On the reactions of the tetraindium cluster $In_4[C(SiMe_3)_3]_4$: Insertion of the monomeric fragments $InC(SiMe_3)_3$ into chalcogen–chalcogen bonds

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ABSTRACT

Treatment of the tetraindium cluster $In_4[C(SiMe_3)_3]_4$ (**1**) with diaryl dichalcogenides Aryl-E-E-Aryl (E = S, Se and Te) afforded the corresponding $RIn(E-Aryl)_2$ [R = $C(SiMe_3)_3$] compounds by insertion of the monomeric fragments InR into the chalcogen–chalcogen bonds. The dimeric formula units adopt different conformations in the solid state (C_i vs. C_{2h}).

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1. Introduction

For many years, cyclopentadienyl derivatives [1–6] and the monomeric compound with the crowded *o*-terphenyl ligand C_6H_3-2,6-$Trip_2$ (Trip = $-C_6H_2$-2,4,6-*i*-Pr_3) [7] were the only well characterized organanometallic indium(I) compounds. About a decade ago, the first alkylindium(I) derivative, $In_4[C(SiMe_3)_3]_4$ (**1**), was obtained by the reaction of InBr with $LiC(SiMe_3)_3$. In contrast to the cyclopentadienyl compounds it exhibits strong In-In bonding interactions and has an almost undistorted tetrahedral cluster of four indium atoms in an oxidation state of +I [8,9]. Compound **1** is soluble in hydrocarbons and is applicable as a facile source of monomeric InR fragments [R = $C(SiMe_3)_3$] in a number of unprecedented and remarkable chemical reactions [10–18]. For instance, novel indium(III) chalcogenides were obtained through the complete oxidation of the cluster atoms by elemental chalcogens or suitable chalcogen atom donors to give heterocubane-type molecules $In_4R_4E_4$ (E = O, S, Se, Te) [8,19–21]. Reactions with phenylchalcogen bromides, H_5C_6-E-Br (E = Se, Te), afforded the dimeric chalcogenolates $[PhE(R)InBr]_2$ (E = Se, Te) [10]. Indium(III) chalcogenolates obtained from indium monohalides and diphenyl dichalcogenides [22] have been extensively applied in organic synthesis to generate carbon–chalcogen bonds. Reactions of interest include: ring opening reactions of epoxides with $IIn(EPh)_2$ (E = S, Se) to the corresponding β-hydroxy selenides [23] and sulfides [24], ring opening reactions of aziridines with $IIn(SePh)_2$ to selenocysteine derivatives and selenotreonine [25],

hydrochalcogenation of terminal alkynes, alkynols and aminoalkynes with $XIn(EPh)_2$ (X = Br, I; E = S, Se, Te] [26–29], Pd(0) catalyzed coupling between $IIn(EPh)_2$ (E = S, Se) with vinyl bromides to vinylic chalcogenides [30], condensations of $IIn(EPh)_2$ (E = S, Se) with alkyl and acyl halides for the synthesis of unsymmetrical chalcogenides [31,32]. Some of these reactions are highly stereoselective, particularly those leading to vinylic chalcogenides. In order to gain a better insight into the properties of these reagents, we started to investigate oxidative reactions involving the tetraindium cluster **1** to generate organoelement indium(III) chalcogenolates. We discuss here the insertion of monomeric fragments InR into the chalcogen–chalcogen bonds of Aryl-E-E-Aryl (E = S, Se, Te).

2. Results and discussion

2.1. Synthesis of $[RIn(\mu$-EAryl$)EAryl]_2$ (Aryl = C_6H_5, E = S (**2**), Se (**3**), Te (**4**); Aryl = p-Me-C_6H_4, E = Te, **5**)

Hexane solutions containing 1 equiv. of the tetraindium cluster **1** and 4 equiv. of the corresponding diaryl dichalcogenide (Eq. (1)) were heated under reflux until the characteristic violet color of the cluster disappeared after about 45 min. Colorless crystals of the product **2** (92% yield) precipitated directly from the reaction mixture after cooling to room temperature; compounds **3** (89%) and **5** (41%) were obtained as yellow single crystals by adding cyclopentane to the reaction mixtures and cooling to −20 °C. We were not able to grow single crystals of compound **4**, which was isolated as a yellow powder in 43% yield after concentration of the hexane solution at room temperature.

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(1)

Aryl = C_6H_5, E = S, **2**; E = Se, **3**; E = Te, **4**;
Aryl = p-Me-C_6H_4, E = Te, **5**.
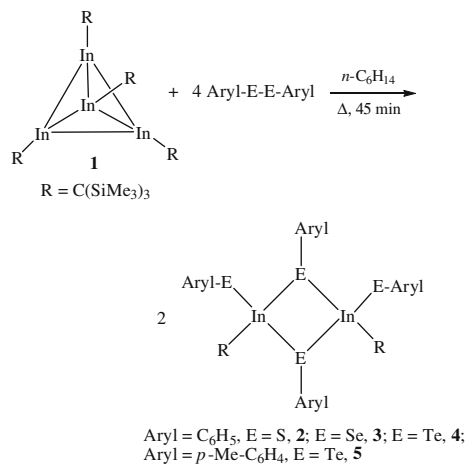
2.2. Spectroscopic and structural characterization of compounds 2–5

NMR (^{1}H and ^{13}C) studies in benzene-d_6 or toluene-d_8 solutions revealed the equivalence of the aryl groups of the arylchalcogenolato ligands. In all cases only four resonances were detected in the ^{13}C NMR spectra for phenyl carbon atoms which may indicate the existence of monomeric entities RIn(E-Aryl)$_2$ in solution. A fast exchange may occur between bridging and terminal chalcogenolato groups, however, we did not observe any alteration upon cooling. Only the mass spectrum of compound **2** revealed higher masses than calculated for the monomeric formula unit RIn(E-Aryl)$_2$ in accordance with the association observed for the solid phase. In all other cases the highest masses correspond to those of the monomeric formula units. The molecular structures of compounds **2**, **3** and **5** are depicted in Figs. 1–3, respectively. They are dimeric in the solid state containing four-membered In$_2$E$_2$ heterocycles. A centrosymmetric structure with the bulky alkyl groups on different sides of the inner ring might be expected as the most favorable one for these heterocycles, but only **2** adopts the corresponding conformation (C_i symmetry). In contrast, both bulky tris(trimethyl-silyl)methyl groups are on the same side of the inner heterocycle
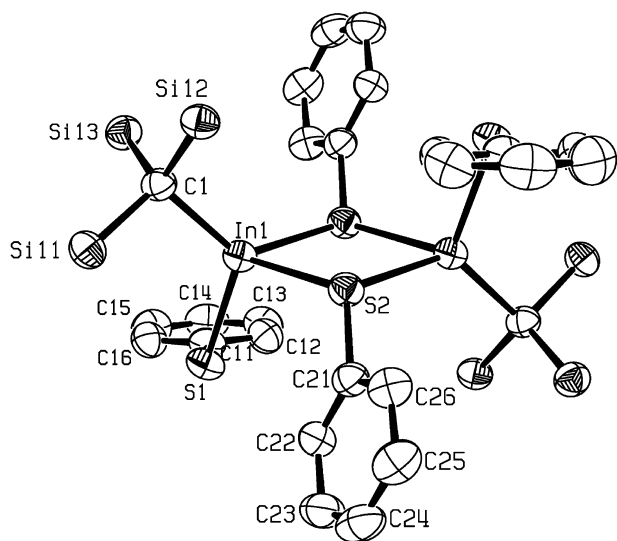

Fig. 2. Molecular structure of **3**. The thermal ellipsoids are drawn at the 50% probability level. Methyl groups and phenyl hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): In1–Se1 2.7525(8), In1–Se2 2.7312(9), In1–Se3 2.554(1), In2–Se1 2.7601(9), In2–Se2 2.7311(9), In2–Se4 2.553(1), In1–Se1–In2 91.83(2), In1–Se2–In2 92.92(2), Se1–In1–Se2 79.26(2), Se1–In2–Se2 79.13(2).
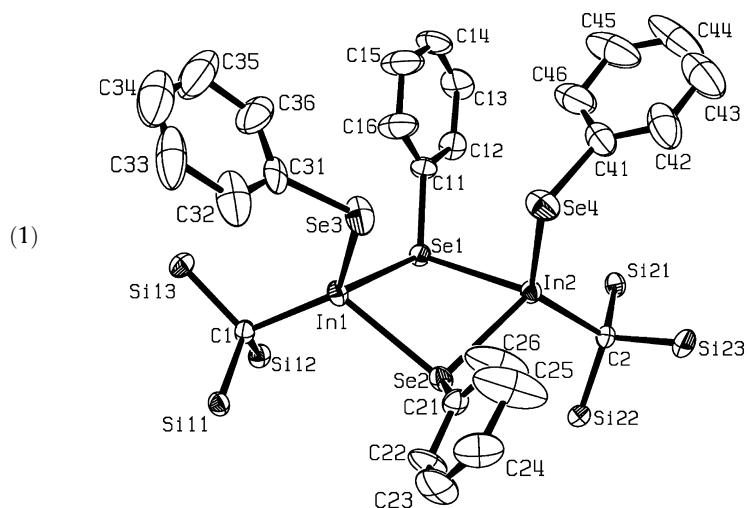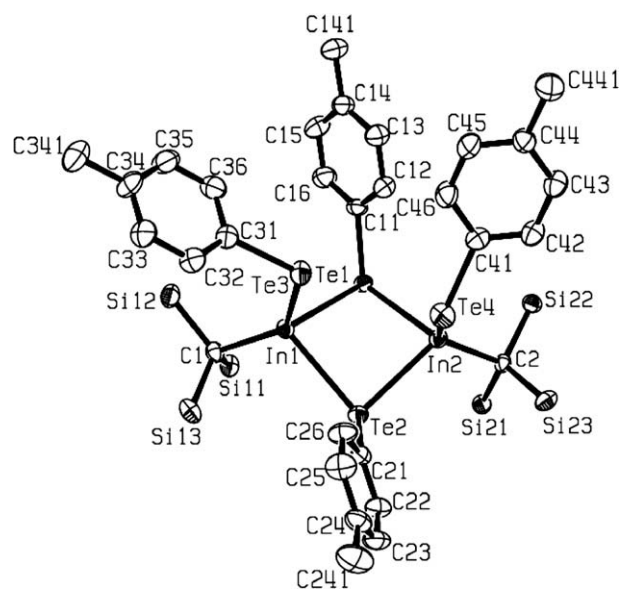

Fig. 3. Molecular structure of **5**. The thermal ellipsoids are drawn at the 50% probability level. Methyl groups and phenyl hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): In1–Te1 2.948(1), In1–Te2 2.939(1), In1–Te3 2.7632(9), In2–Te1 2.9298(8), In2–Te2 2.8981(9), In2–Te4 2.7646(9), In1–Te1–In2 87.26(2), In1–Te2–In2 88.02(2), Te1–In1–Te2 81.94(2), Te1–In2–Te2 82.97(2).

(C_{2v} symmetry) in compounds **3** and **5**. Both terminal chalcogenolato ligands and the phenyl rings attached to the bridging chalcogen atoms occupy the opposite side. Molecular symmetry causes a planar heterocycle in **2**, while the inner rings are strongly folded in **3** and **5** with angles between the normals of the respective InSe$_2$ planes of 41.06(3)° and 45.97(2)°, respectively. By this folding the steric repulsion between the bulky alkyl groups is considerably diminished, following the example of dimeric hydrazides which behave similarly [33,34]. However, the indium atoms approach to relatively short distances of 3.96 and 4.06 Å. A similar transannular In–In distance (4.00 Å) results already for the planar heterocycle of **2** which is caused by the relatively short In–S bonds. Folding and formation of a hypothetical C_{2v} isomer of **2** may be

Fig. 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and phenyl hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): In1–S1 2.452(1), In1–S2 2.626(1), In1–S2′ 2.561(1), In1–S2–In1′ 101.10(3), S2–In1–S2– 78.89(3); In1′ and S2′ generated by 1 − x, 1 − y, −z.

prevented by a further approach of the indium atoms and, hence, an enhanced electrostatic repulsion. The terminal In–E bond lengths are 2.452(1), 2.554 (av.) and 2.764 (av.) Å in **2**, **3** and **5**, respectively, while expectedly the bond lengths to the bridging chalcogen atoms are lengthened to 2.594, 2.744 and 2.929 Å on average. These values correspond well to those reported previously [10–18,35–40]. All bridging chalcogen atoms adopt a trigonal pyramidal coordination sphere. Compounds similar to **2**, **3** and **5** with arylchalcogenolato ligands in terminal and bridging positions at indium(III) centers are rare.

3. Experimental

All procedures were carried out under purified argon. *n*-Hexane and cyclopentane were dried over $LiAlH_4$. $In_4[C(SiMe_3)_3]_4$ (**1**) was prepared according to a literature procedure [2]. Diphenyl dichalcogenides (chalcogen = sulfur, selenium and tellurium) were obtained from commercial sources and used as purchased.

3.1. Synthesis of [RIn(E-Aryl)(μ-E-Aryl)]$_2$, general procedure

About 200 mg of **1** (0.14 mmol) and 4 equiv. of the corresponding diaryldichalcogenide (0.56 mmol) were dissolved in *n*-hexane (40 mL). The solutions were heated under reflux for 45 min, until the color changed from violet to pale yellow. Small quantities of colorless solids precipitated, which were filtered off. The products **2**–**5** were isolated from the reaction mixtures as described below.

3.2. [RIn(SPh)(μ-SPh)]$_2$ (**2**) [R = C(SiMe$_3$)$_3$]

Yield: 292 mg (93%, based on 0.14 mmol of **1**); colorless crystals spontaneously precipitated from the solution at 25 °C. M.p. (argon, sealed capillary): 233 °C (dec.). ^{1}H NMR (toluene-d_8, 400 MHz, 298 K): δ = 8.18 (4H, pseudo-d, *ortho*-H of phenyl), 7.05 (4H, pseudo-t, *meta*-H of phenyl), 6.95 (2H, pseudo-t, *para*-H of phenyl), 0.26 (27H, s, SiMe$_3$). ^{13}C NMR (toluene-d_8, 100 MHz, 298 K): δ = 134.9, 129.96, 129.57, 127.45 (all phenyl), 23.2 (InC), 6.1 (SiMe$_3$). IR (cm^{-1}, paraffin, CsBr): 1579m, 1404w, 1260m, 1078m,

1023m, 686m, 676m, 654m. MS (EI, 70 eV): *m/z* (%, only the most intense peak, M based on the dimer): 788 (0.5) 1/2M$^+$ + InSC$_6$H$_5$, 679 (1) 1/2M$^+$ + In, 564 (5) 1/2M$^+$, 455 (100) 1/2M$^+$ − SC$_6$H$_5$.

3.3. [RIn(SePh)(μ-SePh)]$_2$ (**3**) [R = C(SiMe$_3$)$_3$]

Yield: 296 mg (94%, based on 0.12 mmol of **1**); pale yellow crystals precipitated upon addition of cyclopentane to the *n*-hexane solution and cooling of the resulting solution to −20 °C. M.p. (argon sealed capillary): 190–192 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ = 8.38 (4H, m, *ortho*-H of phenyl), 7.69 (4H, m, *meta*-H of phenyl), 6.92 (2H, m, *para*-H of phenyl), 0.28 (27H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K): δ = 138.48, 135.89, 129.70, 128.86 (all phenyl), 25.01 (In–C), 6.29 (SiMe$_3$). IR (cm^{-1}, paraffin, CsBr): 1574m, 1257m, 1248m, 1066m, 1020m, 999m, 686m, 666m, 652m. MS (EI, 70 eV, both most intense peaks, M based on the dimer): *m/z* (%): 658 (1), 660 (1) 1/2M$^+$; 501 (60), 503 (100) 1/2M$^+$ − SeC$_6$H$_5$.

3.4. [RIn(TePh)(μ-TePh)]$_2$ (**4**) [R = C(SiMe$_3$)$_3$]

Yield: 201 mg (44%, based on 0.15 mmol of **1**); a pale yellow powder precipitated upon concentration and cooling of the *n*-hexane solution to −20 °C. M.p. (argon sealed capillary): 106–108 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K): δ = 8.24 (4H, m, *ortho*-H of phenyl), 7.86 (4H, m, *meta*-H of phenyl), 6.95 (2H, m, *para*-H of phenyl), 0.30 (27H, s, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K): δ = 141.02, 129.97, 128.32, 127.11 (all phenyl), 5.72 (SiMe$_3$), InC not detected. IR (cm^{-1}, paraffin, CsBr): 1570m, 1256m, 1015m, 997m, 687m, 652m. MS (EI, 70 eV, M based on the dimer): *m/z* (%): 523 (1), 525 (1), 527 (1) 1/2M$^+$ − C(SiMe$_3$)$_3$; 408 (65), 410 (91), 412 (80) Te$_2$(C$_6$H$_5$)$_2$.

3.5. [RIn(TeC$_6$H$_4$CH$_3$)(μ-TeC$_6$H$_4$CH$_3$)]$_2$ (**5**) [R = C(SiMe$_3$)$_3$]

Yield: 206 mg (51%, based on 0.16 mmol of **1**); yellow crystals precipitated upon addition of cyclopentane to the reaction mixture

Table 1
Crystal data and structure refinement of **2**, **3** and **5**.

	2	**3**	**5**
Formula	C$_{44}$H$_{74}$In$_2$Si$_6$S$_4$	C$_{44}$H$_{74}$In$_2$Si$_6$Se$_4$	C$_{48}$H$_{82}$In$_2$Si$_6$Te$_4$
Temperature (K)	193(2)	153(2)	153(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group [43]	P2$_1$/n (no. 14)	P2$_1$/c (no. 14)	P$\bar{1}$ (no. 2)
a (Å)	13.7490(8)	19.112(3)	10.509(3)
b (Å)	12.9662(6)	12.042(2)	13.937(4)
c (Å)	15.907(1)	24.767(4)	22.016(7)
α (°)	90	90	100.734(6)
β (°)	108.594(4)	91.358(3)	95.638(6)
γ (°)	90	90	104.470(6)
V (10^{-30} m^3)	2687.7(3)	5699(2)	3032(2)
Z	2	4	2
D$_{calc}$ (g cm^{-3})	1.396	1.535	1.717
μ (mm^{-1})	1.176	3.518	2.794
Crystal size (mm)	0.25 × 0.12 × 0.12	0.27 × 0.12 × 0.06	0.18 × 0.12 × 0.06
Radiation	Mo Kα; graphite monochromator		
Theta range (°)	1.71 ⩽ θ ⩽ 26.21	1.64 ⩽ θ ⩽ 31.43	1.50 ⩽ θ ⩽ 30.04
Index ranges	−17 ⩽ h ⩽ 16	−27 ⩽ h ⩽ 27	−14 ⩽ h ⩽ 14
	−16 ⩽ k ⩽ 15	−17 ⩽ k ⩽ 16	−19 ⩽ k ⩽ 19
	−19 ⩽ l ⩽ 19	−35 ⩽ l ⩽ 35	−30 ⩽ l ⩽ 30
Independent reflections (R$_{int}$)	3518 (0.0502)	17 447 (0.0750)	17 445 (0,0404)
Reflections observed	2900	11 039	12 181
Parameters	263	578	563
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|[I > 2\sigma(I)]$	0.0357	0.0718	0.0465
$wR_2 = \{\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2/\Sigma\|F_o\|^2\}^{1/2}$ (all data)	0.0944	0.1853	0.1044
Maximum/minimum residual (10^{30} e m^{-3})[a]	0.470/−0.478	3.085[a]/−1.262	1.376/−1.602

[a] At the indium atoms.

and cooling to −20 °C. M.p. (argon sealed capillary): 122–124 °C. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 7.99 (4H, m, *ortho*-H of phenyl), 6.79 (4H, m, *para*-H of phenyl), 2.01 (6H, s, Me of *p*-tolyl), 0.30 (27H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ = 143.65, 138.41, 130.33, 128.32 (all phenyl), 20.88 (Me of *p*-tolyl), 5.71 ($SiMe_3$), InC not detected. IR (cm^{-1}, paraffin, CsBr): 1559m, 1260m, 1246m, 1184m, 1007m, 673m, 652m. MS (EI, 70 eV, three most intense peaks, M based on the dimer): *m/z* (%): 551 (1), 553 (2), 555 (2) $1/2\ M^+ - C(SiMe_3)_3$; 436 (70), 438 (100), 440 (90) $Te_2(C_6H_4Me)_2$.

3.6. Crystal structure determinations of compounds *2, 3* and *5*

Single crystals were obtained as described before. The crystallographic data were collected with a BRUKER apex diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 [41,42] by a full-matrix least-squares method based on F^2. Crystal data, data collection parameters and structure refinement details are given in Table 1. Twinned crystals were obtained for compound **2**. A data set of a single individual could be generated at the diffractometer. The molecular structure of **3** showed a disorder of the phenyl group attached to the terminal selenium atom Se3. Its atoms were refined on split positions with occupancy factors of 0.52 and 0.48.

4. Supplementary material

CCDC 709974, 709975 and 709976 contain supplementary crystallographic data for **2**, **3** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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