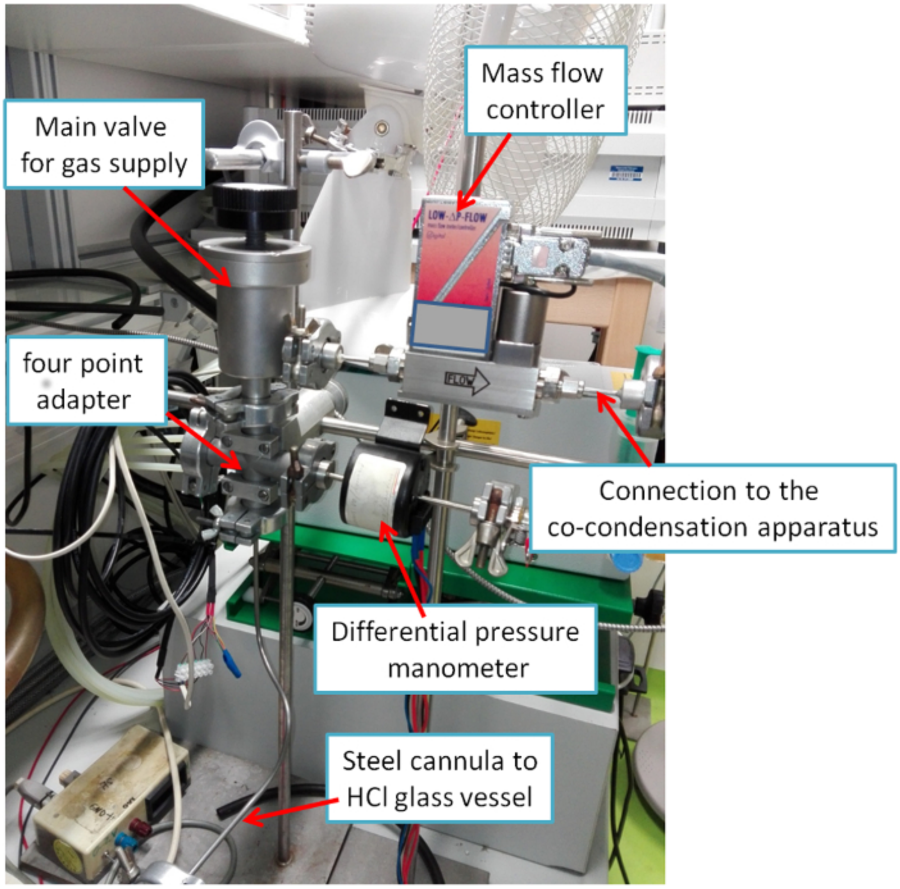

Figure 6. Gas supply part. Photo of the assembled gas supply components. The HCl glass vessel is attached to the steel cannula at the bottom of the picture and is not shown. Please click here to view a larger version of this figure.

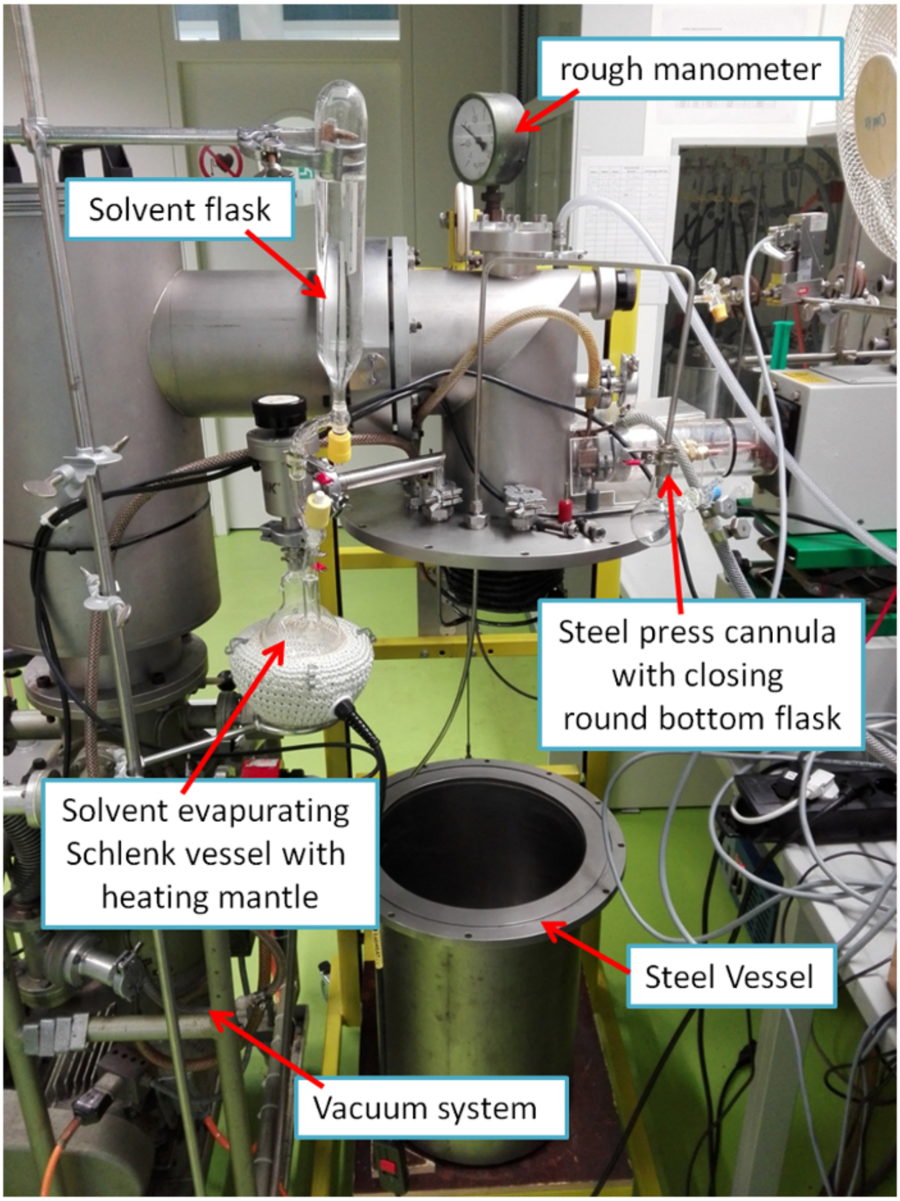

Figure 7. Open apparatus. Photo of the co-condensation apparatus during assembly shortly before the steel vessel is fixed. Please click here to view a larger version of this figure.

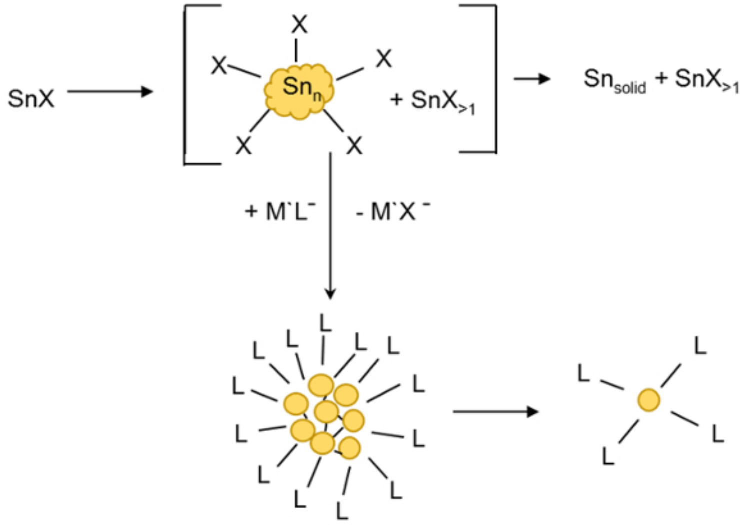

Figure 8. Formation of a metalloid tin cluster applying the disproportionation reaction. General scheme for the synthesis of a metalloid tin cluster applying the disproportionation reaction of a metastable Sn(I)halide. At the bottom, the subsequent degradation of the primarily formed, bigger metalloid clusters into smaller basic units (yellow spheres) is shown. This second step thereby yields even smaller units (bottom right), with an open ligand shell as the final product (X = halide, here Cl; L = bulky ligand, here $Si(SiMe_3)_3$).

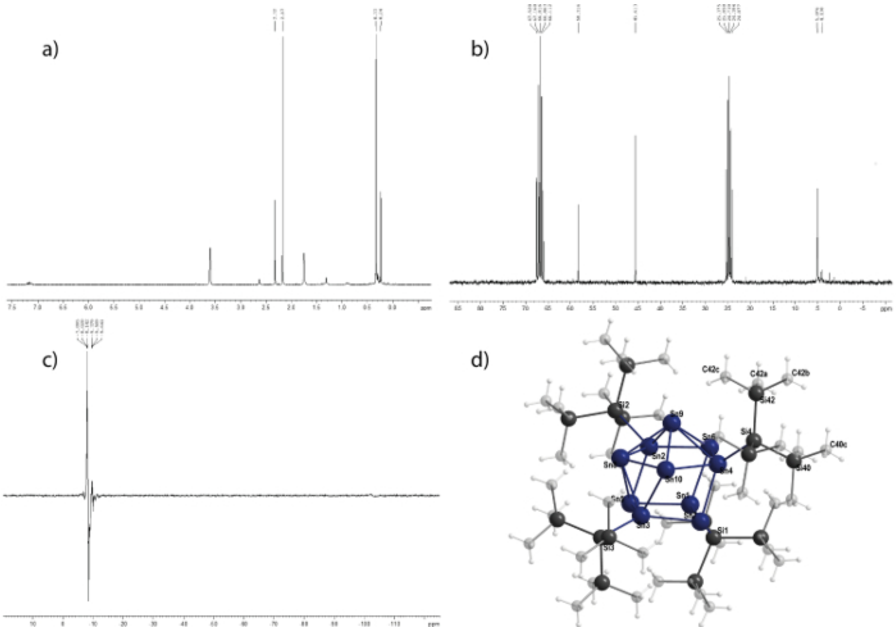

Figure 9. Characterization of $[Li(tmeda)_2]_2Sn_{10}Hyp_4$. The respective NMR spectra for crystals of $[Li(tmeda)_2]_2Sn_{10}Hyp_4$ (solvent: THF-d_8): (**a**) ^{1}H-NMR spectra; (**b**) ^{13}C-NMR spectra; (**c**) ^{29}Si-NMR spectra. In (**d**), the molecular structure of $[Sn_{10}Hyp_4]$ **1** is shown. Thermal ellipsoids are shown at 25% probability, and the CH_3 groups are shown transparent for clarity. Please click here to view a larger version of this figure.

Discussion

By applying the preparative co-condensation technique (**Figure 1**)[25], novel materials based on molecules like SnBr are obtained. Due to the high flexibility in temperature, pressure, metal, and reactive gas, a large variety of metastable solutions of high reactive species can be synthesized. For example, subhalides of silicon and germanium are already obtained in this way. However, finding the right conditions to obtain a metastable solution for further synthesis is not trivial, and the solutions usually must be handled at very low temperatures (*e.g.,* -78 °C). Additionally, the synthesis needs a co-condensation apparatus that is not standard equipment for a chemical laboratory. However, after solving this primary aspect, novel materials are available that might open new doors of chemical syntheses based on metastable solutions of somehow unattainable or even esoteric molecules. Nevertheless, these metastable solutions were up to now the best starting compounds for the synthesis of metalloid group 14 clusters, especially for Ge and Sn[6,7]. Thus, the intrinsic reactivity of the disproportionation reaction ($4\ MX \rightarrow 3M + MX_4$; M = Ge, Sn) is combined with a salt metathesis reaction by reacting the solutions with an organolithium compound like LiHyp or $LiN(SiMe_3)_2$.

The reaction path starting from a binary halide like SnCl and ending with a metalloid cluster like $[Sn_{10}Hyp_4]^{2-}$ **1**, as exemplified in **Figure 8**, is very complex, and finding the right reaction conditions for a successful synthesis might not be possible. However, although such a complex reaction system is present, the reaction of SnCl with LiHyp, as described above, gives the metalloid cluster $[Sn_{10}Hyp_4]^{2-}$ **1** with a high yield of 60%. This behavior might be explained by a second degradation step of the primarily formed mixture of metalloid tin clusters (**Figure 8**). Luckily, the ratio of SnCl and $SnCl_2$ of the metastable solution plays only a minor role during the synthesis of $[Sn_{10}Hyp_4]^{2-}$ **1**. Hence, applying different solutions with different tin:halide ratios, we found that **1** can be isolated in good yield within a tin:halide ratio of 1:1.05 to 1:1.35. Due to the robust reaction, as well as the high yield of isolated compounds, the metalloid cluster $[Sn_{10}Hyp_4]^{2-}$ **1** is an ideal compound for further reactions[26,27]. The major drawback of the high reactivity of the metalloid cluster $[Sn_{10}Hyp_4]^{2-}$ **1** is that it is not stable in solution at room temperature, so the subsequent reactions have to be performed at -78 °C, restricting certain reagents.

1 is isolated in the form of single crystals; thus, its molecular structure can be experimentally determined by single crystal X-ray structural analysis. This first insight into the structural behavior of nanoscaled metalloid tin clusters on an atomic scale is a good basis to establish a structure-property relationship in the field of tin nanoparticles or group 14 nanoparticles in general. We have demonstrated a convenient synthesis of the metalloid tin cluster $[Sn_{10}Hyp_4]^{2-}$ **1** using a metastable Sn(I) chloride solution synthesized via a co-condensation technique. The synthesis applies the disproportionation reaction, which is an intrinsic ability of the metastable monohalide solutions.

Disclosures

The authors do not declare any conflicts of interest.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial support, and we thank Dr. Daniel Werner for helpful discussions.

References

1. Goesmann, H., Feldmann, C. Nanoparticulate Functional Materials. *Angew. Chem. Int. Ed.* **49**, 1362-1395 (2010).
2. Purath, A., Köppe, R., Schnöckel, H. $[Al_7\{N(SiMe_3)_2\}_6]^-$: A first step towards aluminum metal formation by disproportionation. *Angew. Chem. Int. Ed.* **38**, 2926-2927 (1999).
3. Schnöckel, H. Metalloid Al- and Ga-clusters: a novel dimension in organometallic chemistry linking the molecular and the solid-state areas? *Dalton Trans.* 3131 - 3136 (2005).
4. Hu, K.-J., Plant, S. R., Ellis, P. R., Brown, C. M., Bishop, P. T., Palmer, R. E. Atomic Resolution Observation of a Size-Dependent Change in the Ripening Modes of Mass-Selected Au Nanoclusters Involved in CO Oxidation. *J. Am. Chem. Soc.* **137**(48), 15161-15168 (2015).
5. Schnöckel, H. Structures and Properties of Metalloid Al and Ga Clusters Open Our Eyes to the Diversity and Complexity of Fundamental Chemical and Physical Processes during Formation and Dissolution of Metals. *Chem. Rev.* **110**, 4125−4163 (2010).
6. Schnepf, A. Metalloid Cluster Compounds of Germanium: Novel Structural Motives on the Way to Elemental Germanium! *New J. Chem.* **34**, 2079−2092 (2010).
7. Schrenk, C.; Schnepf, A. Metalloid Sn clusters: properties and the novel synthesis via a disproportionation reaction of a monohalide. *Rev. Inorg. Chem.* **34**, 93−118 (2014).
8. Jin, R. Atomically precise metal nanoclusters: stable sizes and optical properties. *Nanoscale.* **7**, 1549-1565 (2015).
9. Schnepf, A. Metalloid Clusters *in Structure and Bonding - Clusters - Contemporary Insight in Structure and Bonding.* (Ed. S. Dehnen) accepted (2016).
10. Brynda, M., Herber, R., Hitchcock, P. B., Lappert, M. F., Nowik, I., Power, P. P., Protchenko, A. V., Ruzicka, A., Steiner, J. Higher-Nuclearity Group 14 Metalloid Clusters: $Sn_9\{Sn(NRR')\}_6]$. *Angew. Chem. Int. Ed.* **45**, 4333-4337 (2006).
11. Klinkhammer, K. W., Xiong, Y., Yao, S. Molecular lead clusters - from unexpected discovery to rational synthesis. *Angew. Chem. Int. Ed.* **43**, 6202-6204 (2004).
12. Richards, A. F., Brynda, M., Olmstead, M. M., Power, P. P. Characterization of Ge_5R_4($R = CH(SiMe_3)_2$, C_6H_3-2,6-Mes_2): Germanium Clusters of a New Structural Type with Singlet Biradical Character. *Organometallics.* **23**, 2841-2844 (2004).
13. Desireddy, A. *et al.* Ultrastable silver nanoparticles. *Nature* **501**, 399-402 (2013).
14. Jadzinsky, P. D., Calero, G., Ackerson, C. J., Bushnell, D. A., Kornberg, R. D. Structure of a Thiol Monolayer-Protected Gold Nanoparticle at 1.1 Å Resolution. *Science.* **318**, 430-433 (2007).
15. Schnepf, A., Schnöckel, H. Metalloid aluminum and gallium clusters: Element modifications on the molecular scale? *Angew. Chem., Int. Ed.* **41**, 3532- 3554 (2002).
16. Ecker, A., Weckert, E., Schnöckel, H. Synthesis and structural characterization of an Al_{77}cluster. *Nature.* **387**, 379-381 (1997).
17. Schnepf, A., Schnöckel, H. Synthesis and structure of a $Ga_{84}R_{20}{}^{4-}$ cluster-a link between metalloid clusters and fullerenes? *Angew. Chem. Int. Ed.* **40**, 712-715 (2001).
18. Schrenk, C., Köppe, R., Schellenberg, I., Pöttgen, R., Schnepf, A. Synthesis of tin(I)bromide. A novel binary halide for synthetic chemistry. *Z. Anorg. Allg. Chem.* **635**, 1541-1548 (2009).
19. Schnepf, A., Köppe, R. Synthese von Germanium(I)bromid. Ein erster Schritt zu neuen Clusterverbindungen des Germaniums ? *Z. Anorg. Allg. Chem.* **628**, 2914-2918 (2002).
20. Uhlemann, F., Köppe, R., Schnepf, A. Synthesis of metastable $Si(II)X_2$solutions (X = F, Cl). A Novel Binary Halide for Synthesis. *Z. Anorg. Allg. Chem.* **640**, 1658 - 1664 (2014).
21. Schenk,C. *et al.* The Formal Combination of Three Singlet Biradicaloid Entities to a Singlet Hexaradicaloid Metalloid $Ge_{14}[Si(SiMe_3)_3]_5Li_3(THF)_6$Cluster. *J. Am. Chem. Soc.* **133**, 2518 - 2524 (2011).
22. Schrenk, C., Schellenberg, I., Pöttgen, R., Schnepf, A. The formation of a metalloid $Sn_{10}[Si(SiMe_3)_3]_6$cluster compound and its relation to the α↔β tin phase transition. *Dalton Trans.* **39**, 1872-1876 (2010).
23. Schrenk, C., Winter, F., Pöttgen, R., Schnepf, A. $\{Sn_{10}[Si(SiMe_3)_3]_4\}^{2-}$: A high reactive metalloid tin cluster with an open ligand shell for further applications. *Chem. Eur. J.* **21**, 2992 - 2997 (2015).
24. Gutekunst, G., Brook, A. G. Tris(trimethylsilyl)silyllithium.3 THF: a stable crystalline silyllithium reagent. *J. Organomet. Chem.* **225**, 1-3 (1982).

25. Timms, P. L. Techniques of Preparative Cryochemistry. *Cryochemistry.* Wiley, New York, 61 - 136 (1976).
26. Schrenk, C., Gerke, B., Pöttgen, R., Clayborne, A., Schnepf, A. „Reactions with a Metalloid Tin Cluster $\{Sn_{10}[Si(SiMe_3)_3]_4\}^{2-}$: Ligand Elimination versus Coordination Chemistry. *Chemistry.* **21**, 8222 - 8228 (2015).
27. Schnepf, A. Chemistry Applying Metalloid Tin Clusters. *Phosphorus, Sulfur and Silicon and the Related Elements.* **191**, 662-664 (2016).