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On the reactions of the tetraindiumcluster In$_4$[C(SiMe$_3$)$_3$]$_4$ with phenylselenium and phenyltellurium bromides

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Abstract

The tetraindiumcluster In$_4$[C(SiMe$_3$)$_3$]$_4$ **1** reacted with phenylselenium bromide and phenyltellurium bromide by the insertion of InR groups into the chalcogen–bromine bonds. The oxidation state of the indium atoms increased from +1 to +3. Compounds were obtained in which the indium atoms bear three different substituents (alkyl groups, phenylchalcogenido ligands, and bromine atoms). The products form dimers in the solid state via In–Se–In and In–Te–In bridges, respectively, and the bromine atoms are in terminal positions.
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1. Introduction

The tetraindiumcluster In$_4$[C(SiMe$_3$)$_3$]$_4$ **1** was obtained in our group about a decade ago [1,2]. It has an almost undistorted tetrahedron of four indium atoms in an oxidation state of +I and is available in a high yield by the reaction on indium(I) bromide with the corresponding organo lithium compound. **1** shows a remarkable and unprecedented chemical reactivity. For instance, its monomeric fragments InR are isolobal to carbon monoxide and many transition metal complexes could be synthesized in which bridging carbonyl ligands were replaced by InR groups [3]. The most interesting derivatives were the tetracarbonylnickel analogous compounds M(InR)$_4$ (M = Ni, Pt), which have a tetrahedrally coordinated central atom and for which quantum-chemical calculations verified a very efficient π-back bonding of electron density from the nickel or platinum atoms into the empty p-orbitals local-

ized at the indium atoms [4,5]. The monomeric fragments of the cluster could also be trapped by cycloaddition reactions [6]. Organoindium subhalides were formed by the careful oxidation of the cluster with halogens or halogen donors. Depending on the reaction conditions different oxidation states at the indium atoms were obtained which led to different structural motifs with two (In$_2$R$_2$X$_2$) or three indium atoms (In$_3$R$_3$X$_2$) connected by In–In single bonds or a cluster-like tetrahedral arrangement of the metal atoms (In$_4$R$_4$X$_2$) (X = Cl, Br, I) [7]. These subhalides are excellent starting materials for the generation of secondary products [8]. Chalcogen derivatives were obtained by treatment of the cluster **1** with chalcogen atom donors. Complete oxidation gave heterocubane-type molecules In$_4$R$_4$X$_4$ (X = O, S, Se, Te) [1,9], while an only partial oxidation was observed for the cluster compound In$_4$R$_4$S [10]. In order to systematically investigate oxidative addition reactions with the alkylindium(I) compound and to generate molecules possessing different functionalities for the application in secondary processes we treated the tetraindium cluster **1** with phenyl substituted selenium and tellurium bromides.

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2. Results and discussion

2.1. Synthesis of [RIn(μ-SeC₆H₅)Br]₂ 2 and [RIn(μ-TeC₆H₅)Br]₂ 3 [R = C(SiMe₃)₃]

2.1. Synthesis of $[RIn(\mu\text{-}SeC_6H_5)Br]_2$ 2 and $[RIn(\mu\text{-}TeC_6H_5)Br]_2$ 3 $[R = C(SiMe_3)_3]$

The tetraindium compound **1** and 4 equiv. of phenylselenium bromide or the corresponding tellurium compound were dissolved in *n*-hexane. A reaction did not occur upon stirring at room temperature. But relatively fast reactions occurred in boiling hexane, Eq. (1), and the violet color characteristic of the tetraindium compound disappeared within 35 or 45 min, respectively. This observation is in accordance with the usual reactivity pattern of compound **1**, and it seems that in most cases at least partial dissociation into the monomeric cluster fragments is required to initiate the formation of secondary products. In the reactions reported here small quantities of brown solids precipitated, which were filtered off. Owing to their insolubility in organic solvents their constitution remained unknown. The products **2** and **3** were isolated as pale yellow crystals after concentration of the filtrate and cooling of the solutions to 0 °C. The yields were 73% and 68%, respectively.

$$\text{(1)}$$
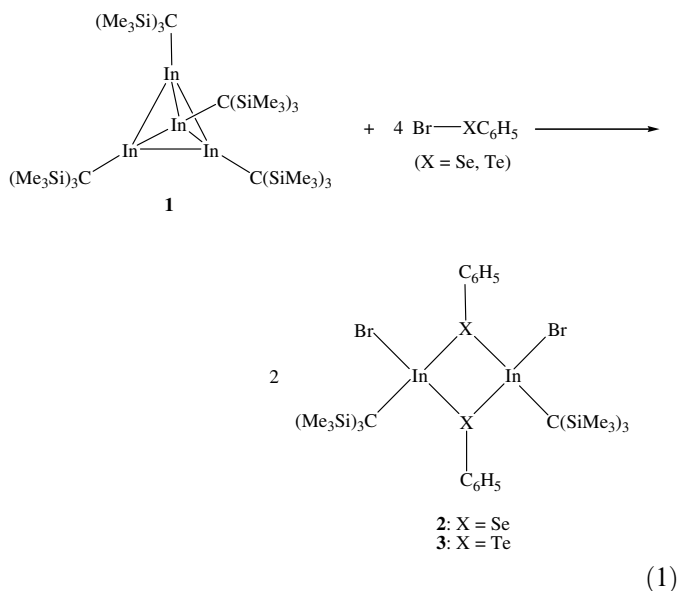
A schematic representation of the molecular structures of compounds **2** and **3** is depicted in Eq. (1). Dimers are formed in the solid state via selenium or tellurium bridges, as discussed in detail below. Each indium atom is attached to three different substituents, one bromine atom, one bulky tris(trimethylsilyl)methyl group and two phenylchalcogenide residues which act as bridging ligands to form the dimeric compounds. Thus, the formation of the products may be described by the oxidative addition of selenium–bromine or tellurium–bromine bonds to the indium(I) atoms of the starting cluster. The constitution is in accordance with the spectroscopic findings. In the ^{1}H NMR spectra we observed singlets for the trimethylsilyl groups and the characteristic pseudo-doublets and -triplets of the hydrogen atoms attached to the phenyl rings with the correct integration ratios. All resonances including those of the ^{13}C NMR spectrum are in the expected ranges and do not require a more detailed discussion. The resonance of the selenium atom in the ^{77}Se NMR spectrum of **2** occurred at $\delta = 234$ [11]. Interestingly, the EI mass spectrum of **2** showed the molecular peak of the intact dimer minus the mass of one methyl group in a low intensity. The mass of the monomer has a much higher intensity, but the most intense peak was observed for the monomer minus its phenylselenium group. In contrast the dimeric formula unit could not be detected in the EI mass spectrum of the tellurium compound **3**. The monomer occurred in a relative intensity of 4%, and once again one of the most intense peaks arose from the loss of the phenylchalcogenido group from the monomer.

The corresponding sulphur bromide starting compound, Br–S–C₆H₅, is reported to be relatively unstable [12]. We tried to generate it on a route similar to that one given in the Experimental Section for the synthesis of Br–Te–C₆H₅ by the reaction of diphenyldisulphide with elemental bromine. We reacted the product in situ with the tetraindium cluster **1**, but could not isolate any compound analogous to **2** or **3**.

2.2. Molecular structures

The molecular structures of the compounds **2** and **3** are depicted in Figs. 1 and 2, respectively. They possess four-membered In₂Se₂ or In₂Te₂ heterocycles in their molecular centres with the bromine atoms in a terminal position at each indium atom. The molecules do not have a centre of symmetry as might be expected for those heterocyclic com-
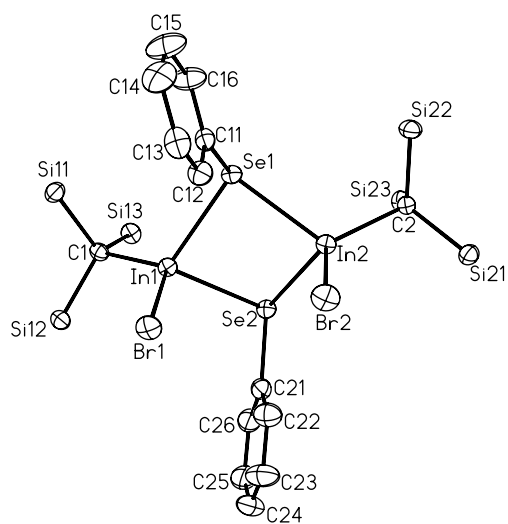

Fig. 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and phenyl hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): In1–Br1 250.01(5), In2–Br2 250.05(5), In1–Se1 268.49(5), In1–Se2 270.26(5), In2–Se1 269.78(5), In2–Se2 272.44(5), In1–C1 218.1(4), In2–C2 217.8(3), Se1–C11 193.3(4), Se2–C21 193.6(4), In1–Se1–In2 89.76(2), Se1–In1–Se2 84.19(2), Se1–In2–Se2 83.52(2), In1–Se2–In2 88.83(2).
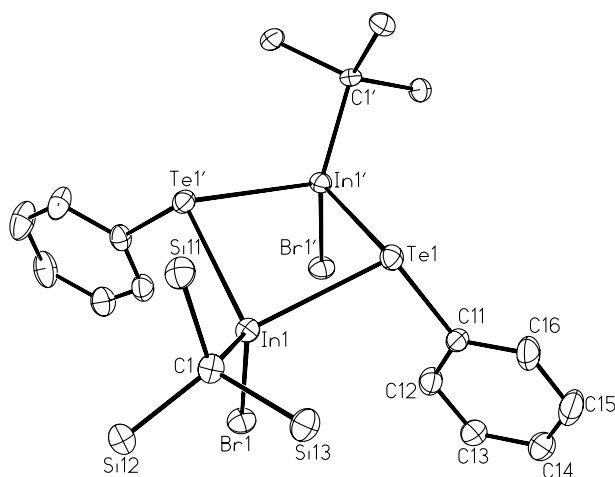
Fig. 2. Molecular structure of **3**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and phenyl hydrogen atoms are omitted. Important bond lengths (pm) and angles (°): In1–Br1 251.40(6), In1–Te1 289.35(4), In1–Te1′ 288.19(5), In1–C1 218.7(4), Te1–C11 212.2(4), In1–Te1–In1′ 86.76(1), Te1–In1–Te1′ 87.55(1); In1′ and Te1′ were generated by $-x$, y, $-z + 0.5$.

pounds. Instead the bromine atoms attached to indium and the phenyl groups at the chalcogen atoms are on the same side of the inner heterocycle (C_{2v} symmetry). This arrangement may be favoured by the bulky tris(trimethylsilyl)methyl groups which have the lowest possible steric interaction in this particular structure [13]. As a result, a strong folding across the In–In axes of the molecules was detected (40.2° and 35.7°, respectively). The In–Se (270.2 pm on average), the In–Te (288.8 pm) and the In–Br distances (250.5 pm) are in the ranges characteristic of the respective bonding situation with tricoordinated chalcogen [14–16] or terminal bromine atoms [16,17]. Owing to the considerable puckering of the heterocycles all angles of the rings are smaller than 90° (**2**: In–Se–In 89.3°; Se–In–Se 83.9°; **3**: In–Te–In 86.8°; Te–In–Te 87.5°). Thus, in the tellurium compound the slightly larger angle is observed at indium, while for the selenium compound the most acute angle occurs at indium. Clearly this is due to the relatively large radius of the tellurium atoms. The indium atoms have a strongly distorted tetrahedral surrounding, while the selenium or tellurium atoms have a pyramidal coordination sphere.

3. Experimental

All procedures were carried out under purified argon. n-Hexane was dried over $LiAlH_4$. $In_4[C(SiMe_3)_3]_4$ **1** was obtained according to a literature procedure [1]. Commercially available $Br–Se–C_6H_5$ and $Te_2(C_6H_5)_2$ (Sigma–Aldrich) were employed without further purification. $Br–Te–C_6H_5$ [18] was obtained according to a procedure reported for the synthesis of the corresponding selenium derivative [12,19]: Diphenylditelluride was dissolved in 20 ml of $CHCl_3$, cooled to 0 °C and treated with the stoichiometric quantity of elemental bromine dissolved in the

same solvent. After stirring for 1 h at 0 °C the solvent was removed in vacuum. $Br–Te–C_6H_5$ remained as a brownish oil, which was directly employed for further reactions.

3.1. Synthesis of $[RIn(Br)(\mu-Se–C_6H_5)]_2$ **2**

$In_4[C(SiMe_3)_3]_4$ **1** (0.180 g, 0.130 mmol) and phenylselenium bromide (0.123 g, 0.521 mmol) were dissolved in 40 ml of n-hexane. The solution was heated under reflux for 35 min, until the color changed from violet of **1** to pale yellow. A small quantity of a brown amorphous solid precipitated, which was filtered off. The filtrate was concentrated and cooled to −15 °C to yield pale yellow crystals of the product **2**. Yield: 0.237 g (73%); the crystals of **2** include one molecule of n-hexane per formula unit of the dimer. M.p. (argon, sealed capillary): 209 °C (dec.). ^1H NMR (C_6D_6, 400 MHz, 298 K): $\delta = 8.24$ (4H, pseudo-d, o-H of phenyl), 7.04 (4H, pseudo-t, m-H of phenyl), 6.93 (2H, pseudo-t, p-H of phenyl), 0.31 (54H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): $\delta = 135.1$ (o-C of phenyl), 129.9 (m-C of phenyl), 129.3 (p-C of phenyl), 124.2 (i-C of phenyl), 23.1 (In–C), 5.7 ($SiMe_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz, 298 K): $\delta = -2.0$. ^{77}Se NMR (C_6D_6, 76.3 MHz, 298 K): $\delta = 234$. IR (cm^{-1}; paraffin; CsBr): 1576 w (phenyl); 1463 vs, 1377 vs (paraffin); 1297 vw, 1251 m δCH_3; 1157 w, 1060 vw, 1018 w, 998 w νCC; 855 vs, 777 w, 734 m ρCH_3(Si); 720 m (paraffin); 686 m, 674 m phenyl, $\nu_{as}SiC$; 653 m $\nu_s SiC$; 608 m, 461 m νInC, νSeC. MS (EI, 70 eV): m (%) (the most intense peaks only, isotopic patterns are in agreement with calculated spectra) = 1149 [M(dimer)$^+$−CH_3, 0.03], 1009 (M$^+$−SeC_6H_5, 1), 582 (1/2M$^+$, 12), 427 (1/2M$^+$−SeC_6H_5, 100).

3.2. Synthesis of $[RIn(Br)(\mu-Te–C_6H_5)]_2$ **3**

$In_4[C(SiMe_3)_3]_4$ **1** (0.210 g, 0.152 mmol) was dissolved in 40 ml of n-hexane and added to phenyltellurium bromide (0.177 g, 0.622 mmol; generated in situ as described before). The solution was heated under reflux for 45 min, until the color changed from violet of **1** to pale yellow. A small quantity of a brown solid precipitated, which was filtered off. The filtrate was concentrated and cooled to −15 °C to yield pale yellow crystals of the product **3**. Yield: 0.262 g (68%). M.p. (argon, sealed capillary): 180 °C (dec.). ^1H NMR (C_6D_6, 400 MHz, 298 K): $\delta = 8.26$ (4H, pseudo-d, o-H of phenyl), 7.01 (4H, pseudo-t, m-H of phenyl), 6.94 (2H, pseudo-t, p-H of phenyl), 0.35 (54H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 100 MHz, 298 K): $\delta = 138.9$ (o-C of phenyl), 130.3 (m-C of phenyl), 129.8 (p-C of phenyl), 110.2 (i-C of phenyl), 19.5 (In–C), 5.9 ($SiMe_3$). IR (cm^{-1}; paraffin; CsBr): 1571 s (phenyl); 1464 vs (paraffin); 1435 vs, 1403 m δCH_3; 1377 vs (paraffin); 1329 vw, 1291 w, 1257 vs δCH_3; 1190 vw, 1178 vw, 1157 vw, 1065 vw, 1055 vw, 1013 s, 996 s νCC; 853 vs, 777 s, 731 vs ρCH_3(Si); 686 s, 673 vs phenyl, $\nu_{as}SiC$; 652 vs $\nu_s SiC$; 606 m, 449 m νInC, νTeC. MS (EI, 70 eV): m (%) (the most intense peaks only,

Table 1
Crystal data and structure refinement of **2** and **3**[a]

	2	**3**
Formula	$C_{38}H_{78}Br_2In_2Se_2Si_6$	$C_{37}H_{64}Br_2In_2Si_6Te_2$
Temperature (K)	153(2)	153(2)
Crystal system	Monoclinic	Orthorhombic
Space group [21]	$P2_1/n$ (no. 14)	$Pbcn$ (no. 60)
a (pm)	1371.4(1)	1735.2(1)
b (pm)	1878.5(2)	1409.2(1)
c (pm)	2074.9(2)	2150.7(2)
α (°)	90	90
β (°)	94.675(2)	90
γ (°)	90	90
V (10^{-30} m^3)	5327.7(8)	5259.1(7)
Z	4	4
D_{calc} (g cm^{-3})	1.560	1.670
μ (mm^{-1})	3.891	3.644
Crystal size (mm)	$0.25 \times 0.06 \times 0.03$	$0.18 \times 0.12 \times 0.07$
Radiation	Mo Kα; graphite monochromator	Mo Kα; graphite monochromator
θ Range for data collection (°)	$1.46 \leqslant \theta \leqslant 30.03$	$1.86 \leqslant \theta \leqslant 28.05$
Index ranges	$-19 \leqslant h \leqslant 19$, $-26 \leqslant k \leqslant 26$, $-28 \leqslant l \leqslant 29$	$-22 \leqslant h \leqslant 22$, $-18 \leqslant k \leqslant 18$, $-27 \leqslant l \leqslant 28$
Reflections observed	8589	5118
Independent reflections (R_{int})	15 449 (0.0734)	6377 (0.0762)
Parameters	471	244
$R = \sum||F_o| - |F_c||/\sum|F_o|$ $[I > 2\sigma(I)]$	0.0390	0.0415
$w_2 = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum|F_o|^2\}^{1/2}$ (all data)	0.0687	0.0939
Maximum/minimum residual electron density (10^{30} e m^{-3})	1.072/−0.557	0.926/−0.732

[a] Programme SHELXL-97 [20]; solutions by direct methods, full matrix refinement with all independent structure factors.

isotopic patterns are in agreement with calculated spectra) = 632 (1/2M$^+$, 4), 617 (1/2M$^+$−CH$_3$, 3), 427 (1/2M$^+$−TeC$_6$H$_5$, 72).

3.3. Crystal structure determinations of compounds 2 to 3

Single crystals were obtained on cooling of saturated solutions in *n*-hexane (**2**) or cyclopentane (**3**) (20/−15 °C). The crystallographic data were collected with a Bruker Smart APEX diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 [20] 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. The crystals of **2** enclose one *n*-hexane molecule per formula unit. One cyclopentane molecule per formula unit was detected in the structure of **3**. It is disordered over a twofold crystallographic rotation axis. Its hydrogen atoms were not considered.

4. Supplementary material

CCDC 619212 and 619213 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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