

Synthesis of (RSn)₄X₆ Adamantanes (X = O, S, Se) in Liquid Ammonia and in the Two-Phase System Liquid Ammonia/THF

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Dedicated to Professor Dietmar Seyferth on the occasion of his 70th birthday

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The reactions of trisSnBr₃ (**1**) [tris = (Me₃Si)₃C] and *n*BuSnCl₃ with Na₂X (X = O, S, Se) yield the heterocyclic adamantanes **2–6**. The reaction of **1** with Na₂O is carried out in liquid ammonia under normal pressure at –78 °C to give (trisSn)₄O₆ (**2**). However, the reaction of **1** with Na₂S and Na₂Se under

pressure at room temperature results in the formation of (trisSn)₄S₆ (**3**) and (trisSn)₄Se₆ (**4**). *n*BuSnCl₃ reacts with Na₂S and Na₂Se in liquid ammonia at –33 °C under normal pressure to give (*n*BuSn)₄S₆ (**5**) and (*n*BuSn)₄Se₆ (**6**), respectively.

Introduction

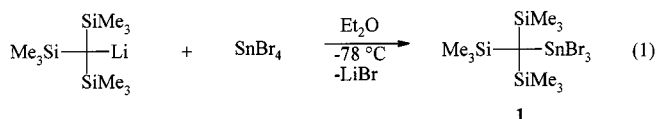
Compounds of the type (RE)₄X₆ (E = Si, Ge, Sn; X = S, Se) with an adamantane or a double-decker structure have been reported.^[1–3] Unno et al. described the synthesis of (RE)₄X₆ compounds (E = Si and Ge; X = S and Se), with a double-decker structure, which afforded the corresponding adamantane upon heating.^[1] Another contribution by Berwe and Haas dealt with the reaction of RSnCl₃ with Na₂S · 9 H₂O and Me₃SiSSiMe₃, where a heterocyclic adamantane (RSn)₄S₆ was reported to be the major product.^[2]

Herein the synthesis of the hitherto unknown trisSnBr₃ (**1**) [tris = (Me₃Si)₃C] and a general method for the preparation of (RSn)₄X₆ [R = tris; X = O (**2**), S (**3**), Se (**4**); R = *n*Bu; X = S (**5**), Se (**6**)] are reported.

Results and Discussion

Synthesis and Spectra

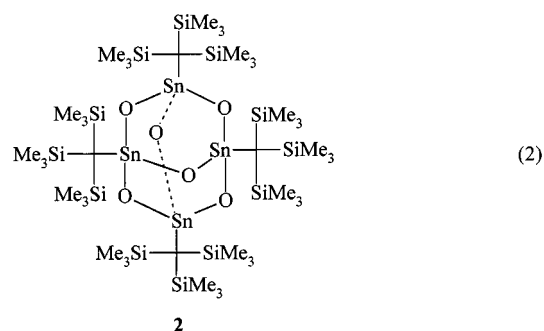
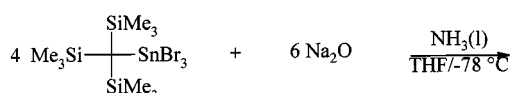
trisSnBr₃ (**1**) is easily obtained by the treatment of tin tetrabromide with tris(trimethylsilyl)methyl lithium in diethyl ether (Equation 1).^[4] Compound **1** is a colorless, sublimable crystalline solid, whereas *n*-butyltin trichloride is a liquid.



Compound **1** was characterized by mass spectrometry and NMR-spectral studies. The ¹H-NMR spectrum of **1**

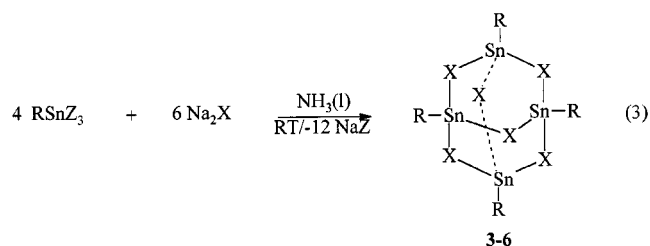
gives a singlet at δ = 0.32 for the protons of the methyl groups of the tris ligand, and ¹¹⁹Sn- and ²⁹Si-NMR spectra also show singlets (at δ = –237.4 and 1.8, respectively). The mass spectrum exhibits a peak at *m/z* 575 [M⁺ – Me]. The spectral data and elemental analysis confirm the composition of the compound to be C₁₀H₂₇Br₃Si₃Sn (**1**).

Compound **1** reacts with Na₂X (X = O, S, Se) in liquid ammonia to give (RSn)₄X₆ [R = tris; X = O (**2**), S (**3**), Se (**4**)]. While Na₂O reacts with **1** at –78 °C under normal pressure in liquid ammonia, Na₂S and Na₂Se, generated in situ in liquid ammonia at –78 °C, react under pressure in liquid ammonia (Equations 2 and 3). The formation of Na₂S and Na₂Se in situ is indicated by a color change of the reaction medium from blue to yellow and red, respectively.



The proton-NMR spectrum of (trisSn)₄O₆ (**2**) shows four singlets (δ = 0.13, 0.24, 0.28, 0.51), as does the ²⁹Si-NMR spectrum (δ = –1.0, –0.42, –0.27, –0.17), which indicates that the tris groups are not equivalent. However, the four tin atoms are equivalent and the compound gives only one ¹¹⁹Sn resonance (δ = 94.3). The mass spectrum exhibits the molecular ion peak at *m/z* (%) 1496 (100) [M⁺].

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R = tris, *n*-Bu Z = Cl, Br X = S, Se

Compounds (trisSn)₄S₆ (**3**) and (trisSn)₄Se₆ (**4**) were characterized by elemental analysis, multinuclear NMR spectra and mass spectrometry. Unlike in the case of **2**, the ¹H-NMR spectra of both compounds **3** and **4** show singlets at δ = 0.22 and 0.20, respectively. Similarly, the ²⁹Si-NMR spectra of **3** and **4** give singlets at δ = 4.5. This indicates that in both compounds the tris ligands are equivalent, unlike in the case of **2**. The ¹¹⁹Sn-NMR spectrum of **3** shows a singlet (δ = 72.8) which is downfield shifted compared to that of **1** (δ = −237.4) due to the formation of the heterocyclic adamantane. It should be pointed out that ¹¹⁹Sn- and ⁷⁷Se-NMR spectra could not be recorded in the case of **4** due to its instability in solution. Compound **4** decomposed with the formation of selenium. The same behavior was observed for the corresponding tellurium derivative.

The mass spectrum of **3** exhibits two intense peaks (*m/z* 1594 [M⁺], 1579 [M⁺ − CH₃]). However, no molecular ion peak [M⁺] could be observed for compound **4**, instead a peak at *m/z* (%) 1645 (100) [M⁺ − tris] was observed.

Similar to **1**, *n*BuSnCl₃ reacts with Na₂S and Na₂Se in liquid ammonia at refluxing temp. (−33°C) to give (nBuSn)₄S₆ (**5**) and (nBuSn)₄Se₆ (**6**), respectively.

Compounds **5** and **6** were characterized by elemental analysis, mass spectrometry and multinuclear NMR-spectral studies. The ¹H-NMR spectra of **5** and **6** give a typical spectral pattern due to the *n*butyl group. The ¹¹⁹Sn-NMR spectra of **5** and **6** show singlets at δ = 144 and −22, respectively. This difference in resonances is due to the difference in electronegativities of S and Se. The ⁷⁷Se-NMR spectrum of **6** exhibits a singlet at δ = −169.9. Thus, the NMR-spectral studies agree well with the proposed adamantane structure. The mass spectrum of **5** shows a peak at *m/z* (%) 839 (70) [M⁺ − *n*-butyl]. **6** is characterized in the gas phase by two peaks: first the molecular ion peak at *m/z* (%) 1177 (20) and second the fragment at *m/z* (%) 1120 (90) [M⁺ − *n*-butyl].

In all cases we were unable to detect the coupling constants of ¹¹⁷Sn/¹¹⁹Sn, ¹¹⁹Sn/⁷⁷Se and ¹¹⁹Sn/²⁹Si.

X-ray Structures of **2** and **3**

The structure of **2** (see Figure 1) shows a highly symmetric, regular adamantane core (point group *T*) consisting of tin and oxygen atoms. This geometry is defined by a threefold axis through the Sn–C bond and three equivalent twofold axes through two opposite O atoms, so that only 1/

12 of the whole molecule exists in the asymmetric unit. Due to this symmetry, each of the Sn atoms shows a distorted tetrahedral geometry with three equivalent bridging oxygen atoms and a terminal tris(trimethylsilyl)methyl group heading away from the core. All Sn–O bond lengths are equal [196.8(1) pm], as well as the Sn–C bond lengths [213.4(3) pm] and the corresponding bond angles [O–Sn–O 103.8(1)°, O–Sn–C 114.7(1)°]. Two solvent molecules of benzene exist close to the special position 1/4, 1/4, 0 and appear to rotate freely.

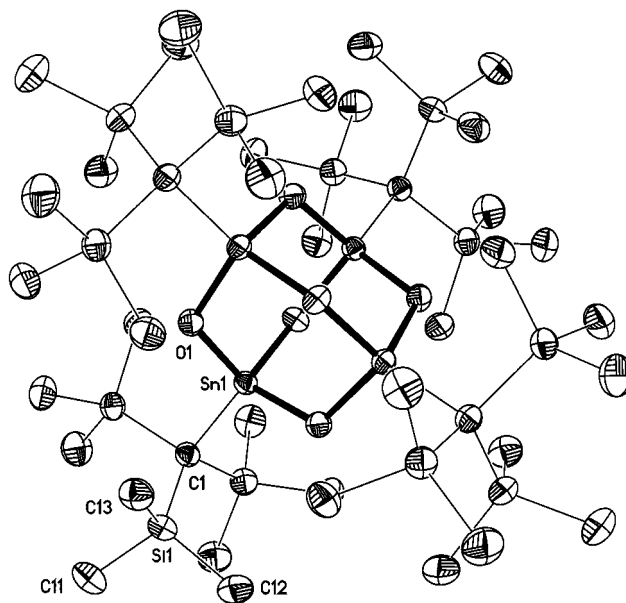


Figure 1. Crystal structure of **2**

3 (see Figure 2) is isomorphous with **2** but the O atoms are replaced by S. This substitution leads to longer bonds in the adamantane core [Sn–S 240.8(3) pm] and a longer Sn–C bond [223(2) pm] in **3**, causing the terminal tris(trimethylsilyl)methyl group to be disordered. Because of this

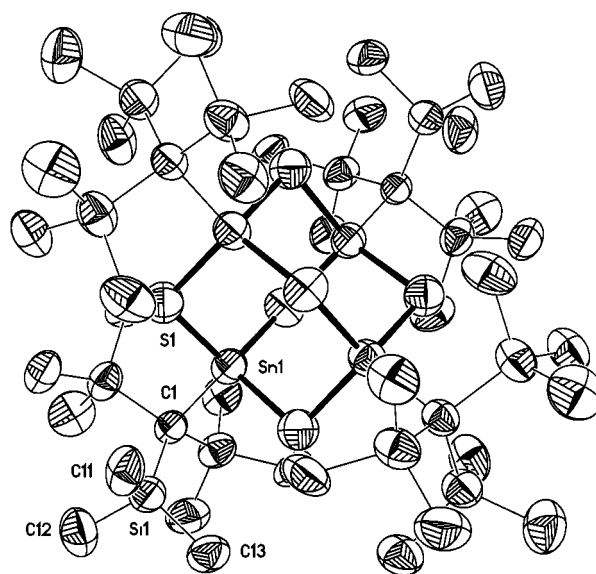


Figure 2. Crystal structure of **3**

disorder a mirror plane is added to the symmetry of the data, the space group is *Fd*–*3m* instead of *Fd*–*3* as in **2**.

Conclusion

In summary, we have shown that tin adamantanes containing the chalcogens oxygen, sulfur and selenium are easily accessible using liquid ammonia as a reaction media. The structure of (trisSn)₄O₆ has been shown to have the most regular adamantane core of this series

Experimental Section

General: All reactions were carried out under dry nitrogen using Schlenk techniques and a drybox. Solvents were dried and distilled under nitrogen prior to use. – ¹H NMR (200 MHz): Bruker AM 200. – ²⁹Si NMR (49.7 MHz), ¹¹⁹Sn NMR (93.3 MHz), ⁷⁷Se NMR (47.7 MHz): Bruker AC 250 NMR, tetramethylsilane, tetramethyltin and dimethylselenium, respectively, as external standards. – MS: Bruker AM 200 MS, Bruker MSL 400 MS. – M.p.: Bühler SPA-1. – The starting materials trisLi^[4] and Na₂X (X = S, Se)^[5] were prepared by literature methods. Tin tetrabromide and *n*-butyltin trichloride were commercially available.

Synthesis of 1: A solution of (trisLi)₂ · 4 THF (4.4 g, 5.7 mmol, dissolved in 40 mL of diethyl ether) was added dropwise to a solution of SnBr₄ (5.0 g, 11.4 mmol, dissolved in 30 mL of diethyl ether) at –78°C while stirring. The reaction mixture was allowed to warm up to room temp., and the residue was dissolved in 50 mL of *n*-hexane and the precipitate of lithium bromide filtered off. 50% of the solvent was removed in vacuo. Recrystallization of the crude product at –30°C afforded 6.0 g (89%) of a colorless crystalline solid (sublimation at 155°C). – ¹H NMR (200 MHz, C₆D₆): δ = 0.32 {s, 27 H, C[Si(CH₃)₃]₃}. – ²⁹Si NMR (49.7 MHz, C₆D₆): δ = 1.8 [C(SiMe₃)₃]. – ¹¹⁹Sn NMR (93.3 MHz, C₆D₆): δ = –237.4 (trisSnBr₃). – MS (EI); *m/z* (%): 575 (100) [M⁺ – Me].

Synthesis of 2: Na₂O (0.093 g, 1.5 mmol) was suspended in 30 g of liquid ammonia at –78°C. **1** (0.59 g, 1 mmol) was dissolved in 20 mL of THF and added dropwise to the suspension of Na₂O while stirring. The reaction mixture was cooled at –78°C for 6 h and then warmed up slowly to room temp. THF was removed in vacuo. The remaining solid was dissolved in 50 mL of *n*-hexane, the precipitate of sodium bromide filtered off and the filtrate concentrated in vacuo. The residue was a white solid (0.28 g, 80%). Recrystallization from benzene resulted in colorless single crystals (m.p. > 250°C). – C₄₀H₁₀₈Si₁₂Sn₄O₆ (1398.38): calcd. C 32.11, H 7.71; found C 31.9, H 7.7. – ¹H NMR (200 MHz, C₆D₆): δ = 0.13 {s, 27 H, C[Si(CH₃)₃]₃}, 0.24 {s, 27 H, C[Si(CH₃)₃]₃}, 0.28 {s, 27 H, C[Si(CH₃)₃]₃}, 0.51 {s, 27 H, C[Si(CH₃)₃]₃}. – ²⁹Si NMR (49.7 MHz, C₆D₆): δ = –1.0 (SiMe₃), –0.42 (SiMe₃), –0.27 (SiMe₃), –0.17 (SiMe₃). – ¹¹⁹Sn NMR (93.3 MHz, C₆D₆): δ = 94.3 (Sn_{ad}) (ad = adamantane). – MS (EI); *m/z* (%): 1496 (100) [M⁺], 1481 (75) [M⁺ – Me].

Synthesis of 3: Sulfur (0.096 g, 3 mmol) was suspended in liquid ammonia in a glass autoclave at –78°C. Sodium (0.138 g, 6 mmol) was added to the suspension while stirring. The stirring was continued until the color changed from blue to yellow. Solid **1** (1.18 g, 2 mmol) was added to the stirred suspension of sodium sulfide, and the glass autoclave was closed. The reaction mixture was allowed to warm up to room temp. After 25 min, the color of the reaction mixture changed from yellow to green. After 24 h, the autoclave

was opened and the liquid ammonia vaporized. Subsequently, the residue was dissolved in 20 mL of toluene, the sodium bromide filtered off and the filtrate concentrated in vacuo. Recrystallization from benzene afforded 0.6 g (75%) of yellow crystals (decomp. 168°C). – C₄₀H₁₀₈Se₆Si₁₂Sn₄ (1593.56): calcd. C 30.15, H 6.78, S 12.07, Si 21.15; found C 31.3, H 7.1, S 11.8., Si 21.3. – ¹H NMR (200 MHz, C₆D₆): δ = 0.22 {s, 108 H, 4 C[Si(CH₃)₃]₃}. – ²⁹Si NMR (49.7 MHz, C₆D₆): δ = 4.5 (SiMe₃). – ¹¹⁹Sn NMR (93.3 MHz, C₆D₆): δ = 72.8 (Sn_{ad}). – MS (EI); *m/z* (%): 1579 (100) [M⁺ – Me], 1594 (45) [M⁺].

Syntheses of 4: Compound **4** was synthesized in an analogous manner to that of **3**. The reaction and isolation afforded 0.38 g (81%) of a yellow/red powder (decomp. 195–205°C). – C₄₀H₁₀₈Se₆Si₁₂Sn₄ (1874.92): calcd. C 25.62, H 5.81; found C 26.0, H 5.7. – ¹H NMR (200 MHz, CDCl₃): δ = 0.20 {s, 108 H, C[Si(CH₃)₃]₃}. – ²⁹Si NMR (49.7 MHz, CDCl₃): δ = 4.5 (SiMe₃). – MS (EI); *m/z* (%): 1645 (100) [M⁺ – tris].

Synthesis of 5: Sulfur (0.144 g, 4.5 mmol) was suspended in 40 g of liquid ammonia in a 100-mL Schlenk flask at –78°C. Sodium (0.207 g, 9 mmol) was slowly added to this mixture. The reaction mixture was stirred until it became yellow. *n*BuSnCl₃ (0.847 g, 3 mmol) was then added to the suspension which was then allowed to warm up to –33°C and refluxed in liquid ammonia for 2 h. The liquid ammonia vaporized overnight. The residue was dissolved in 20 mL of *n*-hexane, the precipitate of sodium chloride filtered off and the filtrate concentrated in vacuo, yielding 0.3 g (45%) of a yellow powder (decomp. 130°C). – C₁₆H₃₆S₆Sn₄ (895.7): calcd. C 21.46, H 4.05, S 21.48; found C 20.9, H 4.2, S 22.3. – ¹H NMR (200 MHz, CDCl₃): δ = 0.85–0.95 (t, 12 H, CH₃CH₂CH₂CH₂Sn_{ad}), 1.35–1.50 (m, 8 H, CH₃CH₂CH₂CH₂Sn_{ad}), 1.70–1.80 (m, 16 H, CH₃CH₂CH₂CH₂Sn_{ad}). – ¹¹⁹Sn NMR (93.3 MHz, CDCl₃): δ = 144 (Sn_{ad}). – MS (EI); *m/z* (%): 839 (70) [M⁺ – *n*Bu], 655 (100) [M⁺ – *n*Bu – Sn – 2 S].

Synthesis of 6: Selenium (0.355 g, 4.5 mmol) was suspended in 40 g of liquid ammonia in a 100-mL Schlenk flask at –78°C. Sodium (0.207 g, 9 mmol) was added slowly to this mixture while stirring, until the solution became red. Finally, *n*-butyltin trichloride (0.847 g, 3 mmol) was added. After warming up to –33°C, the mixture was refluxed for 5 h. The liquid ammonia was vaporized overnight. The residue was dissolved in 20 mL of *n*-hexane, the precipitated sodium chloride filtered off and the solvent removed in vacuo to yield 0.6 g (68%) of a yellow powder (decomp. 118°C). – C₁₆H₃₆Se₆Sn₄ (1177.06): calcd. Sn 40.34; found Sn 40.5. – ¹H NMR (200 MHz, CDCl₃): δ = 0.90–1.00 (t, 12 H, 4 CH₃CH₂CH₂CH₂Sn_{ad}), 1.35–1.55 (sext, 8 H, 4 CH₃CH₂CH₂CH₂Sn_{ad}), 1.65–1.80 (quint, 8 H, 4 CH₃CH₂CH₂CH₂Sn_{ad}), 1.90–1.98 (t, 8 H, 4 CH₃CH₂CH₂CH₂Sn_{ad}). – ¹¹⁹Sn NMR (93 MHz, CDCl₃): δ = –22 (Sn_{ad}). – ⁷⁷Se NMR (47 MHz, CDCl₃): δ = –165.5 (Sn_{ad}Se_{1.5ad}). – MS (EI); *m/z* (%): 1120.4 (90) [M⁺ – *n*Bu], 1177 (20) [M⁺].

X-ray Crystallographic Study:^[6] Crystals were grown by cooling a saturated solution of benzene (**2**) or benzene/trichloromethane (**3**) to 8°C and then mounted on a glass fiber in a rapidly cooled perfluoro polyether.^[7] – Crystal data for **2**: C₄₀H₁₀₈O₆Si₁₂Sn₄ + 3 C₆H₆, *M* = 1731.43, space group *Fd*–*3*, *a* = 2541.2(3) pm, *V* = 16.41(10) nm³, *Z* = 8, ρ_{calcd.} = 1.402 g cm^{–3}, data collection: Stoe-Siemens-Huber four-circle diffractometer, coupled to a Siemens CCD area detector, graphite-monochromated Mo-*K*_α radiation, crystal size 0.5 × 0.4 × 0.4 mm, all measurements at 133(2) K, φ- and ω-collecting mode, 4.5° ≤ 2θ ≤ 59.5°, 92370 reflections measured, 1940 unique (*R*_{int} = 0.0270), 1795 with *I* > 2σ(*I*), 1.419 mm^{–1} absorption coefficient, semi-empirical absorption correction from

Table 1. Selected bond lengths [pm] and angles [°] of **2**; symmetry transformations for equivalent atoms are indicated

Sn(1)–O(1)	196.8(1)
Sn(1)–C(1)	213.4(3)
Si(1)–C(1)	190.8(1)
O(1)–Sn(1)–O(1) ^[a]	103.8(1)
O(1)–Sn(1)–C(1)	114.7(1)
Sn(1)–O(1)–Sn(1) ^[b]	120.0(1)
Si(1) ^[c] –C(1)–Si(1)	112.9(1)
Si(1) ^[c] –C(1)–Sn(1)	105.8(1)

^[a] $-x + 3/4, -y + 3/4, z$. – ^[b] $-x + 5/4, y, -z + 1/4$. – ^[c] $x - 1/2, -y + 3/4, -z + 1/4$.

Table 2. Selected bond lengths [pm] and angles [°] of **3**; symmetry transformations for equivalent atoms are indicated

Sn(1)–C(1)	223(2)
Sn(1)–S(1)	240.8(3)
C(1)–Si(1)	191.2(7)
C(1)–Sn(1)–S(1)	108.1(1)
S(1) ^[a] –Sn(1)–S(1)	110.8(1)
Sn(1)–S(1)–Sn(1) ^[b]	106.7(2)
Si(1)–C(1)–Si(1) ^[a]	112.3(5)
Si(1)–C(1)–Sn(1)	106.5(6)

^[a] $-x + 3/4, -y + 1/4, z + 1/2$. – ^[b] $-x + 5/4, y + 0, -z + 1/4$.

equivalents (0.5373–0.6007 transmission factors). Data/restraints/parameters: 1940/181/124, final $R1 = 0.0265$ for $I > 2 \sigma(I)$ and $wR2 = 0.0635$ for all data [$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o)^2 + (0.0180 \cdot P)^2 + 79.5121 \cdot P$, $P = [F_o^2 + 2F_c^2]/3$], largest peak and hole in final diff. map = 642 and -745 e nm^{-3} . – Crystal data for **3**: $\text{C}_{40}\text{H}_{108}\text{S}_6\text{Si}_{12}\text{Sn}_4 + 1.57 \text{ C}_6\text{H}_6 + 0.43 \text{ CHCl}_3$, $M = 1767.39$, space group $Fd\bar{3}m$, $a = 2554.1(3) \text{ pm}$, $V = 16.66(10) \text{ nm}^3$, $Z = 8$, $\rho_{\text{calcd.}} = 1.409 \text{ g cm}^{-3}$, data collection: Stoe-Siemens-AED2 four-circle diffractometer, graphite-monochromated Mo- K_α radiation, crystal size $0.5 \times 0.4 \times 0.4 \text{ mm}$, all measurements at 150(2) K, learnt-profile method, $7.8^\circ \leq 2\theta \leq 49.3^\circ$, 6642 reflections measured, 713 unique ($R_{\text{int}} = 0.1007$), 544 with $I > 2\sigma(I)$, data/restraints/parameters: 713/33/76, final $R1 = 0.0673$ for $I > 2\sigma(I)$ and $wR2 = 0.2304$ for all data, $w^{-1} = \sigma^2(F_o)^2 + (0.1268 \cdot P)^2 + 304.6513 \cdot P$, largest peak and hole in final diff. map = 1260 and -1049 e nm^{-3} . – Structural analysis and refinement: Both struc-

tures (see Tables 1 and 2) were solved by direct methods using SHELXS-97^[8] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.^[9] All non-hydrogen atoms except those of the solvent molecules were refined anisotropically. Hydrogen atom positions were calculated from idealized geometries and refined using a riding model. In **2** solvent benzene molecules close to the special position $1/4, 1/4, 0$ could not be resolved properly, and were refined using strong restraints on geometry and displacement parameters. Special position constraints were suppressed. In **3** the electron density for the solvent showed an even more disordered site than in **2** so that the solvent molecules were refined as a rigid benzene molecule and a strongly restrained trichloromethane molecule. The two molecules share the same position, the sum of their occupation factors is 1. Since this model does not describe the true situation very well the difference electron density is comparatively high. The severe disorder in structure **3** leads to a significantly worse refinement compared to structure **2**.

Acknowledgments

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