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The chemistry of trityl isoselenocyanate revisited: A preparative and structural investigation

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ABSTRACT

The reaction of trityl chloride with KSeCN gives trityl isoselenocyanate which was structurally characterised by X-ray diffraction. Trityl isoselenocyanate reacts with hydrazine to give trityl selenosemicarbazide and with primary amines to give selenourea derivatives. However, with secondary amines mixtures of selenoureas and substitution products are formed. Trityl selenosemicarbazide undergoes a condensation reaction with salicylaldehyde to give the corresponding trityl selenosemicarbazone. In the case of 2-pyridinecarboxaldehyde, the analogous selenosemicarbazone cannot be isolated, instead a small quantity of the diselenide was isolated from the reaction mixture. The compounds prepared here were fully characterised spectroscopically and several also by X-ray diffraction.

1. Introduction

Isoselenocyanates RN=C=Se are useful synthetic precursors for a variety of organoselenium compounds containing the –NHC(Se)– unit including selenoamides and selenocarbamate esters which can act as monoanionic Se^- ligands towards a metal upon deprotonation. In our laboratories we are studying various aspects of the coordination chemistry of these types of organoselenium compounds with both transition- and main-group-metals, and have previously reported some results with gold [1–3]. Isoselenocyanates are generally prepared in a one-pot procedure from the corresponding formamides, phosgene and Se metal in the presence of a base [4]. Alternatively, the reaction of an isocyanide with Se metal in $CHCl_3$ also gives reasonable yields of isoselenocyanates [5]. In either case, use of highly toxic phosgene (or one of its derivatives) is required. In search for a safer and simple preparation for isoselenocyanates we came across a report that trityl isoselenocyanate could be prepared simply from trityl chloride and KSeCN [6], although the exact same procedure had previously been reported to yield trityl selenocyanate [7]. Given this apparent contradiction, we wished to re-examine the reaction of trityl chloride with KSeCN and use modern characterisation methods to unambiguously identify the product. Should the isoselenocyanate indeed be formed, we wished to examine its reactivity and to see if any organoselenium compounds suitable as ligands could be prepared from it. The results of this investigation are reported herein.

2. Results and discussion

Trityl isoselenocyanate (**1**) was prepared from the reaction of trityl chloride and KSeCN (Scheme 1) as previously described [6]. The compound was obtained as colourless needles after recrystallisation from hexane. We observed that the compound turned red upon standing at room temperature in the presence of light over a period of *ca.* 12 h. To prevent this decomposition, the material was stored in amber bottles in the freezer. In solution (acetone or CH_2Cl_2) decomposition also occurs: the formation of a red precipitate (presumably elemental Se) can be observed after a period of several hours. Since there has been some debate in the past if the seleno- or iso-selenocyanate derivative is formed by the reaction of KSeCN and Ph_3CCl, we wished to unambiguously confirm the identity of the material in the solid state using single crystal X-ray diffraction. The molecular structure of **1** is shown in Fig. 1, important bond distances and angles are included in the figure caption.

The compound crystallises in the space group $P2_1/c$ with two independent molecules in the asymmetric unit. From the molecular structure it is immediately apparent that the compound is indeed the isoselenocyanate and not the selenocyanate as was suggested by Rheinboldt and de Campos [7]. Based on the C–N distance of 1.458(3) Å, which is typical for a nitrogen–carbon-single bond, an ionic structure $[Ph_3C][NCSe]$ can also be ruled out. The Se=C=N unit is, as expected, virtually linear [178.8(2)°] and the quite short Se=C and C=N bond distances [1.740(3) and 1.149(3) Å, respectively], are also virtually identical to those observed in the ferrocene derivative $[Fe\{\eta^5\text{-}C_5H_4NCSe\}_2]$, the only other isoselenocyanate that has been structurally characterised

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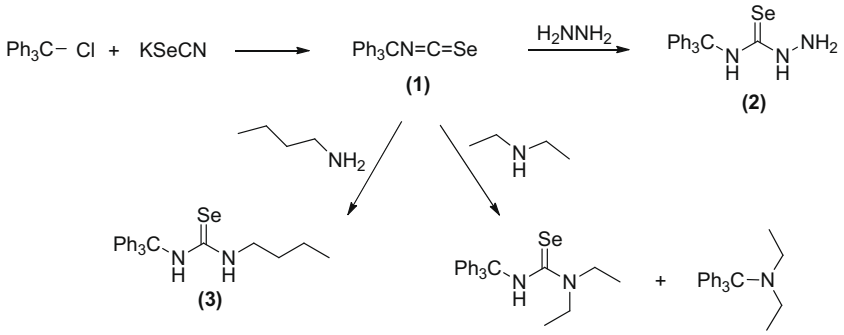


Scheme 1.

[8]. These rather short bond distances are indicative of the strong π-interactions between the three atoms of the NCSe unit. The bond distances and angles of the two independent molecules of **1** are identical within experimental error, except the Ph_3C–N═C angles, which differ by *ca.* 6° probably due to packing effects in the crystal.

The reaction of trityl isoselenocyanate with hydrazine hydrate in cyclohexane affords trityl selenosemicarbazide $Ph_3CNHC(Se)NHNH_2$ (**2**) (Scheme 1) in good yield as colourless, crystalline solid [6]. In contrast to the isoselenocyanate, compound **2** can be kept at room temperature in the absence of light for several weeks without any sign of decomposition. Given this stability both in the solid state and in solution, we were able to spectroscopically characterise this compound for the first time: The ^{77}Se NMR spectrum shows a singlet at 319.4 ppm, whilst the ^{13}C NMR spectrum of **2** displays a singlet resonance due to the C═Se carbon atom at 179.20 ppm (in addition to the signals of the Ph_3C unit). We were also able to obtain X-ray quality crystals of **2** and determined the solid state structure (Fig. 2).

This compound also crystallises in the space group $P2_1/c$ with two independent molecules in the asymmetric unit. The $NHC(Se)NHNH_2$ unit is held in an *E* configuration through an intramolecular H-bond N(6)H···N(5) of *ca.* 2.09 Å forming a five-membered quasi cyclic structure. The Se–C bond distance [1.862(6) Å] in **2** is longer than that in the isoselenocyanate **1**, reflecting the perturbation of the cumulated π-system and the high degree of delocalisation. The increase of the C–N bond distances is also consistent with the change of bond order; the Ph_3C–N bond distances in **1** and **2** are essentially identical.

The reactivity of trityl isoselenocyanate with *n*-butylamine and diethylamine was also investigated (Scheme 1). In the case of *n*-butylamine, the selenourea derivative $Ph_3CNHC(Se)NH^nBu$ (**3**) was obtained as colourless solid in good yield. The compound was spectroscopically characterised, the data being fully consistent with the proposed structure (see Experimental). The same reaction with the Et_2NH also gave a colourless solid; however, this material was shown by ^1H NMR spectroscopy to consist of a *ca.* 1:1 mixture of the selenourea $Ph_3CNHC(Se)NEt_2$ and the substitution product Ph_3CNEt_2. This reactivity mimics that reported for the sulphur analogue: Trityl isothiocyanate reacts with *n*-butylamine to give exclusively the thiourea derivative whereas Et_2NH gives the thiourea only in poor yield (the other component is the substitution product, which is simply removed in the purification process). Furthermore, other secondary amines such as piperidine and morpholine react with trityl isothiocyanate to give exclusively the substitution products [9]. It appears that in the case of the

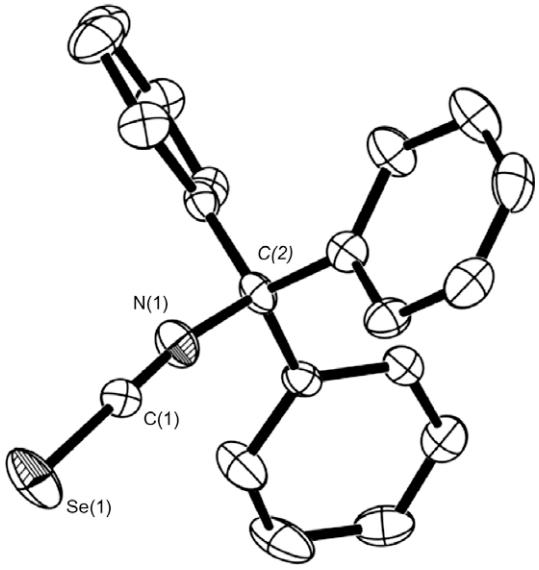


Fig. 1. Molecular structure of one of the independent molecules of compound **1**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å]: Se(1)–C(1) 1.740(3), C(1)–N(1) 1.149(3), N(1)–C(2) 1.458(3). Selected bond angles [°]: Se(1)–C(1)–N(1) 178.8(2), C(1)–N(1)–C(2) 169.7(3).

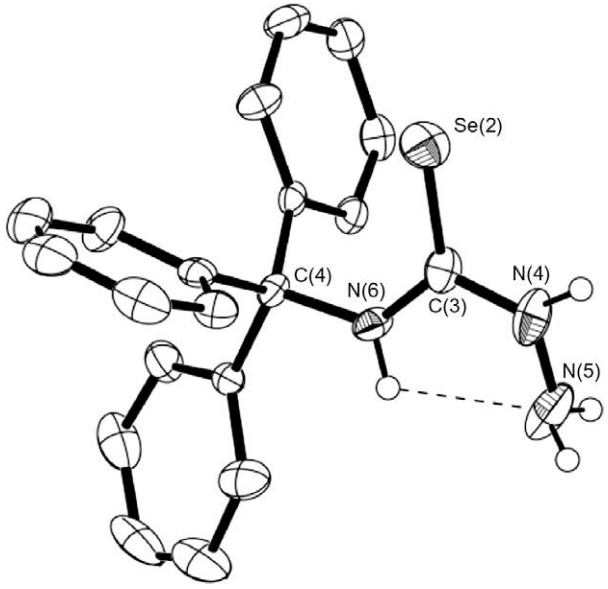
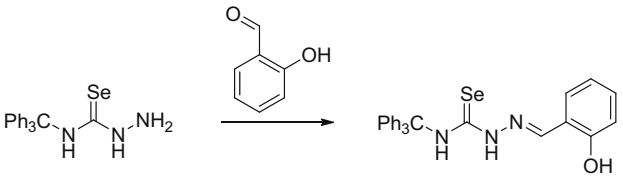


Fig. 2. Molecular structure of one of the independent molecules of compound **2**. Ellipsoids show 50% probability levels. Only the NH hydrogen atoms are shown as spheres with arbitrary radii. Selected bond distances [Å]: C(3)–Se(2) 1.862(6), C(3)–N(6) 1.310(9), C(3)–N(4) 1.361(7), C(4)–N(6) 1.439(8), N(4)–N(5) 1.393(8). Selected angles [°]: C(4)–N(6)–C(3) 129.2(7), N(6)–C(3)–N(4) 116.2(6), N(6)–C(3)–Se(2) 126.6(5).



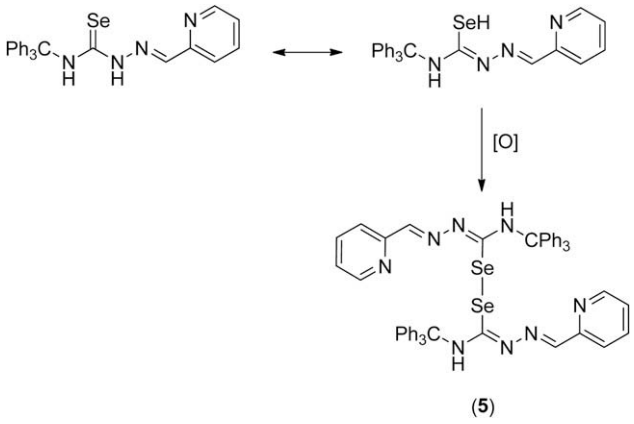
Scheme 2.

selenium derivative too, substitution accompanied by release of selenocyanate is also a competing reaction when an amine reacts with trityl isoselenocyanate. Depending on the nature of the amine, either exclusively addition products (selenoureas) or mixtures of addition and substitution products are formed.

Trityl selenosemicarbazide undergoes a condensation reaction with salicylaldehyde to give the imine $Ph_3CNHC(Se)NHN{=}CH(C_6H_4\text{-}2\text{-}OH)$ **4** in reasonable yield (Scheme 2).

The compound's identity could be unambiguously established by using ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy (see Experimental section for details), since no crystals suitable for X-ray diffraction could be obtained. In contrast, under the same conditions 2-pyridinecarboxaldehyde gave after work-up a dark gum which contained a few large yellow crystals after standing for some time. Evidently, significant decomposition occurs during the reaction. The crystals however, could be studied by X-ray diffraction after manually removing them from the gum, which revealed them to be the diselenide **5** (Fig. 3)

The compound crystallises in the space group $P\bar{1}$. Its overall geometry i.e. the Se–Se distance [2.3300(3) Å] as well as the C–Se–Se angles [99.56(6)°] and the C–Se–Se–C torsion angle close



Scheme 3.

to 90° is typical for a diselenide. This result suggests that the desired condensation product from 2-pyridinecarboxaldehyde and trityl selenosemicarbazide had formed at some point during the reaction but this is then transformed into the diselenide which crystallises out from the reaction mixture accompanied by other decomposition products. Heimgartner also reported the isolation of a diselenide obtained by recrystallisation of a 1,2,4-triazole-3-selenone [10]. We propose that the diselenide **5** was formed by oxidative coupling of the selenol tautomer of the selenosemicarbazone (Scheme 3). Unfortunately, we were not able to recover any crystals of the compound for solution spectroscopic studies.

In summary, we have confirmed by X-ray crystallography and by preparing derivatives with amines and hydrazine that the reaction of trityl chloride with KSeCN gives trityl isoselenocyanate and

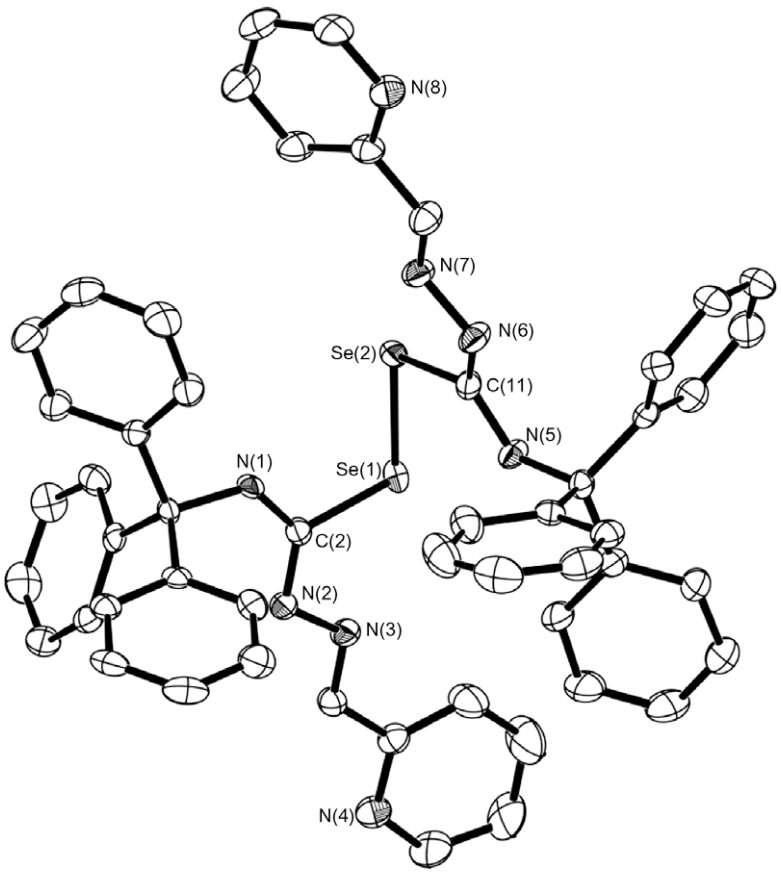


Fig. 3. Molecular structure of compound **5**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

not trityl selenocyanate. We have also examined the preparation of functionalised organoselenium compounds derived from trityl selenosemicarbazide which are potential ligands. We are currently developing this chemistry further and are examining the use of these compounds as ligands in various metal complexes.

3. Experimental

3.1. General

^{1}H, ^{13}C and ^{77}Se NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^{1}H, ^{13}C) and $SeMe_2$ (^{77}Se). Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. All reactions were carried out under aerobic conditions unless stated otherwise. KSeCN was prepared as described in the literature [11] and all other chemicals and solvents (HPLC grade) were sourced commercially and used as received.

3.2. Trityl isoselenocyanate (**1**)

This was prepared by a slightly modified literature procedure: Trityl chloride (7.2 g, 29.5 mmol) was added to a solution of KSeCN (3.6 g, 34.3 mmol) in acetone (80 ml). The mixture was stirred at room temperature for *ca.* 3 h. The precipitated KCl was removed by filtration and the filtrate was evaporated to dryness. The residue was recrystallised from hexane to afford the product as colourless needles in 64% (6.5 g) yield. The compound should be stored in an amber bottle in the freezer. X-ray quality crystals were selected from the bulk sample.

3.3. Trityl selenosemicarbazide (**2**)

This was prepared by a slightly modified literature procedure: To a solution of tityl isoselenocyanate (0.500 g, 1.44 mmol) in cyclohexane (15 mL) and Et_2O (10 mL) was added hydrazine hydrate (0.1 mL). The mixture was stirred at room temperature for *ca.* 10 min. The colourless solid that formed was isolated by filtration and dried. Recrystallisation from EtOH gave the product as colourless crystals in 76% yield (0.415 g). ^{1}H NMR (acetone-d_6) δ = 7.21–7.37 (m, 19 H, Ph_3C, NH), 9.21 (br. s, 1 H, NH_2), 9.52 (br. s, 1 H, NH_2). ^{13}C NMR (acetone-d_6) δ = 73.62, 127.79, 128.49, 130.35, 145.51 (CPh_3), 178.62 (C=Se). ^{77}Se NMR (acetone-d_6) δ = 319.36.

3.4. 1-Trityl-3-n-butylselenourea (**3**)

To a solution of trityl isoselenocyanate (0.348 g, 1.00 mmol) in cyclohexane (10 mL) was added *n*-butylamine (0.08 g, 1.10 mmol) and the mixture was heated at *ca.* 40° for a few hours. The resulting precipitate was isolated by filtration and recrystallised from EtOH to give 0.190 g (45%) of a colourless solid. ^{1}H NMR (acetone-d_6) δ = 0.70 (t, *J* = 7.8 Hz, 3 H, CH_3), 0.86 (sext., *J* = 7.6 Hz, 2 H, CH_3CH_2), 1.05 (quint., *J* = 7.6 Hz, 2 H, $CH_3CH_2CH_2$), 3.38 (quart., *J* = 6.8 Hz, 2 H, CH_2N), 5.71 (br. s, 1 H, NH), 7.28–745 (m, 15 H, Ph_3C), 7.69 (s, 1H, NH). ^{13}C NMR (acetone-d_6) δ = 13.86, 20.15, 31.33, 49.22 (^{n}Bu) 74,72, 128.79, 129.37, 129.53, 143.85 (CPh_3), 180.61 (C=Se), ^{77}Se NMR (acetone-d_6) δ = 245.52.

The same reaction carried out with Et_2NH gave a *ca.* 1:1 mixture (before recrystallisation) of the selenourea and the substitution product Ph_3CNEt_2, as determined by ^{1}H NMR spectroscopy and comparison with an authentic sample of Ph_3CNEt_2. Data for the mixture is given here: ^{1}H NMR (acetone-d_6) δ = 1.15 (t, *J* = 6.9 Hz, 6 H, CH_3 Ph_3CNEt_2), 1.26 (t, *J* = 7.3 Hz, 7 H, CH_3 $Ph_3CNHC(Se)NEt_2$), 2.81 (quart., *J* = 6.9 Hz, 4 H, CH_2 Ph_3CNEt_2), 3.89 (quart., *J* = 7.1 Hz, 5 H, CH_2 $Ph_3CNHC(Se)NEt_2$), 7.13–7.48 (m, 33 H, Ph_3C, NH).

Table 1
Crystal data and refinement details of compounds **1**, **2** and **5**.

	1	**2**	**5**
Empirical formula	$C_{40}H_{30}N_2Se_2$	$C_{40}H_{37}Se_2N_6$	$C_{52}H_{42}Se_2N_8$
Colour	colourless	colourless	yellow
M_r, (g mol^{-1})	696.58	759.68	936.86
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	20.3163(6)	14.7937(8)	11.1128(5)
b (Å)	8.48624(18)	9.6345(5)	13.8305(3)
c (Å)	20.0327(6)	24.9993(13)	16.8335(7)
α (°)	90	90	101.174(3)
β (°)	109.984(3)	101.075(5)	99.377(4)
γ (°)	90	90	112.017(3)
V (Å^3)	3245.85(14)	3496.8(3)	2272.76(15)
Z	4	4	2
D_{calc} (g cm^{-3})	1.425	1.443	1.369
μ (mm^{-1})	2.309	2.153	1.672
F (0 0 0)	1408	1548	956
Crystal size (mm^3)	0.22 × 0.10 × 0.02	0.11 × 0.04 × 0.03	0.14 × 0.08 × 0.05
θ Range for data collection (°)	2.70–29.52	2.97–29.51	3.07–29.51
Reflections collected	19232	17860	18330
Independent reflection	7677	8225	10498
Abs. corr.	empirical	empirical	empirical
Max./min. trans.	1.00/0.60	1.00/0.88	1.00/0.88
Parameters	397	436	559
Goodness-of-fit	0.915	0.842	0.862
R_1 [$I > 2\sigma(I)$]	0.0394	0.0517	0.0318
wR_2 (all data)	0.0968	0.1120	0.0581
Largest diff. peak/hole (e Å^{-3})	1.021/−1.277	1.961/−0.434	0.513/−0.474

3.5. Reaction of trityl selenosemicarbazide with salicylaldehyde

To a solution of trityl selenosemicarbazide (0.300 g, 0.789 mmol) in hot EtOH (40 mL) was added salicylaldehyde (0.08 mL, 0.789 mmol) and the mixture was heated to reflux for *ca.* 4 h. The resulting solution was filtered and the filtrate taken to dryness in vacuum. The resulting pale yellow solid was extracted into CH_2Cl_2 and passed through Celite. The filtrate was concentrated in vacuum and the solid which was isolated by filtration and recrystallised from EtOH. 0.208 g (54%) of a pale yellow solid was obtained. ^{1}H NMR (CD_3Cl) δ = 6.91 (dt, *J* = 7.5/1.0 Hz, 1 H, H4), 6.97 (d, *J* = 8.3 Hz, 1 H, H3), 7.09–7.31 (m, 19 H, Ph_3C, NH, H5, H6), 7.84 (s, 1 H, HC=N), 10.46 (s, 1 H, OH). ^{13}C NMR (CD_3Cl) δ = 74.19 (CPh_3), 116.61 (C3), 118.09 (C1), 119.43 (C5), 127.14 (*p*-Ph), 127.96 (Ph), 128.93 (Ph), 131.36 (C6), 131.57 (C4), 144.01 (*ipso*-Ph), 146.63 (C=N), 157.88 (COH), 158.53 (C=Se). ^{77}Se NMR (CD_3Cl) δ = 402.58.

3.6. Reaction of trityl selenosemicarbazide with 2-pyridinecarboxaldehyde

To a solution of trityl selenosemicarbazide (0.300 g, 0.789 mmol) in EtOH (10 mL) was added 2-pyridinecarboxaldehyde (slight excess) and the mixture was heated to reflux for *ca.* 4 h. The resulting dark-yellow solution was filtered and the filtrate was concentrated in vacuum. On cooling a dark gum remained which was found to contain some large yellow crystals after standing for a few days. The crystals were manually separated from the gum, cleaned and subsequently used for the X-ray diffraction experiment.

3.7. X-ray crystallography

Diffraction data were collected at 170 K using an Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area

detector and a four-circle kappa goniometer. For the data collection the Mo source emitting graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used. Data integration, scaling and empirical absorption correction was carried out using the CrysAlis Pro program package [12]. The structure was solved using Direct Methods and refined by Full-Matrix-Least-Squares against F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were carried out using the program Olex2 [13]. Important crystallographic data and refinement details are summarised in Table 1.

Acknowledgements

We thank RETORTE GmbH, Germany for a generous donation of selenium metal and the DFG for a grant to purchase the diffractometer.

Appendix A. Supplementary material

CCDC compounds **1**, **2** and **5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.02.021.

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