

Special  
Issue

# Chalcogenido-Dimethylgallates and -Indates DMPyr<sub>2</sub>[Me<sub>2</sub>M(μ<sub>2</sub>-E)]<sub>2</sub> (M=Ga, In; E=S, Se): Building Blocks for Higher and Lower Order Chalcogenidoindates

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This account is dedicated to Professor Herbert Roesky on the occasion of his 85th birthday

Metalation of the anions in the ionic liquids DMPyr[SH] and DMPyr[SeH] (DMPyr=1,1-dimethylpyrrolidinium) by trimethylgallium and trimethylindium is investigated. The reaction proceeds via pre-coordination of [EH]<sup>-</sup>, methane elimination and formation of an unprecedented series of chalcogenido metalates DMPyr<sub>2</sub>[Me<sub>2</sub>M(μ<sub>2</sub>-E)]<sub>2</sub> (M=Ga, In; E=S, Se). These show the presences of dinuclear dianions with four-membered ring structures displaying highly nucleophilic bridging chalcogenide ligands in their crystallographically determined molecular structures. Some representative reactions of these building blocks with amphoteric electrophiles were studied: Addition of two equivalents of E(SiMe<sub>3</sub>)<sub>2</sub> (E=S, Se) to the indates

DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-S)]<sub>2</sub> and DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-Se)]<sub>2</sub> leads to a cleavage of the ring, E silylation and formation of mononuclear, monoanionic indates DMPyr[Me<sub>2</sub>In(SSiMe<sub>3</sub>)<sub>2</sub>], DMPyr[Me<sub>2</sub>In(SeSiMe<sub>3</sub>)<sub>2</sub>], and even a mixed sulfido-selenido dimethylindate DMPyr[Me<sub>2</sub>In(SSiMe<sub>3</sub>)(SeSiMe<sub>3</sub>)]. Reaction of DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-S)]<sub>2</sub> with two equivalents of Lewis acid Me<sub>3</sub>In leads to charge delocalization, ring expansion and formation of six-membered ring DMPyr<sub>3</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-S-InMe<sub>3</sub>)<sub>3</sub>]. The latter is a key intermediate in the formation of dianionic sulfidoindate DMPyr<sub>2</sub>[(Me<sub>2</sub>In)<sub>2</sub>(μ<sub>3</sub>-S)<sub>4</sub>] displaying an unusual inverse hetero-adamantane cage structure with four capping sulfido ligands.

## 1. Introduction

Recently, we reported an atom economic synthesis of analytically pure ionic liquids and organic cation salts comprising hydrochalcogenide anions [SH]<sup>-</sup>, [SeH]<sup>-</sup>, [TeH]<sup>-</sup>.<sup>[1,2,3]</sup> Readily available methycarbonate ionic liquids Cat[OCO<sub>2</sub>Me] served as starting materials. We became interested to investigate the deprotonation and metalation of hydrosulfide and hydroselenide anions by trimethylgallium and -indium. Metal organic molecular compounds incorporating group 13 and 16 elements are of interest due to their potential to act as thermally labile precursors for triel-chalcogenide-based III-VI semiconductor materials.<sup>[4]</sup> Particular interest is focussing on binary chalcogenides such as 2D-GaSe, a photoconductor applied in non-linear optics for frequency doubling<sup>[5]</sup> or sesquiselenide In<sub>2</sub>Se<sub>3</sub>,<sup>[6]</sup> but also on molecular precursors<sup>[7]</sup> for ternary and quaternary members of the CIGS family of materials Cu(In<sub>x</sub>Ga<sub>1-x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub>

with their remarkable performance in optoelectronic<sup>[6]</sup> and photovoltaic<sup>[8]</sup> devices, respectively.

Common strategies to incorporate purely inorganic sulfur and selenium ions into molecular precursor compounds or clusters involve deprotonation of H<sub>2</sub>E (E=S, Se) with metal compounds containing basic leaving groups such as alkyl or amido ligands or salt elimination reactions of alkali metal chalcogenides M<sub>2</sub>E, M[EH], Li[ESiMe<sub>3</sub>]<sup>[9]</sup> or Na[ESiMe<sub>3</sub>] with group 13 metal halides.<sup>[10,11]</sup> Trimethylgallium and -indium are widely used group 13 precursors, which can be thermally decomposed to yield high purity semiconductor materials in MOCVD processes.<sup>[12]</sup> Alkyltrienes are Lewis-acids but can also act as Brønsted bases or nucleophiles towards H<sub>2</sub>E, E<sub>8</sub> and (Me<sub>3</sub>Si)<sub>2</sub>E (E=S, Se). Scheme 1 displays representative reaction patterns of organotriels with such chalcogen sources.

When H<sub>2</sub>E or elemental chalcogens are reacted with trialkyltrienes, heterocubane compounds [(μ<sub>3</sub>-E)<sub>4</sub>(MR)<sub>4</sub>] (M=Al, Ga, In; R=Me<sub>2</sub>EtC, tBu) emerge (Scheme 1,i).<sup>[13,14]</sup> By deprotonation of mercapto silanes HSSiR'<sub>3</sub> (R'=alkyl), or by desilylation of bistralkylsilylchalcogenides with trialkyltrienes, the formation of dinuclear neutral complexes with bridging silylchalcogenido ligands [R<sub>2</sub>M(μ<sub>2</sub>-ESiR'<sub>3</sub>)<sub>2</sub>] was observed (Scheme 1,ii).<sup>[15,16]</sup> The availability of highly pure, water and chloride free organic cation salts Cat[SH] and Cat[SeH] inspired us to follow up a new strategy for synthesizing anionic chalcogenido metalates via metalation and protolysis of Cat[EH] by Me<sub>3</sub>M (Ga, In). The primary products 3–6 of this investigation are displayed in Scheme 1,iii.

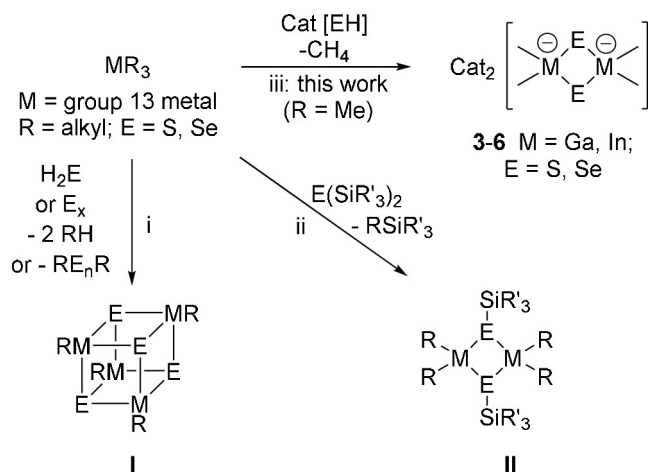
Very few examples of such lower nuclearity chalcogenido gallates and indates with purely inorganic chalcogenido ligands are known such as the trinuclear six-membered ring com-

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An invited contribution to a Special Issue dedicated to Material Synthesis in Ionic Liquids

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**Scheme 1.** Syntheses of group 13/16 metal chalcogenido compounds: i: heterocubanes  $[RM(\mu_3-E)]_3^{3-}$  (I)<sup>[13,14]</sup> ii: silylchalcogenide dimers  $[R_2M(\mu_2-ESiR'_3)]_2$  (II)<sup>[15,16]</sup> and iii: new chalcogenido-organometalates 3–6.

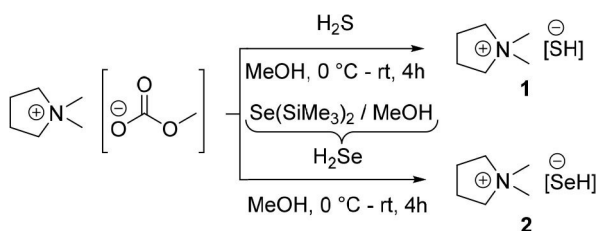
pounds  $[(Cl_2M)(\mu_2-E)]_3^{3-}$  (M=Ga, In; E=S, Se).<sup>[17]</sup> They were obtained by reaction of alkali metal hydrochalcogenides with  $MCl_3$  and characterized after cation exchange for quaternary ammonium cations. It seems, that their existence requires a highly negative, trianionic charge in order to inhibit the formation of higher nuclear clusters.

## 2. Results and discussion

### 2.1. Synthesis and Characterisation of the Chalcogenide IL Building Blocks

First, the synthesis of better crystallizing symmetric 1,1-dimethylpyrrolidinium (DMPyr) hydrochalcogenide salts was performed following our protocol described for corresponding 1-butyl-1-methylpyrrolidinium (BMPyr) salts (Scheme 2).<sup>[2]</sup> DMPyr[SH] (1) was prepared by deprotonation of  $H_2S$  with DMPyr[OCO<sub>2</sub>Me] in methanol. DMPyr[SeH] (2) was prepared by adding  $Se(SiMe_3)_2$  to a solution of DMPyr[OCO<sub>2</sub>Me] in methanol.

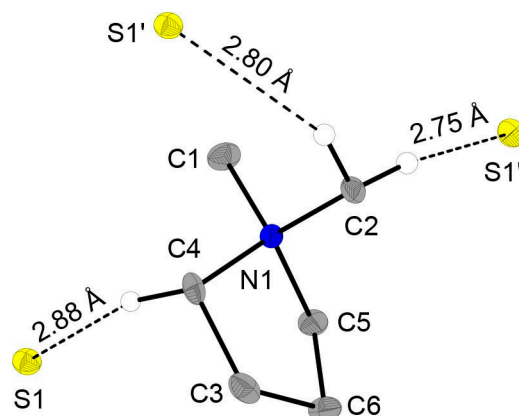
Single crystals of DMPyr[SH] (1) suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of 1 in acetonitrile at room temperature. 1 crystallizes in space group  $P2_1/n$  with four formula units per unit cell. In the lattice, one DMPyr<sup>+</sup> cation is non-covalently bonded to three hydro-sulfide anions via H-bonds ranging from 2.75 Å to 2.88 Å



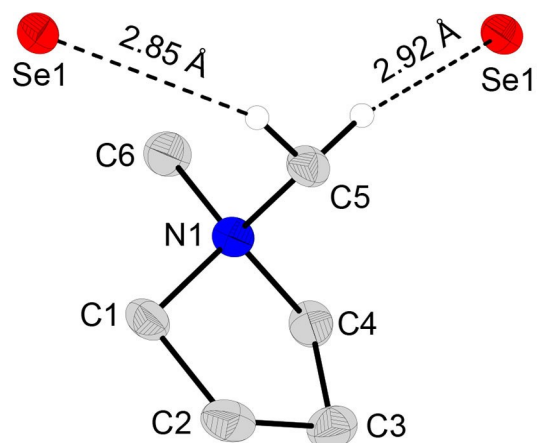
**Scheme 2.** Preparation of DMPyr[SH] (1) and DMPyr[SeH] (2).

(Figure 1). Crystalline BMPyr[SH] does show exactly the same coordination pattern of the cation to three sulfur atoms and H-bonds ranging from 2.64 Å to 2.87 Å.<sup>[2]</sup>

X-ray diffractive single-crystals of DMPyr[SeH] (2) were obtained by slow gas phase diffusion of diethyl ether into a saturated solution of 2 in a mixture of acetonitrile and diethyl ether. DMPyr[SeH] (2) crystallizes in space group  $P2_1/n$  with four ion pairs per unit cell. One DMPyr<sup>+</sup> cation is non-covalently bonded to two selenium atoms by two H-bonds to two protons of one and the same *N*-methyl group ranging from 2.85 Å to 2.92 Å (Figure 2).



**Figure 1.** Molecular structure of DMPyr[SH] (1). Only H-atoms involved in H-bonds are shown. Ellipsoids shown at the 50% level. Symmetry operations I:  $-1+x, y, z$ ; II:  $-1/2+x, 1/2-y, 1/2+z$ . Selected bond lengths (in Å) and angles (in °): C1–N1 1.493(2), C2–N1 1.503(1), C4–N1 1.511(1), C5–N1 1.511(1), C4–C3 1.527(2), C3–C6 1.550(2), C5–C6 1.526(2), C1–N1–C2 109.95(8), C1–N1–C5 111.67(8), C1–N1–C5–C6 161.66(9), C5–C6–C3 104.96(9), C5–C6–C3–C4 2.2(1), C6–C3–C4 105.59(9), C6–C3–C4–N1 23.7(1), C3–C4–N1–C2 77.3(1), S1–C4 3.776(1), S1–C4–N1 94.00(6), S1–C4–N1–C5 64.6(7).



**Figure 2.** Molecular structure of DMPyr[SeH] (2). Only H-atoms involved in H-bonds are shown. Ellipsoids shown at the 50% level. Symmetry operations I:  $1/2+x, 1/2-y, 1/2+z$ . Selected bond lengths (in Å) and angles (in °): C6–N1 1.495(4), C5–N1 1.497(4), C1–N1 1.511(4), C4–N1 1.513(4), C1–C2 1.529(5), C2–C3 1.546(5), C4–C3 1.528(5), C6–N1–C5 109.9(2), C6–N1–C4 111.3(2), C6–N1–C4–C3 159.4(3), C4–C3–C2 105.8(2), C4–C3–C2–C1 3.9(3), C3–C2–C1 104.9(3), C3–C2–C1–N1 28.7(3), C2–C1–N1–C5 75.0(3), Se1–C5 3.758(3), Se1–C5–N1 92.8(2), Se1–C5–N1–C4 170.6(2).

The closest interionic contacts of non-cyclic quaternary ammonium salts  $R_4N[SeH]$  ( $R=Me$ ,<sup>[20]</sup> (3.12 Å) and  $Bu$ <sup>[19]</sup> (3.06 Å)) are longer, while those of imidazolium salt  $EMIm[SeH]$ <sup>[2]</sup> are in a similar short range 2.81 Å to 2.95 Å as observed in 2.

The <sup>1</sup>H NMR spectra of the salts 1 and 2 confirm previously reported proton shifts of the weakly solvated anions  $[SH]^-$  (−4.04 ppm) in 1 and  $[SeH]^-$  (−6.62 ppm) in 2.<sup>[2]</sup> The distinctive proton NMR spectra are presented in Figure 3.

## 2.2. Synthesis and Characterisation of the Chalcogenido Metalate Building Blocks

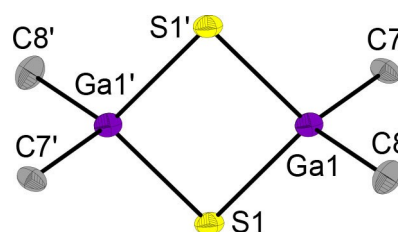
When a solution of  $Me_3M$  ( $M=Ga, In$ ) in THF is added to a THF suspension of  $DMPyr[EH]$  ( $E=S, Se$ ) at  $-20$  °C, a clear solution is obtained within a few minutes. This might be explained by the formation of lipophilic intermediates  $DMPyr[Me_3M-EH]$  ( $M=Ga, In; E=S, Se$ ) (Scheme 3,I). After warming this solution to room temperature, a colourless precipitate emerges within few hours. <sup>1</sup>H NMR spectra and elemental analyses of these isolated precipitates confirm the presence of the dianionic title compounds  $DMPyr_2[Me_2M(\mu_2-E)]_2$  3–6 formed via methane elimination. Single-crystal X-ray analyses prove the presence of four-membered ring structures of dianions  $[Me_2M(\mu_2-E)]_2^{2-}$  for all four combinations of  $E=S, Se$  and  $M=Ga, In$  (Scheme 3).

Single crystals of  $DMPyr_2[Me_2Ga(\mu_2-S)]_2$  (3) were obtained by diffusion of pentane into a saturated solution of 3 in tetrahydrofuran at room temperature. 3 crystallizes in the monoclinic space group  $P2_1/n$  with two ion pairs per unit cell. Due to crystallographically disordered cations the interionic

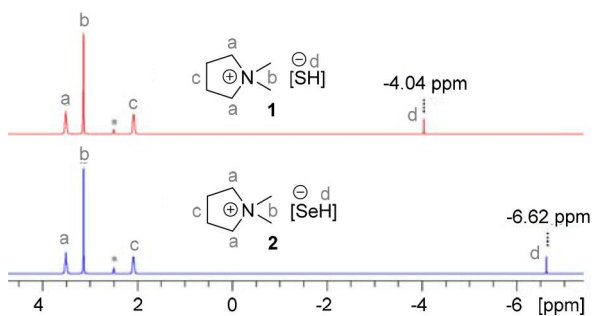
interactions could not be reliably identified in this particular case (Figure 4).

Single crystals of  $DMPyr_2[Me_2Ga(\mu_2-Se)]_2$  (4) were obtained by diffusion of pentane into a saturated solution of 4 in tetrahydrofuran at 0 °C. 4 crystallizes in the monoclinic space group  $P2_1/n$  with two ion pairs per unit cell. The compound displays a crystallographic center of symmetry. One crystallographically unique interionic H-bond of 2.93 Å is identified as shortest anion-cation contact (Figure 5).

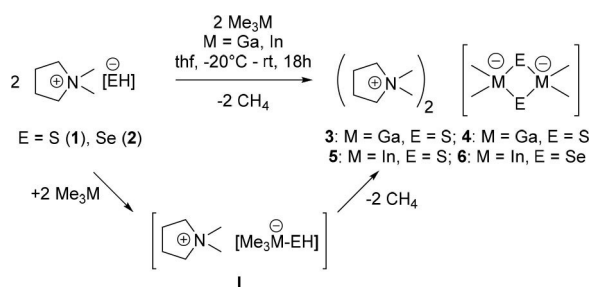
Single crystals of  $DMPyr_2[Me_2In(\mu_2-S)]_2$  (5) obtained by diffusion of pentane into a saturated solution of 5 in tetrahydrofuran at room temperature. 5 crystallizes in the monoclinic space group  $P2_1/n$  with two ion pairs per unit cell. The non-covalent interactions show remarkable similarity to those identified in the case of the selenium/gallium homologue 4. Again, one crystallographically unique interionic H-bond (2.83 Å) between



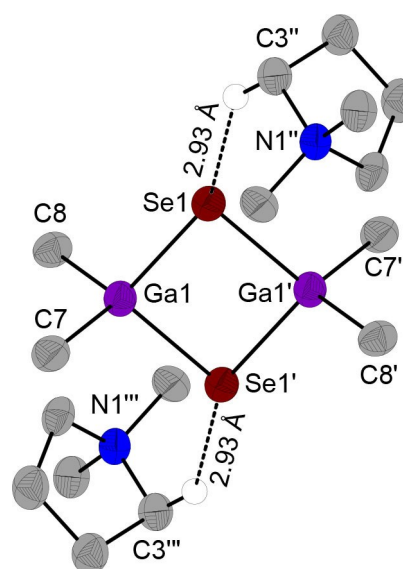
**Figure 4.** Molecular structure of the dianion present in  $DMPyr_2[Me_2Ga(\mu_2-S)]_2$  (3). Cations and H-atoms are not shown for clarity. Due to disordered cations, non-covalent interionic interactions cannot be discussed. Ellipsoids shown at the 50% level. Symmetry operations I:  $1-x, -y, 1-z$ . Selected bond lengths (in Å) and angles (in °) of the anion: Ga1–S1 2.3225(5), Ga1–S1' 2.3293(4), S1–Ga1–S1' 97.27(1), Ga1–S1'–Ga1' 82.73(1), Ga1–C7 2.032(2), Ga1–C8 2.012(2), C7–Ga1–C8 108.62(7), Ga1'–S1'–Ga1–C7 117.38(5), Ga1'–S1'–Ga1–C8 119.00(5).



**Figure 3.** <sup>1</sup>H NMR (300.3 MHz, \*dms $_6$ -d $_6$ ) of  $DMPyr[SH]$  (1) and  $DMPyr[SeH]$  (2).



**Scheme 3.** Preparation 3–6 from 1 and 2 via plausible intermediates I.

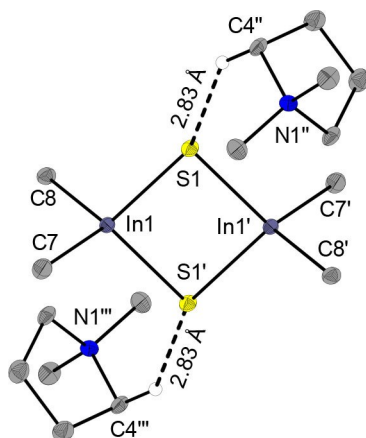


**Figure 5.** Molecular structure of  $DMPyr_2[Me_2Ga(\mu_2-Se)]_2$  (4). Only H-atoms active in H-bonds shown. Ellipsoids shown at the 50% level. Symmetry operations I:  $1-x, 1-y, 1-z$ ; II:  $-1/2+x, 1/2-y, 1/2+z$ ; III:  $3/2-x, 1/2+y, 1/2-z$ . Selected bond lengths (in Å) and angles (in °) of the anion: Ga1–Se1 2.453(1), Ga1–Se1' 2.461(1), Se1–Ga1–Se1' 82.41(4), Ga1–Se1–Ga1' 82.59(4), Ga1–C7 2.017(9), Ga1–C8 2.014(9), C7–Ga1–C8 109.0(4), Ga1'–Se1'–Ga1–C7–118.4(3), Ga1'–Se1'–Ga1–C8–117.6(3).

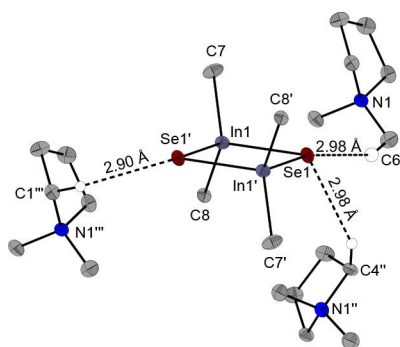
one sulfur atom and the same ring C–H bond of the cation DMPyr<sup>+</sup> is identified (Figure 6).

While DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-Se)]<sub>2</sub> (**6**) can be synthesized according to Scheme 3, single crystals suitable for X-ray analysis were obtained by a different synthesis route: Leaving a solution of equimolar amounts of DMPyr[SeSiMe<sub>3</sub>]<sup>[20]</sup> and Me<sub>3</sub>In standing for five days at room temperature in C<sub>6</sub>D<sub>6</sub> leads to growth of single crystals of **6**. As very slow formation of Me<sub>4</sub>Si is observed in the NMR spectrum, it is proposed, that **6** was formed by Se–Si bond cleavage induced via nucleophilic methyl group transfer to the Se–SiMe<sub>3</sub> group in plausible anionic intermediate [Me<sub>3</sub>In–Se–SiMe<sub>3</sub>]<sup>−</sup>. **6** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with two ion pairs per unit cell. The three shortest interionic H-bonds to different protons of three DMPyr<sup>+</sup> cations are ranging from 2.98 Å to 2.90 Å (Figure 7).

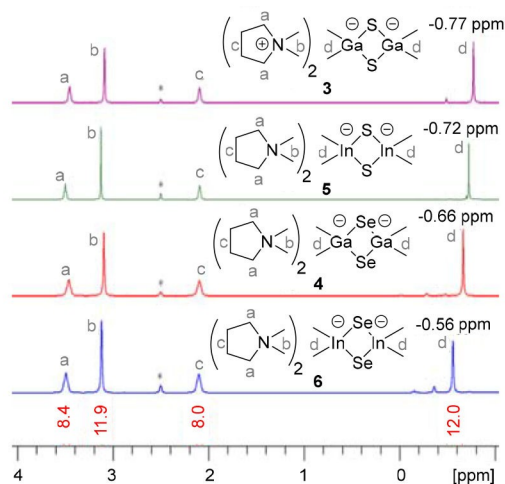
The <sup>1</sup>H NMR spectra of the title compounds show a simple pattern of signals for two DMPyr<sup>+</sup> cations and one dianion, as



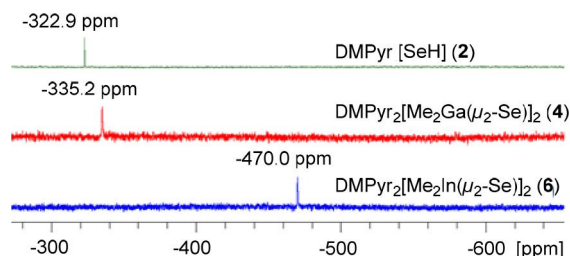
**Figure 6.** Molecular structure of DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-S)]<sub>2</sub> (**5**). Only H-atoms active in H-bonds are shown. Ellipsoids shown at the 50% level. Symmetry operations I:  $-x, -y, -z$ ; II:  $1-x, -y, -z$ ; III:  $-1+x, y, z$ . Selected bond lengths (in Å) and angles (in °) of the anion: In1–S1 2.5040(5), In1–S1' 2.5067(4), S1–In1–S1' 96.15(1), In1–S1–In1' 83.85(1), In1–C7 2.206(2), In1–C8 2.205(2), C7–In1–C8 108.45(6), In1'–S1'–In1–C7 118.81(5), In1'–S1–In1–C8 116.64(4).



**Figure 7.** Molecular structure of DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-Se)]<sub>2</sub> (**6**). Only H-atoms active in crystallographically unique H-bonds are shown. Ellipsoids shown at the 50% level. Symmetry operations I:  $2-x, -y, 2-z$ ; II:  $1/2+x, 1/2-y, 1/2+z$ ; III:  $1+x, y, z$ . Selected bond lengths (in Å) and angles (in °) of the anion: In1–Se1 2.6208(4), In1–Se1' 2.6177(4), Se1–In1–Se1' 96.72(1), In1–Se1–In1' 83.28(1), In1–C7 2.209(3), In1–C8 2.212(3), C7–In1–C8 110.2(1), In1'–Se1'–In1–C7 117.35(9), In1'–Se1–In1–C8 116.58(8).



**Figure 8.** <sup>1</sup>H NMR spectra (**3**, **5**: 500.2 MHz; **4**, **5**: 300.3 MHz, \*dms<sub>o</sub>-d<sub>6</sub>) of DMPyr<sub>2</sub>[Me<sub>2</sub>M(μ<sub>2</sub>-E)]<sub>2</sub> **3–6**.



**Figure 9.** <sup>77</sup>Se NMR spectra (57.3 MHz, dms<sub>o</sub>-d<sub>6</sub>) of the selenium containing title compounds DMPyr[SeH] (**2**, top row), DMPyr<sub>2</sub>[Me<sub>2</sub>Ga(μ<sub>2</sub>-Se)]<sub>2</sub> (**4**, middle row), and DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-Se)]<sub>2</sub> (**6**, bottom row).

indicated by the corresponding integrals (Figure 8). For the dianions a general trend towards more low-field shifted M–Me signals is observed with increasing molecular weight  $S < Se$  and  $Ga < In$ . The shifts are stronger affected by the chalcogen atoms than by the metal atoms: The M–Me protons of the selenium compounds **4** and **6** are more low-field shifted than the corresponding signals of the sulfur homologues **3** and **5**, while the corresponding signals of the gallates **3** and **4** are slightly more high-field shifted compared to the indates **5** and **6**.

In contrast, <sup>77</sup>Se NMR spectra show a more pronounced high-field shift with increasing molecular weight  $Ga < In$ : The hydrochalcogenide anion in DMPyr[SeH] (**2**) displays a pronounced low-field shift, while the anion in DMPyr<sub>2</sub>[Me<sub>2</sub>In(μ<sub>2</sub>-Se)]<sub>2</sub> (**6**) is showing the strongest high-field shifted signal (Figure 9).

## 2.3. Reactivity Studies with Chalcogenido Indates 5 and 6

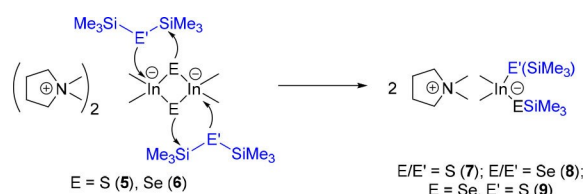
### 2.3.1. Ring Cleavage Reactions

Preliminary studies show, that these easily obtained dianionic building blocks are reactive towards other electrophilic and Lewis acidic element or metal species. The scope of using **3–6**

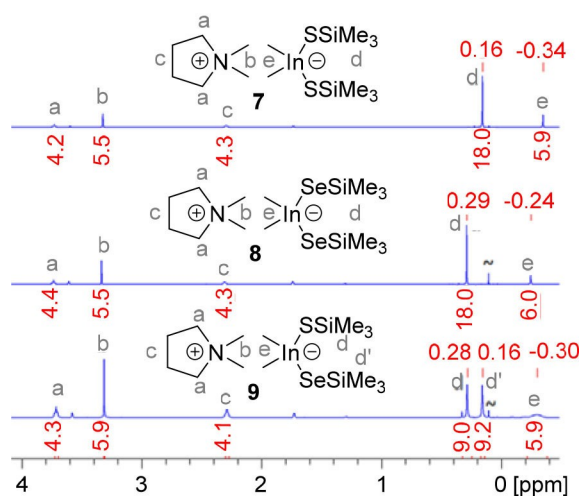


as ligands to transfer  $[\text{Me}_2\text{M}-\text{E}]_n^{n-}$  anions to other metals and to form heteronuclear clusters has not systematically been studied so far. In this chapter we focus on reactions of the indium compounds **5** and **6** with silicon and indium electrophiles. The reason for choosing indium and not gallium homologues is the higher electron density and nucleophilicity expected at the bridging sulfido or selenido ligands in the anionic backbone  $[\text{In}-(\mu-\text{E})-\text{In}]$  compared to  $[\text{Ga}-(\mu-\text{E})-\text{Ga}]$ : Gallium has a higher Allred-Rochow electronegativity 1.8 compared to aluminium (1.5) and indium (1.5).<sup>[21]</sup> Therefore, the charge of the chalcogen dianions is believed to be much better stabilized in gallium than in indium compounds. This prognosis is reflected in the observable higher reactivity of **5** and **6** towards amphoteric electrophiles such as  $\text{Me}_3\text{Si}-\text{E}-\text{SiMe}_3$  and  $\text{Me}_3\text{In}$  compared to **3** and **4**.

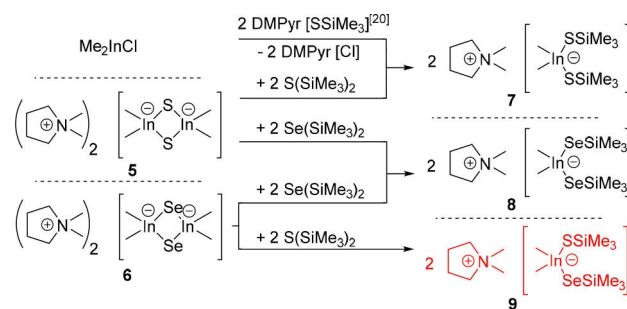
The indates  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2-\text{S})_2]$  (**5**) and  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2-\text{Se})_2]$  (**6**) react with two equivalents of  $(\text{Me}_3\text{Si})_2\text{E}$  under cleavage of the four-membered ring to yield bis(trimethylsilylchalcogenido)-dimethylindates  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SSiMe}_3)_2]$  (**7**) and  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SeSiMe}_3)_2]$  (**8**) (Scheme 4). A dipolar intramolecular addition mechanism is suggested, as we were able to isolate even a mixed silylsulfido-selenido derivative  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SSiMe}_3)(\text{SeSiMe}_3)]$  (**9**) via selective cleavage of the ring  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2-\text{Se})_2]$  (**6**) by addition of  $\text{S}(\text{SiMe}_3)_2$ . The formation of mononuclear silylchalcogenidoindates can easily be monitored by the observation of a new



**Scheme 4.** Suggested dipolar addition mechanism towards mononuclear silylchalcogenido indates **7–9**.



**Figure 10.**  $^1\text{H}$  NMR spectra (250.1 MHz,  $^*\text{dmsO}-d_6$ ) of the indates **7**, **8**, and **9**. The shift of the indium attached methyl groups of **9** implies the presence of a sulfido- and selenido-substituted metalate anion.



**Scheme 5.** Reactions of **5** and **6** to silylchalcogenido-dimethylindates **7**, **8**, and mixed **9**.

signal for indium attached methyl groups in the proton NMR spectra (Figure 10).

Interestingly, the reaction of  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2-\text{S})_2]$  (**5**) with  $>5$  molar excess of  $\text{Se}(\text{SiMe}_3)_2$  leads to  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SeSiMe}_3)_2]$  (**8**), indicating that a terminal  $[\text{In}-\text{S}-\text{SiMe}_3]$  functionality of plausible mixed intermediate  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SSiMe}_3)(\text{SeSiMe}_3)]$  (**9**) can be replaced by a probably more stable  $[\text{In}-\text{Se}-\text{SiMe}_3]$  functionality – taking also the formation of a more stable  $\text{Si}-\text{S}$  bond into consideration. Therefore, the other synthesis strategy laid out in Scheme 5 is more selective for the simple isolation of pure **9**. Finally,  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SSiMe}_3)_2]$  (**7**) can be prepared by reaction of two equivalents of  $\text{DMPyr}[\text{SSiMe}_3]$  with  $\text{Me}_2\text{InCl}$ . This strategy has the disadvantage, that another salt,  $\text{DMPyr}[\text{Cl}]$ , has to be separated from much better soluble **7**, but this is the overall cheapest large scale method to synthesize such synthons for planning further condensation reaction steps with Lewis acids involving  $-\text{Me}$  and  $-\text{SiMe}_3$  leaving groups (Scheme 5).

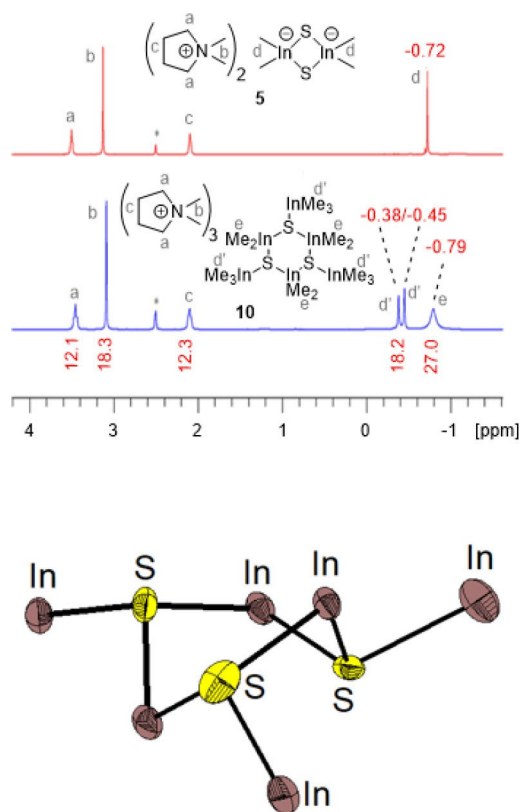
Complexes containing silylchalcogenido ligands  $[\text{M}-\text{E}-\text{SiMe}_3]$  are attractive synthons for condensation reactions e.g. with heterometal acetates  $\text{M}'\text{OAc}$  in order to selectively synthesize heteronuclear linkages  $\text{M}-\text{E}-\text{M}'$  by elimination of  $\text{Me}_3\text{SiOAc}$ .<sup>[11,15,22–24]</sup> For a long time, only two structural motives with heavy silylchalcogenido ligands were known: the spirocyclic compounds  $[(\text{Me}_2\text{M})_6\text{E}(\text{ESiMe}_3)_4]$  ( $\text{M}=\text{Ga}, \text{In}; \text{E}=\text{S}, \text{Se}$ ),<sup>[25]</sup> and  $[\text{iPr}_3\text{PCu}(\mu_2-\text{SeSiMe}_3)(\text{InMe}_3)]$  ( $\text{E}=\text{S}, \text{Se}$ ).<sup>[26]</sup> The latter is the addition product of  $\text{Me}_3\text{In}$  and  $\text{iPr}_3\text{PCuESiMe}_3$ . It unites all atoms necessary to act as single-source precursor for  $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$  materials.<sup>[23,26]</sup> Recently, we established a series of homoleptic trielates  $\text{Cat}[\text{M}(\text{ESSiMe}_3)_4]$  which can act as versatile precursors for binary ( $\text{Cat}^+ = \text{organic cation}$ ) and ternary materials ( $\text{Cat}^+ = [\text{Cu}]^+$ ).<sup>[7]</sup>

### 2.3.2. Condensation to Higher Nuclear Clusters

Furthermore, we investigated the reaction of Lewis base  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2-\text{S})_2]$  (**5**) with two equivalents of trimethylindium as Lewis acid. **5** dissolved upon 1:2 adduct formation according to the results of an elemental analysis. Proton NMR spectra of product **10** indicated a broad signal corresponding to  $\text{Me}_3\text{In}$  units, while  $\text{Me}_2\text{In}$  groups are split into two signals matching in their sum with the expected 2:3 integral (Fig-

ure 11): This observation would be in accord with a four-membered ring structure with either *syn*- or *anti*- $[\mu_2\text{-S-InMe}_3]$  bridging groups. The real situation turned out to be more interesting: Crystals of **10** were grown from THF/pentane. They were of poor quality due to multiple disorder problems, but the results of a preliminary XRD analysis allowed to determine the inner core of **10** to be a hexanuclear trimer  $\text{DMPyr}_3[\text{Me}_2\text{In}(\mu_2\text{-S-InMe}_3)]_3$ . The six-membered ring adopts a twisted boat conformation with bulky terminal  $[\mu_2\text{-S-InMe}_3]$  groups in *syn*- or *anti*-configuration with respect to each other, thus minimizing their steric interaction and releasing ring strain. This explains the proton NMR results. As a matter of fact, the highly negative charge loaded four membered ring suffered a ring expansion to a six-membered ring upon delocalizing the high negative charge per sulfido ligand over double as much indium atoms.

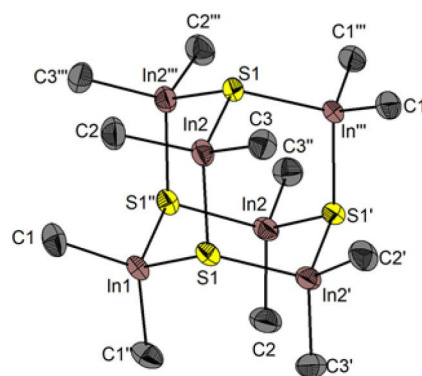
During our many attempts to grow single crystals of **10** with less disorder problems we realized, that both, the relative ratio and absolute shifts of In-CH<sub>3</sub> protons changed with time after taking NMR samples. Figure 13 displays the typical proton NMR after a 14 days crystallization period in THF/pentane via a NMR sample taken in  $\text{dms}\text{-d}_6$ . Repeated recrystallisation of such samples revealed, that the ratio of protons of type (d) and (e) vary a bit. This means, these signals belong to different



**Figure 11.**  $^1\text{H}$  NMR spectra (500.1 MHz for **5**, 300.1 MHz for **10**, \* $\text{dms}\text{-d}_6$ ) of  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2\text{-S})]_2$  (**5**) before (top row), and after addition of two equivalents of  $\text{Me}_3\text{In}$ . Presentation of the inner core of formed asymmetric trimer  $\text{DMPyr}_3[\text{Me}_2\text{In}(\mu_2\text{-S-InMe}_3)]_3$  (**10**) with *syn*- and *anti*- $\text{S-InMe}_3$  groups as shown by a preliminary XRD analysis (see discussion in SI, Figure S1, page S22).

species. However, the species with chemically equivalent In-CH<sub>3</sub> protons at  $\delta_{\text{H}} = -0.64$  ppm could not fully be separated from the species with  $\delta_{\text{H}} = -0.38$  ppm so far: Both belong to ionic methylindate species with the same cation. Finally, a few single crystals suitable for XRD analysis were separated mechanically. They turned out to be the salt  $\text{DMPyr}_2[(\text{Me}_2\text{In})_6(\mu_3\text{-S})_4]$  (**11**) (Figure 12). The latter crystallizes in the tetragonal space group  $I4_1/acd$  with  $Z=8$  ion pairs per unit cell and one molecule of tetrahydrofuran per formula unit. The cations show in part some disorder.

The structure refinement reveals, that a dianionic hexanuclear inverse heteroadamantane cage had been formed. In contrast to archetypical metal chalcogenide adamantane cage structures, the metals are not located in the capping positions whereas chalcogen atoms in the bridging positions, but inverse:  $[\text{Me}_2\text{In}]$  units are bridging and sulfido ligands are capping  $[\mu_3\text{-S}]$ . Comparable inverse adamantane anion structures have been reported for the chalcogenidohydroborates  $\text{Cs}[(\text{H}_2\text{B})_6(\mu_3\text{-E})_4]$  ( $\text{E}=\text{S}, \text{Se}$ ).<sup>[27]</sup> A plausible path of formation of this dianion might be induced by an irreversible dissociation of  $\text{Me}_3\text{In}$  from one of the sulfide bridges in **10**. Dissociated  $\text{Me}_3\text{In}$  might then abstract a methyl group from a neighbouring  $[\mu_2\text{-S-InMe}_3]$  unit forming the known tetramethylindate anion and a formally coordinatively unsaturated  $[\text{In}_2\text{-S-InMe}_2]^+$  unit which is folding up with the formed nucleophilic  $[\text{In}(\mu\text{-S})\text{-In}]^-$  units to build up the cluster framework. The dislocation of accumulated negative charge in such charge dissociation reactions is probably the trigger for the formation of the dianionic cluster cage. Another trigger might be the fact, that  $\text{DMPyr}[\text{InMe}_4]$  tends to be not stable for extended periods of time. It decomposes, thus shifting the reaction from metastable **10** to more stable **11** by irreversible decay of proposed by-product  $\text{DMPyr}[\text{InMe}_4]$ . We tried hard to develop a synthesis method on a gram scale for **11** – without full success up to

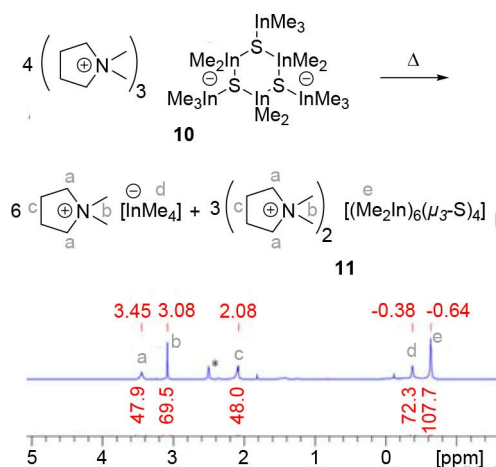


**Figure 12.** Molecular structure of the dianion in  $\text{DMPyr}_2[(\text{Me}_2\text{In})_6(\mu_3\text{-S})_4]$  (**11**). H-atoms, cations, and solvent molecules are not shown for clarity. Ellipsoids shown at the 50% level. Symmetry operations I:  $3/4-y, -1/4+x, 1/4-z$ ; II:  $1-x, 1/2-y, z$ ; III:  $1/4+y, 3/4-x, 1/4-z$ . Selected bond lengths (in Å) and angles (in  $^\circ$ ) of the anion: S1-In1 2.522(1), S1-In2 2.522(1), S1-In2' 2.522(1), S1'-In1-S1 106.96(4), S1-In2-S1''' 107.15(4), In1-S1-In2' 111.80(5), In1-S1-In2 109.60(5), In1-C1 2.174(5), In2-C2 2.177(6), In2-C3 2.181(5), C1-In1-C1'' 118.5(2), C2-In2-C3 118.0(2), S1-In1-C1 108.2(1), S1-In1-C1''' 107.3(1), In2-S1-In1-C1'' 177.9(2), C1-In1-S1-In2' -176.0(2), C2-In2-S1-In2' 174.4(2), C2-In2-S1-In1 178.8(2), In1-S1-In2-S1' 59.65(6), In1-S1-In2-S1''' -63.5(6).

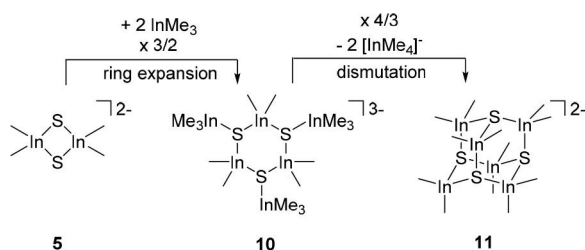
date: The thermal dissociation of metastable **10** can be accelerated in diglyme: After 18 h at 100 °C and after removing all volatiles in vacuo, the colourless solid obtained shows the same signals and similar integrals in the  $^1\text{H}$  NMR spectrum, which is taken as an indication for an overall stoichiometric transformation displayed in Figure 13.

We assume, that the formation of cluster dianion **11** with the lowest negative real charge per sulfido group is the result of accumulated charge reduction starting from low nuclearity (dinuclear) dianion **5** with the highest charge at sulfur, via metalation with  $\text{Me}_3\text{In}$  and ring expansion towards metastable **10** and its dismutation and charge dissociation into  $[\text{InMe}_4]^-$  and  $[(\text{Me}_2\text{In})_6(\mu_3\text{-S})_4]^{2-}$  (Scheme 6).

This mechanism has to be further confirmed in future research and alternative synthesis strategies have to be developed in order to synthesize such inverse adamantane cage compounds with all combinations of Ga/In and S/Se. The SI describes first encouraging experiments indicating that the mononuclear silylchalcogenido-dimethylindates **7**, **8** and **9** described above are indeed useful building blocks to approach clusters of type **11** under thermodynamic reaction control via condensation of metastable intermediates formed by reactions of **7–9** with  $\text{Me}_2\text{InCl}$  and  $\text{Me}_3\text{In}$  (Scheme S2 and Figures S3–S6).



**Figure 13.**  $^1\text{H}$  NMR spectra (300.2 MHz,  $^*\text{dms}\text{-d}_6$ ) pointing out an assumed dismutation mechanism for the formation of **11**.



**Scheme 6.** Assumed mechanism for the formation of cage compound **11** via **10** starting from **5**.

### 3. Conclusions

Deprotonation of hydrochalcogenide anions of organic salts  $\text{DMPyr}[\text{EH}]$  ( $\text{E}=\text{S}$  (**1**),  $\text{Se}$  (**2**)) with trimethylgallium and indium  $\text{Me}_3\text{M}$  ( $\text{M}=\text{Ga}$ ,  $\text{In}$ ) leads to a comprehensive series of dinuclear chalcogenidogallates  $\text{DMPyr}_2[\text{Me}_2\text{Ga}(\mu_2\text{-E})_2]$ ,  $\text{E}=\text{S}$  (**3**);  $\text{E}=\text{Se}$  (**4**), and chalcogenido indates  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2\text{-E})_2]$ ,  $\text{E}=\text{S}$  (**5**),  $\text{Se}$  (**6**). These are valuable building blocks for reactivity studies: Dinuclear and dianionic chalcogenido indates **5** and **6** were shown to be ring cleaved into mononuclear indates  $\text{DMPyr}[\text{Me}_2\text{In}(\text{ESiMe}_3)_2]$ ,  $\text{E}=\text{S}$  (**7**),  $\text{Se}$  (**8**), while  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2\text{-Se})_2]$  (**6**) is cleaved by  $\text{S}(\text{SiMe}_3)_2$  to mixed silylsulfido-selenido indate  $\text{DMPyr}[\text{Me}_2\text{In}(\text{SSiMe}_3)(\text{SeSiMe}_3)]$  (**9**). By addition of two equivalents of trimethylindium to  $\text{DMPyr}_2[\text{Me}_2\text{In}(\mu_2\text{-S})_2]$  (**5**) a terminal trimethylindate unit is added to each highly charged sulfur atom resulting in better charge delocalization and ring expansion into hexanuclear trianionic ring compound  $\text{DMPyr}_3[\text{Me}_2\text{In}(\mu_2\text{-S-InMe}_3)]_3$  (**10**). Long term storage of **10** in solution leads to dimutation into  $\text{DMPyr}_2[(\text{Me}_2\text{In})_6(\mu_3\text{-S})_4]$  (**11**) displaying an interesting inverse heteroadamantane cage identified crystallographically. Based on model reactions it is likely, that **10** decomposes to **11** by thermolysis and under elimination of  $\text{DMPyr}[\text{InMe}_4]$ . All in all, new valuable triel chalcogenido metalate building blocks and a first set of their further transformations were presented.

### Experimental Section

For methods and devices please refer to the General Consideration section in the Supporting Information.

#### XRD Analyses

Please refer to the Crystallographic Information section in the Supporting Information concerning the used hardware and software used for data collection. For cell refinement and data reduction as well as structure refinement of molecular structures of chapter 3 please check Table S1–Table S5 in the Supporting Information. Deposition Number(s) 1910795 (for **3**), 1910796 (for **5**), 1910797 (for **2**), 1910798 (for **1**), 1910799 (for **11**), 1910800 (for **4**), 1910794 (for **6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

#### Representative Synthetic Procedures

Synthetic procedures for **1**, **3**, **4**, **6**, **8**, **9** and strategies to synthesize **11** on large scale by alternative synthetic routes are provided in the Supporting Information.

#### Synthesis of *N,N*-Dimethylpyrrolidinium Hydroselenide $\text{DMPyr}[\text{SeH}]$ (**2**)

$\text{Se}(\text{SiMe}_3)_2$  (6.88 g, 30.5 mmol, 1.1 eq.) was added to a solution of *N,N*-dimethylpyrrolidinium methylcarbonat (4.86 g, 27.8 mmol, 1.0 eq) in 30 mL methanol at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and for 1 hour at room temperature. All volatiles

were removed in fine vacuum and the residue was diluted in acetonitrile until a saturated solution is obtained. Storing this saturated solution at  $-30^{\circ}\text{C}$  yields greenish crystals that are collected by filtration and washed two times with 10 mL diethyl ether. DMPyr[SeH] (**2**, 3.90 g, 21.6 mmol, 78%) was obtained as slightly greenish crystals. The yield can be enhanced by further saturation of the mother liquor and subsequent recrystallisation cycles.  $^1\text{H}$  NMR (300.3 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{H}}=3.51$  (m, 4H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 3.14 (s, 6H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 2.09 (m, 4H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ),  $-6.62$  (s, 1H, HSe) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{C}}=64.6$  (t,  $^1J_{\text{CN}}=3.2$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 50.9 (t,  $^1J_{\text{CN}}=3.9$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 21.3 (s,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ) ppm.  $^{77}\text{Se}$  NMR (57.3 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{Se}}=-322.9$  (s, SeH) ppm. Anal. calcd. for  $\text{C}_6\text{H}_{15}\text{N}_2\text{Se}$ : C, 40.0; H, 8.4; N, 7.8. Found: C, 40.0; H, 8.5; N, 8.0.

### Synthesis of *N,N*-Dimethylpyrrolidinium Dimethylsulfidoindate DMPyr<sub>2</sub>[Me<sub>2</sub>In( $\mu_2$ -S)]<sub>2</sub> (**5**)

To a suspension of DMPyr[SH] (0.096 g, 0.73 mmol, 2.0 eq.) in 10 mL thf a solution of Me<sub>2</sub>In (0.121 g, 0.76 mmol, 2.1 eq.) in 10 mL thf was slowly added at  $-20^{\circ}\text{C}$ . The reaction mixture is allowed to obtain room temperature within 18 h under continuous stirring. The mixture becomes clear after approximately 15 min, and after approximately 2 hours a colorless solid precipitates. After the 18 h a colorless cloudy suspension is obtained. All volatiles were removed in fine vacuum and the residue was washed twice with 10 mL of pentane. DMPyr<sub>2</sub>[Me<sub>2</sub>MIn( $\mu_2$ -S)]<sub>2</sub> (**0.170** g, 0.31 mmol, 87%) is obtained as colorless powder.  $^1\text{H}$  NMR (500.2 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{H}}=3.50$  (m, 8H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 3.13 (s, 12H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 2.09 (m, 8H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ),  $-0.72$  (s, 12H, In( $\text{CH}_2$ )<sub>2</sub>×2) ppm.  $^{13}\text{C}$  NMR (125.8 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{C}}=64.6$  (t,  $^1J_{\text{CN}}=3.2$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 50.9 (t,  $^1J_{\text{CN}}=3.9$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 21.3 (s,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ),  $-0.3$  (s, In( $\text{CH}_2$ )<sub>2</sub>) ppm. Anal. calcd. for  $\text{C}_{16}\text{H}_{40}\text{In}_2\text{N}_2\text{S}_2$ : C, 34.7; H, 7.3; N, 5.1; S, 11.6. Found: C, 34.5; H, 7.6; N, 5.2; S, 11.3.

### Synthesis of *N,N*-Dimethylpyrrolidinium bis(trimethylsilylsulfo)dimethylindate DMPyr[Me<sub>2</sub>In(SSiMe<sub>3</sub>)<sub>2</sub>] (**7**)

S(SiMe<sub>3</sub>)<sub>2</sub> (0.057 g, 0.32 mmol, 1.5 eq.) is slowly added to a suspension of DMPyr<sub>2</sub>[Me<sub>2</sub>In( $\mu_2$ -S)]<sub>2</sub> (**5**) (0.060 g, 0.11 mmol, 0.5 eq.) in 10 mL thf at  $-78^{\circ}\text{C}$ . The reaction mixture is slowly allowed to obtain room temperature within 18 h and stirred, until a clear solution is obtained. After removing all volatiles in fine vacuum, the oily residues are washed with 5 mL pentane and dried in fine vacuum. DMPyr[Me<sub>2</sub>In(SSiMe<sub>3</sub>)<sub>2</sub>] (**7**, 0.087 g, 0.20 mmol, 88%) is obtained as colorless and oily wax.  $^1\text{H}$  NMR (500.2 MHz, THF- $\text{d}_8$ )  $\delta_{\text{H}}=3.71$  (m, 4H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 3.31 (s, 6H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 2.29 (m, 4H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 0.16 (s, 18H, (H<sub>3</sub>C)<sub>2</sub>In(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>),  $-0.34$  (s, 6H, (H<sub>3</sub>C)<sub>2</sub>In(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>) ppm.  $^{13}\text{C}$  NMR (125.8 MHz, THF- $\text{d}_8$ )  $\delta_{\text{C}}=66.5$  (t,  $^1J_{\text{CN}}=3.2$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 52.5 (t,  $^1J_{\text{CN}}=4.0$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 22.6 (s,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 6.5 (s, (H<sub>3</sub>C)<sub>2</sub>In(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>),  $-1.9$  (s, (H<sub>3</sub>C)<sub>2</sub>In(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>) ppm.  $^{29}\text{Si}$  NMR (99.4 MHz, THF- $\text{d}_8$ )  $\delta_{\text{Si}}=8.6$  (s, (H<sub>3</sub>C)<sub>2</sub>In(SSi(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>) ppm. Anal. calcd. for  $\text{C}_{14}\text{H}_{38}\text{InNS}_2\text{Si}_2$ : C, 36.9; H, 8.4; N, 3.1; S, 14.1. Found: C, 36.9; H, 8.2; N, 3.6; S, 13.1. Note that crude product was investigated.

### Synthesis of DMPyr<sub>3</sub>[Me<sub>2</sub>In( $\mu_2$ -S-InMe<sub>3</sub>)<sub>3</sub>] (**10**)

To a suspension of DMPyr<sub>2</sub>[Me<sub>2</sub>In( $\mu_2$ -S)]<sub>2</sub> (**5**) (0.100 g, 0.180 mmol, 1.5 eq.) in 3 mL thf a solution of 0.058 g Me<sub>2</sub>In (0.058 g, 0.361 mmol, 3.0 eq.) in 5 mL thf was added dropwise at  $-78^{\circ}\text{C}$ . The reaction mixture was allowed to obtain room temperature within 18 h. A clear solution is obtained, that is separated from all volatiles in fine vacuum. The colorless residue is washed with 5 mL pentane and dried in fine vacuum. DMPyr<sub>3</sub>[Me<sub>2</sub>In( $\mu_2$ -S-InMe<sub>3</sub>)<sub>3</sub>] (**10**) was

obtained as colorless solid with a yield of 0.145 g (0.111 mmol, 92%).  $^1\text{H}$  NMR (300.1 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{H}}=3.45$  (m, 12H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 3.08 (s, 18H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 2.10 (m, 12H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ),  $-0.38$  &  $-0.45$  (2×s, 18H, (H<sub>3</sub>C)<sub>2</sub>In),  $-0.79$  (bs, 27H,  $\mu_2$ -S-In(CH<sub>3</sub>)<sub>3</sub>) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{C}}=64.8$  (t,  $^1J_{\text{CN}}=3.1$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 51.0 (t,  $^1J_{\text{CN}}=4.1$  Hz,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 21.3 (m, 12H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ),  $-0.79$  &  $-0.88$  (2×s, (H<sub>3</sub>C)<sub>2</sub>In),  $-0.79$  (bs, 27H,  $\mu_2$ -S-In(CH<sub>3</sub>)<sub>3</sub>) ppm.\* Anal. calcd. for  $\text{C}_{33}\text{H}_{87}\text{In}_6\text{N}_6\text{S}_3$ : C, 30.2; H, 6.7; N, 3.2; S, 7.3. Found: C, 30.9; H, 6.7; N, 3.5; S, 6.6. Note that crude product was investigated.\*The signals in the  $^{13}\text{C}$  NMR spectrum are quite weak. The split signal for the indium attached methyl groups is hardly determinable. The  $^{13}\text{C}$  NMR signal for the  $\mu_2$ -S-InMe<sub>3</sub> groups cannot be identified clearly. This is due to a dynamic conformational rearrangement also displayed in the proton spectra.

### Synthesis of DMPyr<sub>2</sub>[(Me<sub>2</sub>In)<sub>6</sub>( $\mu_3$ -S)<sub>4</sub>] (**11**)

A 30 mg sample of **10** was dissolved in THF and layered with pentane. After 14 days in the dark under argon protective gas, a crop of colorless crystals next to colorless microcrystalline material had formed. The NMR sample of a representative sample of this precipitate dissolved in  $\text{dms}\text{-d}_6$  is presented in Figure 13. It reveals a mix of what is presumed to be DMPyr[InMe<sub>4</sub>] and **11**. Single crystals of **11** were mechanically separated and submitted to XRD analysis. Estimated yield of separated **11**: <10%.  $^1\text{H}$  NMR (300.1 MHz,  $\text{dms}\text{-d}_6$ )  $\delta_{\text{H}}=3.45$  (m, 12H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 3.08 (s, 18H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ), 2.10 (m, 12H,  $(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2$ ),  $-0.45$  (2×s, 18H, (H<sub>3</sub>C)<sub>2</sub>In),  $-0.64$  (12H,  $\mu_2$ -In(CH<sub>3</sub>)<sub>3</sub>) ppm.

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### Conflict of Interest

The authors declare no conflict of interest.

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