The insertion of chalcogen atoms into the In–In bond of tetrakis[bis(trimethylsilyl)methyl]diindane(4): monomeric compounds with In–S–In, In–Se–In, and In–Te–In groups [1]

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Abstract

The insertion of chalcogen atoms into the indium–indium bond of tetrakis[bis(trimethylsilyl)methyl]diindane(4) (1) by the reaction of 1 with the chalcogen atom donors propylene sulphide, triethyl phosphonium selenide or telluride yields homoleptic compounds with up to now unknown $R_2In-S-InR_2$ (2), $R_2In-Se-InR_2$ (3), and $R_2In-Te-InR_2$ (4) groups. All products are monomeric, both in solution and in the solid state, as shown by the cryoscopically determined molar masses and crystal structure determinations. The indium–chalcogen–indium bridges are bent and exhibit angles of 112.4(1) and 116.8(2)° (2), 109.96(3)° (3), and 105.42(2)° (4).

Keywords: Indium–indium bond; Chalcogen insertion; Indium–sulphur bond; Indium–selenium bond; Indium–tellurium bond

1. Introduction

Tetrakis[bis(trimethylsilyl)methyl]diindane(4) 1 was the first isolated and fully characterized organoindium derivative with the indium atoms in an oxidation state of +II and an In–In single bond [1]. While many successful reactions with the dialuminium(4) [2] and digallium(4) analogues [3] reveal remarkable reactivity of these compounds with the formation of radical anions, deprotonation and insertion of atoms and molecules [4–10], little is known about the reactivity of the di-indium(4) derivative 1. We wish to report here on the insertion of sulphur, selenium, and tellurium atoms into the indium–indium bond of 1; up to now all attempts to insert an oxygen atom have been unsuccessful. As apparent from a large number of recent publications, organochalcogenides of Al, Ga, and In are at present of great interest in third main-group chemistry [11].
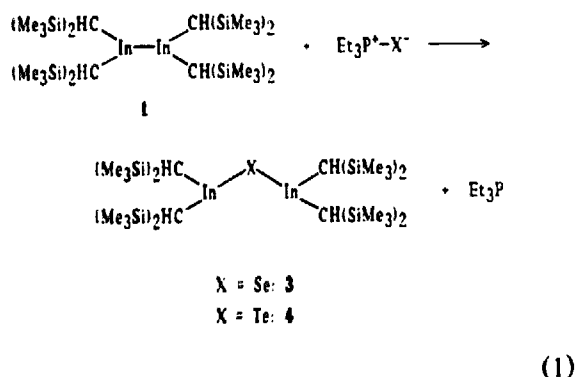
2. Syntheses of the tetraalkyl diindium sulphide (2), selenide (3), and telluride (4) derivates

Triethylphosphonium chalcogenides Et_3PX (X = S [12], Se, Te [13]) were successfully applied to the insertion of sulphur [6,7], selenium [7], and tellurium atoms [8,9] into Al–Al or Ga–Ga bonds, and gave the chalcogen-bridged dialuminium and digallium derivatives in more than 80% yield by reaction with the dialuminium(4) [2] and digallium(4) [3] compounds. Correspondingly, the orange–red colour of 1 disappears immediately when the diindane(4) 1 is treated with a stoichiometric amount of Et_3PSe or Et_3PTe in toluene at room temperature. After evaporation of the solvent and recrystallization from n-pentane, colourless crystals of the diindium selenide 3 and yellowish crystals of the
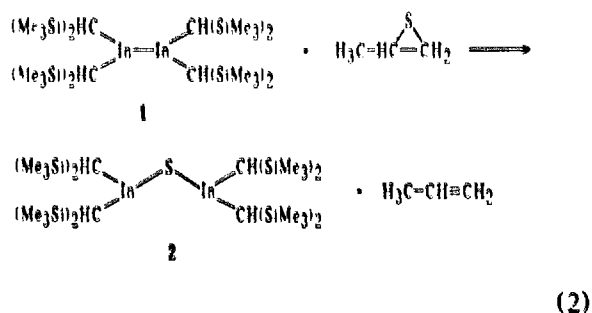
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[1] Dedicated to Professor Dr. R. Blachnik on the occasion of his 60th birthday.

telluride **4** can be isolated in more than 85% yield (Eq. (1)):

(Me₃Si)₂HC CH(SiMe₃)₂
         In—In   · Et₃P⁺–X⁻ ——→
(Me₃Si)₂HC CH(SiMe₃)₂

1

(Me₃Si)₂HC X CH(SiMe₃)₂
         In   In   · Et₃P
(Me₃Si)₂HC   CH(SiMe₃)₂

X = Se: **3**
X = Te: **4**

(1)

With Et₃PS and **1**, however, no reaction was observed under similar conditions over a period of several days. Owing to the lower thermal stability of **1** compared with the corresponding dialuminium(4) or digallium(4) compounds, complete decomposition occurred in boiling n-hexane with precipitation of elemental indium and formation of tris[bis(trimethylsilyl)methyl]indane [1]; the In₂S derivative **2** could not be detected NMR spectroscopically. As a sulphur donor we finally used propylene sulphide, which reacts with **1** at room temperature within 3 h to yield almost quantitatively the diindium sulphide derivative **2** (Eq. (2)):

(Me₃Si)₂HC CH(SiMe₃)₂   S
         In—In   · H₃C–HC—CH₂ ——→
(Me₃Si)₂HC CH(SiMe₃)₂

1

(Me₃Si)₂HC S CH(SiMe₃)₂
         In   In   · H₃C–CH=CH₂
(Me₃Si)₂HC   CH(SiMe₃)₂

2

(2)

All three products **2** (X = S), **3** (X = Se), and **4** (X = Te) are monomeric in benzene solutions, as shown by the cryoscopically determined molar masses. While both compounds **2** and **3** are colourless, the tellurium derivative **4** crystallizes as a yellowish solid. **2** and **3** show only one absorption in the UV/vis spectra, at 220 and 240 nm respectively, which are characteristic of bis(trimethylsilyl)methyl compounds with three-coordinated aluminium, gallium [3] or indium atoms [1] and possibly indicate an interaction between C–Si bonds of the substituents with the empty p-orbital at the central atom by hyperconjugation [14]. Besides the absorption at 240 nm, the UV/vis spectrum of the tellurium compound **4** exhibits a broad shoulder at about 320 nm

with a half-width of approximately 100 nm, which corresponds to its yellow colour. The IR spectra of **2**, **3** and **4** are almost identical due to their similar molecular structures, and only a very small shift of the In–C stretching vibrations is observed on going from sulphur to the heavier tellurium atom (**2**: 496, 480; **3**: 494, 478; **4**: 492, 476 cm⁻¹). The In₂S stretching vibration could be detected at 370 cm⁻¹; the In₂Se and In₂Te bands are out of range of conventional IR techniques (less than 225 cm⁻¹). While the chemical shift of the SiMe₃ resonances is not affected by the different chalcogen atoms in both ¹H and ¹³C NMR spectra, the resonances of the CH group bound to indium show a significant shift to higher field with the lighter chalcogen atom; similar effects are observed in the series with the corresponding aluminium [6–8] and gallium [7,9] compounds. All derivatives with two aluminium or gallium atoms bridged by a chalcogen atom (without oxygen) [6–9] or a CH₂ group [15] and coordinated by four bulky bis(trimethylsilyl)methyl substituents show, in low-temperature NMR experiments in toluene-d₈, a hindered rotation, which is probably caused by sterical interactions. A similar effect could not be observed with the products **2** to **4**, possibly due to the larger radius of the indium atom with respect to aluminium or gallium and as a consequence a smaller hindrance of the free rotation by sterical restrictions. The melting points of the three derivatives **2** to **4** are, independent of the chalcogen atom, determined to 130°C.

3. Crystal structures

All bis(trimethylsilyl)methyl compounds with Al–CH₂–Al [15], Al–S–Al [6], Al–Se–Al [7], Al–Te–Al [8], Ga–S–Ga [7], Ga–Se–Ga [7], Ga–Te–Ga [9] bridges crystallize isotypically in the space group *Pcca* with the bridging atom located on a two-fold crystallographic rotation axis and a bent element–heteroatom–element group. The corresponding Al–O–Al derivative exhibits, however, another crystal structure and shows a linear Al–O–Al group with NMR evidence for some π-interactions between the oxygen lone pairs and the empty p-orbitals at the aluminium atoms [10]. The In–S–In derivative **2** (Fig. 1) crystallizes in the space group *P*1̄ (Tables 1 and 2), with the sulphur atom disordered in two positions and a quite different molecular conformation compared with the Al or Ga analogues. Only the In–Se–In derivative **3** (Fig. 2) crystallizes isotypic to the aluminium or gallium chalcogenides in the orthorhombic space group *Pcca* with half a molecule in the asymmetric unit (Table 3). **4** (X = Te) reveals the monoclinic space group *C*2/*c* (Table 4) with a whole molecule in the asymmetric unit. Nevertheless, its molecular structure is, as shown in Figs. 2 and 3, very similar to that of the Al or Ga derivatives.
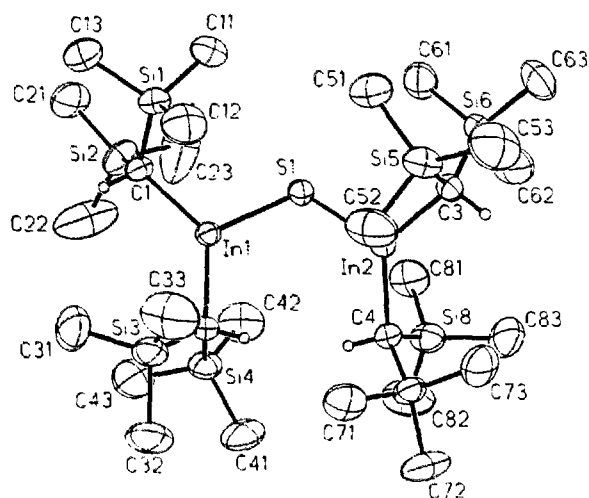
Fig. 1. Molecular structure and numbering scheme of 2 (X = S); the thermal ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity; methine hydrogen atoms with arbitrary radius. Only one position of the disordered sulphur atom is included; the atoms Si7 and C2 are not labelled.

The In-X-In groups are bent with the most acute angle (105.42°, Table 5) at the Te atom in compound 4 (In-S-In 112.4 and 116.8°; In-Se-In 109.96°). The

magnitude of the angle is, as in the Al or Ga derivatives, probably determined mainly by sterical requirements and the long In-Te bonds allow the closest approach to the ideal value of 90°, as found for instance in the H_2X compounds [18]. As expected, the indium-chalcogen bond lengths become larger with the heavier chalcogen atom (In-S 242.6 and 236.6 pm, In-Se 251.9 pm, In-Te 271.7 pm). While a multitude of organo element compounds is known with In-S bonds [11,19-22], only a few derivatives are described with In-Se [11,19,21,23,24] or In-Te [11,21,22,25] bonds. As recently discussed [7], a strong correlation exists in these derivatives between the bond lengths (Al-X, Ga-X) and the coordination number of the chalcogen atom, and the shortest bonds are observed with two-coordinated chalcogen atoms. Accordingly, the In-X bonds in compounds 2 to 4 are among the shortest found in the literature. A very short In-Se bond length of 237.6 pm was recently observed in a compound with a terminal selenium atom and a coordination number of 1 at selenium [26]. The In-X bonds are shorter than calculated from the covalent radii of indium (from the In-In bond in 1 [1]) and sulphur, selenium or tellurium [27] (calculated: In-S 243, In-Se 258, In-Te 276). A much

Table 1
Crystal data and data collection parameters for the diindium chalcogenides 2, 3, and 4

	2	3	4
Formula	$C_{28}H_{76}In_2SSi_8$	$C_{28}H_{76}In_2SeSi_8$	$C_{28}H_{76}In_2Si_8Te$
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$; No. 2 [16]	Pcca; Nr. 54 [16]	C2/c; Nr. 15 [16]
Z	2	4	8
Temperature (K)	293(2)	293(2)	293(2)
d_{calc} (g cm^{-1})	1.228	1.287	1.324
a (pm)	923.3(2)	2382.3(8)	3618.2(7)
b (pm)	1199.4(2)	1666.34(6)	1237.7(2)
c (pm)	2381.3(3)	1230.59(5)	2359.6(5)
α (°)	92.73(1)	90	90
β (°)	92.39(1)	90	109.10(3)
γ (°)	112.27(1)	90	90
V (10^{-30} m^3)	2432.5(7)	4885.2(3)	9985(3)
μ (mm^{-1})	1.204	1.901; empirical absorption correction	1.704; empirical absorption correction
Crystal size (mm^3)	0.3 × 0.25 × 0.22	0.7 × 0.5 × 0.4	0.7 × 0.5 × 0.4
Four-cycle diffractometer	Siemens P4	AED 2	AED 2
Radiation	Mo Kα graphite monochromator		
Range	$3.4 \le 2\theta \le 60°$	$3.4 \le 2\theta \le 52°$	$3.5 \le 2\theta \le 50°$
Reciprocal space	$-1 \le h \le 9$	$0 \le h \le 29$	$0 \le h \le 42$
	$-15 \le k \le 12$	$-20 \le k \le 0$	$0 \le k \le 14$
	$-25 \le l \le 25$	$0 \le l \le 15$	$-28 \le l \le 26$
Scan mode	ω	ω	ω
Independent reflections	5968	4793	8794
Number of reflections with $F > 4\sigma(F)$	5540	3057	6144
Program	SHELXTL, SHELXL-93 [17]; solution by direct methods; full-matrix refinement with all independent structure factors		
Parameters	352	189	376
R, wR^2	0.035; 0.128	0.042; 0.068	0.040; 0.070
Max. residual (10^{-30} e m^{-3})	0.70	0.56	0.63
Min. residual (10^{-30} e m^{-3})	-0.41	-0.38	-0.57

$R = \Sigma ||F_0| - |F_c||/\Sigma |F_0| (F > 4\sigma(F))$; $wR^2 = \{\Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma w (F_0^2)^2\}^{1/2}$ (all data)

more pronounced shortening is observed with the aluminium–chalcogen bonds, while the gallium–chalcogen bond lengths are in excellent agreement with the sum of the covalent radii [7]. This is a clear indication that the most part of the shortening is due to different ionic contributions caused by the electronegativity differences between the third main-group elements with aluminium as the most electropositive and gallium the most electronegative element in the series Al, Ga, and In [23]. The In–C bond lengths are within the range normally observed in organo indium derivatives (2: 215.9 pm; 3: 216.9 pm; 4: 217.5 pm); they are about 2 pm shorter than in the starting compound 1 (218.9(5) pm), with indium in the oxidation state of +II [1].

The molecular conformation is approximately staggered in the compounds 3 and 4, similar to the aluminium or gallium derivatives and probably due to a minimization of sterical interactions between the bulky substituents; the angles between the normals of the InC_2 planes amount to 80.3° (3) and 72.2° (4). The molecular centre is much more flattened in the diindium sulphide 2, with an angle of 41.7° between the normals of the InC_2 planes. The structure approaches planarity, which is expected for an effective π-interaction between one lone-pair of the sulphur atom and the empty p-orbitals at indium. Each of the disordered sulphur atoms lies almost ideally within one of the InC_2 planes (S1 9 pm above In1C1C2, 33 pm above In2C3C4; S2 11 pm

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (10^{-22} m^2) for the atoms of the asymmetric unit in 2 (excluding hydrogen atoms)

Atom	x	y	z	U_{eq}
In1	0.08870(4)	0.77241(3)	0.17247(2)	4.36(1)
In2	0.26879(5)	0.83623(3)	0.33331(2)	4.86(2)
S1*	0.0505(3)	0.7130(2)	0.2681(1)	4.81(5)
S2*	0.0962(4)	0.6989(3)	0.2621(2)	4.81(5)
C1	−0.0309(6)	0.6223(4)	0.1116(2)	4.8(1)
S11	0.0230(2)	0.4912(1)	0.12506(7)	5.91(4)
C11	−0.080(1)	0.4038(6)	0.1832(3)	9.8(3)
C12	0.2362(9)	0.5437(7)	0.1410(4)	9.9(3)
C13	−0.025(1)	0.3849(7)	0.0613(3)	10.6(3)
S12	··0.2417(2)	0.5975(2)	0.1023(1)	8.15(6)
C21	−0.360(1)	0.4623(7)	0.0573(4)	11.2(3)
C22	−0.263(1)	0.7235(9)	0.0661(6)	19.0(7)
C23	−0.328(1)	0.585(2)	0.1695(5)	23.3(9)
C2	0.2247(7)	0.9607(5)	0.1613(2)	5.1(1)
S13	0.3531(3)	0.9773(2)	0.10186(9)	8.2(6)
C31	0.242(1)	0.9158(9)	0.0347(3)	14.8(5)
C32	0.480(1)	1.1376(7)	0.0940(4)	13.7(4)
C33	0.482(1)	0.8959(9)	0.1141(5)	14.3(4)
S14	0.1098(2)	1.0574(2)	0.16822(9)	7.56(5)
C41	0.239(1)	1.2106(6)	0.1987(4)	11.3(3)
C42	−0.052(1)	0.9926(8)	0.2165(4)	11.7(3)
C43	0.019(1)	1.0735(9)	0.0995(4)	14.1(4)
C3	0.3576(7)	0.7312(5)	0.3854(2)	5.6(1)
S15	0.4771(2)	0.6693(2)	0.34233(9)	7.27(5)
C51	0.357(1)	0.5241(6)	0.3037(3)	9.3(2)
C52	0.573(1)	0.7761(7)	0.2881(4)	11.2(3)
C53	0.636(1)	0.6513(9)	0.3872(4)	12.6(3)
S16	0.2101(2)	0.6259(2)	0.42894(7)	6.96(5)
C61	0.0400(9)	0.5143(7)	0.3870(3)	10.1(3)
C62	0.135(1)	0.7129(8)	0.4787(4)	12.7(4)
C63	0.299(1)	0.5425(8)	0.4728(4)	11.7(3)
C4	0.3235(7)	1.0287(5)	0.3375(2)	5.3(1)
S17	0.5357(2)	1.1241(2)	0.33759(8)	6.51(5)
C71	0.6084(8)	1.1120(7)	0.2672(3)	9.1(2)
C72	0.579(1)	1.2874(6)	0.3538(4)	11.5(3)
C73	0.6516(9)	1.0764(8)	0.3898(4)	10.7(3)
S18	0.2083(3)	1.0636(2)	0.39316(9)	7.66(6)
C81	0.0112(9)	0.9426(8)	0.3924(4)	10.5(3)
C82	0.174(1)	1.2035(8)	0.3803(5)	13.9(4)
C83	0.307(1)	1.0788(9)	0.4644(3)	12.4(3)

* Statistically disordered sulphur atom.

above In2C3C4, 42 pm above In1C1C2), but there are no correlations with the In–S bond lengths, which are both short for S2 (236.6 pm) and both long for S1 (242.6 pm on average). Though the singular structure of 2 might be interpreted in terms of an approach to a conformation which is optimal for a π-interaction, there is, in contrast to the Al–O–Al derivative [10], no spectroscopic evidence that such an interaction plays an important role in describing this molecule.

4. Experimental

All procedures were carried out under an atmosphere of purified argon in dried solvents (n-pentane over LiAlH$_4$; toluene over Na/benzophenone). Compound 1 was prepared according to Ref. [1], Et$_3$PSe and Et$_3$PTe according to Ref. [13]; Et$_3$PTe crystallizes from toluene with half a molecule of the solvent per formula unit; propylene sulphide from Aldrich-Chemie was employed without further purification.

4.1. Synthesis of Tetrakis[bis(trimethsilyl)methyl]diindium sulphide 2

10.2 ml of a 0.064 M solution of propylene sulphide (0.65 mmol) in toluene was added to a solution of 0.56 g (0.65 mmol) of 1 in toluene. After 3 h at room temperature the colour of the solution changed from orange–red to colourless. The solvent was removed in vacuo and the residue recrystallized from n-pentane. Yield: 0.54 g (92%) colourless, slightly air-sensitive platelets. M.p. (under Ar, closed capillary) 130.5°C.
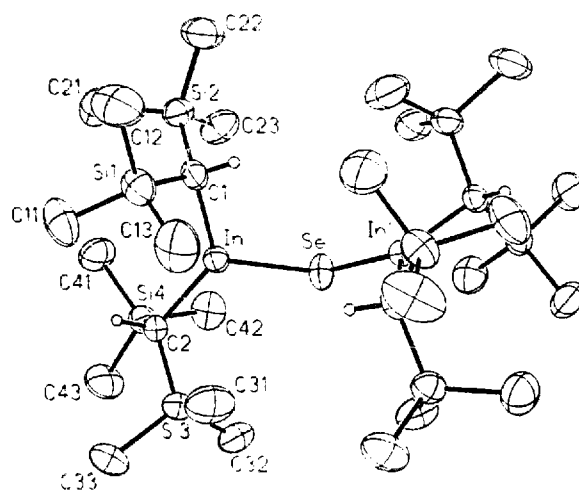

Fig. 2. Molecular structure and numbering scheme of 3 (X = Se); the thermal ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity.

Molar mass (cryoscopically in benzene): obs. 915, calc. 899.3 g mol^{-1}. Mass spectrum (CI, isobutane): 433.1 (100%), 434.1 (40%), 435.1 (20%) In[CH(SiMe$_3$)$_2$]$_2$; 738.7 (0.4%), 739.5 (0.1%) M$^+$-CH(SiMe$_3$)$_2$; 882.7 (0.3%), 883.8 (0.1%) M$^+$-CH$_3$; 898.5 (0.1%) M$^+$. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.63 (InCH), 0.31 ppm (SiMe$_3$). ^{13}C NMR (C$_6$D$_6$ 75.5 MHz): δ 25.2 (InC), 4.6 ppm (SiMe$_3$). IR (paraffin, CsBr plates, cm^{-1}): 1292 m, 1246 vs δCH$_3$; 1018 vs δCH; 936 s, 906 m, 841 vs, 785 s, 770 vs, 754 vs, 727 m ρCH$_3$(Si); 685 s, 660 vs ν$_{as}$SiC; 610 s ν$_s$SiC; 496 s, 480 m νInC; 370 s νIn$_2$S; 330 w, 285 w, 278 w δSiC. UV/vis (n-pentane) (ε): 220 nm (86000).

Table 3
Atomic coordinates and equivalent isotropic displacement parameters (10^{-22} m^2) for the atoms of the asymmetric unit in 3 (excluding hydrogen atoms)

Atom	x	y	z	U$_{eq}$
In	0.58018(1)	0.73573(2)	0.18673(2)	4.439(9)
Se	0.5000	0.64899(4)	0.2500	6.21(2)
C1	0.6071(2)	0.8324(2)	0.2929(3)	5.1(1)
Si1	0.62468(6)	0.92662(8)	0.2176(1)	6.79(4)
C11	0.6823(2)	0.9101(3)	0.1195(4)	9.9(2)
C12	0.6471(3)	1.0086(3)	0.3102(4)	12.2(2)
C13	0.5618(2)	0.9628(3)	0.1416(5)	11.3(2)
Si2	0.65659(6)	0.79294(8)	0.3979(1)	6.20(4)
C21	0.7313(2)	0.8000(3)	0.3541(4)	9.1(2)
C22	0.6495(2)	0.8504(3)	0.5280(4)	9.8(2)
C23	0.6414(2)	0.6863(3)	0.4305(4)	8.5(2)
C2	0.6188(2)	0.6947(2)	0.0373(3)	4.9(1)
Si3	0.56716(6)	0.70070(9)	−0.0771(1)	6.42(4)
C31	0.5202(2)	0.7896(3)	−0.0593(4)	10.8(2)
C32	0.5228(2)	0.6093(3)	−0.084(4)	9.2(2)
C33	0.6049(2)	0.7167(4)	−0.2094(3)	10.2(2)
Si4	0.65886(5)	0.59969(8)	0.0548(1)	5.93(3)
C41	0.7240(2)	0.6214(3)	0.1350(4)	9.3(2)
C42	0.6178(2)	0.5216(3)	0.1276(4)	8.9(2)
C43	0.6815(2)	0.5568(3)	−0.0783(4)	10.0(2)

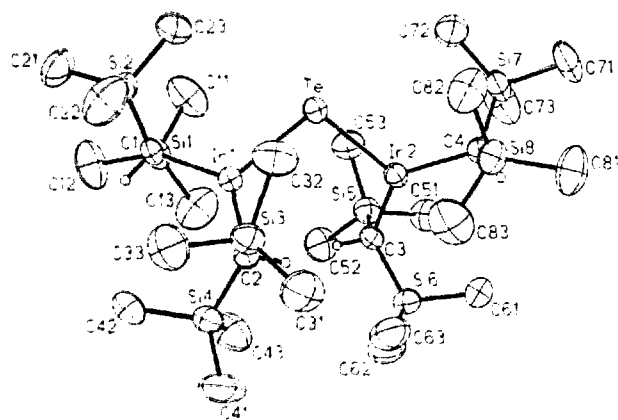Fig. 3. Molecular structure of 4 (X = Te); the thermal ellipsoids are drawn at the 40% probability level; methyl hydrogen atoms are omitted for clarity.

4.2. Synthesis of Tetrakis[bis(trimethsilyl)methyl]diindiumselenide 3

A solution of 0.178 g (0.90 mmol) of Et_3PSe in 25 ml of toluene was added to a solution of 0.754 g (0.87 mmol) of 1 in 25 ml of toluene. The colour changed immediately from orange–red to colourless. The solution was stirred at room temperature for 1 h, the solvent evaporated and the residue recrystallized from n-pentane. Yield: 0.728 g (88%), colourless, slightly air-sensitive platelets. M.p. (under Ar closed capillary) 130°C. Molar mass (cryoscopically in benzene): obs. 895, calc. 946.2 g mol^{-1}. Mass spectrum (CI, isobutane): 433.3 (100%) $In[CH(SiMe_3)_2]_2$; 947.2 (0.4%), 948.0 (1.1%), 949.3 (0.9%) $M + H^+$. ^1H NMR $(C_6D_6$, 300 MHz): δ 0.75 (InCH), 0.30 ppm $(SiMe_3)$. ^{13}C NMR $(C_6D_6$, 75.5

Table 4
Atomic coordinates and equivalent isotropic displacement parameters $(10^{-22}$ $m^2)$ for the atoms of the asymmetric unit in 4 (excluding hydrogen atoms)

Atom	x	y	z	U_{eq}
Te	0.319024(9)	0.75144(3)	−0.09014(1)	6.06(1)
In1	0.368276(9)	0.67751(3)	0.01632(1)	4.697(9)
In2	0.366003(9)	0.82087(3)	−0.15183(1)	4.689(9)
C1	0.3502(1)	0.5282(3)	0.0474(2)	4.8(1)
Si1	0.35323(5)	0.4129(1)	−0.00206(7)	6.79(4)
C11	0.3091(2)	0.4034(5)	−0.0685(3)	12.1(3)
C12	0.3626(2)	0.2833(5)	0.0409(3)	13.0(3)
C13	0.3954(2)	0.4311(6)	−0.0306(3)	13.3(3)
Si2	0.30452(4)	0.5438(1)	0.06727(7)	6.66(4)
C21	0.2908(2)	0.4150(5)	0.0953(3)	11.6(2)
C22	0.3141(2)	0.6435(6)	0.1304(3)	13.3(3)
C23	0.2623(2)	0.5908(6)	0.0036(3)	11.7(3)
C2	0.4177(1)	0.7808(4)	0.0628(2)	5.6(1)
Si3	0.40198(4)	0.8914(1)	0.10376(7)	6.76(4)
C31	0.4320(2)	1.0150(4)	0.1071(3)	11.0(2)
C32	0.3502(2)	0.9339(5)	0.0645(3)	9.5(2)
C33	0.4056(2)	0.8515(5)	0.1816(2)	10.5(2)
Si4	0.46340(4)	0.7046(1)	0.10140(7)	7.16(4)
C41	0.5045(2)	0.7954(5)	0.1415(3)	12.5(3)
C42	0.4560(2)	0.6064(5)	0.1565(3)	10.4(2)
C43	0.4796(2)	0.6276(6)	0.0453(3)	11.9(2)
C3	0.4152(1)	0.7168(4)	−0.1489(2)	5.5(1)
Si5	0.39865(4)	0.6086(1)	−0.20668(7)	6.63(4)
C51	0.4032(2)	0.6513(5)	−0.2796(2)	9.9(2)
C52	0.4279(2)	0.4825(5)	−0.1810(3)	10.6(2)
C53	0.3467(2)	0.5704(5)	−0.2193(2)	8.5(2)
Si6	0.46121(4)	0.7929(1)	−0.14087(8)	7.09(4)
C61	0.4540(2)	0.8931(5)	−0.2025(3)	10.0(2)
C62	0.5022(2)	0.7010(5)	−0.1408(4)	12.1(3)
C63	0.4778(2)	0.8674(6)	−0.0676(3)	11.3(2)
C4	0.3467(1)	0.9677(3)	−0.2037(2)	4.9(1)
Si7	0.30051(5)	0.9491(1)	−0.26875(6)	6.79(4)
C71	0.2831(2)	1.0781(5)	−0.3080(3)	10.9(2)
C72	0.2603(2)	0.8893(6)	−0.2469(3)	12.5(3)
C73	0.3112(2)	0.8599(5)	−0.3252(3)	12.7(3)
Si8	0.34994(5)	1.0836(1)	−0.15252(7)	6.82(4)
C81	0.3579(2)	1.2134(4)	−0.1880(3)	11.0(2)
C82	0.3054(2)	1.0925(5)	−0.1304(3)	10.6(2)
C83	0.3927(2)	1.0666(6)	−0.0827(3)	12.4(3)

MHz): δ 26.2 (InC), 4.6 ppm (SiMe₃). IR (paraffin, CsBr plates, cm⁻¹): 1290 w, 1256 sh, 1244 s δCH₃; 1017 s δCH; 928 m, 910 m, 837 vs, 785 s, 768 s, 754 s, 725 m ρCH₃(Si); 683 s, 658 s ν_{as}SiC; 608 m ν_sSiC; 494 s, 478 m νInC; 332 vw δSiC. UV/vis (n-pentane) (ε): 240 nm (44000).

4.3. Synthesis of Tetrakis[bis(trimethsilyl)methyl]diindiumtelluride 4

A solution of 0.159 g (0.55 mmol) of Et₃PTe · 0.5 toluene in 25 ml of toluene was added to a solution of 0.443 g (0.51 mmol) of 1 in 25 ml of toluene. The

Table 5
Important bond lengths (pm) and angles (°) of the diindium chalcogenides 2, 3 and 4

2

In1–S1 *	241.9(3)	In2–S1 *	243.3(3)
In1–S2 *	235.6(4)	In2–S2 *	237.6(4)
In1–C1	216.1(5)	In2–C3	215.5(5)
In1–C2	216.5(5)	In2–C4	216.4(5)
C1–Si1	185.7(5)	C3–Si5	186.1(6)
C1–Si2	185.6(5)	C3–Si6	186.1(6)
C2–Si3	185.4(6)	C4–Si7	185.8(6)
C2–Si4	185.0(6)	C4–Si8	186.2(6)
In1–S1 *–In2	112.4(1)	In1–S2 *–In2	116.8(2)
C1–In1–S1 *	111.8(2)	C3–In2–S1 *	113.2(2)
C1–In1–S2 *	109.3(2)	C3–In2–S2 *	106.4(2)
C2–In1–S1 *	117.2(2)	C4–In2–S1 *	116.1(2)
C2–In1–S2 *	118.9(2)	C4–In2–S2 *	123.4(2)
C2–In1–C1	131.0(2)	C4–In2–C3	130.1(2)
In1–C1–Si1	111.4(2)	In2–C3–Si5	108.7(3)
In1–C1–Si2	110.2(3)	In2–C3–Si6	114.7(3)
In1–C2–Si3	111.1(3)	In2–C4–Si7	114.8(3)
In1–C2–Si4	113.2(3)	In2–C4–Si8	107.9(3)
Si1–C1–Si2	118.7(3)	Si5–C3–Si6	117.8(3)
Si3–C2–Si4	119.6(3)	Si7–C4–Si8	118.2(3)

3

In–Se	251.87(5)	In–C2	216.6(4)
In–C1	217.2(4)	C1–Si2	186.9(4)
C1–Si1	187.0(4)	C2–Si4	186.2(4)
C2–Si3	187.2(4)		
In–Se–In′	109.96(3)	C2–In–C1	128.3(2)
C1–In–Se	117.6(1)	C2–In–Se	113.8(1)
Si1–C1–Si2	119.8(2)	Si3–C2–Si4	118.0(2)
In–C1–Si1	113.0(2)	In–C1–Si2	109.9(2)
In–C2–Si3	110.1(2)	In–C2–Si4	112.8(2)

4

In1–Te	271.9(1)	In2–Te	271.40(7)
In1–C1	216.7(4)	In2–C3	217.9(4)
In1–C2	217.9(4)	In2–C4	217.4(4)
C1–Si1	186.9(4)	C3–Si5	186.5(5)
C1–Si2	187.0(5)	C3–Si6	186.9(5)
C2–Si3	186.7(5)	C4–Si7	187.7(5)
C2–Si4	186.4(5)	C4–Si8	185.3(5)
In1–Te–In2	105.42(2)	C3–In2–Te	116.3(1)
C1–In1–Te	114.9(1)	C4–In2–Te	115.1(1)
C2–In1–Te	116.7(1)	C4–In2–C3	128.4(2)
C2–In1–C1	128.2(2)	In2–C3–Si5	109.8(2)
In1–C1–Si1	110.7(2)	In2–C3–Si6	113.4(2)
In1–C1–Si2	112.7(2)	In2–C4–Si7	113.2(2)
In1–C2–Si3	110.7(2)	In2–C4–Si8	109.9(2)
In1–C2–Si4	113.5(2)	Si5–C3–Si6	119.8(2)
Si1–C1–Si2	118.2(2)	Si7–C4–Si8	118.5(2)
Si3–C2–Si4	119.3(2)		

* Statistically disordered sulphur atom.
The atom In′ is calculated from the symmetry operation −x + 1, y, −z + ½.

colour changed immediately from orange–red to pale yellow. The solution was stirred at room temperature for 1 h, the solvent evaporated and the residue recrystallized from n-pentane. Yield: 0.44 g (87%), yellowish, slightly air-sensitive crystals. M.p. (under Ar, closed capillary) 130°C. Molar mass (cryoscopically in benzene): obs. 805 (slow decomposition), calc. 994.8 g mol^{-1}. Mass spectrum (EI): 433.6 (24%), 434.6 (10%), 435.6(5%) In[CH(SiMe$_3$)$_2$]$_2$; 835.8 (0.4%), 837.8 (0.4%), 838.7 (0.3%) M$^+$–CH(SiMe$_3$)$_2$; 996.1 (0.03%) M$^+$. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.95 (InCH), 0.30 ppm (SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 75.5 MHz): δ 27.5 (InC), 4.6 ppm (SiMe$_3$). IR (paraffin, CsBr plates, cm^{-1}): 1289 w, 1246 vs δCH$_3$; 1017 vs δCH; 928 s, 912 s, 845 vs, 783 vs, 770 vs, 754 vs, 727 s ρCH$_3$(Si); 685 vs, 658 vs ν_{as}SiC; 608 s ν_sSiC; 492 vs, 476 s νInC; 334 w, 276 w δSiC. UV/vis (n-pentane) (ε): 240 nm (62000), 320 nm (sh, br, 9000).

5. Supplementary material available

Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository numbers CSD-404955 (2), CSD-404956 (3) and CSD-404957 (4), the names of the authors, and the journal citation.

Acknowledgements

References

[1] W. Uhl, M. Layh and W. Hiller, J. Organomet. Chem., 368 (1989) 139.

[2] W. Uhl, Z. Naturforsch., Teil B, 43 (1988) 1113.

[3] W. Uhl, M. Layh and T. Hildenbrand, J. Organomet. Chem., 364 (1989) 289.

[4] W. Uhl and A. Vester, Chem. Ber., 126 (1993) 941; W. Uhl, A. Vester, W. Kaim and J. Poppe, J. Organomet. Chem., 454 (1993) 9; C. Pluta, K.R. Pörschke, C. Krüger and K. Hildenbrand, Angew. Chem., 105 (1993) 451; W. Uhl, H.H. Karsch, U. Schütz and A. Vester, Chem. Ber., 126 (1993) 2637; W. Uhl, U. Schütz, S. Pohl and W. Saak, Z. Naturforsch., Teil B, 49 (1994) 637; W. Uhl, U. Schütz, W. Hiller and M. Heckel, Chem. Ber., 127 (1994) 1587; W. Uhl, R. Gerding, S. Pohl and W. Saak, Chem. Ber., 128 (1995) 81.

[5] W. Uhl, M. Layh, G. Becker, K.W. Klinkhammer and T. Hildenbrand, Chem. Ber., 125 (1992) 1547; W. Uhl, U. Schütz, W. Kaim and E. Waldhör, J. Organomet. Chem., 501 (1995) 79.

[6] W. Uhl, A. Vester and W. Hiller, J. Organomet. Chem., 443 (1993) 9.

[7] W. Uhl, R. Gerding, I. Hahn, S. Pohl, W. Saak and H. Reuter, Polyhedron in press.

[8] W. Uhl and U. Schütz, Z. Naturforsch., Teil B, 49 (1994) 931.

[9] W. Uhl, U. Schütz, W. Hiller and M. Heckel, Organometallics, 14 (1995) 1073.

[10] W. Uhl, M. Koch, W. Hiller and M. Heckel, Angew. Chem. Int. Ed. Engl., 34 (1995) 989.

[11] J.P. Oliver, J. Organomet. Chem., 500 (1995) 269.

[12] H. Heydt and M. Regitz, in Houben-Weyl, Methoden der Organischen Chemie, Vol. E2, Thieme, Stuttgart, 4th edn., 1982, p. 84.

[13] R$_3$PTe: D. Klamann and K.J. Irgolic, in Houben-Weyl, Methods of Organic Chemistry, Vol. E12b, Thieme, Stuttgart, 4th edn., 1990, p. 22; a similar method was used for the preparation of Et$_3$PSe.

[14] H. Bock and W. Kaim, Acc. Chem. Res., 15 (1982) 9.

[15] M. Layh and W. Uhl, Polyhedron, 9 (1990) 277.

[16] T. Hahn (ed.), International Tables for Crystallography, Space Group Symmetry, Vol. A, Kluwer Academic, Dordrecht, 1989.

[17] SHELXTL PLUS Vers. 4.1, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1990; G.M. Sheldrick, SHELXL-93, Program for the Refinement of Structures, Universität Göttingen, 1993.

[18] N.N. Greenwood and A. Earnshaw, Chemie der Elemente, VCH, Weinheim, 1990, p. 996.

[19] K. Ruhlandt-Senge and P.P. Power, Inorg. Chem., 32 (1993) 3478; B. Krebs, W. Bobb, H.-J. Wellmer and K. Wiesmann, Z. Anorg. Allg. Chem., 620 (1994) 1234.

[20] Some recent results (without typical solid state structures): W. Hirpo, A.C. Sutorik, S. Dhingra and M.G. Kanatzidis, Polyhedron, 13 (1994) 2797; H. Rahbarnoohi, M. Taghiof, M.J. Heeg, D.G. Dick and J.P. Oliver, Inorg. Chem., 33 (1994) 6307; S.U. Ghazi, M.J. Heeg and J.P. Oliver, Inorg. Chem., 33 (1994) 4517; W. Bubenheim and U. Müller, Z. Anorg. Allg. Chem., 620 (1994) 1607; Yu.A. Bankovsky, I.R. Berzinya, Yu.V. Ashaks, I.A. Ephimenko and V.S. Fundamensky, Zh. Neorg. Khim., 39 (1994) 603; D.J. Rose, Y.D. Chang, Q. Chen, P.B. Kettler and J. Zubieta, Inorg. Chem., 34 (1995) 3973; D.L. Reger and P.S. Coan, Inorg. Chem., 34 (1995) 6226; J. Zukermann-Schpector, I. Haiduc, C. Silvestru and R. Cea-Olivares, Polyhedron, 14 (1995) 3087.

[21] K. Merzweiler, F. Rudolph and L. Brands, Z. Naturforsch., Teil B, 47 (1992) 470.

[22] W. Uhl, R. Graupner, M. Pohlmann, S. Pohl and W. Saak, Chem. Ber., 129 (1996) 143.

[23] M.G. Kanatzidis and S. Dhingra, Inorg. Chem., 28 (1989) 2024; T.A. Annan, R. Kumar, H.E. Mabrouk, D.G. Tuck and R.K. Chadha, Polyhedron, 8 (1989) 865; O.T. Beachley, Jr., J.C. Lee. Jr., H.J. Gysling, S.H.L. Chao, M.R. Churchill and C.H. Lake, Organometallics, 11 (1992) 3144; S.S. Dhingra and M.G. Kanatzidis, Inorg. Chem., 32 (1993) 1350; O.T. Beachley, Jr., S.H.L. Chao, M.R. Churchill and C.H. Lake, Organometallics, 12 (1993) 5025; W. Hirpo, S. Dhingra, A.C. Sutorik and M.G. Kanatzidis, J. Am. Chem. Soc., 115 (1993) 1597; S. Saluschke, M. Pink, W. Dietzsch, R. Kirmse and N. Law, Z. Anorg. Allg. Chem., 619 (1993) 1862; M. Schuster and W. Bensch, Z. Anorg. Allg. Chem., 620 (1994) 737; S.P. Wuller, A.L. Seligson, G.P. Mitchell and J. Arnold, Inorg. Chem., 34 (1995) 4854; H. Rahbarnoohi, R. Kumar, M.J. Heeg and J.P. Oliver, Organometallics, 14 (1995) 3869.

[24] W. Uhl, R. Graupner, M. Layh and U. Schütz, J. Organomet. Chem., 493 (1995) C1.

[25] H. Rahbarnoohi, R. Kumar, M.J. Heeg and J.P. Oliver, Organometallics, 14 (1995) 502.

[26] M.C. Kuchta and G. Parkin, J. Am. Chem. Soc., 117 (1995) 12651.

[27] J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry, fourth edition, Harper Collins College Editions, New York, 4th edn., 1993.