



Sn(I) halides: Novel binary compounds of tin and their application in synthetic chemistry

Andreas Pacher, Claudio Schrenk, Andreas Schnepf*

Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstraße 15, Geb. 30.45, 76128 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 4 August 2009

Accepted 26 August 2009

Available online 31 August 2009

Keywords:

Metalloid clusters

Tin

Subhalides

Thermodynamics

ABSTRACT

Metalloid cluster compounds are ideal model compounds for the area between the molecular and solid state, i.e. the nanometer regime. For the synthesis of metalloid cluster compounds, the disproportionation reaction of a metastable subhalide is a fruitful synthetic route. In the case of tin, monohalides are needed for this synthetic route as tin(II) halides are too stable to be used. Due to thermodynamic data, gaseous SnBr should be formed at 1370 °C, and by applying a co-condensation technique it can be trapped at –196 °C and prepared in synthetic scale. Herein first analyses of SnBr are presented, showing that SnBr is more reactive than the corresponding GeBr, already disproportionating quantitatively to elemental tin and SnBr₂ on heating to room temperature. By applying nitrogen-based donor molecules like *n*Bu₃ or pyridine, the reactivity can be moderated and the solubility is enhanced leading e.g. to an SnBr emulsion, which can be used for the synthesis of metalloid cluster compounds of tin.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Metalloid cluster compounds are ideal model compounds to get an insight into the area between the molecular and solid state, i.e. the nanometer regime [1]. This borderland is of particular interest especially for metals or semi-metals as a drastic change of the physical properties takes place from oxidized species (salts, non-conducting behaviour) to the bulk phase (metals/semi-metals, conducting/semi-conducting behaviour) [2]. For the heavier group 14 elements [3] this area is also of great technical interest as the module size in computer industry reaches more and more the nanometer range [4]. During the last years metalloid cluster compounds of germanium of the general formulae Ge_{*n*}R_{*m*} (*n* > *m*) could be established as a novel group of substances [5]. Thereby we have been able to establish a fruitful synthetic route via the disproportionation reaction of a metastable Ge(I) halide (GeBr or GeCl), leading to cluster compounds with up to 14 germanium atoms in the cluster core [6]. The structural characterization of the so far synthesized compounds reveals that novel structural motives can be realized on the way to the bulk phase of elemental germanium. Thus the arrangement of the 10 germanium atoms in (THF)₁₈Na₆Ge₁₀[Fe(CO)₄]₈ **1** could be described as a centaur polyhedron [7], a motif known from solid state chemistry for coordination number 10. However, in the case of **1**, the polyhedron is empty. Additionally the 14 germanium atoms in (THF)₆Li₃Ge₁₄[Ge(SiMe₃)₃]₅ **2** [8] form an empty polyhedron (Fig. 1), showing that larger empty

polyhedrons are even stable for the higher congeners of carbon hinting to a possible route to “germa-fullerenes”.

Due to these achievements in germanium chemistry we asked ourselves if this synthetic concept might be extended to other group 14 elements. Among these, tin is most interesting as here, due to the more metallic character, a greater structural diversity might be expected [3]. Some examples of metalloid cluster compounds of tin could be synthesized by the groups of Power and co-workers [9] and Fischer and co-workers [10] in recent years via a reductive coupling reaction. Thereby the more metallic character of tin becomes obvious in the case of the metalloid cluster compound Sn₁₅Dipp₆ **3** (Dipp = NArSiMe₃; Ar = 2,6-*i*Pr₂-C₆H₃), where the central tin atom (Fig. 1) exhibits the coordination number 8 + 6 (tungsten type).

2. Results and discussion

The disproportionation reaction of a metastable tin halide leads at the end to elemental tin and a halide in a higher oxidation state. During this disproportionation reaction tin-rich compounds are formed on the way to elemental tin as sketched in Scheme 1. These intermedially formed metalloid cluster compounds might be kinetically stabilized by substituting the halides by bulky ligands as the reactive metal core is then shielded by a ligand shell. This synthetic concept can lead to giant metalloid cluster compounds, first of all shown for group 13, as the metalloid clusters Al₇₇[N(SiMe₃)₂]₂₀²⁻ [11] and Ga₈₄[N(SiMe₃)₂]₂₀^{x-} (*x* = 3, 4) [12] are synthesized applying the disproportionation reaction of a metastable Al(I) or Ga(I) solution, respectively.

* Corresponding author.

E-mail address: schnepf@chemie.uni-karlsruhe.de (A. Schnepf).

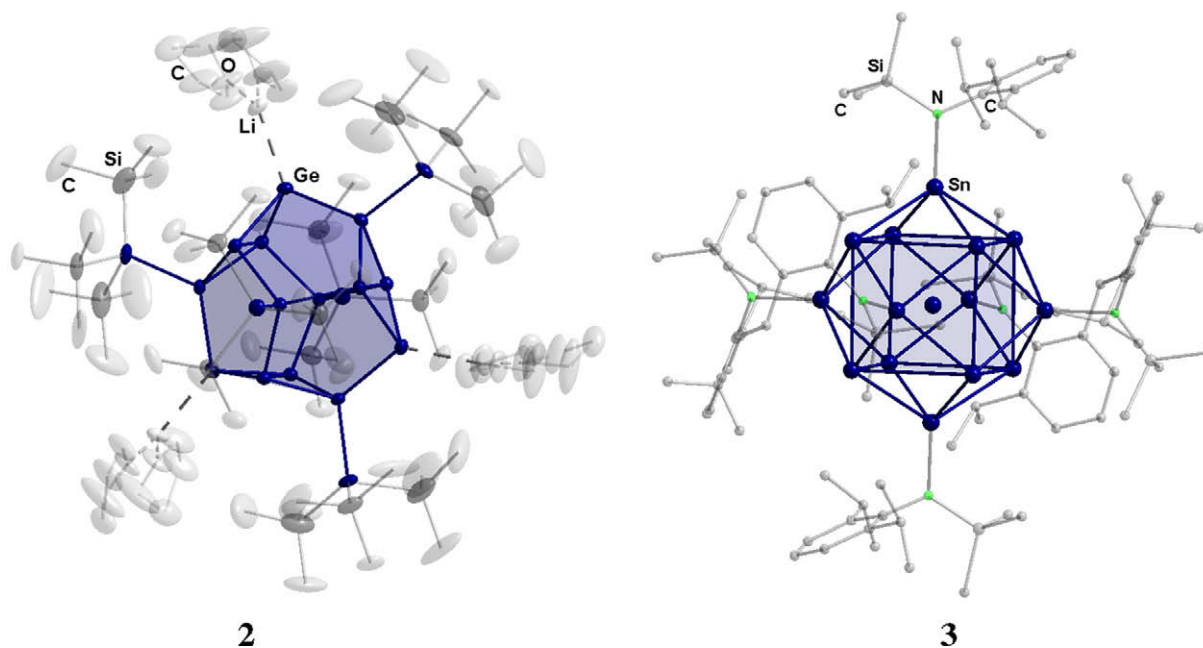
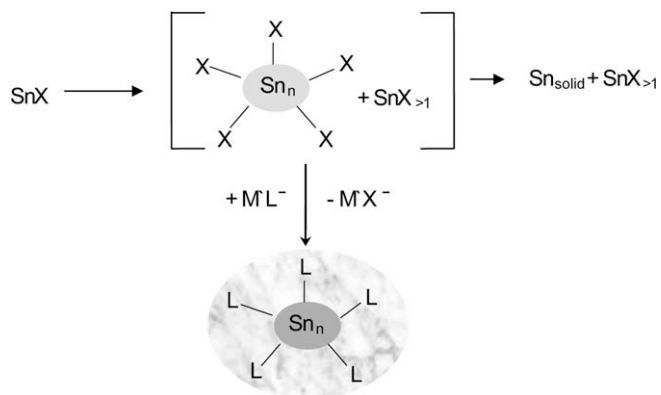


Fig. 1. Molecular structure of selected metalloids cluster compounds of germanium (left) and tin (right) without hydrogen atoms: $(\text{THF})_6\text{Li}_3\text{Ge}_{14}[\text{Ge}(\text{SiMe}_3)_3]_5$ **2** and $\text{Sn}_{15}\text{Dipp}_6$ **3** (Dipp = NArSiMe_3 ; Ar = 2,6-*i*-Pr₂-C₆H₃). The arrangement of the germanium as well as tin atoms is highlighted by a polyhedral presentation.

However, for a kinetic stabilization low reaction temperatures are needed and therefore the well known Sn(II) halides do not represent suitable starting materials as e.g. SnBr_2 is stable up to the boiling point of 619 °C [13]. Consequently, to establish a synthetic route to metalloids cluster compounds *via* a disproportionation reaction, a more reactive subhalide is needed; a promising candidate might be a Sn(I) halide, which has been spectroscopically analyzed in the gas phase [14]. For the synthesis of this monohalide in the gas phase drastic reaction conditions are needed, so a first estimation based on quantum chemically computed thermodynamic data shows that Sn(I)Br should be formed as the major gaseous compound by reaction (1) at 1370 °C at a reaction pressure of 10^{-2} mbar [16].



For the synthesis of SnBr in preparative scale the preparative co-condensation is applied, which is useful to trap such reactive species and which is performed in a home made apparatus, whose principal construction is shown in Fig. 2.



Scheme 1. Schematic presentation of the synthetic concept of the synthesis of a metalloids cluster compound of tin via the disproportionation reaction of a metastable subvalent subhalide.

For the synthesis, elemental tin is placed in the graphite reactor (a in Fig. 2), which is heated inductively to ca. 1240 °C – measured via a spectral pyrometer (c in Fig. 2). Afterwards HBr is passed through the reactor and the resulting gaseous products are condensed together with an added solvent at –196 °C. The simultaneously formed hydrogen gas is pumped off by a high vacuum pumping system (oil diffusion pump) leading to a constant pressure of 5×10^{-5} mbar during the reaction. After the reaction, the liquid nitrogen is removed and the apparatus is vented with nitrogen. During the slow warming, the internal matrix melts and the resulting solution can be transferred into a cooled Schlenk vessel by overpressure via a steel cannula (h in Fig. 2).

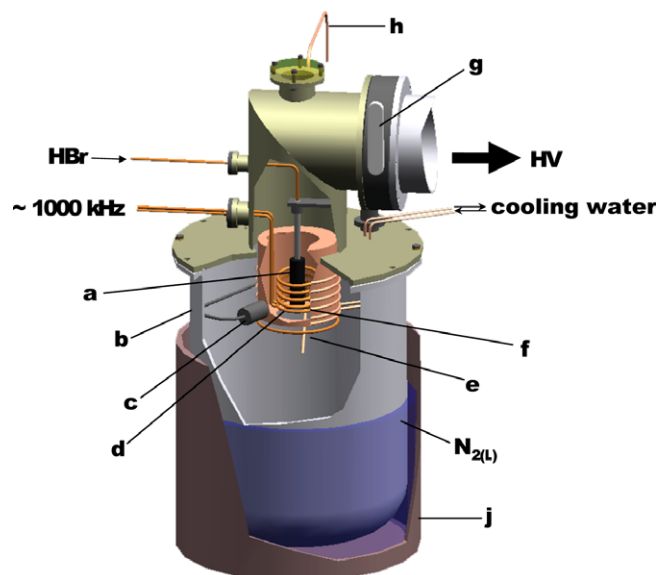


Fig. 2. Schematic presentation of the co-condensation apparatus: (a) graphite reactor; (b) stainless steel vessel; (c) optic with glass fibre to spectral pyrometer; (d) induction coil; (e) solvent inlet; (f) copper cooling shield; (g) main lock valve; (h) steel cannula; (i) HV = high vacuum.

When toluene is used as solvent, a colourless solution is obtained, in which a black solid is suspended, that looks dark red in small layers. During the reaction normally 17–19 mmol tin are consumed when 20 mmol HBr are used, thus SnBr is formed nearly quantitatively during the high temperature reaction. The black residue can be filtered and dried under vacuum, while it is heated to room temperature, leading to a dark grey solid, in which a Sn:Br ratio of nearly 1:1 is found. However powder diffraction studies as well as ^{119}Sn Mössbauer spectroscopy show that the residue is a 1:1 mixture of Sn and SnBr₂ indicating that the disproportionation reaction ($2\text{SnBr} \rightarrow \text{Sn} + \text{SnBr}_2$) has quantitatively taken place [16]. However the dark red colour at low temperatures hints to a certain amount of subhalides. Consequently Sn(I)Br is more reactive than the corresponding Ge(I)Br, which is stable in the solid state up to 90 °C [15].

Further co-condensation reactions with solvent mixtures containing oxygen-based donor molecules like acetone or thf show that the disproportionation reaction is the favourable reaction channel of Sn(I)Br. Thus no reaction products with e.g. acetone are observed and only SnBr₂(acetone)₂ and elemental tin are obtained [16]. Thus we changed to nitrogen-based donor molecules like pyridine and *Nn*Bu₃ and also used a solvent that exhibits a high dielectric constant, which in the case of Ge(I) halides has led to isolable solutions [7]. First of all we performed a co-condensation reaction with a 4:1 mixture of dichloromethane and pyridine, leading at –78 °C to a dark red solution, in which a small amount of an orange solid is suspended. This result looks quite promising. However, after a couple of days, the colour of the solution vanishes even at –78 °C leading to more orange precipitate, in which due to an X-ray fluorescence analysis, a nearly equimolar amount of tin, bromine and chlorine is present. The presence of chlorine indicates that chlorinated solvents are not useful as they seem to react with the subhalide leading to an orange precipitate. The solvent of the overlaying solution was evaporated leading to a pale yellow residue which was redissolved in thf. On cooling this solution to –28 °C colourless rod-like crystals of SnBr₂·thf·pyridine **5** were obtained (Fig. 3). In the crystal of **5**, SnBr₂ molecules are present (Sn1–Br2: 261.96(15) pm, Sn1–Br3: 263.89(14) pm), which are coordinated by a pyridine (Sn–N: 238.5(8) pm) as well as a thf (Sn–O 270.8(3) pm) molecule. Additionally two longer Sn–Br con-

tacts (Sn1–Br2': 356.0(2) pm, Sn1–Br3': 353.8(2) pm) are formed leading to a distorted octahedral arrangement around the central Sn atom, a similar situation as found in SnBr₂(acetone)₂ and SnBr₂(thf)₂ [16].

The appearance of larger amounts of SnBr₂ (1.7 g of **5**) shows that beside the reaction with dichloromethane leading to an orange solid, a disproportionation reaction has taken place leading to SnBr₂. Interestingly, although the primary product was redissolved in thf, one pyridine molecule is present in the crystal, indicating that pyridine is a stronger donor for tin subhalides than thf. As chlorinated solvents are not inert against tin monohalides, we changed to fluorinated ones as the C–F bond is more stable than the C–Cl bond. Thus the co-condensation reaction with a 4:1 mixture of α,α,α -trifluorotoluene yields a suspension of a black residue and a colourless solution. The solution is filtered and stored at –15 °C leading to colourless rod-like crystals of SnBr₂·pyridine₂ **6** (figures can be found in the Supporting information). The black residue exhibits a Sn:Br ratio of 1:1.18 being nearly a 1:1 mixture of Sn and SnBr₂. This result indicates that the disproportionation reaction has quantitatively taken place; this might be due to the high temperature (–35°), which has to be used with respect to the melting point of α,α,α -trifluorotoluene of –35 °C.

Thus in the following we performed a co-condensation reaction with a 4:1 mixture of toluene and *Nn*Bu₃ leading at –78 °C to a dark emulsion of a black oil in a colourless solution. When this emulsion is treated with a –78 °C cold toluene solution of Li-Si(SiMe₃)₃ and subsequently heated to room temperature a black reaction solution is isolated with no residue remaining in the co-condensation apparatus. After work-up procedures, dark red crystals of Sn₁₀[Si(SiMe₃)₃]₆ **7** are obtained [17], representing the first metalloid cluster compound synthesized via a disproportionation reaction of a Sn(I) halide and showing that the oily form of the subhalide can be used for the synthetic route emphasized in Scheme 1.

3. Conclusions

Sn(I) halides can be synthesized in preparative scale via a co-condensation technique. These Sn(I) halides already disproportion-

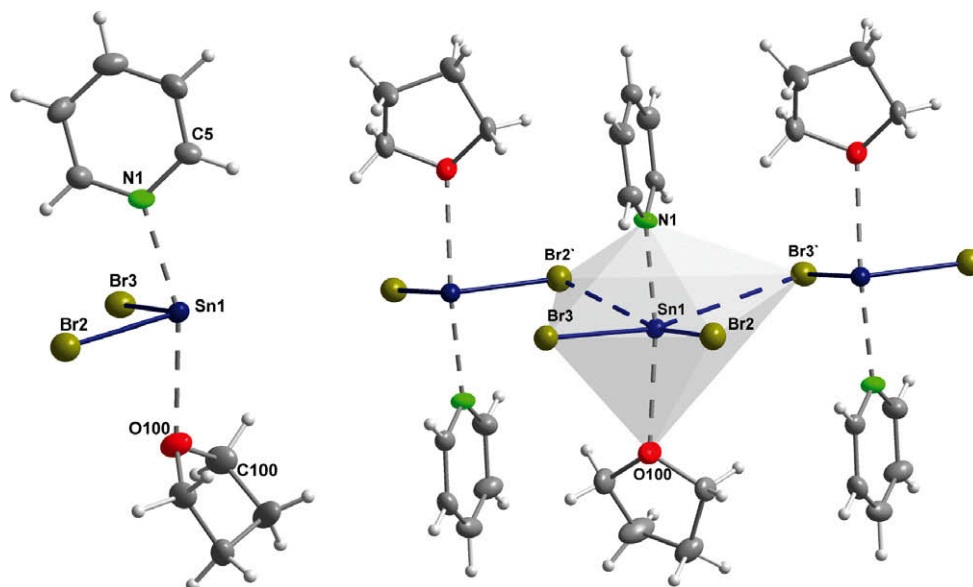


Fig. 3. Left: molecular structure of SnBr₂·pyridine·thf **5**; right: first coordination sphere of the tin atom within the crystal, the pseudo octahedral arrangement is emphasized via a polyhedral presentation: (displacement ellipsoids with 50% probability).

tionate quantitatively to tin and Sn(II) halides when heated to room temperature, being more reactive than the corresponding Ge(II) halides. Nitrogen-based donor molecules are capable to stabilize the monohalides, leading in the case of NnBu_3 to an oily form of the subhalide, which can be used for the synthesis of metalloid cluster compounds of tin, as the reaction with $\text{LiSi}(\text{SiMe}_3)_3$ leads to the metalloid cluster compound $\text{Sn}_{10}[\text{Si}(\text{SiMe}_3)_3]_6$ **7**, in which beside 10 tin atoms only 6 ligands are present and where the 10 tin atoms are arranged in the form of a centaur polyhedron, being a novel structural motif in tin chemistry. This synthetic route might now be extended to other substituents, leading to larger metalloid cluster compounds, shedding more light onto the area between the molecular and solid state. Furthermore changing the donor component from hard nitrogen bases to softer phosphorous bases might further stabilize the monohalide, leading to, at least at low temperature, stable solutions.

4. Experimental

The co-condensation reaction is performed in the apparatus shown in Fig. 2 which is evacuated to a pressure of 5×10^{-6} mbar. In the graphite reactor elemental tin is placed and the reactor is heated inductively to 1240 °C. Afterwards, the liquid tin is treated with a constant flow rate of HBr (0.2 mmol/min), leading to a constant working pressure of ca. 5×10^{-5} mbar. The resulting gaseous products are condensed together with a solvent mixture (ca. 150 ml) at the surface of the stainless steel vessel, which is cooled to -196 °C with liquid nitrogen. After the reaction, the inductive heating is switched off and the graphite reactor is allowed to cool for ca. 20 min. Then the main lock valve is closed and the apparatus is vented with nitrogen. Afterwards the stain-

less steel vessel is heated with dry ice to -78 °C. After the melting of the matrix the resulting solution is decanted to a cooled schlenk vessel (dry ice) via a steel cannula with overpressure.

4.1. $\text{SnBr}_2\cdot\text{thf}\cdot\text{pyridine}$ **5**

During the co-condensation reaction 2.13 g Sn (17.94 mmol) and 20 mmol HBr are consumed. The gaseous products were condensed with a solvent mixture of dichloromethane/pyridine (4:1), leading to a dark red solution with a small amount of an orange solid at -78 °C. At -78 °C the solution bleaches, while more orange precipitate is obtained. The colourless solution is filtered and concentrated to dryness. The pale yellow residue is dissolved in thf leading to a pale yellow solution. From this solution colourless crystals (Table 1) of $\text{SnBr}_2\cdot\text{thf}\cdot\text{pyridine}$ **5** are obtained after storage at -28 °C (1.74 g, 22.5%).

4.2. $\text{SnBr}_2\cdot(\text{pyridine})_2$ **6**

During the co-condensation reaction 2.42 g Sn (20.4 mmol) and 20 mmol HBr are consumed. The gaseous products were condensed with a solvent mixture of α,α,α -tri-fluorotoluene/pyridine (4:1), leading to a black suspension of a colourless solution and a black residue at -35 °C. The colourless solution is filtered and stored at -15 °C leading to colourless rod-like crystals (Table 1) of $\text{SnBr}_2\cdot\text{thf}$ **6** (510 mg, 5.72%).

Appendix A. Supplementary material

CCDC 742644 and 742645 contain the supplementary crystallographic data for compounds **5** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.08.038](https://doi.org/10.1016/j.jorganchem.2009.08.038).

Table 1
Crystallographic data and structural refinement details of $\text{SnBr}_2\cdot\text{thf}\cdot\text{pyridine}$ **5** and $\text{SnBr}_2\cdot(\text{pyridine})_2$ **6**.

Compound formula	$\text{SnBr}_2\text{ONC}_9\text{H}_{13}$ 5	$\text{SnBr}_2\text{N}_2\text{C}_{10}\text{H}_{10}$ 6
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$\text{Pmm}2_1$
Cell parameters [Å respectively °]		
<i>a</i>	8.4698(17)	15.110(3)
<i>b</i>	9.3422(19)	6.8999(14)
<i>c</i>	16.424(3)	6.1950(12)
β	100.82(3)	
Cell volume [Å ³]	1276.4(4)	645.9(2)
<i>Z</i>	4	2
Density [g cm ⁻³]	2.236	2.246
Absorption coefficient μ [mm ⁻¹]	8.234	8.135
<i>F</i> (0 0 0)	808	408
Crystal dimensions [mm]	0.5 × 0.1 × 0.05	0.6 × 0.1 × 0.1
Diffractometer	STOE IPDS	STOE IPDS
Temperature [K]	150	200
Wavelength [Å]	0.71073	0.71073
θ Range [°]	2.52–26.76	2.95–26.68
Measured reflections	6100	4487
Independent reflections	2669	1269
Observed reflections with $F^2 > 2\sigma$	2009	1253
Programs used	SHELXL and SHELXS	SHELXL and SHELXS
Number of parameters	127	73
<i>R</i> -value [$I > 2\sigma(I)$]	0.0630	0.0336
<i>R</i> -value (all data)	0.1952	0.0913
Goodness of fit		
Remaining electron density minimum/ maximum [e Å ⁻³]	1.702 and –2.292	1.093 and –0.830

References

- [1] A. Schnepf, H. Schnöckel, *Angew. Chem., Int. Ed.* 41 (2002) 3532–3554; A. Schnepf, *Angew. Chem., Int. Ed.* 43 (2004) 664–666.
- [2] H. Schnöckel, *Dalton Trans.* 19 (2005) 3131–3136.
- [3] A. Schnepf, *Chem. Soc. Rev.* 36 (2007) 745–758.
- [4] R.S. Chau, *Nanotechnol. Briefs* 2 (3) (2005).
- [5] A. Schnepf, *Coord. Chem. Rev.* 250 (2006) 2758–2770.
- [6] A. Schnepf, *Eur. J. Inorg. Chem.* (2008) 1007–1018.
- [7] A. Schnepf, C. Schenk, *Angew. Chem., Int. Ed.* 45 (2006) 5373–5376.
- [8] C. Schenk, A. Schnepf, *Chem. Commun.* (2008) 4643–4645.
- [9] (a) B.E. Eichler, P.P. Power, *Angew. Chem., Int. Ed.* 40 (2001) 796–797; (b) A.F. Richards, B.E. Eichler, M. Brynda, M.M. Olmstead, P.P. Power, *Angew. Chem., Int. Ed.* 44 (2005) 2546–2548; (c) M. Brynda, R. Herber, P.B. Hitchcock, M.F. Lappert, I. Nowik, P.P. Power, A.V. Protchenko, A. Ruzicka, J. Steiner, *Angew. Chem., Int. Ed.* 45 (2006) 4333–4337; (d) E. Rivard, J. Steiner, J.C. Fettingner, J.R. Giuliani, M.P. Augustine, P.P. Power, *Chem. Commun.* (2007) 4919–4921.
- [10] G. Prabusankar, A. Kempter, C. Gemel, M.-K. Schröter, R.A. Fischer, *Angew. Chem., Int. Ed.* 47 (2008) 7234–7237.
- [11] A. Ecker, E. Weckert, H. Schnöckel, *Nature* 387 (1997) 379–381.
- [12] (a) A. Schnepf, H. Schnöckel, *Angew. Chem., Int. Ed.* 40 (2001) 711–715; (b) A. Schnepf, B. Jee, H. Schnöckel, E. Weckert, A. Meents, D. Luebbert, E. Herling, B. Pilawa, *Inorg. Chem.* 42 (2003) 7731–7733.
- [13] Holleman-Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Auflage, Walter de Gruyter, Berlin, 2007, p. 1012.
- [14] K. Balasubramanian, *J. Mol. Spectrosc.* 132 (1988) 280–283.
- [15] R. Köppe, A. Schnepf, *Z. Anorg. Allg. Chem.* 628 (2002) 2914–2918.
- [16] C. Schrenk, R. Köppe, I. Schellenberg, R. Pöttgen, A. Schnepf, *Z. Anorg. Allg. Chem.* 635 (2009) 1541–1548.
- [17] C. Schrenk, I. Schellenberg, R. Pöttgen, A. Schnepf, *Chemistry*, submitted for publication.