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Masaichi Saito[a]; Yoshihiko Kanatomi[a]
[a] Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Saitama-city, Saitama, Japan

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Reinvestigation on the synthesis of hexakis(phenylseleno)benzene

Masaichi Saito* and Yoshihiko Kanatomi

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Saitama-city, Saitama 338-8570, Japan

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This article is dedicated to Professor Juzo Nakamaya on the occasion of his retirement from Saitama University.

Reactions of hexafluorobenzene with PhSeNa in dimethylformamide (DMF) afforded 1,4-bis (phenylseleno)benzene **3** and 1,2,4,5-tetrakis(phenylseleno)benzene **4**, instead of the reported product, hexakis(phenylseleno) benzene **1**. Reactions of hexabromobenzene with PhSeNa in hexamethylphosphoric triamide (HMPA) afforded 1,4-bis-**6**, 1,2,4,5-tetrakis-**7** and hexakis(phenylseleno)benzene **1**. The structures of the products were established by X-ray crystallographic analysis.

Keywords: hexafluorobenzene; hexabromobenzene; 1,4-bis(phenylseleno)benzene; 1,2,4,5-tetrakis (phenylseleno)benzene; hexakis(phenylseleno)benzene

1. Introduction

Persulfurated aromatic compounds are of growing interest from the viewpoint of their structural diversity, building blocks for dendric molecules, and application to advanced organic materials, and a comprehensive review has recently been published (*1*). Quite recently, novel hexakis(arylthio)benzenes have been synthesized (*2*, *3*) and used as stabilizers of palladium nanoparticles (*3*). On the other hand, with regard to the corresponding heavier analogues, only a few examples of perselenated aromatic compounds have appeared (*4*, *5*) and no reports on the synthesis of the corresponding tellurium derivatives have been published. Hexakis(phenylseleno)benzene **1** was first synthesized by the reaction of hexachlorobenzene with PhSeNa, prepared from diphenyl diselenide and sodium hydride, and the structure was estimated by elemental analysis of its CBr_4 adduct (*4*). Later, the structure of the CBr_4 adduct of **1** was finally established by X-ray crystallographic analysis (*6*). Most recently, hexakis(phenylseleno)benzene **1** has been efficiently synthesized by the reaction of hexafluorobenzene **2** with PhSeNa in DMF (*7*). To the best of our knowledge, however, spectral details of **1** have not appeared in any previous reports. We became interested in the investigation on the reactivities of hexakis(phenylseleno)benzene **1** which could be utilized as a new building block of new advanced

*Corresponding author. Email: masaichi@chem.saitama-u.ac.jp

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materials and hence we examined the synthesis of **1** according to the literature. We report here a new reaction mode which was not reported in the previous report (*7*). An alternative method for the synthesis of **1** is also described.

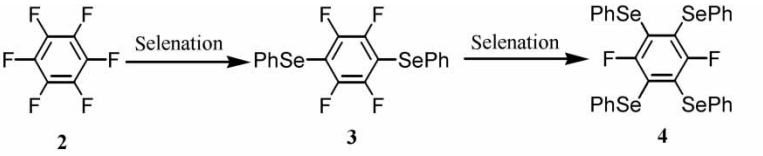
2. Results and discussion

2.1. *Reactions of hexafluorebenzene 2 with PhSeNa*

Firstly, we examined the reaction of hexafluorobenzene **2** with PhSeNa according to the previous report (*7*). After treatment of diphenyl diselenide (3 mmol) with an equimolar amount of sodium hydride (assay, 60%) in DMF, to the resulting mixture was added a DMF solution of hexafluorobenzene **2** (0.5 mmol) and it was stirred for 2 h. However, 1,4-bis(phenylseleno)-substituted compound **3** was obtained in 88% yield instead of the reported hexakis(phenylseleno)benzene **1** (Scheme 1) (*7*). The structure of the 1,4-bis adduct **3** was estimated by NMR and elemental analysis and finally established by X-ray crystallographic analysis. Prolonged stirring (3 days) of the reaction mixture in DMF, formed from hexafluorobenzene **2**, diphenyl diselenide (6 eq.) and sodium hydride (6 eq.), afforded tetrakis-substituted derivative **4** in 19% yield (Scheme 1). The tetrakis-substituted derivative **4** was also formed by the reaction of the 1,4-bis adduct **3** with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in 76% yield. Although a mixture of the tetrakis-substituted derivative **4** and PhSeNa in DMF was stirred for 3 days at 0°C, the starting **4** was recovered and hence we concluded that hexakis(phenylseleno)benzene **1** could not be synthesized by ourselves under the same conditions as the previous ones (*7*). Secondly, in order to obtain compound **1**, the reaction of hexafluorobenzene **2** with PhSeNa in HMPA was examined, because the first synthesis of **1** was achieved by the reaction of hexachlorobenzene with PhSeNa in HMPA (*4*). However, stirring the reaction mixture from hexafluorobenzene **2**, diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in HMPA for 4 days afforded tetrakis(phenylseleno)-substituted compound **4** in 45% yields. The compounds **3** and **4** were not reported in the previous literature (*7*). Reaction of **4** with PhSeNa in HMPA did not proceed and the compound **4** was recovered. The reason that further substitution of **4** did not proceed was probably caused by the fact that electron deficiency of the phenylseleno-substituted derivatives decreases with an increase in the number of phenylseleno groups, suppressing an addition–elimination reaction. A similar limitation in the substitution of hexafluorobenzene **2** was also reported in the literature (*3*).

2.2. *Reactions of hexabromobenzene 5 with PhSeNa*

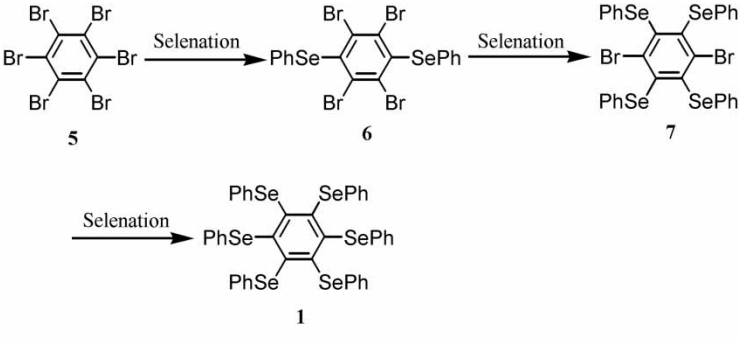
Although the first synthesis of **1** was achieved from hexachlorobenzene (*4*), we independently examined reactions of hexabromobenzene **5** with PhSeNa in HMPA. After treatment of hexabromobenzene **5** with PhSeNa prepared from diphenyl diselenide (2 eq.) and sodium hydride (2 eq.), the reaction mixture was stirred at room temperature for 2 h to afford 1,4-bis(phenylseleno)-substituted derivative **6** in 70% yield (Scheme 2). Treatment of hexabromobenzene **5** with PhSeNa, prepared from diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) for 12 h afforded tetrakis-substituted derivative **7** in 62% yield (Scheme 2). Finally, the targeted hexakis-substituted compound **1** was obtained in 33% yield by the reaction of hexabromobenzene **5** with PhSeNa prepared from diphenyl diselenide (6 eq.) and sodium hydride (12 eq.) for 12 h (Scheme 2). The hexakis derivative **1** was also synthesized by the reaction of tetrakis derivative **7** with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in 91% yield. The structure of **1** was estimated by NMR and elemental analysis and finally established by X-ray crystallographic analysis.



2 **3** **4**

Starting compound	Solvent	PhSeSePh	NaH	Stirring	Temp.	Products
2	DMF	6 eq.	6 eq.	2 h	0 °C	**3** (88%)
2	DMF	6 eq.	6 eq.	3 d	0 °C	**4** (18%)
3	DMF	6 eq.	6 eq.	12 h	0 °C	**4** (76%)
4	DMF	6 eq.	6 eq.	3 d	0 °C	**4** (81%)
2	HMPA	6 eq.	6 eq.	4 d	r.t.	**3** (3%), **4** (45%)
4	HMPA	6 eq.	6 eq.	4 d	r.t.	**4** (82%)

Scheme 1. Selenation of hexafluorobenzene **2**.



5 **6** **7** **1**

Starting compound	Solvent	PhSeSePh	NaH	Stirring	Temp.	Products
5	HMPA	2 eq.	2 eq.	2 h	r.t.	**6** (70%)
5	HMPA	6 eq.	6 eq.	12 h	r.t.	**7** (62%)
5	HMPA	6 eq.	12 eq.	12 h	r.t.	**1** (32%)
7	HMPA	6 eq.	6 eq.	12 h	r.t.	**1** (91%)

Scheme 2. Selenation of hexabromobenzene **5**.

2.3. *Molecular stucture of phenylselenobenzenes 1, 3 and 7*

Figure 1 reveals the first solid-state structure of hexakis derivative **1** without any other molecules in the unit cell, even though the structure of the CBr_4-adduct of **1** has already been reported (*4*). The asymmetric unit has two independent half molecules which lie about independent inversion centers, and the only one of these molecules is shown in Figure 1. The bonding situation of the aromatic ring and the six selenium atoms slightly deviates from planarity, and the dihedral angles, for example, between the Se(1)−C(1)−C(2) and C(1)−C(2)−Se(2) planes, are about from 10 ° to 15 ° with an up-and-down conformation. The six phenyl rings are situated in an up-and-down conformation, with each of the rings located nearly perpendicularly to the next phenyl rings. No bonding interactions were found in any combination of the selenium atoms and the distances range from 3.2 to 3.5 Å, which are much longer than the Se–Se bond (2.31 Å) in dimethyl diselenide (*8*). Because of the up-and-down conformation of phenylseleno groups, leading to steric bulkiness, no π–π stacking is found in the unit cell.

Figure 2 reveals the molecular structure of the tetrakis adduct **7**. The molecule lies about an inversion center. In contrast to the hexakis adduct **1** whose phenyl rings are located in an

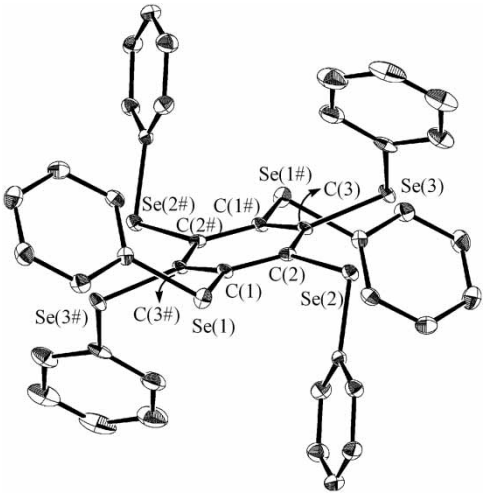


Figure 1. ORTEP drawing of **1** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). Only one of the two independent molecules is shown and the # character in the atom labels shows that these atoms are at equivalent position $(1-x, 1-y, -z)$. All hydrogen atoms are omitted for clarity.

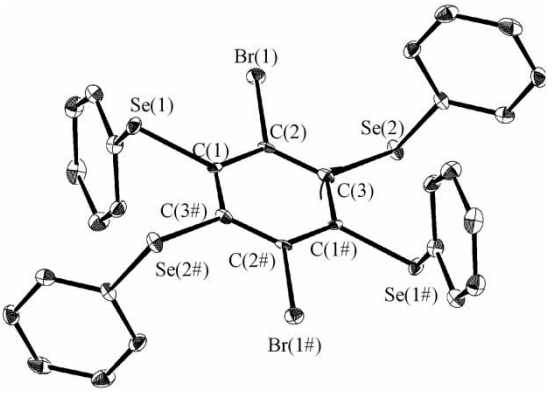


Figure 2. ORTEP drawing of **7** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). The # character in the atom labels shows that these atoms are at equivalent position $(-x, -y, -z)$. All hydrogen atoms are omitted for clarity.

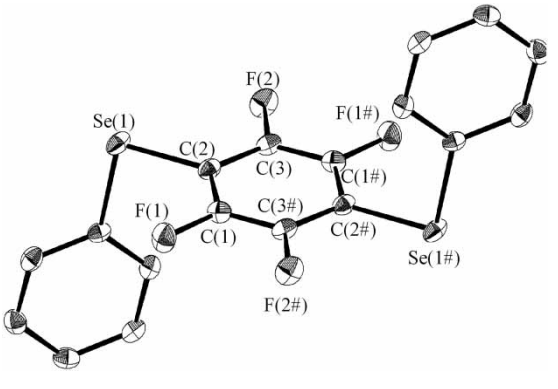


Figure 3. ORTEP drawing of **3** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). Only one of the two independent molecules is shown and the # character in the atom labels shows that these atoms are at equivalent position $(-1-x, -1-y, -z)$. All hydrogen atoms are omitted for clarity.

up-and-down fashion, the phenyl rings on the 1- and 2-positions are both located on the same side of the central phenyl ring.

Figure 3 reveals the molecular structure of the bis(phenylseleno) adduct **3**. The asymmetric unit has two independent half molecules which lie about independent inversion centers, and the only one of these molecules is shown in Figure 3. The two phenyl rings are located in opposite positions. Since the shortest distance between the phenyl rings is 5.657 Å, no significant interactions derived from π–π stacking are found in the unit cell.

3. Conclusion

Reactions of hexafluorobenzene **2** with PhSeNa in DMF afforded 1,4-bis(phenylseleno)benzene **3** and 1,2,4,5-tetrakis(phenylseleno)benzene **4**, instead of the reported product, hexakis(phenylseleno)benzene **1**. The stepwise introduction of phenylseleno groups resulted in the decrease of the electron deficiency of the benzene ring, suppressing further substitution by phenylseleno groups. Reactions of hexabromobenzene **5** with PhSeNa in HMPA afforded 1,4-bis- **6**, 1,2,4,5-tetrakis- **7** and hexakis(phenylseleno)benzene **1**. Therefore, the stepwise introduction of phenylseleno groups into hexabromobenzene **5** was achieved. The structures of the products were established by X-ray crystallographic analysis.

4. Experimental

4.1. *General procedures*

DMF and HMPA were distilled over calcium hydride. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz), and ^{77}Se NMR (76 MHz) spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$. Wet column chromatography (WCC) was carried out with Kanto silica gel 60N. Preparative gel permeation chromatography was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL- 1H and -2H columns with $CHCl_3$ as the eluant. Data for the X-ray crystallographic analyses were collected at 103 K on a Bruker SMART APEX diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) and the structures were solved by direct methods. All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

4.2. *Reaction of hexafluorobenzene 2 with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in DMF (2 h)*

A DMF (10 mL) suspension of diphenyl diselenide (941 mg, 3.01 mmol) and sodium hydride (127 mg, 3.2 mmol; assay 60%) was stirred for 30 min at 0 °C. To the suspension was added a DMF (5 mL) solution of hexafluorobenzene **2** (0.055 mL, 0.48 mmol) and the resulting mixture was stirred for 2 h at the same temperature. The reaction mixture was poured into ice water and insoluble materials (877 mg) were collected by filtration. The residue was subjected to WCC (eluant: hexane:ethyl acetate = 50:1) to afford 1,2,4,5-tetrafluoro-3,6-bis(phenylseleno)benzene (**3**) (193 mg, 88%). **3**: mp 126.5–127.3°C(hexane). ^{1}H NMR: δ 7.24–7.34(m, 6H), 7.53–7.58(m, 4H); ^{13}C NMR: δ 109.80–110.52(C), 127.99(C), 128.51(CH), 129.49(CH), 133.68(CH), 145.09–147.86(C); ^{77}Se NMR: δ 281.6–282.4. The ^{13}C signals at about 146 ppm and the ^{77}Se signals are very complicated because of couplings with ^{19}F nuclei. Anal. calcd for $C_{18}H_{10}F_4Se_2$: C, 46.98; H, 2.19. Found: C, 47.06; H, 2.07.

4.3. *Reaction of hexafluorobenzene 2 with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in DMF (3 days)*

A DMF (5 mL) suspension of diphenyl diselenide (490 mg, 1.57 mmol) and sodium hydride (63 mg, 1.6 mmol; assay 60%) was stirred for 30 min at 0 °C. To the suspension was added a DMF (3 mL) solution of hexafluorobenzene **2** (0.03 mL, 0.3 mmol) and the resulting mixture was stirred for 3 days at the same temperature. The reaction mixture was poured into ice water and insoluble materials (397 mg) were collected by filtration. The residue was washed by hexane and 1,4-difluoro-2,3,5,6-tetrakis(phenylseleno)benzene (**4**) (36 mg, 19%) was collected as an insoluble material. **4**: mp 152.0–152.8°C(hexane). ^{1}H NMR: δ 7.13–7.24(m, 12H), 7.28–7.32(m, 8H); ^{13}C NMR: δ 100.12(C), 126.42(C, d, J(C-F) = 27 Hz), 127.48(CH), 129.24(CH), 130.81(C), 132.44(CH); ^{77}Se NMR: δ 379.7–380.0. The ^{77}Se signals are very complicated because of couplings with ^{19}F nuclei. Anal. calcd for $C_{30}H_{20}F_2Se_4$: C, 49.07; H, 2.75. Found: C, 48.86; H, 2.51.

4.4. *Reaction of bis(phenylseleno)benzene 3 with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in DMF*

A DMF (4 mL) suspension of diphenyl diselenide (404 mg, 1.30 mmol) and sodium hydride (56 mg, 1.4 mmol; assay 60%) was stirred for 30 min at 0 °C. The suspension was added to bis(phenylseleno)benzene **3** (98 mg, 0.21 mmol) and the resulting mixture was stirred for 12 h at the same temperature. The reaction mixture was poured into ice water and insoluble materials (386 mg) were collected by filtration. The residue was washed with hexane and tetrakis(phenylseleno)benzene **4** (118 mg, 76%) was collected as an insoluble material.

4.5. *Reaction of 1,4-difluoro-2,3,5,6-tetrakis(phenylseleno)benzene (4) with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in DMF (3 days)*

A DMF (3 mL) suspension of diphenyl diselenide (206 mg, 0.66 mmol) and sodium hydride (35 mg, 0.88 mmol; assay 60%) was stirred for 30 min at 0 °C. The resulting suspension was added to tetrakis(phenylseleno)benzene **4** (79 mg, 0.11 mmol) and the resulting mixture was stirred for 3 days at the same temperature. The reaction mixture was poured into ice water and insoluble materials (201 mg) were collected by filtration. The residue was washed with hexane and tetrakis(phenylseleno)benzene **4** (65 mg, 81%) was recovered.

4.6. *Reaction of hexafluorobenzene 2 with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in HMPA (4 days)*

An HMPA (10 mL) suspension of diphenyl diselenide (938 mg, 3.01 mmol) and sodium hydride (127 mg, 3.2 mmol; assay 60%) was stirred for 30 min at room temperature. To the suspension was added an HMPA (6 mL) solution of hexafluorobenzene **2** (0.06 mL, 0.5 mmol) and the resulting mixture was stirred for 4 days. The reaction mixture was poured into ice water and insoluble materials (206 mg) were collected by filtration. The residue was subjected to WCC (eluant: hexane : ethyl acetate = 50:1) to afford tetrakis(phenylseleno)benzene **4** (174 mg, 45%) and bis(phenylseleno)benzene **3** (7 mg, 3%).

4.7. *Reaction of 1,4-difluoro-2,3,5,6-tetrakis(phenylseleno)benzene (4) with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in HMPA (4 days)*

An HMPA (5 mL) suspension of diphenyl diselenide (192 mg, 0.62 mmol) and sodium hydride (27 mg, 0.66 mmol; assay 60%) was stirred for 30 min at room temperature. The resulting

suspension was added to tetrakis(phenylseleno)benzene **4** (109 mg, 0.15 mmol) and the resulting mixture was stirred for 4 days at the same temperature. The reaction mixture was poured into ice water and insoluble materials (236 mg) were collected by filtration. The residue was washed with hexane and tetrakis(phenylseleno)benzene **4** (89 mg, 82%) was recovered.

4.8. *Reaction of hexabromobenzene 5 with diphenyl diselenide (2 eq.) and sodium hydride (2 eq.) in HMPA*

An HMPA (3 mL) suspension of diphenyl diselenide (314 mg, 1.01 mmol) and sodium hydride (43 mg, 1.1 mmol; assay 60%) was stirred for 30 min at room temperature. The suspension was added to an HMPA (5 mL) solution of hexabromobenzene **5** (273 mg, 0.50 mmol) and the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was poured into ice water and insoluble materials (484 mg) were collected by filtration. The residue was washed with hexane and 1,2,4,5-tetrabromo-3,6-bis(phenylseleno)benzene (**6**) (243 mg, 70%) was collected as an insoluble material. **6**: mp 225.0–226.3°C (dichloromethane + hexane). ^{1}H NMR: δ 7.26–7.31(m, 6H), 7.33–7.38(m, 4H); ^{13}C NMR: δ 127.53(CH), 128.48(C), 129.62(CH), 131.09(CH), 132.07(C), 134.03(C); ^{77}Se NMR: δ 611.9. Anal. calcd for $C_{18}H_{10}Br_4Se_2$: C, 30.72; H, 1.43. Found: C, 30.12; H, 1.05.

4.9. *Reaction of hexabromobenzene 5 with diphenyl diselenide (6 eq.) and sodium hydride (6 eq.) in HMPA*

An HMPA (10 mL) suspension of diphenyl diselenide (944 mg, 3.03 mmol) and sodium hydride (126 mg, 3.2 mmol; assay 60%) was stirred for 30 min at room temperature. The suspension was added to an HMPA (5 mL) solution of hexabromobenzene **5** (275 mg, 0.50 mmol) and the resulting mixture was stirred for 12 h at room temperature. The reaction mixture was poured into ice water and insoluble materials (888 mg) were collected by filtration. The residue was washed with hexane and 1,4-dibromo-2,3,5,6-tetrakis(phenylseleno)benzene (**7**) (265 mg, 62%) was collected as an insoluble material. **7**: mp 199–201 °C (chloroform). ^{1}H NMR: δ 7.19(s, 20H); ^{13}C NMR: δ 126.96(CH), 129.41(CH), 130.59(CH), 134.03(C), 138.14(C), 144.24(C); ^{77}Se NMR: δ 588.7. Anal. calcd for $C_{30}H_{20}Br_2Se_4$: C, 42.09; H, 2.36. Found: C, 41.72; H, 1.98.

4.10. *Reaction of hexabromobenzene 5 with diphenyl diselenide (6 eq.) and sodium hydride (12 eq.) in HMPA: formation of hexakis(phenylseleno)benzene 1*

An HMPA (10 mL) suspension of diphenyl diselenide (946 mg, 3.03 mmol) and sodium hydride (245 mg, 6.1 mmol; assay 60%) was stirred for 30 min at room temperature. The suspension was added to hexabromobenzene **5** (330 mg, 0.59 mmol) and the resulting mixture was stirred for 15 h at room temperature. The reaction mixture was poured into ice water and insoluble materials (1157 mg) were collected by filtration. The residue was washed with ethanol and 1,2,3,4,5,6-hexakiskis(phenylseleno)benzene (**1**) (168 mg, 33%) was collected as an insoluble material. **1**: mp 194–195 °C (dichloromethane). ^{1}H NMR: δ 7.08–7.18(m, 30H); ^{13}C NMR: δ 126.71(CH), 129.24(CH), 130.87(CH), 135.49(C), 148.36(C); ^{77}Se NMR: δ 558.6. Anal. Calcd for $C_{42}H_{30}Se_6$: C, 50.02; H, 3.00. Found: C, 50.15; H, 2.84.

4.11. *Preparation of hexakis(phenylseleno)benzene 1 from tetrakis(phenylseleno)-benzene 7*

An HMPA (5 mL) suspension of diphenyl diselenide (590 mg, 1.89 mmol) and sodium hydride (79 mg, 2.0 mmol; assay 60%) was stirred for 1 h at room temperature. The suspension was

added to tetrakis(phenylseleno)benzene **7** (255 mg, 0.30 mmol) and the resulting mixture was stirred for 12 h at room temperature. The reaction mixture was poured into ice water and insoluble materials (1.061 g) were collected by filtration. The residue was washed with hexane and hexakis(phenylseleno)benzene **1** (274 mg, 91%) was collected as an insoluble material.

4.12. *Crystallographic data for 1*

$C_{42}H_{30}Se_6$, $M = 1008.42$, $0.50 \times 0.45 \times 0.30$ mm, triclinic, $a = 11.0877(13)$, $b = 11.0999(13)$, $c = 15.8195(19)$ Å, $\alpha = 97.159(3)$, $\beta = 100.566(2)$, $\gamma = 100.771(2)^\circ$, $V = 1854.6(4)$ Å^3, $\rho_{calc} = 1.806$ g cm^{-3}, $Z = 2$, space group $P-1$, $R_1 = 0.029$ ($I > 2\sigma(I)$, 5964 reflections), $wR_2 = 0.077$ (for all reflections) for 6723 reflections and 433 parameters. goodness of fit (GOF) = 1.047. CCDC-725309 contains the supplementary crystallographic data for this compound.

4.13. *Crystallographic data for 3*

$C_{18}H_{10}F_4Se_2$, $M = 460.18$, $0.30 \times 0.20 \times 0.10$ mm, monoclinic, $a = 15.6199(11)$, $b = 5.6565(4)$, $c = 18.7242(13)$ Å, $\beta = 107.202(1)^\circ$, $V = 1580.35(19)$ Å^3, $\rho_{calc} = 1.934$ g cm^{-3}, $Z = 4$, space group $P2_1/n$, $R_1 = 0.029$ ($I > 2\sigma(I)$, 3149 reflections), $wR_2 = 0.069$ (for all reflections) for 3787 reflections and 217 parameters. GOF = 1.014. CCDC-725308 contains the supplementary crystallographic data for this compound.

4.14. *Crystallographic data for 7*

$C_{30}H_{20}Br_2Se_4$, $M = 856.10$, $0.50 \times 0.20 \times 0.20$ mm, triclinic, $a = 8.3203(17)$, $b = 9.4611(18)$, $c = 9.4660(17)$ Å, $\alpha = 107.373(4)$, $\beta = 94.986(3)$, $\gamma = 105.393(3)^\circ$, $V = 674.4(2)$ Å^3, $\rho_{calc} = 2.108$ g cm^{-3}, $Z = 1$, space group P-1, $R_1 = 0.050$ ($I > 2\sigma(I)$, 2278 reflections), $wR_2 = 0.144$ (for all reflections) for 2427 reflections and 163 parameters. GOF = 1.279. CCDC-725310 contains the supplementary crystallographic data for this compound.

Acknowledgements

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