Synthesis, structures and reactivity of novel germanium(II) aryloxide and arylsulfide complexes

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The protonolysis reactions between $Ge[N(SiMe_3)_2]_2$ and substituted phenols give rise to new germanium(II) aryloxide complexes $[Ge(OAr)_2]_n$ (n = 2, ArO = $OC_6H_2Me_3$-2,4,6 **1** or $OC_6H_3{}^iPr_2$-2,6 **2**; n = 1, ArO = $OC_6H_3Ph_2$-2,6 **3** or OC_6HPh_4-2,3,5,6 **4**). The solid state structures of **1**–**4** have been determined by X-ray diffraction and compared to their spectroscopic properties. Compounds **1** and **2** contain bridging aryloxide ligands and the environment about the germanium atoms is pyramidal. Compound **1** reacts with benzil to yield a five-coordinate germanium complex $[Ge(OC_6H_2Me_3$-2,4,6)$(O_2C_2Ph_2)(O_2C_2HPh_2)]$ **5**, while compound **4** reacts with the same reagent to give $[Ge(OC_6HPh_4$-2,3,5,6)$_2(O_2C_2Ph_2)]$ **6**. The X-ray crystal structures of **5** and **6** have also been determined. Compound **4** also undergoes an oxidative addition reaction with CH_3I to yield the germane $[Ge(OC_6HPh_4$-2,3,5,6)$_2(Me)(I)]$ (**7**). A novel arylsulfidegermane, $[HGe(SC_6H_2{}^iPr_3$-2,4,6)$_3]$ **8**, was isolated in the reaction between $Ge[N(SiMe_3)_2]_2$ and $HSC_6H_2{}^iPr_3$-2,4,6 and was characterized by NMR spectroscopy and an X-ray crystal structure.

Introduction

Metal aryloxide complexes are known for the majority of main-group and transition metals.[1] However, aryloxide complexes of germanium are uncommon, especially when germanium is in the +2 oxidation state. Structurally characterized germanium(IV) aryloxide compounds include $[Ge(OC_6H_3Ph_2$-2,6)$_3$-Cl],[2] $[Ge(OC_6H_3Ph_2$-2,6)$_2(NMe_2)]$,[2] and $[Ge(OC_6H_5)(CNO)\{N(SiMe_3)(C_6H_2Me_3$-2,4,6)$\}]$.[3] Examples of germanium(II) aryloxide compounds include $[Ge(OC_6H_2\{CH_2NMe_2\}_3$-2,4,6)$_2]$,[4] $[Ge(OC_6H^tBu_2$-2,6-Me-4)$_2]$,[5] and $[Ge(OC_6H^tBu_2$-2,6-Me-4)$_2Fe(CO)_4]$.[6] A number of germanium(II) calixarene complexes, including $Ge[{}^tBucalix^{(TMS)2}]$[7] and $Ge_2[{}^tBucalix]$,[8] have also been reported.

Recently, we reported the synthesis and characterization of two novel germanium(II) binaphthoxide complexes, (R,R)-$[Ge\{OC_{20}H_{10}(OSiMe_3)$-2'-$(SiMe_3)_2$-3,3'$\}_2]$ and (R)-$[Ge\{O_2C_{20}H_{10}(SiMe_2Ph)_2$-3,3'$\}\{NH_3\}]$, and described the catalytic activity of $Ge[N(SiMe_3)_2]_2$ for the monosilylation of 3,3'-disubstituted-1,1'-bi-2,2'-naphthols.[9] We now wish to report the preparation and properties of several new germanium(II) aryloxide compounds and present some aspects of their reaction chemistry.

Results and discussion

Synthesis, NMR spectroscopy, and structure of $[Ge(OAr)_2]_n$ (n = 1 or 2)

The germanium(II) aryloxide compounds **1**–**4** were synthesized by the protonolysis reaction between $Ge[N(SiMe_3)_2]_2$ and the substituted phenols ArOH, as shown in Scheme 1. The products were obtained in pure form by recrystallization from hot benzene and were typically isolated in moderate to excellent yields. Compounds **1** and **4** are very sparingly soluble in benzene or toluene while **2** and **3** are substantially more soluble.

Complexes **1**–**4** were characterized by ^1H NMR spectroscopy, elemental analysis, and X-ray crystallography. The identity of the ancillary aryloxide ligands has an important effect on the nature of the products. Compounds **1** and **2** adopt a dimeric structure in the solid state, as shown by their X-ray crystal structures. ORTEP diagrams for **1** and **2** are shown in Figs. 1 and 2, and selected bond lengths and angles are summarized in Tables 1 and 2. Complexes of germanium containing bridging alkoxide ligands, such as $[Ge(O^tBu)_2]_2$[10] and $[\{Ge(\mu-O^tBu)$-

Scheme 1
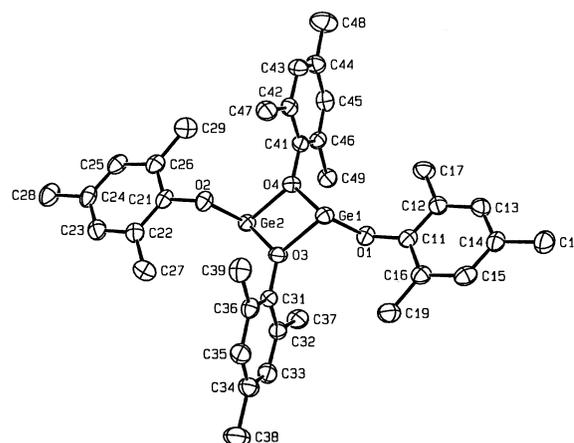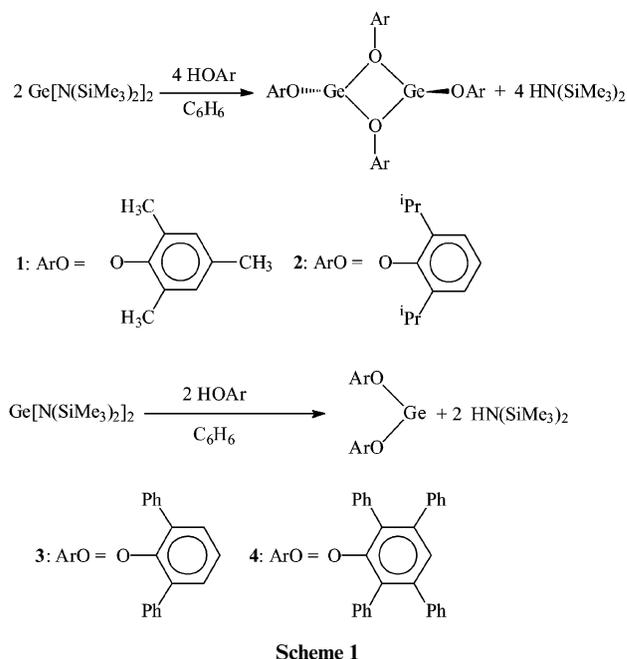
Fig. 1 ORTEP plot of $[Ge(OC_6H_2Me_3$-2,4,6)$_2]_2$ (**1**). Thermal ellipsoids are drawn at 50% probability.

Table 1 Selected bond lengths (Å) and angles (°) for $[Ge(OC_6H_2Me_3\text{-}2,4,6)_2]_2$ (**1**)

Ge(1)–O(1)	1.828(3)	Ge(2)–O(2)	1.822(3)
Ge(1)–O(3)	1.984(3)	Ge(2)–O(3)	1.987(3)
Ge(1)–O(4)	1.984(3)	Ge(2)–O(4)	1.981(3)
O(1)–Ge(1)–O(4)	94.8(1)	O(2)–Ge(2)–O(3)	95.7(1)
O(1)–Ge(1)–O(3)	94.6(1)	O(2)–Ge(2)–O(4)	93.7(1)
O(3)–Ge(1)–O(4)	72.0(1)	O(3)–Ge(2)–O(4)	72.0(1)

Table 2 Selected bond lengths (Å) and angles (°) for $[Ge(OC_6H_3{}^iPr_2\text{-}2,6)_2]_2$ (**2**)

Ge(1)–O(1)	1.823(2)	Ge(2)–O(2)	1.824(2)
Ge(1)–O(3)	1.981(2)	Ge(2)–O(3)	2.008(2)
Ge(1)–O(4)	2.012(2)	Ge(2)–O(4)	1.988(2)
O(1)–Ge(1)–O(4)	91.88(7)	O(2)–Ge(2)–O(3)	96.75(7)
O(1)–Ge(1)–O(3)	95.19(7)	O(2)–Ge(2)–O(4)	95.17(7)
O(3)–Ge(1)–O(4)	72.40(6)	O(3)–Ge(2)–O(4)	72.35(6)

Fig. 3 Diagram illustrating the pyramidal germanium atoms and transoid arrangement of the terminal aryloxide ligands in **2**.
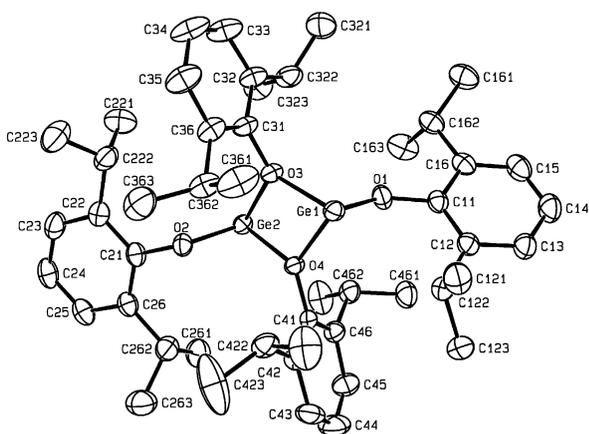
Fig. 2 ORTEP plot of $[Ge(OC_6H_3{}^iPr_2\text{-}2,6)_2]_2$ (**2**). Thermal ellipsoids are drawn at 50% probability.

$(OSiPh_3)\}_2]$[11] have been reported, as have oxo-bridged germanium(IV) complexes including $[Ge\{N(SiMe_3)_2\}_2(\mu\text{-}O)_2]$[12] and $[Ge\{C_6H_3Et_2\text{-}2,6\}_2(\mu\text{-}O)_2]$.[13] The germanium metal centers of **1** and **2** are bridged by two aryloxide ligands and represent the first examples of germanium(II) compounds exhibiting this structural motif.

The Ge–$O_{terminal}$ bond lengths in **1** have values of 1.828(3) and 1.822(3) Å, while the Ge–$O_{bridging}$ bonds are significantly longer, ranging from 1.981(3) to 1.987(3) Å. These values are similar to those of $[\{Ge(\mu\text{-}O^tBu)(OSiPh_3)\}_2]$ $d(Ge\text{–}O_{terminal}) =$ 1.814(2) Å, $d(Ge\text{–}O_{br}) = 1.966(2)$ Å[11] and $[Ni(CO)_3Ge(O^tBu)_2]_2$ $d(Ge\text{–}O_{terminal}) = 1.780(6)$ Å, $d(Ge\text{–}O_{br}) = 1.932(6)$ Å.[10] All of the Ge–$O_{bridging}$ bond lengths of **1** are nearly identical. The Ge–$O_{terminal}$ bond lengths in **2** are similar to that of **1**, having values of 1.823(2) and 1.824(2) Å. The Ge–O_{br} bonds in **2** vary over a wider range than those of **1**, with values between 1.981(2) Å and 2.012(2) Å. This is possibly a result of the increased steric bulk of the 2,6-isopropylphenoxide ligands of **2** relative to the 2,4,6-trimethylphenoxide ligands of **1**.

The parallelogram composed by the two germanium and two bridging oxygen atoms is completely planar in **1**, but is slightly puckered by approximately 8.5° in **2**. The phenyl rings of the bridging aryloxide ligands in both **1** and **2** are approximately perpendicular to the plane defined by the Ge–O–Ge trapezoids in order to minimize the steric repulsion between substituents on the bridging and terminal aryloxide groups. The germanium metal centers in both **1** and **2** are pyramidal. The terminal aryloxide ligands are arranged in a transoid fashion, as illustrated for **2** in Fig. 3. The group 12 metal(II) aryloxide complexes $[Cd(OC_6H_3{}^tBu_2\text{-}2,6)_2]_2$[14] and $[Zn(OC_6H_3{}^tBu_2\text{-}2,6)_2]_2$,[15] both of
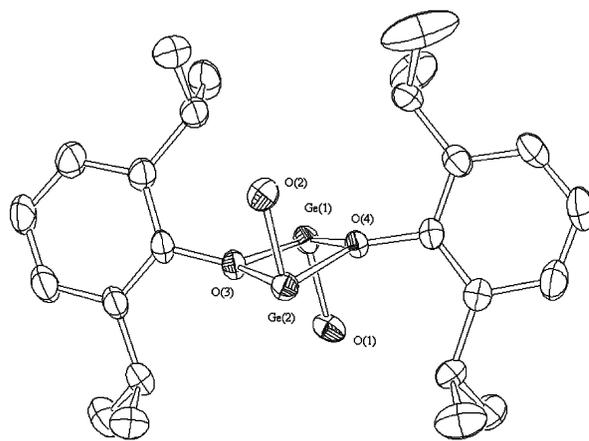
which contain bridging ArO ligands, were recently reported. The disposition of the bridging ArO ligands in these complexes are similar to that in **1**; however, these species lack the lone pair of electrons present in their Group 14 analogs, and thus adopt a distorted trigonal planar rather than a pyramidal environment about the Zn or Cd metal centers.

The germanium–germanium separation is 3.209 Å in **1** and is 3.212 Å in **2**, both of which are well outside the range (typically 2.4–2.6 Å) normally attributed to direct Ge–Ge bonding.[16–23] Germylenes containing ligands bound though a N- or O-atom typically do not dimerize to form digermenes while this process is common in alkyl-substituted germylenes with carbon-bound ligands. This has been attributed to the lone pair of electrons being more tightly held to the Ge metal center in these types of materials relative to their alkyl-substituted counterparts.[24] Thus, it is not surprising that neither **1** nor **2** form a digermene species, but instead contain bridging aryloxide ligands.

The 2,6-diphenylphenoxide and 2,3,5,6-tetraphenylphenoxide complexes **3** and **4** are monomeric in the solid state as indicated by their X-ray crystal structures. ORTEP diagrams for **3** and **4** are shown in Figs. 4 and 5, and bond lengths and
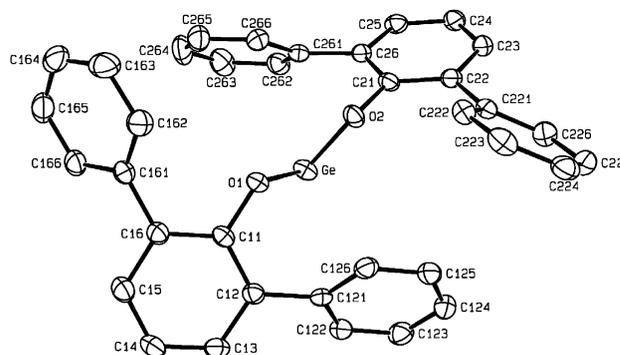
Fig. 4 ORTEP plot of $[Ge(OC_6H_3Ph_2\text{-}2,6)_2]$ (**3**). Thermal ellipsoids are drawn at 50% probability.

angles for both compounds are listed in Table 3. The ligands of **3** and **4** are presumably sufficiently bulky to prevent dimerization. The complex $[Ge(OC_6H_2Me\text{-}4\text{-}{}^tBu\text{-}2,6)_2]$ was also found to be monomeric in the solid state.[5] The Ge–O bond lengths in **3** are 1.817(1) and 1.822(1) Å, while the Ge–O bond length in **4** is slightly longer, with a value of 1.826(1) Å. The O–Ge–O bond angle in **3** is 92.10(5)° and is 91.09(7)° in **4**. The cadmium bis-(diphenylphenoxide) complex $[Cd(OC_6H_3Ph_2\text{-}2,6)_2]_2$ was found to be dimeric in the solid state, and exhibits π-interactions between the cadmium metal centers and the *ortho*-carbons of the phenyl substituents $d(Cd\text{–}C) = 2.680(5)$ and 2.622(5) Å.[14]

Table 3 Selected bond lengths (Å) and angles (°) for [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$] (**3**) and [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$] (**4·3C$_6$H$_6$**)

Compound **3**			
Ge–O(1)	1.817(1)	O(1)–Ge–O(2)	92.10(5)
Ge–O(2)	1.822(1)		
Compound **4**			
Ge–O(1)	1.826(1)	O(1)–Ge–O(1′)	91.09(7)
Ge–O(1′)	1.827(1)		
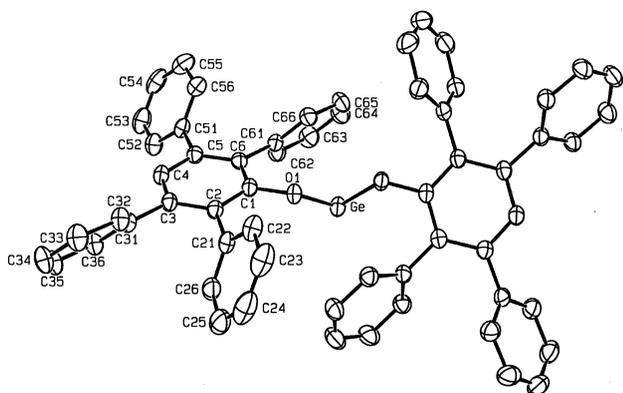
Fig. 5 ORTEP plot of [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$]·3C$_6$H$_6$ (**4·3C$_6$H$_6$**). Thermal ellipsoids are drawn at 50% probability.

The closest Ge–C contact in **3** is 3.072 Å, and thus such interactions appear to be absent in this complex.

The bridging and terminal aryloxide ligands of **1** and **2** undergo fast exchange on the NMR timescale at room temperature resulting in broadened resonances, and this process proceeds more rapidly in **1** than in **2**. The ^{1}H NMR resonance in C$_6$D$_6$ at 300 MHz for the *ortho*-methyl groups of **1** is extremely broad at room temperature ($\Delta v_{1/2}$ = 96 Hz), as a result of their proximity to the bridging oxygen atoms. The more isolated *para*-methyl groups exhibit a much sharper signal ($\Delta v_{1/2}$ = 6 Hz).

The *ortho*-isopropyl groups of **2** also give rise to slightly broadened NMR signals at 25 °C, but to a much lesser extent than the 2,6-methyl groups of **1**. The bridging/terminal ligand exchange processes of **1** and **2** were investigated using variable-temperature NMR spectroscopy. At 25 °C in toluene-d_8, the signal for the 2,6-methyl groups of **1** is broadened into the baseline. A defined signal begins to appear at 2.28 ppm upon heating to 45 °C, which increases in intensity and sharpness as the temperature is increased. However, even at 100 °C, the $\Delta v_{1/2}$ for this resonance has a value of 12.5 Hz (at 300 MHz), indicating that complete exchange does not occur even at this temperature. The signals for the isopropyl groups of **2** become sharp at 40 °C, indicating a faster exchange process for **2** than for **1**.

At 25 °C in toluene-d_8, compound **2** exhibits a slightly broadened doublet for the methyl groups of the *ortho*-isopropyl ligands at δ 1.11 ppm, as well as a broad signal for the methyne protons of these groups at 3.57 ppm. Upon cooling the solution to 5 °C, the signal for the methyne protons is broadened into the baseline and the doublet at δ 1.11 ppm is no longer resolved. At −20 °C, two distinct methyne resonances are visible at δ 4.28

and 2.90 ppm, for the bridging and terminal aryloxide groups, respectively. The signal for the methyl groups is also split into two broadened signals at δ 1.27 and 0.98 ppm at this temperature. At −60 °C, two septets at δ 4.30 (J = 6.0 Hz) and 2.98 (J = 5.7 Hz) are present in a 1:1 intensity ratio. There are three distinct doublets for the methyl groups of the isopropyl ligands at δ 1.31 (J = 5.7 Hz), 1.24 (J = 5.7 Hz), and 1.00 (J = 6.0 Hz) ppm, in a 1:1:2 intensity ratio. The methyl groups of the bridging 2,6-diisopropylphenoxide ligands are diastereotopic as a result of the transoid ligand disposition about the pyramidal germanium atoms (Fig. 3). The poor solubility properties of **1** precluded a variable-temperature NMR study at low temperatures. It is also of note that neither **1** nor **2** undergo exchange with trace amounts of the free phenol in solution at high temperature.

There are two distinct structural changes of interest. First, there is the issue of inversion of configuration about the germanium atoms in dimeric **1** and **2**; the second involves bridge–terminal aryloxide exchange in these molecules. The ground state structures of **1** and **2** exhibit a transoid arrangement of the terminal aryloxide ligands. In solution at low temperature, the presence of diastereotopic bridge aryloxide methyl groups indicate this structure is present. A cisoid structure leads to a plane of symmetry through the bridging aryloxide ligands. Rapid (on the NMR timescale) inversion at germanium, resulting in interconversion between the cisoid and transoid structural isomers, would lead to exchange of the diastereotopic bridge methyl groups. This is illustrated in Scheme 2A.

However, in this system we are unable to observe whether or not this process occurs due to the exchange of bridging and terminal aryloxide ligands. Hence, broadening of the signals for the diastereotopic bridge methyl groups occurs due to the exchange of these ligands with the terminal aryloxide groups. The barrier to inversion about the pyramidal germanium atoms is less than 13.5 kcal mol^{-1} as the diastereotopic methyl groups are well resolved at −60 °C and begin to coalesce at −20 °C. The mechanism of bridge/terminal ligand exchange is unknown. It is possible that dissociation to trace amounts of monomer is occurring (*cf.* **3** and **4**). However, it is also possible that a pathway involving bridge opening is taking place, as shown in Scheme 2B.

Reaction chemistry of [Ge(OAr)$_2$]$_n$

Compound **1** was treated with 2 molar equivalents of benzil in an attempt to trap the [Ge(OAr)$_2$] moiety as the complex [Ge(OAr)$_2$(O$_2$C$_2$Ph$_2$)] (Scheme 3). Instead of the expected product, a mixture of species was obtained, as shown by NMR spectroscopy. Complex **5** was obtained in 44% yield by recrystallization of the crude reaction mixture from hot benzene and was characterized by an X-ray crystal structure. Evaporation of the mother liquor yielded an intractable red/brown oil. Addition of germylenes to benzil and other non-enolizable α-diketones proceeds by a concerted 1,4-addition reaction,[25] and isolated yields of the adducts are often low.[26,27] Compound **5** was formed even after drying the benzil reagent *in vacuo* for 48 h, after which time there was no evidence for adventitious water in the IR spectrum of this material. Although we are uncertain of the nature of the other products formed in the reaction,
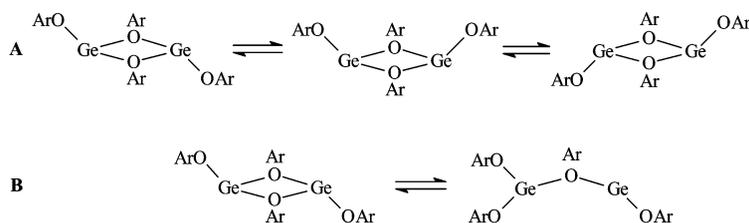
Scheme 2
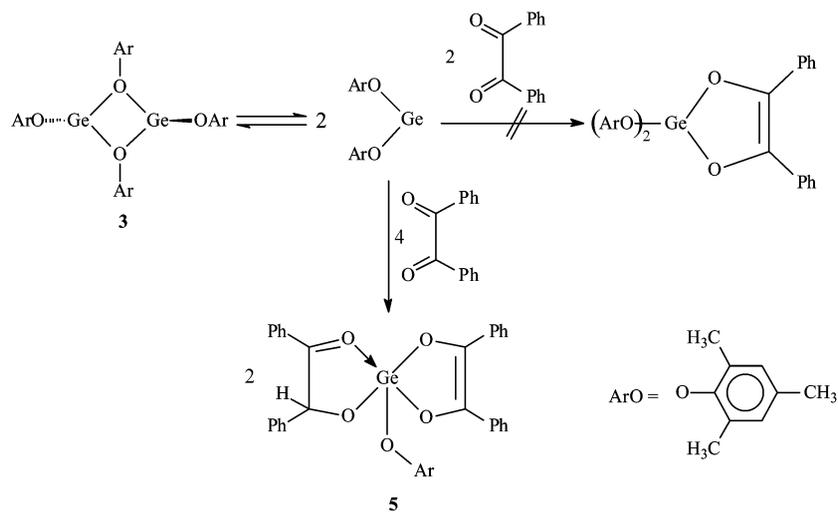
Scheme 3

Table 4 Selected bond lengths (Å) and angles (°) for [Ge(OC$_6$H$_2$Me$_3$-2,4,6)(O$_2$C$_2$Ph$_2$)(O$_2$C$_2$HPh$_2$)]·C$_6$H$_6$ (**5**·C$_6$H$_6$)

Ge–O(1)	1.773(2)	Ge–O(2)	2.037(1)
Ge–O(3)	1.794(1)	Ge–O(4)	1.813(1)
Ge–O(5)	1.773(1)	C(1)–O(1)	1.421(2)
C(2)–O(2)	1.248(2)	C(1)–C(2)	1.521(3)
C(3)–C(4)	1.339(3)		
O(1)–Ge–O(2)	83.09(6)	O(1)–Ge–O(3)	124.38(7)
O(1)–Ge–O(4)	93.20(6)	O(1)–Ge–O(5)	116.87(7)
O(2)–Ge–O(3)	87.10(6)	O(2)–Ge–O(4)	172.66(6)
O(2)–Ge–O(5)	85.96(6)	O(3)–Ge–O(4)	89.71(6)
O(3)–Ge–O(5)	116.80(7)	Ge(4)–Ge–O(5)	101.48(7)

Table 5 Selected bond lengths (Å) and angles (°) for [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$(O$_2$C$_2$Ph$_2$)]·0.5C$_6$H$_6$ (**6**·0.5C$_6$H$_6$)

Ge–O(11)	1.772(4)	Ge–O(14)	1.770(4)
Ge–O(2)	1.720(4)	Ge–O(3)	1.733(4)
O(11)–Ge–O(14)	94.8(2)	O(11)–Ge–O(2)	110.8(2)
O(11)–Ge–O(3)	115.54(2)	O(14)–Ge–O(2)	121.6(2)
O(14)–Ge–O(3)	111.3(2)	O(2)–Ge–O(3)	103.4(2)

and these high coordination numbers are very common in open-framework germinates.[34–36]

One of the chelating ligands of **5** is bound to the germanium(IV) metal center in the expected fashion through two single Ge(IV)–O bonds with lengths of 1.794(1) and 1.813(1) Å. The C(3)–C(4) bond length is 1.339(3) Å, indicative of a C–C double bond. The second chelate is attached to the germanium center in a different fashion. The Ge–O(1) distance of 1.774(1) Å is typical for a formal Ge(IV)–O single bond while the Ge–O(2) distance of 2.037(1) Å indicates the presence of a dative bond between the germanium atom and the carbonyl moiety of the chelating ligand (Table 5). The two carbon atoms of the ligand backbone are singly bound and a hydrogen atom, refined in the X-ray structure of **5**, is bound to C(1). This ligand undoubtedly arises from the protonation of a benzil molecule, but the exact pathway of its formation is unknown.

In contrast to **1**, the monomeric germylene **4** cleanly reacts with benzil to give the expected product **6**. An ORTEP diagram for **6** is shown in Fig. 7, and selected bond lengths and angles are collected in Table 5. The Ge–O bond lengths of the bound aryloxide ligands in **6** are 1.720(4) and 1.733(4) Å, which are
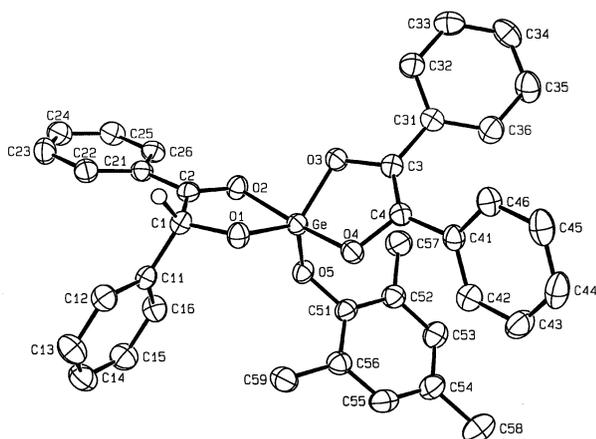
Fig. 6 ORTEP plot of [Ge(OC$_6$H$_2$Me$_3$-2,4,6)(O$_2$C$_2$Ph$_2$)(O$_2$C$_2$HPh$_2$)]· C$_6$H$_6$ (**5**·C$_6$H$_6$). Thermal ellipsoids are drawn at 50% probability.

5 could reproducibly be prepared from **1** and benzil in benzene or toluene solvent.

An ORTEP diagram of **5** is shown in Fig. 6, and selected bond lengths and angles are collected in Table 4. Compound **5** contains a five-coordinate germanium metal center, with one 2,4,6-trimethylphenoxide ligand and two different chelating ligands. The ligands are arranged in a distorted square base pyramidal geometry, with the two chelating ligands being slightly twisted relative to one another and the phenoxide ligand forming the apex of the pyramid. Compound **5** is a rare example of a neutral five-coordinate germanium(IV) complex. Reported examples of these species are often salt complexes,[28,29] such as [Et$_4$N][(C$_6$H$_4$O$_2$)$_2$GePh], although neutral complexes containing coordinated donor ligands are also known.[30,31] Six-coordinate germanium species have also been reported[30–33]
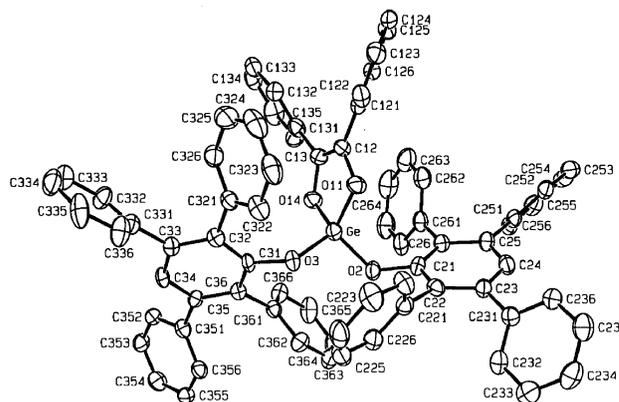
Fig. 7 ORTEP plot of [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$(O$_2$C$_2$Ph$_2$)]·0.5C$_6$H$_6$ (**6**·0.5C$_6$H$_6$). Thermal ellipsoids are drawn at 50% probability.

slightly shorter than those of the chelating 1,2-dialkoxide moiety, d(Ge–O) = 1.772(4) and 1.770(4) Å. The Ge–OAr distances in **6** are shorter than the Ge–OAr distance of **4**, d(Ge–O) = 1.826(1) Å, reflecting the higher formal charge on the germanium metal center. The four oxygen atoms are arranged about the metal center in an approximately tetrahedral fashion.

Compound **4** undergoes insertion into the carbon-iodine bond of MeI (Scheme 4) to give the germane [Ge(OC$_6$HPh$_4$-

Scheme 4
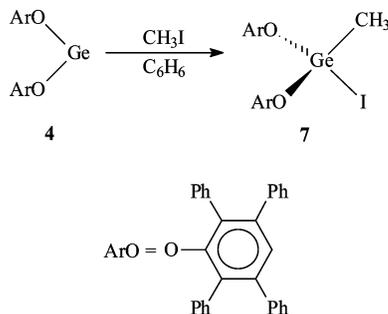
2,3,5,6)$_2$(Me)(I)], which was characterized by elemental analysis and ^{1}H NMR spectroscopy. The resonance for the methyl protons is found relatively far upfield at δ −0.24 ppm, while the methyl groups of [(PhO)Me$_2$GeH] and [(PhS)Me$_2$GeH] exhibit signals at δ 0.75 and 0.54 ppm, respectively.[37] The upfield shift of the methyl resonance of **7** is likely a result of the diamagnetic anisotropy of the *ortho*-phenyl rings of the tetraphenyl-phenoxide ligands, which provides increased shielding for the methyl protons.

Synthesis and structure of a germanium(IV) arylsulfide complex

In an attempt to compare the properties of arylsulfide complexes with those of aryloxide complexes, Ge[N(SiMe$_3$)$_2$]$_2$ was reacted with 2 equivalents of HSC$_6$H$_2$^{i}Pr$_3$-2,4,6. Thiolate complexes of germanium(II) are unusual, although [Ge(SC$_6$H$_2$Me$_3$-2,4,6)$_2$] has been reported and its Cr(CO)$_5$ complex has been structurally characterized.[38,39] Other structurally characterized examples include [Et$_4$N][Ge(SPh)$_3$], [Ph$_4$P]$_2$[Ge$_2$(SCH$_2$-CH$_2$S)$_3$],[40] and [Ge(S^{t}Bu)$_2$]$_2$,[41] and the arylthiolate complexes [Ge(SC$_6$H$_2$^{t}Bu$_3$-2,4,6)][42] and [PhSGeH$_3$][43] have also been reported.

Instead of the expected product [Ge(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_2$]$_n$ (n = 1 or 2), a germane-hydride complex [HGe(SC$_6$H$_2$^{i}Pr$_3$)$_3$] (**8**) was isolated as shown in Scheme 5. Compound **8** likely forms in a two-step process, involving formation of [Ge(SAr)$_2$] followed by insertion of this species into the S–H bond of HSC$_6$H$_2$^{i}Pr$_3$-2,4,6. When three equivalents of the arylthiol are used in the reaction, complex **8** can be isolated and residual Ge[N(SiMe$_3$)$_2$]$_2$ can be detected by ^{1}H NMR spectroscopy. Theoretical studies indicate that S–H bonds undergo germylene insertion reactions more readily than do O–H bonds.[44] Thus, it appears that once the [Ge(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_2$] (**8a**) complex is formed, it undergoes
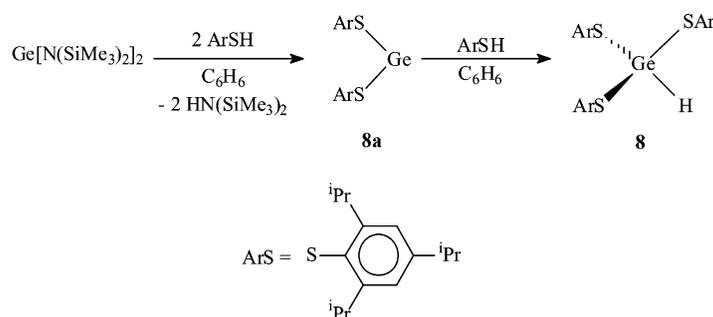
Table 6 Selected bond lengths (Å) and angles (°) for one molecule of [HGe(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_3$] (**8**)

Ge(1)–S(11)	2.2160(7)	Ge(1)–S(12)	2.2150(7)
Ge(1)–S(31)	2.2154(2)	Ge(1)–H(1)	1.45(2)
S(11)–Ge(1)–S(12)	110.77(3)	S(11)–Ge(1)–S(13)	109.80(3)
S(12)–Ge(1)–S(13)	111.70(3)	S(11)–Ge(1)–H(1)	110.(1)
S(12)–Ge(1)–H(1)	106.5(9)	S(13)–Ge(1)–H(1)	107.9(9)
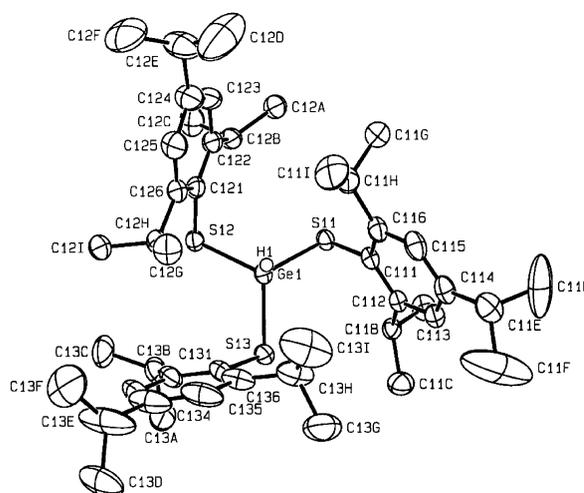
Fig. 8 ORTEP plot of one molecule of [HGe(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_3$] (**8**). Thermal ellipsoids are drawn at 50% probability.

insertion into the S–H bond more rapidly than the protonolysis reaction between HSC$_6$H$_2$^{i}Pr$_3$-2,4,6 and Ge[N(SiMe$_3$)$_2$]$_2$ occurs. In contrast, no reaction was observed between the aryloxide complex **4** and HSC$_6$H$_2$^{i}Pr-2,4,6. The more electron withdrawing phenoxide ligands of **4**, relative to the arylthiolato ligands of the intermediate **8a**, likely result in **4** being less nucleophilic than **8a**. Additionally, the S–H bond of the arylthiol is weaker than the O–H bond of the phenol. These two factors serve to explain the formation of **8** rather than **8a**.

Compound **8** was characterized by NMR spectroscopy and an X-ray crystal structure. An ORTEP diagram of **8** is shown in Fig. 8 and selected bond distances and angles are summarized in Table 6. The ^{1}H NMR signal for the proton of **8** appears at δ 5.73 ppm, which is shifted downfield from the resonance observed for [H$_2$Ge{CH(SiMe$_3$)$_2$}$_2$] at δ 4.23 ppm[45] and from that of PhSGeH$_3$ at δ 4.65 ppm[43] due to the presence of three electronegative groups attached to the germanium atom in **8**. Compound **8** contains two different molecules of the same formulation in the unit cell. The Ge–S and Ge–H bonds of the respective molecules are within one standard deviation of each other, with the exception of the Ge(2)–S(21) bond, which is 0.067 Å shorter than the shortest Ge(1)–S bond. The Ge–S bond lengths in **8** range from 2.2150(7) to 2.2160(7) Å, and are similar to that of [Ge(SC$_6$H$_4$Me-4)$_4$], d(Ge–S)$_{avg}$ = 2.218 Å[40] and are slightly shorter than the mixed alkyl/thiolate

Scheme 5

germanium(IV) complex [Ph$_3$Ge(SC$_6$H$_4$^{t}Bu-4)], d(Ge–S) = 2.229(2) Å.[46] The environment about the germanium atom is approximately tetrahedral, with an average S–Ge–S bond angle of 110.76°.

Conclusions

Germanium aryloxide complexes have been prepared by the protonolysis reaction between Ge[N(SiMe$_3$)$_2$]$_2$ and phenols ArOH, and the nature of the incoming phenoxide ligand dictates the nature of the product obtained. Less bulky ligands give rise to dimeric structures containing bridging phenoxide ligands and pyramidalized germanium atoms, while more sterically encumbering ligands result in monomeric complexes. The complex [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$] (**4**) undergoes reactions typical of germylene complexes, including oxidative addition to α-diketones and alkyl halides. The new arylthiolato germane species [HGe(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_3$] (**8**) has been prepared from Ge[N(SiMe$_3$)$_2$]$_2$, and presumably forms by a two-step process involving metathesis to yield [Ge(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_2$] followed by insertion of this materials into the S–H bond of HSC$_6$-H$_2$^{i}Pr$_3$-2,4,6.

Experimental

General considerations

All manipulations were carried out using standard Schlenk, syringe and glovebox techniques.[47] Solvents were purified using an Innovative Technologies solvent purification system. ^{1}H NMR spectra were recorded at 300 MHz using a Varian Inova-300 or at 500 MHz using a Bruker DRX-500 spectrometer. Elemental analyses were carried out in-house at Purdue University. The bisamide Ge[N(SiMe$_3$)$_2$]$_2$ was purchased from Gelest, Inc. or synthesized *via* literature methods.[48–50] The compounds 2,6-diphenylphenol,[51] 2,3,5,6-tetraphenylphenol[52] and 2,4,6-triisopropylbenzenethiol[53] were prepared according to literature methods, while 2,4,6-trimethylphenol, 2,6-diisopropylphenol, and iodomethane were purchased from Aldrich and used without further purification. Benzil was purchased from Aldrich and heated *in vacuo* at 100 °C for 12 h to remove water.

Synthesis of [Ge(OC$_6$H$_2$Me$_3$-2,4,6)$_2$]$_2$ (1)

A solution of 2,4,6-trimethylphenol (0.81 g, 5.9 mmol) in benzene (10 cm^3) was added dropwise to a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (1.05 g, 2.66 mmol) in benzene (10 cm^3) with stirring. The orange color of the solution faded and the mixture was stirred for 6 h, after which time a white precipitate had formed. The solvent was removed *in vacuo* and the crude material was recrystallized from hot benzene (10 cm^3) to yield 0.66 g (73%) of **1** as colorless crystals. Anal. Calc.. for C$_{36}$H$_{44}$-Ge$_2$O$_4$ (**1**): C, 63.04; H, 6.36. Found: C, 62.98; H, 6.37%. ^{1}H NMR (25 °C, C$_6$D$_6$): δ 6.71 (s, 6 H, *m*-H), 2.31 (br s, 24 H, *o*-CH$_3$), 2.10 (s, 12 H, *p*-CH$_3$) ppm.

Synthesis of [Ge(OC$_6$H$_3$^{i}Pr$_2$-2,6)$_2$]$_2$ (2)

To a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.59 g, 1.5 mmol) in benzene (5 cm^3) was added a solution of 2,5-diisopropylphenol (0.58 g, 3.2 mmol) in benzene (5 cm^3) dropwise with stirring. The reaction became colorless and was stirred for 5 h. The volatiles were removed *in vacuo* to yield a pale yellow oil, which solidified after cooling at −15 °C for 2 h. Compound **2** was isolated as 0.39 g (61%) of a pale yellow solid. Anal. Calc. for C$_{48}$H$_{68}$Ge$_2$O$_4$ (**2**): C, 67.48; H, 8.02. Found: C, 67.11; H, 8.18%. ^{1}H NMR (25 °C, C$_6$D$_6$): δ 7.06 (d, *J* = 7.2 Hz, 8 H, *m*-H), 6.96 (t, 4 H, *J* = 6.9 Hz, *p*-H), 3.60 (br s, 8 H), 1.16 (d, *J* = 6.6 Hz, 48 H).

Synthesis of [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$] (3)

A solution of 2,6-diphenylphenol (0.590 g, 1.14 mmol) in benzene (10 cm^3) was added to a solution of Ge[N(SiMe$_3$)$_2$]$_2$

(0.450 g, 2.39 mmol) in benzene (5 cm^3). The solution instantly became colorless and was stirred for 12 h. The volatiles were removed *in vacuo* to yield a white solid which was recrystallized from a warm benzene–hexane (50:50 v/v) solution to yield 0.37 g (58%) of **3** as colorless crystals. Anal. Calc. for C$_{36}$H$_{26}$GeO$_2$ (**3**): C, 76.77; H, 4.65. Found: C, 76.62; H, 4.87%. ^{1}H NMR (C$_6$D$_6$): δ 7.41 (m, 8 H, 2,6-diphenyl groups), 7.17 (d, 4 H, *meta*-Ph$_2$C$_6$H$_3$), 7.00 (m, 12 H, 2,6-diphenyl groups), 6.86 (t, 2 H, *para*-Ph$_2$C$_6$H$_3$).

Synthesis of [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$] (4)

A suspension of 2,3,5,6-tetraphenylphenol (3.10 g, 7.78 mmol) in benzene (20 cm^3) was added to a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (1.32 g, 3.35 mmol) in benzene (5 cm^3). The solution was gently heated until all of the material dissolved, upon which the orange color faded. The mixture was allowed to cool to room temperature and was stirred for 12 h resulting in the formation of a white precipitate. The volatiles were removed *in vacuo* and the resulting solid was washed with 3 × 20 cm^3 of benzene followed by recrystallization from 20 cm^3 of hot benzene to yield 2.43 g (84%) of **4** as colorless crystals. Anal. Calc. for C$_{66}$H$_{48}$GeO$_2$ (**4**·C$_6$H$_6$): C, 83.82; H, 5.12. Found: C, 84.04; H, 5.37%. ^{1}H NMR: δ 7.31–7.23 (m, 15 H, aromatics), 7.02–6.90 (m, 27 H, aromatics) ppm.

Synthesis of [Ge(OC$_6$H$_2$Me$_3$-2,4,6)(O$_2$C$_2$Ph$_2$)(O$_2$C$_2$HPh$_2$)] (5)

A solution of benzil (0.10 g, 0.48 mmol) in benzene (5 cm^3) was added to a suspension of **1** (0.13 g, 0.20 mmol) in benzene (5 cm^3). The resulting yellow solution gradually darkened to orange–red with stirring over 2 h. The volatiles were removed *in vacuo* and the resulting material was recrystallized from 3 cm^3 of hot benzene. The solid was washed with 2 × 3 cm^3 of benzene to yield **5** as a red solid. Yield: 0.11 g (44%). Anal. Calc. for C$_{37}$H$_{32}$GeO$_5$ (**5**): C, 70.62; H, 5.12. Found: C, 70.80; H, 5.25%. ^{1}H NMR: δ 7.91 (d, 2H, *J* = 7.2 Hz, *o*-(Ph)C(=O)), 7.68 (d, 2 H, *J* = 8.1 Hz, *o*-(Ph)C(H)(–O)), 7.57 (pseudo-d, br, 4H, *o*-(Ph)$_2$C$_2$O$_2$), 7.05 (pseudo-t, 2 H, *m*-(Ph)C(=O)), 6.97–6.59 (aromatics, 12 H), 5.78 (s, 1 H, (Ph)C(*H*)(–O)), 2.65 (s, 6 H, *o*-(*Me*)$_3$C$_6$H$_2$O), 2.11 (s, 3 H, *p*-(*Me*)$_3$C$_6$H$_2$O) ppm.

Synthesis of [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$(O$_2$C$_2$Ph$_2$)] (6)

A solution of benzil (0.080 g, 0.38 mmol) in benzene (15 cm^3) was added to a suspension of **4** (0.30 g, 0.35 mmol) in benzene (10 cm^3). The solution was gently heated until all material had dissolved, after which time the solution darkened from yellow to red. The volatiles were removed resulting in a red–brown solid, which was recrystallized from 10 cm^3 of hot benzene. The solid was washed with 3 × 3 cm^3 of benzene to yield 0.19 g (51%) of **6**. ^{1}H NMR: δ 7.91 (d, 4 H, *o*-(Ph)C$_2$O$_2$, *J* = 7.2 Hz), 7.54 (pseudo-t, 4 H, *m*-(Ph)C$_2$O$_2$), 7.32–6.81 (aromatics, 44 H).

Synthesis of [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$(Me)(I)] (7)

Iodomethane (0.5 cm^3, 8.0 mmol) was added *via* syringe to a suspension of **4** (0.50 g, 0.58 mmol) in benzene (10 cm^3). The solution was heated until all of the material dissolved. After cooling, the mixture was stirred for 12 h resulting in the formation of an off-white precipitate. The volatiles were removed *in vacuo* and the resulting solid was recrystallized from 3 cm^3 of hot benzene to **7** as a white powder. Yield: 0.41 g (70%). Anal. Calc. for C$_{61}$H$_{45}$GeIO$_2$: C, 72.58; H, 4.49. Found: C, 72.85; H, 4.67%. ^{1}H NMR: δ 7.30–7.17 (m, 15 H, aromatics), 7.12–6.95 (m, 27 H, aromatics), −0.24 (s, 3 H) ppm.

Synthesis of [HGe(SC$_6$H$_2$^{i}Pr$_3$-2,4,6)$_3$] (8)

A solution of 2,4,6-triisopropylthiophenol (0.87 g, 3.7 mmol) in benzene (10 cm^3) was added *via* syringe to a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.46 g, 1.2 mmol) in benzene (5 cm^3). The solution instantly changed from light orange to deep red–orange in

Table 7 Crystallographic data for compounds **1**–**6** and **8**

	1	**2**	**3**	**4·3C$_6$H$_6$**	**5·C$_6$H$_6$**	**6·0.5C$_6$H$_6$**	**8**
Formula	C$_{36}$H$_{44}$Ge$_2$O$_4$	C$_{48}$H$_{68}$Ge$_2$O$_4$	C$_{36}$H$_{26}$GeO$_2$	C$_{78}$H$_{60}$GeO$_2$	C$_{43}$H$_{38}$GeO$_5$	C$_{77}$H$_{55}$GeO$_4$	C$_{45}$H$_{70}$GeS$_3$
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	7.8478(4)	16.2589(3)	23.9641(3)	23.9853(5)	9.6278(2)	10.9950(5)	14.7180(3)
b/Å	20.535(1)	13.0851(2)	12.3175(2)	11.2746(3)	18.8016(4)	13.7686(5)	18.5142(4)
c/Å	21.148(1)	23.0812(3)	20.0053(3)	22.0664(5)	19.4563(5)	18.964(1)	19.0815(5)
α/°	90	90	90	90	90	87.582(2)	114.7659(9)
β/°	99.804(3)	109.160(1)	111.3914(6)	94.633(1)	92.877(1)	83.360(2)	101.0489(9)
γ/°	90	90	90	90	90	86.501(2)	91.028(2)
V/Å^3	3358.4(6)	4638.5(2)	5498.3(1)	5947.8(4)	3517.5(2)	2844.6(2)	4605.6(4)
Z	4	4	8	4	4	2	4
D_c/g cm^{-3}	1.357	1.223	1.361	1.231	1.336	1.304	1.125
Temperature/K	150	150	150	150	150	150	150
Radiation (wavelength/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
R	0.048	0.039	0.032	0.039	0.038	0.081	0.049
R_w	0.109	0.082	0.083	0.096	0.088	0.144	0.106

color, then became colorless after 5 min. The solution was stirred for 1 h and the volatiles were removed *in vacuo* to yield 0.84 g (92%) of **8** as a pale yellow solid. Anal. Calc. for C$_{45}$H$_{70}$GeS$_3$: C, 69.30; H, 9.04; S, 12.33. Found: C, 68.93; H, 9.28; S, 12.35%. ^{1}H NMR (C$_6$D$_6$): δ 7.10 (s, 6 H, *meta*-H), 5.73 (s, 1 H, Ge–H), 3.77 (sept, 6 H, $J = 6.9$ Hz, *o*-(CH$_3$)$_2$C*H*), 2.74 (sept, 3 H, $J = 6.9$ Hz, *p*-(CH$_3$)$_2$C*H*), 1.21 (d, 54 H, $J = 6.9$ Hz, *ortho*- and *para*-(C*H*$_3$)$_2$CH) ppm.

X-Ray data collection and reduction

Crystal data and data collection parameters are contained in Table 7. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.[54] An empirical absorption correction using SCALEPACK was applied.[55] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[56] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from ref. 57. Refinement was performed on an AlphaServer 2100 using SHELX-97.[58] Crystallographic drawings were obtained using the program ORTEP.[59]

CCDC reference numbers 195678 (**1**), 195676 (**2**), 195674 (**3**), 195679 (**4**), 195677 (**5**), 195680 (**6**), 195675 (**8**).

See http://www.rsc.org/suppdata/dt/b2/b211077f/ for crystallographic data in CIF or other electronic format.

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