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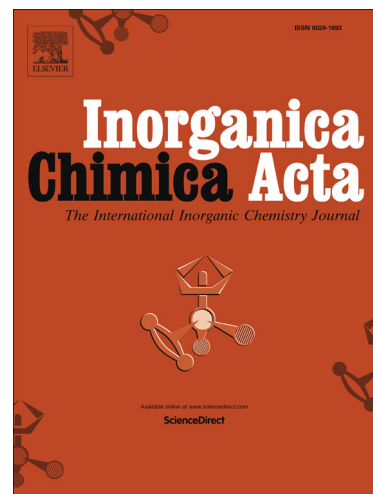
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Complexation of Aromatic Dichalcogen Ligands to Germanium

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Abstract: Eight novel germanium compounds of the type $[R_2Ge(E-Ar-E)]$, where $R = Me, Ph$; $E-Ar-E$ = an aromatic bidentate chalcogen ligand, were successfully synthesised. The effects of changing 3 variables within the series were investigated. These variables included the chalcogen ($E = S/Se$), aromatic backbone ($Ar = Nap/Biphenyl$) and R group (Me/Ph) employed. The choice of aromatic backbone had the greatest effect on the structure. A substantial change in geometry around the germanium centre was observed within the solid state structures depending on whether the backbone was naphthalene or biphenyl. This affected the stability of the compound and resulted in the visible decomposition of two selenium complexes over several days. All novel compounds were characterised by multinuclear NMR, IR, mass spectroscopy and single crystal X-ray diffraction.

Keywords: Germanium; sulfur; selenium; coordination; X-Ray structure

Introduction

Sulfur and selenium donor ligands are soft donor ligands¹⁻⁴ and include, thiolates (**A**), dithiolates (**B, D**) and dithioleenes (**C**) as well as trithiolates (**E**) and tetrathiolates (**F**) (Figure 1).^{5,6}

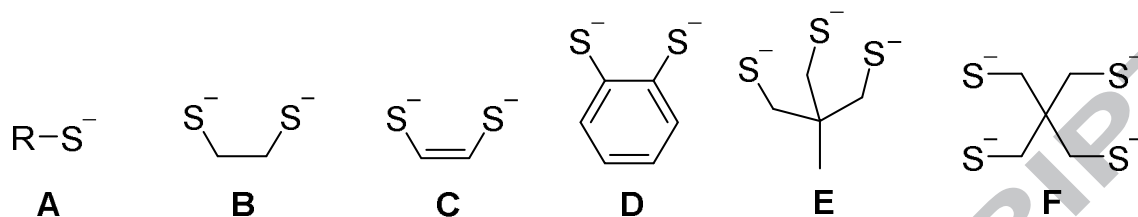


Figure 1: Sulfur donor ligands.

Of particular interest here are dithiolate ligands containing an aromatic backbone. Until recently bidentate dithiolate ligands with larger rigid aromatic backbones, such as naphthalene, biphenyl, anthracene and tetracene, have had relatively little attention in comparison to other dithiolate ligands such as ethane-1,2-dithiolate, **B**, and benzene-1,2-dithiolate, **D**.⁷ Teo reported some systems in the late 1970s (**G-J**, Figure 2) studying a series of singly and doubly bridged transition metal complexes with potential uses as organic solid state semiconductors.⁸⁻¹⁵

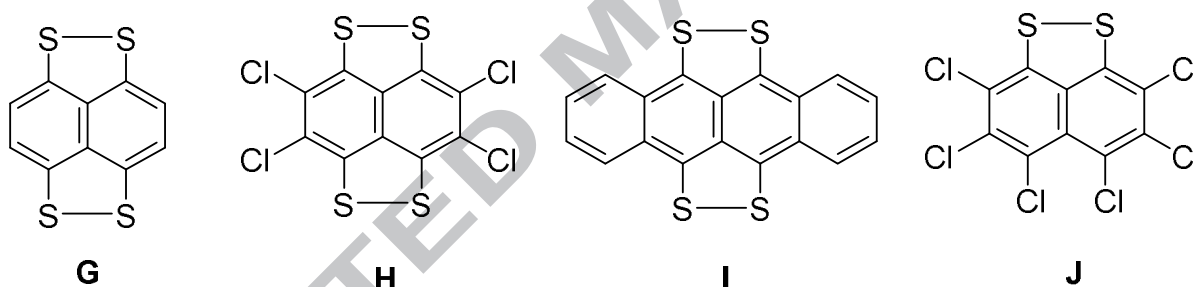


Figure 2: Structurally related naphthalene ligands.

Sulfur ligands can be used in a variety of applications, such as lubricant additives and as catalysts in a range of reactions¹⁶⁻¹⁸ (**K**) and they can support unusual magnetic properties.¹⁹⁻²² Wright and co-workers established that rigid, naphthalene-1,8-dithiolate ligands provide a range of diiron hydrogenase mimics (**L**,

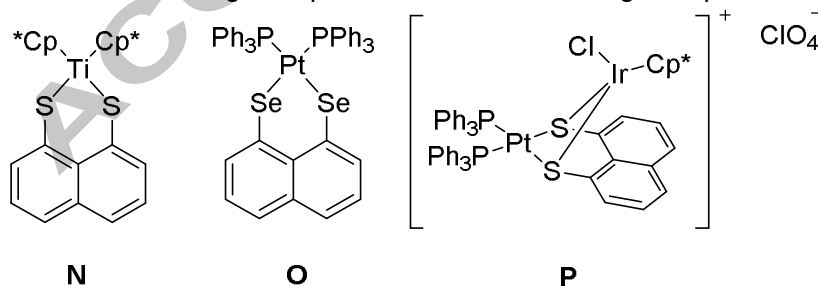
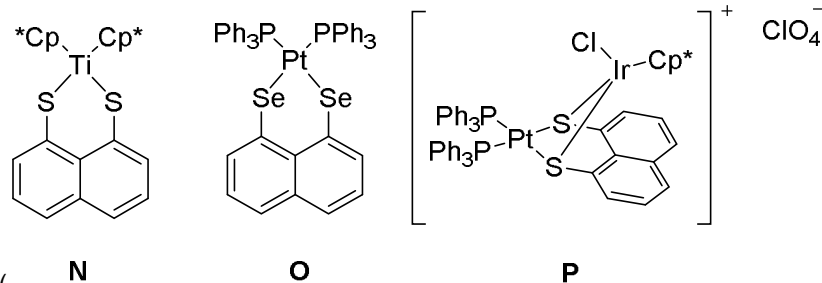


Figure 3) that act as electrocatalysts for the proton reduction of *p*-toluenesulfonic acid.^{23,24} In addition, the



rhodium (I) complex, **M** (

Figure 3), containing the bidentate sulfur ligand 1,1'-binaphthalene-2,2'-dithiol, can be used as a catalyst for the highly regioselective hydroformylation of styrene.²⁵

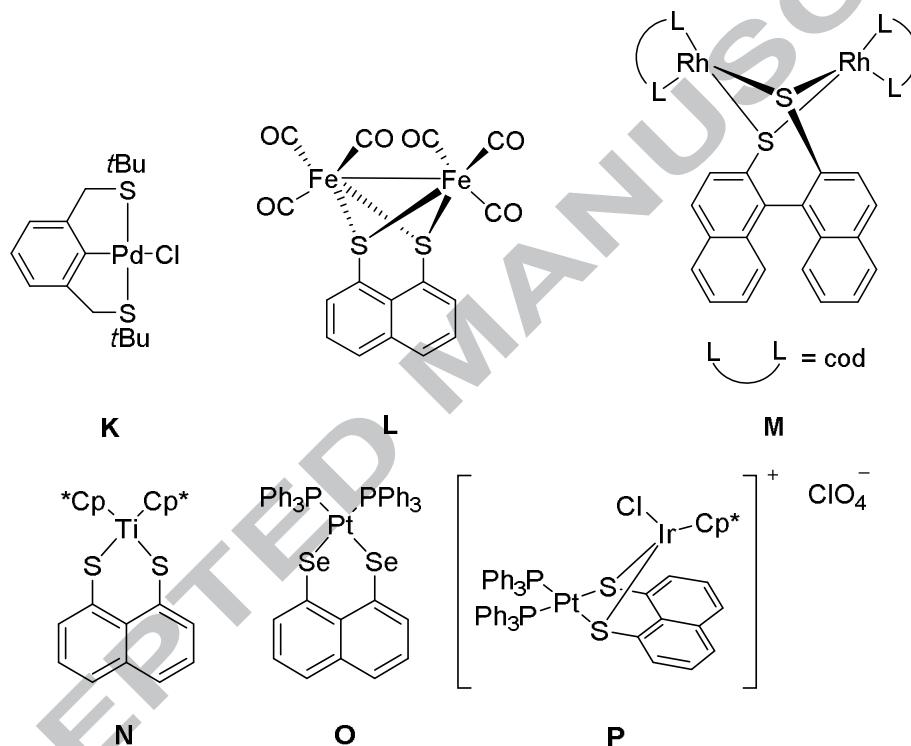
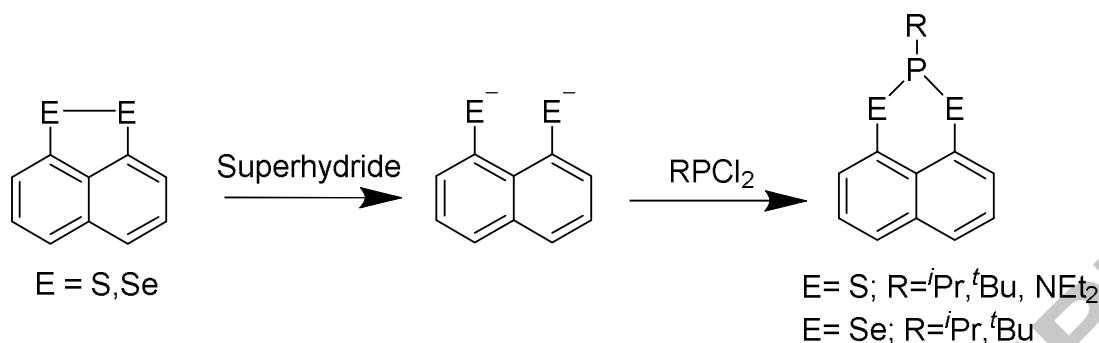


Figure 3: Sulfur containing complexes.

Robertson illustrated the ability of sulfur-donor atoms to bridge a range of metal centres to form species such as the titanium (IV) complex **N**.²⁸ Subsequently, Knight synthesised the platinum (II) complex **O**, which demonstrated that selenium-donor atoms are also capable of binding metal centres.²⁹ The hetero-bimetallic complex **P** demonstrated the ease with which sulfur donor atoms in ligands of this type may increase their coordination number.³⁰ More recently, work has included p-block elements with a series of phosphorus-chalcogen heterocycles being synthesised (Scheme 1). Solid state nmr revealed that the selenium analogues showed intermolecular interactions between the phosphorus and selenium atoms.³¹



Scheme 1: Synthesis of phosphorus-chalcogen heterocycles

There are few examples of compounds involving a germanium atom bound to bidentate chalcogen ligands in the literature (Figure 4).³²⁻³⁵

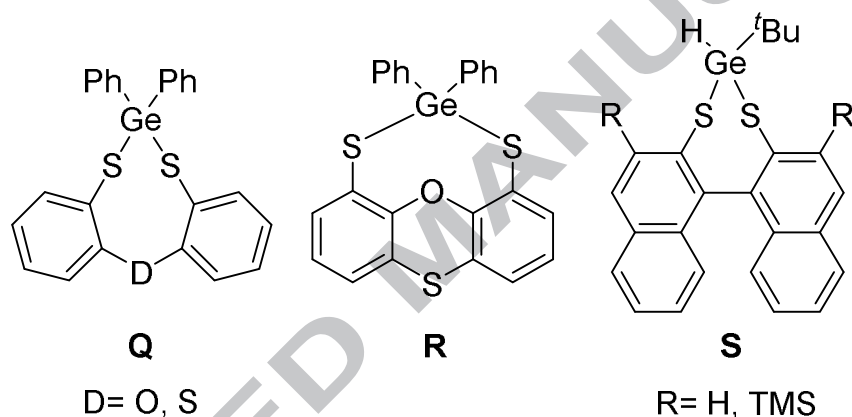


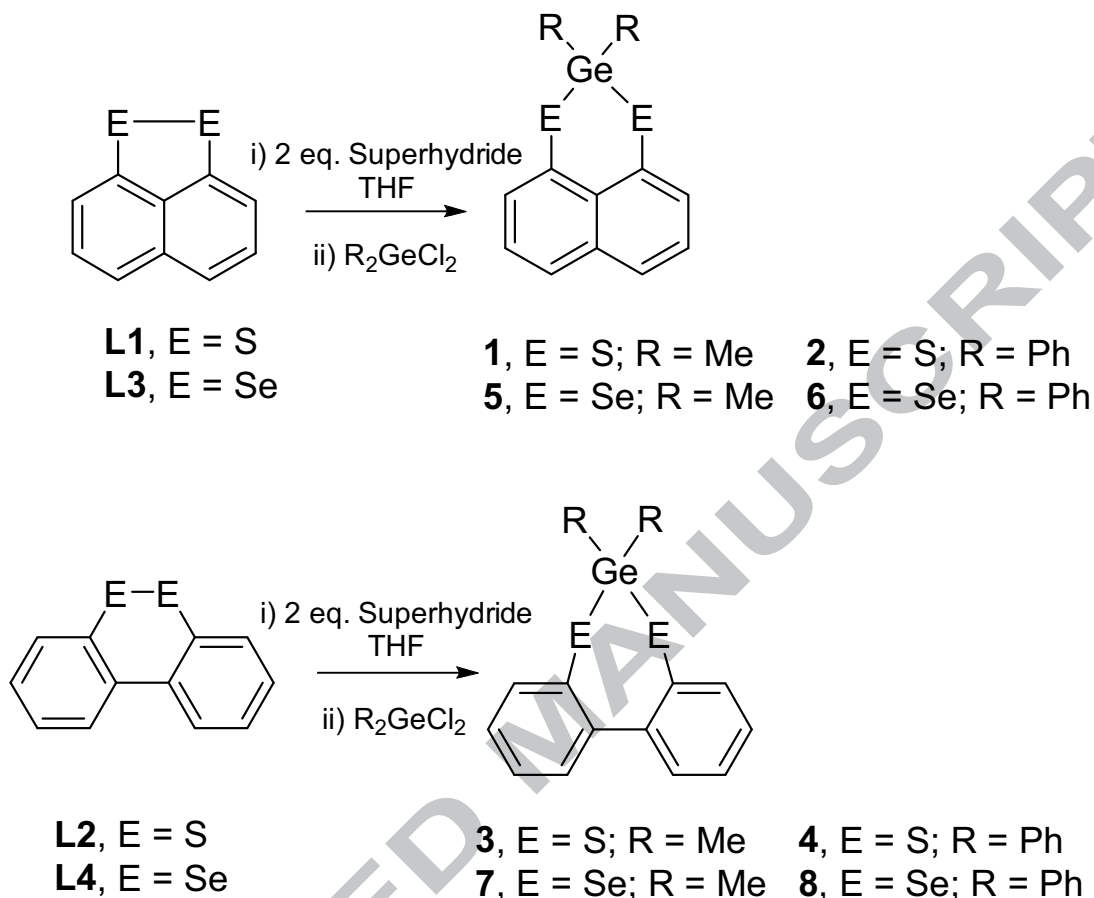
Figure 4. Germanium compounds containing S,S-bidentate ligands.

Q and **R** were synthesised by employing tridentate $[D(C_6H_4S)_2]^{2-}$ (D = O, S) and $[S(C_6H_3S)2O]^{2-}$ ligands in order to study hypercoordination in germanium heterocyclic compounds. **Q** exhibits a bipyramidal-trigonal local geometry of the germanium (IV) atom with intramolecular interactions of D→Ge.³⁹ Compound **R**, displays a distorted tetrahedral local geometry at the Ge (IV) center, however, if the two Ph substituents are replaced by Cl, a trigonal bipyramidal coordination geometry is observed, as well as strong O→Ge intramolecular interactions, due to an increase of the Lewis acidity on the germanium atom.⁴⁰ The first enantiomerically pure chiral germanium hydrides (**S**) were synthesised in 2003 by Gaultieri.³⁸

In this work we describe the synthesis and crystal structures of eight R_2GeL complexes where R = Ph or Me, and L has either a naphthyl or biphenyl backbone with sulfur or selenium donor atoms. Their structural features are compared.

Results and Discussion

The synthetic route to complexes **1-8** is shown in Scheme 2.



Scheme 2: Synthesis of the germanium series.

Complexes **1-4** were obtained in 25-60% yield as cream/white solids. **1** had the lowest yield of the series as it was more soluble in hexane resulting in the loss of some product. Crystals of **1-4** suitable for single crystal X-ray diffraction were grown by slow evaporation from a saturated solution in dichloromethane. The starting material, Me_2GeCl_2 , showed a signal from the methyl protons at δ_{H} 1.21 ppm. Compounds **1** and **3** display a shift in the methyl signal upfield to δ_{H} 0.92 ppm and δ_{H} 0.83 ppm respectively since the two chlorine atoms bound to the germanium centre are changed for two, more donating, sulfur atoms. In a similar manner, the aromatic signals from the phenyl groups bound to the germanium centre in **2** and **4** also shifted upfield compared to the starting material, Ph_2GeCl_2 . The appearance of aromatic signals from the chalcogen ligand provided further evidence of a successful reaction. Usually, for compounds containing the naphthalene backbone, three doublet of doublets would be expected. In **1**, two aromatic peaks are observed, a doublet and a *pseudo* triplet. In this case the signals from the *ortho* and *para* protons perfectly overlap resulting in one doublet with an integral twice that of the *pseudo* triplet. This *pseudo* triplet is

observed as the two coupling constants are of a similar size. In **2** the signals for the *ortho* and *para* protons are separate, with the same apparent triplet present.

For complexes **3** and **4**, which contain the biphenyl backbone, two doublet of doublets and two doublet of doublet signals would be expected from the ligand. Two doublet of doublet signals are observed in the ^1H NMR spectrum of **3** and **4**, in the latter, one of these overlaps with the phenyl group signals. The remaining signals appear as *pseudo* triplet of doublets since the two $^3J_{\text{HH}}$ values are similar in magnitude. ^{13}C NMR was obtained for **1-4**. In all cases the number of signals corresponding to quaternary, CH and CH_3 carbon atoms matched what was expected and there was no indication of any other species being present. High-resolution mass spectroscopy of **1-4** showed the $[\text{M}+\text{H}^+]$ ions each displaying the predicted isotopic distribution pattern.

The selenium analogues were synthesised using the same procedure as for the sulfur complexes (**2**). Complexes **5-8** were obtained in 28-78% yield as cream/white solids. **8** had a lower yield of 28% due to a mishandling during synthesis. Crystals of **5-8** suitable for single crystal X-ray diffraction were grown from a saturated solution in dichloromethane. As with the sulfur series, the ^1H NMR spectra of **5-8** indicated the success of the reactions. The signals from the methyl protons in **5** and **7** were shifted upfield by 0.10 and 0.21 ppm respectively compared to the starting material. The aromatic signals due to the phenyl groups bound to the germanium centre in **6** and **8** also experienced shifts in comparison to the starting material, Ph_2GeCl_2 . For complex **5**, three signals were observed corresponding to the naphthalene backbone, in contrast to **1** discussed earlier. The same number of signals and splitting patterns were observed in **6**, as in the sulfur analogue **2**. This similarity between the two series extended to **7** and **8** which had similar ^1H NMR spectra to **3** and **4**. In the ^{13}C NMR spectra of **5-8** were obtained, as with the sulfur series, for all cases the correct number of signals corresponding to quaternary, CH and CH_3 carbon atoms were observed. The ^{77}Se NMR spectra for compounds **7** and **8** display, as expected, only one singlet signals shifted upfield to δ_{Se} 81.0 ppm and δ_{Se} 59.9 ppm for **7** and **8** respectively when compared to the starting material, **L3**, δ_{Se} 349.5 ppm. The high-resolution mass spectroscopy (ASAP⁺) for **5** to **8** showed appropriate $[\text{M}+\text{H}]^+$ ions.

Compounds **5** and **6** exhibited signs of decomposition after a few hours. A change in the colour of the samples from white/cream to brown/purple was observed. After a few days a number of additional signals were observed in the ^1H and ^{13}C NMR spectra. Analysis of the ^1H NMR spectrum of **5** after one month showed signals corresponding to the starting ligand that suggested that the sample had decomposed into **L3**. This was further supported by single crystal X-ray diffraction of the sample whereupon the structure of the starting material, **L3**, was obtained. The ^1H NMR also showed evidence of a methyl containing germanium product displaying a singlet peak at δ_{H} 0.59 ppm. This is upfield of the signal for the germanium starting material. The singlet signal suggests all methyl groups are in the same environment but currently, the form that the decomposition product takes remains unknown. The synthesis of **5** was repeated and the analysis conducted swiftly to avoid excessive decomposition. This allowed the best quality data (^1H & ^{13}C NMR, IR and MS) to be obtained in addition to successfully growing a crystal of the desired complex and

running it. Following the same protocol complex **6** was spectroscopically characterised and examined by single crystal X-ray diffraction.

Crystal structures of compounds **1**, **2**, **5** and **6** are shown in Figure 5. Selected structural parameters are listed in Table 1.

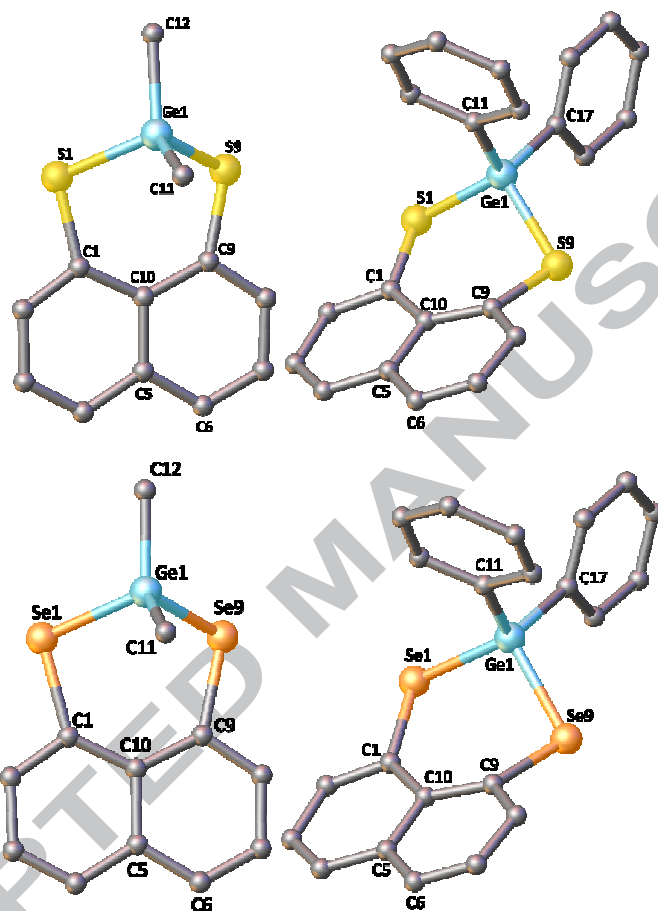


Figure 5. Molecular structures of **1** (top left), **2** (top right), **5** (bottom left) and **6** (bottom right), hydrogen atoms omitted for clarity.

Table 1: Selected Bond Lengths (Å), Angles (°), and Dihedral Angles (°) for **1,2,5,6**

	1	2	5	6
E1–Ge1	2.2100(5)	2.2106(12)	2.3357(4)	2.3319(7)
E9–Ge1	2.2075(5)	2.2005(11)	2.3422(4)	1.926(5)
E1...E9	3.3359(6)	3.390(2)	3.5147(5)	3.5767(8)
E1–Ge1–E9	98.08(2)	100.46(5)	97.413(14)	100.48(3)
C–Ge1–C	116.07(9)	113.50(18)	115.25(13)	113.3(2)
Splay Angle ^Y	+23.7(4)	+23.3(13)	+27.2(6)	+25.5(13)
C1–C10–C5–C6	177.6(2)	–175.3(5)	179.4(2)	–174.1(5)
S1–C1...C9–S9	3.9(1)	–19.6(3)	–1.3(1)	–24.0(3)

$${}^{\vee}\text{Splay Angle} = (\text{S1-C1-C10}) + (\text{C1-C10-C9}) + (\text{C10-C9-P19}) - 360$$

The E-Ge-E angles for **1** and **5**, which both possess methyl R groups, are 98.08(2) and 97.41(1)° respectively. This is well below the expected tetrahedral angle of 109.5°. However, for the phenyl analogues **2** and **6**, the E-Ge-E angles are found to be slightly closer to the ideal tetrahedral angle, at 100.45(5) and 100.47(3)°. This was unexpected as one might assume a bulkier R group would lead to a larger E-Ge-E angle. The S-Ge bond lengths range between 2.206(2) and 2.2088(6) Å and the Se-Ge between 2.3265(8) and 2.3390(6) Å. All bond lengths are similar to those previously reported in the literature (S-Ge; 2.239 Å, Se-Ge; 2.368 Å).³⁶ The sum of the van der Waals radii for S-S and Se-Se is 3.6 and 3.8 Å respectively. The E...E interatomic distances are significantly smaller than the sum of the van der Waals radii for the atoms in all cases. This means that the *peri*-atoms are forced to sit in such close proximity that their orbitals may still overlap. A positive splay angle indicates a repulsive interaction between the chalcogens in the *peri*-positions, whereas a negative angle would indicate an attractive bonding interaction. The pro-ligand starting material for **5** for example, **L3**, has a splay angle of -3.7(13)° as there is a single bond between the two selenium *peri*-atoms. In all cases in the naphthalene series the splay angle is large and positive, ranging between 23.3(13) to 27.2(6)°.

The largest splay angles observed are for complexes **5** (27.2(6)°) and **6** (25.5(13)°). Complex **5** is also found to have the smallest E-Ge-E angle of the series with both **5** and **6** having Se...Se interatomic distances that are much less than the sum of the two atoms' van der Waals radii. These observations suggest that the strain present in the complexes results in them being unstable. This is supported by the fact that they both readily decompose to their respective starting ligands, eliminating a germanium by-product.

A small amount of in-plane distortion of the naphthalene ring can be observed with the C1-C10-C5-C6 dihedral angle ranging from 174.1(5)-179.4(2)°. This distortion is more pronounced when the Ge-R group is phenyl. The S1-C1...C9-S9 torsion angle varies greatly depending on the R group on the germanium; for methyl only a small torsion of 3.9(1)° (**1**) and 1.3(1)° (**5**) is observed whereas for phenyl this increases to 19.6(3)° (**2**) and 24.0(3)° (**6**).

Crystal structures of compounds **3**, **4**, **7** and **8** are shown in Figure 6. Selected structural parameters are listed in Table 2.

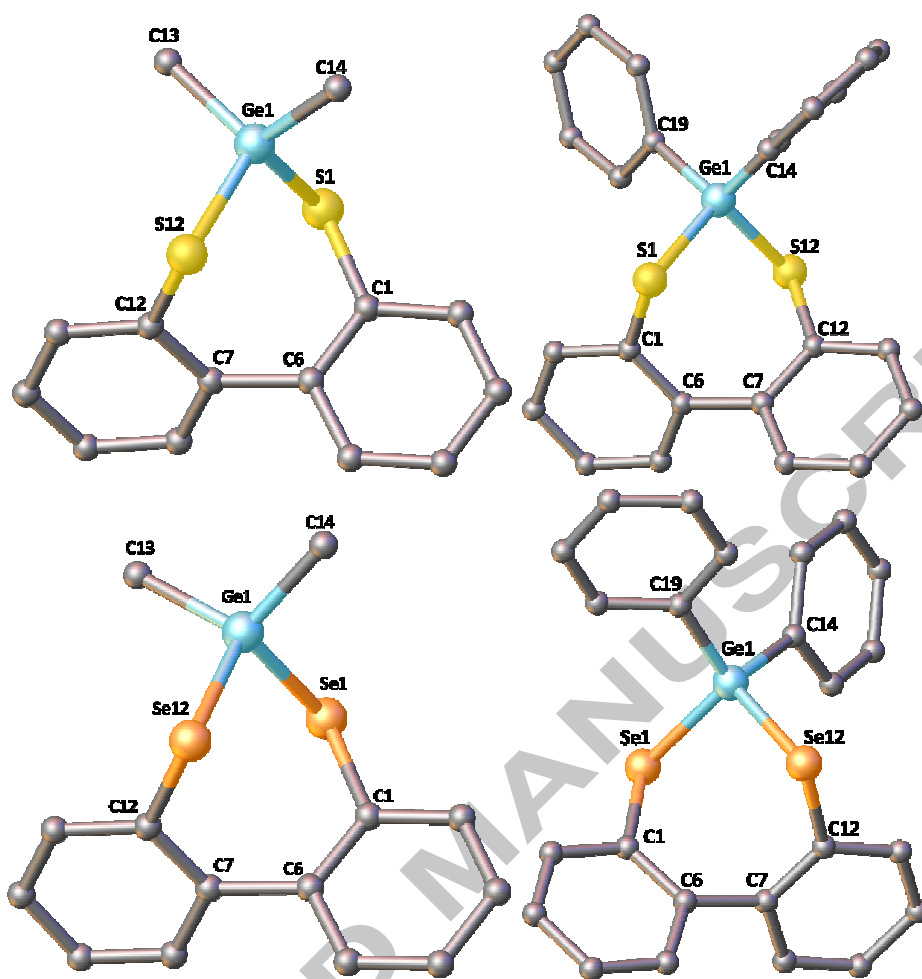


Figure 6. Molecular structures of **3** (top left), **4** (top right), **7** (bottom left) and **8** (bottom right), hydrogen atoms omitted for clarity

Table 2. Selected Bond Lengths (Å), Angles (°), and Dihedral Angles (°) for **3**, **4**, **7** and **8**.

	3	4	7	8
E1–Ge1	2.2311(6)	2.2290(6)	2.3663(5)	2.3612(19)
E12–Ge1	2.2314(6)	2.2276(6)	2.3530(5)	2.3645(9)
E1⋯E12	3.5733(8)	3.5661(8)	3.7536(6)	3.795 (2)
E1–Ge1–E12	106.38(2)	106.29(2)	105.377(13)	106.85(4)
C–Ge1–C	114.86(10)	115.81(10)	113.29(15)	113.6(3)
C1–C6–C7–C12	–69.5(3)	–68.6(3)	–69.1(4)	+75(1)

In these cases, with a flexible biphenyl backbone, the E1–Ge1–E12 angles range from 105.377(13)–106.85(4)° quite close to an ideal tetrahedral angle. In contrast to this the C13–Ge1–C14 angle is larger than the tetrahedral angle by 3.6–6.2°. The C1–C6–C7–C12 torsion angles range from 68.6(3)–75(1)°, notably larger than the 44° found in unsubstituted biphenyl.³⁷ The E⋯E interatomic

distances between the chalcogen atoms in the *bay*-positions are still slightly less than the sum of their van der Waals radii ($\Sigma r_{\text{vdW}}[\text{S-S}] = 3.6 \text{ \AA}$, $\Sigma r_{\text{vdW}}[\text{Se-Se}] = 3.8 \text{ \AA}$). However they are further apart than the naphthalene complexes which may explain why these complexes proved to be more stable over time.

Conclusion

Eight germanium compounds of the type $[\text{R}_2\text{Ge}(\text{E-Ar-E})]$, where $\text{R} = \text{Me}, \text{Ph}$; E-Ar-E = an aromatic bidentate chalcogen ligand, were successfully synthesised. The effects of changing 3 variables within the series were investigated. These variables included the chalcogen ($\text{E} = \text{S/Se}$), aromatic backbone ($\text{Ar} = \text{Nap/Biphenyl}$) and R group (Me/Ph) employed. The choice of aromatic backbone had the greatest effect on the structure. A substantial change in geometry around the germanium centre was observed within the solid state structures depending on whether the backbone was naphthalene or biphenyl.

Experimental

General:

All synthetic manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk-line techniques. Dry solvents were either collected from an *MBraun Solvent Purification System*, or were dried and stored according to common procedures. Chemicals were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar or were taken from the laboratory inventory and used without further purification. Dibenzo[*c,e*][1,2]dithiin and naphtho[1,8-*c,d*]-1,2-diselenole were synthesised according to literature procedures.^{29,38} All NMR spectra were recorded using a *JEOL GSX Delta 270* or a *Bruker Avance III 500* spectrometer at 25 °C. Assignments of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were made with the use of H–H DQF-COSY, H–C HSQC, H–C HMBC two-dimensional experiments. For ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, tetramethylsilane was used as an external standard. For ^{77}Se NMR dimethylselenide was used as an external standard. Residual solvent peaks were also used for calibration (CDCl_3 $\delta_{\text{H}} 7.26$, $\delta_{\text{C}} 77.2$ ppm). Chemical shifts (δ) are given in parts per million (ppm). Coupling constants (J) are given in Hertz (Hz).

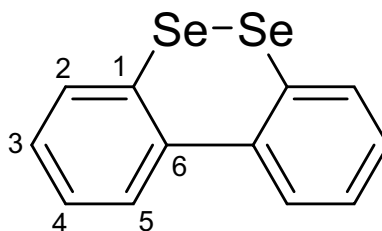
Mass Spectrometry spectra were acquired at the EPSRC UK National Mass Spectrometry Facility in Swansea using a *Waters Xevo G2-S* (ASAP). Infrared spectra were recorded as KBr discs in the range of 4000–400 cm^{-1} using a Perkin-Elmer System 2000 NIR Fourier Transform Spectrometer.

X-Ray Crystallography:

The crystallographic data (Table 3) were collected using a *Rigaku SCX-Mini diffractometer* with graphite monochromated Mo-K α radiation at $-100(1) \text{ }^\circ\text{C}$ (Mo-K $\alpha = \lambda = 0.71073 \text{ \AA}$). The data for all compounds were collected and processed using CrystalClear (Rigaku).³⁹ The crystal structures were solved using direct methods and refined by full-matrix least-squares against F^2 (SHELXL) or heavy-atom Patterson methods and expanded using Fourier techniques.^{40,41} The non-hydrogen atoms were refined anisotropically, hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised

geometries. Searches of the Cambridge Structure Database were performed using the *WebCSD*.³⁶ Images of crystal structures were obtained using *OLEX-2 v1.2.5*, with all other manipulations carried out using *Mercury 3.5*.⁶⁵⁻⁶⁷ These data can be obtained free of charge via 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; e-mail: deposit@ccdc.cam.ac.uk. CCDC Nos 1495912-1495919.

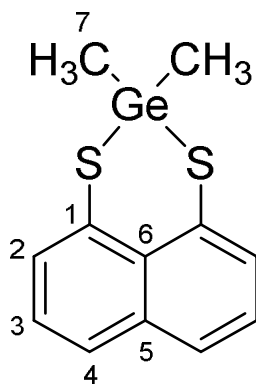
Synthetic Methods:



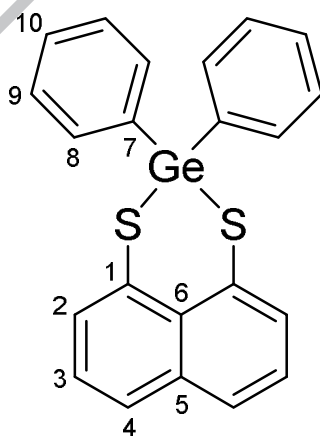
NMR atom numbering for **L4**.

L4 was synthesised following an adapted literature procedure.²⁹

To a stirred solution of biphenyl (5.04 g, 32.4 mmol) in hexane (150 mL) was added TMEDA (12.2 mL, 81.0 mmol) and *n*BuLi (32.4 mL, 81.0 mmol). The solution was heated at 60 °C for 3 hours. The solution was cooled to -78 °C and diluted with THF (30 mL). Selenium (7.675 g, 97.2 mmol) was added with vigorous stirring and the reaction was left stirring overnight. The solution was washed with water until the aqueous layer was colourless. The organic layer was dried over magnesium sulfate and the solvent removed. Purification by flash column chromatography (silica gel/hexane:DCM: 90:10) yielded a red solid (3.802 g, 12.3 mmol, 38%). The analytical data that was obtained was in good agreement with that which was previously reported.⁵⁸ ¹H NMR (500 MHz, CDCl₃): δ_H 7.75 (dd, ³J_{HH} = 7.6, ⁴J_{HH} = 1.4 Hz, 2H, H-2), 7.65 (dd, ³J_{HH} = 7.8, ⁴J_{HH} = 1.5 Hz, 2H, H-5), 7.39 (td, ³J_{HH} = 7.6, ⁴J_{HH} = 1.4 Hz, 2H, H-4), 7.26 (td, ³J_{HH} = 7.6, ⁴J_{HH} = 1.5 Hz, 2H, H-3). ¹³C NMR (125 MHz, CDCl₃): δ_C 141.9 (C_q, C-6), 131.8 (CH, C-2), 131.1 (C_q, C-1), 129.8 (CH, C-5), 128.9 (CH, C-4), 127.68 (CH, C-3).

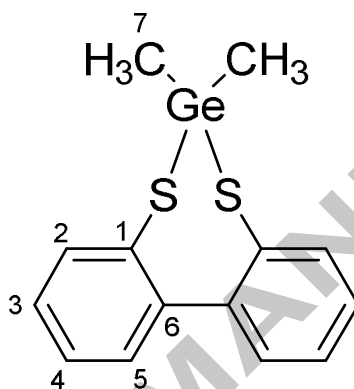
NMR atom numbering for **1**.

To a solution of naphtho[1,8-*c,d*]-1,2-dithiole (0.164 g, 0.860 mmol) in THF (10 mL) was added superhydride (1.72 mL, 1.72 mmol). The solution was stirred for 30 minutes and Me₂GeCl₂ (0.1 mL, 0.860 mmol) was added. The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the product washed with hexane to afford a cream crystalline solid (0.064g, 0.21 mmol, 25%), m.p. 79-80 °C. ¹H NMR (500 MHz, CDCl₃): δ_H 7.71 (d, ³J_{HH} = 7.7 Hz, 4H, H-2,4), 7.31 (pt, ³J_{HH} = 7.7 Hz, 2H, H-3), 0.92 (s, 6H, H-7). ¹³C NMR (125 MHz, CDCl₃): δ_C 136.6 (C_q, C-5), 133.8 (CH, C-2 or 4), 130.1 (C_q, C-6), 129.5 (C_q, C-1), 129.0 (CH, C-2 or 4), 125.2 (CH, C-3), 2.8 (CH₃, C-7). IR (KBr): ν_{max}/cm⁻¹ 3050w (ν_{Ar-H}), 1545s, 1194s, 844s, 812vs, 755vs, 625m, 586s. HRMS (ASAP+): m/z (%) 294.9678 (100) [M+H]⁺.

NMR atom numbering for **2**.

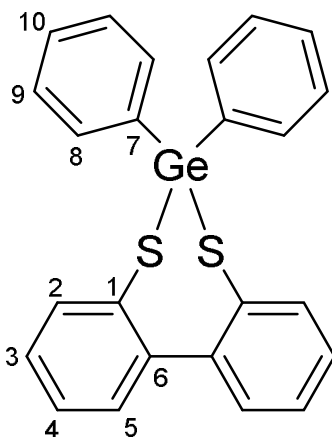
To a solution of naphtho[1,8-*c,d*]-1,2-dithiole (0.064 g, 0.34 mmol) in THF (10 mL) was added superhydride (0.68 mL, 0.68 mmol). The solution was stirred for 30 minutes and Ph₂GeCl₂ (0.07 mL, 0.34 mmol) was added. The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the product washed with hexane to afford a

cream crystalline solid (0.075g, 0.18 mmol, 54%), m.p. 164-165 °C. Anal. calcd. for $C_{22}H_{16}GeS_2$ (417.12 g mol^{-1}): C, 63.35; H, 3.87. Found: C, 63.25; H, 3.99. 1H NMR (500 MHz, $CDCl_3$): δ_H 7.79 (dd, $^3J_{HH} = 7.3$, $^4J_{HH} = 1.4$ Hz, 2H, H-2), 7.70-7.67 (m, 4H, H-8), 7.66 (dd, $^3J_{HH} = 8.2$, $^4J_{HH} = 1.4$ Hz, 2H, H-), 7.46-7.37 (m, 6H, H-9, 10), 7.29 (pt, $^3J_{HH} = 7.8$ Hz, 2H, H-3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 136.5 (C_q , C-5), 134.1 (CH, C-8), 133.5 (CH, C-2), 133.2 (C_q , C-7), 130.8 (CH, C-10), 130.0 (C_q , C-6), 129.2 (C_q , C-1), 129.2 (CH, C-4), 128.8 (CH, C-9), 125.2 (CH, C-3). IR (KBr): ν_{max}/cm^{-1} 3042w (ν_{Ar-H}), 1544s, 1431s, 1197s, 1089s, 877m, 813s, 737vs, 695vs, 457vs. HRMS (ASAP+): m/z (%) 418.9985 (100) $[M+H]^+$.

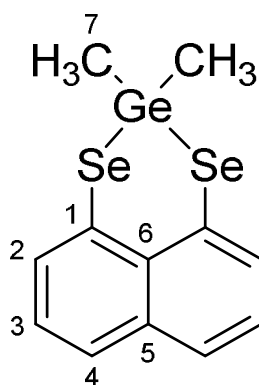


NMR atom numbering for **3**.

To a solution of dibenzo[*c,e*][1,2]dithiin (0.186 g, 0.860 mmol) in THF (10 mL) was added superhydride (1.72 mL, 1.72 mmol). The solution was stirred for 30 minutes and Me_2GeCl_2 (0.1 mL, 0.860 mmol) was added. The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the product washed with hexane to afford a white crystalline solid (0.142g, 0.45 mmol, 52%), m.p. 104-105 °C. Anal. calcd. for $C_{12}H_{12}GeS_2$ (292.98 g mol^{-1}): C, 52.71; H, 4.42. Found: C, 52.55; H, 4.34. 1H NMR (500 MHz, $CDCl_3$): δ_H 7.59 (dd, $^3J_{HH} = 7.7$, $^4J_{HH} = 1.1$ Hz, 2H, H-2), 7.42 (ptd, $^3J_{HH} = 7.5$, $^4J_{HH} = 1.3$ Hz, 2H, H-4), 7.32 (ptd, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.6$ Hz, 2H, H-3), 7.28 (dd, $^3J_{HH} = 7.0$, $^4J_{HH} = 1.5$ Hz, 2H, H-5), 0.83 (s, 6H, H-7). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 147.2 (C_q , C-6), 135.4 (CH, C-2), 131.2 (C_q , C-1), 129.9 (CH, C-5), 128.2 (CH, C-4), 128.1 (CH, C-3), 4.2 (CH₃, C-7). IR (KBr): ν_{max}/cm^{-1} 3052w (ν_{Ar-H}), 1453s, 1422s, 1060m, 1032m, 836vs, 803s, 758vs, 610s, 574vs, 390s. HRMS (ASAP+): m/z (%) 320.9847 (100) $[M+H]^+$.

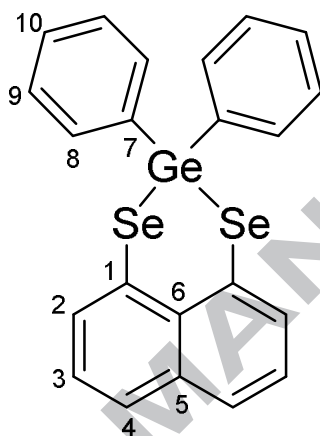
NMR atom numbering for **4**.

To a solution of dibenzo[*c,e*][1,2]dithiin (0.073 g, 0.34 mmol) in THF (10 mL) was added superhydride (0.68 mL, 0.68 mmol). The solution was stirred for 30 minutes and Ph_2GeCl_2 (0.07 mL, 0.34 mmol) was added. The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the product washed with hexane to afford a white crystalline solid (0.089g, 0.20 mmol, 60%), m.p. 155-156 °C. ^1H NMR (500 MHz, CDCl_3): δ_{H} 7.54-7.51 (m, 6H, H-2,8), 7.48-7.44 (m, 4H, H-4,10), 7.43-7.39 (m, 4H, H-9), 7.34 (dd, $^3J_{\text{HH}} = 7.6$, $^4J_{\text{HH}} = 1.6$ Hz, 2H, H-5), 7.28 (ptd, $^3J_{\text{HH}} = 7.5$, $^4J_{\text{HH}} = 1.6$ Hz, 2H, H-3). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 147.3 (C_{q} , C-6), 136.1 (CH, C-2), 135.6 (C_{q} , C-7), 133.7 (CH, C-8), 130.5 (CH, C-10), 130.2 (C_{q} , C-1), 130.0 (CH, C-5), 128.6 (CH, C-9), 128.4 (CH, C-4), 128.1 (CH, C-3). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3047w ($\nu_{\text{Ar-H}}$), 1454m, 1429s, 1088m, 755vs, 737vs, 695vs, 457vs. HRMS (ASAP+): m/z (%) 445.0147 (100) $[\text{M}+\text{H}]^+$.

NMR atom numbering for **5**.

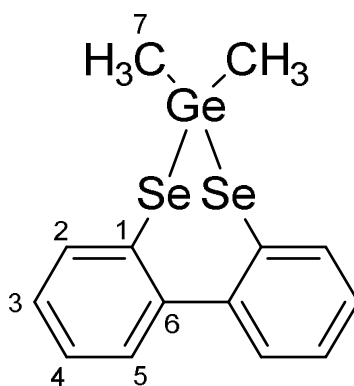
To a solution of naphtho[1,8-*c,d*]-1,2-diselenole (0.244 g, 0.856 mmol) in THF (10 mL) was added superhydride (1.72 mL, 1.72 mmol). The solution was stirred for 30 minutes and Me_2GeCl_2 (0.1 mL, 0.860

mmol) was added. The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the product washed with hexane to afford a white crystalline solid (0.177 g, 0.46 mmol, 53%). ^1H NMR (500 MHz, CDCl_3): δ_{H} 7.94 (dd, $^3J_{\text{HH}} = 7.2$, $^4J_{\text{HH}} = 1.4$ Hz, 2H, H-2), 7.77 (dd, $^3J_{\text{HH}} = 8.2$, $^4J_{\text{HH}} = 1.3$ Hz, 2H, H-4), 7.26 (dd, $^3J_{\text{HH}} = 8.1$, $^3J_{\text{HH}} = 7.2$ Hz, 2H, H-3), 1.11 (s, 6H, H-7). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 136.4 (C_{q} , C-5), 136.1 (CH, C-2), 131.7 (C_{q} , C-6), 130.1 (CH, C-4), 125.5 (C_{q} , C-1), 125.3 (CH, C-3), 4.5 (CH, C-7). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3029w ($\nu_{\text{Ar-H}}$), 1539s, 1196m, 855m, 796vs, 754vs. HRMS (ASAP+): m/z (%) 285.8819 (100) [$\text{C}_{10}\text{H}_7\text{Se}_2$] $^+$, 356.9002 (87) [$\text{M}-2\text{CH}_3+\text{H}$] $^+$, 390.8568 (3) [$\text{M}+\text{H}$] $^+$.

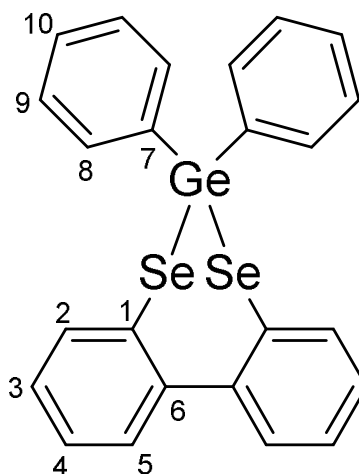


NMR atom numbering for **6**.

To a solution of naphtho[1,8-c,d]-1,2-diselenole (0.135 g, 0.47 mmol) in THF (10 mL) was added superhydride (0.95 mL, 0.95 mmol). The solution was stirred for 30 minutes and Ph_2GeCl_2 (0.1 mL, 0.47 mmol) was added. The resulting pale pink solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the product washed with hexane to afford a yellow crystalline solid (0.183 g, 0.36 mmol, 78%), m.p. 165-168 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ_{H} 7.99 (dd, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 1.4$ Hz, 2H, H-2), 7.72 (dd, $^3J_{\text{HH}} = 8.1$, $^4J_{\text{HH}} = 1.4$ Hz, 2H, H-4), 7.71-7.69 (m, 4H, H-8), 7.42-7.38 (m, 6H, H-9, 10) 7.23 (dd, $^3J_{\text{HH}} = 8.1$, $^3J_{\text{HH}} = 7.2$ Hz, 2H, H-3). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 136.4 (C_{q} , C-5), 135.5 (CH, C-2), 134.1 (CH, C-8), 134.0 (C_{q} , C-7), 131.8 (C_{q} , C-6), 130.6 (CH, C-10), 130.1 (CH, C-4), 128.7 (CH, C-9), 125.5 (C_{q} , C-1), 125.3 (CH, C-3). IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3041 ($\nu_{\text{Ar-H}}$), 1539m, 1431s, 809s, 757s, 735vs, 694vs, 456s, 339s. HRMS (ASAP+): m/z (%) 285.8817 (50) [$\text{C}_{11}\text{H}_7\text{Se}_2$] $^+$, 512.8889 (100) [$\text{M}+\text{H}$] $^+$.

NMR atom numbering for **7**.

To a solution of dibenzo[*c,e*][1,2]diselenin (0.265 g, 0.856 mmol) in THF (10 mL) was added superhydride (1.72 mL, 1.72 mmol). The solution was stirred for 30 minutes and Me_2GeCl_2 (0.1 mL, 0.856 mmol) was added. The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the solid washed with hexane to afford a white solid (0.200 g, 0.484 mmol, 57%), m.p. 143-146 °C. ^1H NMR (500 MHz, CDCl_3): δ_{H} 7.72 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H, H-2), 7.44 (ptd, $^3J_{\text{HH}} = 7.6$, $^4J_{\text{HH}} = 1.3$ Hz, 2H, H-4), 7.29-7.24 (m, 4H, H-3,5), 1.00 (s, 6H, H-7). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 148.4 (C_q , C-6), 137.0 (CH, C-2), 129.6 (CH, C-5), 128.5 (CH, C-4), 127.9 (CH, C-3), 127.2 (C_q , C-1), 6.0 (CH_3 , C-7). ^{77}Se NMR: δ_{Se} (51.52 MHz, CDCl_3) 81.0 (s) IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3062w ($\nu_{\text{Ar-H}}$), 1448s, 1421s, 1024m, 842s, 801s, 751vs, 731s, 616s, 582s, 460s. HRMS (ASAP+): m/z (%) 231.9794 (100) $[\text{C}_{12}\text{H}_9\text{Se}]^+$ 416.8723 (60) $[\text{M}+\text{H}]^+$.

NMR atom numbering for **8**.

To a yellow solution of Biphenyl Se_2 (0.147g, 0.474 mmol) in THF (10 mL) was added superhydride (0.95 mL, 0.95 mmol). The solution was stirred for 30 minutes and Ph_2GeCl_2 (0.1 mL, 0.474 mmol) was added.

The solution was stirred overnight and the solvent was removed. The product was dissolved in DCM and filtered through celite. The solvent was removed and the solid washed with hexane to afford a white solid (0.070 g, 0.130 mmol, 28 %), m.p. 152-154 °C. ^1H NMR (500 MHz, CDCl_3): δ_{H} 7.66 (dd, $^3J_{\text{HH}} = 7.7$, $^4J_{\text{HH}} = 1.1$ Hz, 2H, H-2), 7.55-7.52 (m, 4H, H-8), 7.46 (ptd, $^3J_{\text{HH}} = 7.5$, $^4J_{\text{HH}} = 1.3$ Hz, 2H, H-4), 7.44-7.37 (m, 6H, H-9, 10) 7.33 (dd, $^3J_{\text{HH}} = 7.5$, $^4J_{\text{HH}} = 1.4$ Hz, 2H, H-5), 7.23 (ptd, $^3J_{\text{HH}} = 7.6$, $^4J_{\text{HH}} = 1.6$ Hz, 2H, H-3). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 148.6 (C_q , C-6), 137.7 (CH, C-2), 136.7 (C_q , C-7), 133.7 (CH, C-8), 130.2 (CH, C-10), 129.7 (CH, C-5), 128.7 (CH, C-4), 128.5 (CH, C-9), 128.0 (CH, C-3), 126.5 (C_q , C-1). ^{77}Se NMR: δ_{Se} (51.52 MHz, CDCl_3) 59.9 (s) IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 3047w ($\nu_{\text{Ar-H}}$), 1451m, 1429s, 1086m, 760s, 733vs, 694vs, 455vs. HRMS (ASAP+): m/z (%) 538.9061 (100) $[\text{M}+\text{H}]^+$.

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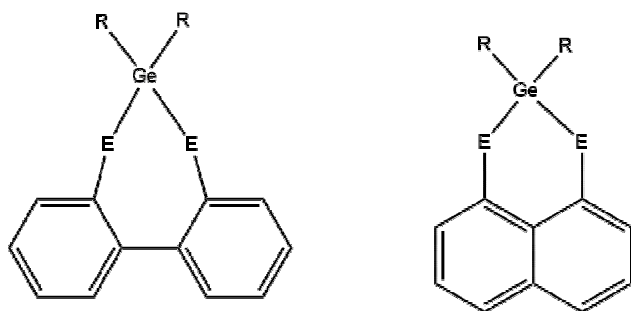
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Table 3 . Details of the X-ray data collections and refinements for compounds **1- 8**

Compound	1	2	3	4	5	6	7	8
Formula	C ₁₂ H ₁₂ S ₂ Ge	C ₂₂ H ₁₆ S ₂ Ge	C ₁₄ H ₁₄ S ₂ Ge	C ₂₄ H ₁₈ S ₂ Ge	C ₁₂ H ₁₂ S ₂ Ge	C ₂₂ H ₁₆ Se ₂ Ge	C ₁₄ H ₁₄ Se ₂ Ge	C ₂₄ H ₁₈ Se ₂ Ge
<i>M</i>	292.94	417.08	318.97	443.12	386.74	510.88	412.77	536.92
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> -1
<i>a</i> /Å	10.6555(7)	10.2885(7)	25.2521(17)	8.9252(6)	12.2243(8)	10.5367(7)	13.269(2)	7.092(5)
<i>b</i> /Å	9.6022(7)	11.1102(7)	7.8269(5)	9.9466(7)	8.0543(5)	11.0880(7)	7.5999(10)	10.528(7)
<i>c</i> /Å	13.0915(9)	16.0857(11)	14.3078(10)	12.2054(8)	14.1487(9)	11.0880(7)	28.851(5)	13.6554(10)
α	90	90	90	108.620(5)	90	90	90	87.845(12)
β	113.158(5)	92.971(5)	101.223(6)	94.157(6)	114.736(5)	92.378(5)	97.208(8)	83.034(11)
γ	90	90	90	95.289(6)	90	90	90	81.783(14)
<i>U</i> /Å ³	1231.54(15)	1836.2(2)	2773.8(3)	1016.47(12)	1265.24(15)	1869.4(2)	2886.5(7)	1001.4(10)
<i>Z</i>	4	4	8	2	4	4	8	2
μ /mm ⁻¹	9919	1.896	2.483	1.717	8.139	5.534	7.142	5.170
Reflections collected	7313	14990	11419	8383	10602	15304	11969	8472
Independent reflections	2174	3267	2509	3489	2302	3283	2634	3605
<i>R</i> _{int}	0.0286	0.0806	0.0678	0.0226	0.0444	0.0660	0.0637	0.0952
<i>R</i> _{oif}	0.0217	0.0620	0.0316	0.0289	0.0289	0.0509	0.0294	0.0807
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0515	0.1080	0.0630	0.0621	0.0534	0.1120	0.0563	0.1653



Sulfur and Selenium complexes of Germanium are rare; four examples of each have been prepared and structurally characterised

Graphical abstract

New Germanium Complexes with S, S bidentate ligands show the difference in behavior of ligands depending on bite

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