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# Synthesis and structures of aryloxo- and binaphthoxogermanium(IV) alkyl iodide complexes

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ABSTRACT

The germanium(II) aryloxide complexes (*S*)-[Ge{O$_2$C$_{20}$H$_{10}$-(SiMe$_2$Ph)$_2$-3,3′}{NH$_3$}] (**1**) and [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$] (**2**) react with either Bu$^t$I or MeI to yield the corresponding germanium(IV) compounds (*S*)-[Ge{O$_2$C$_{20}$H$_{10}$-(SiMe$_2$Ph)$_2$-3,3′}{Bu$^t$}{I}] (**3**), (*S*)-[Ge{O$_2$C$_{20}$H$_{10}$-(SiMe$_2$Ph)$_2$-3,3′}{Me}{I}] (**4**), [Ge(OC$_6$H$_3$-Ph$_2$-2,6)$_2$(Bu$^t$)(I)] (**5**), and [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$(Me)(I)] (**6**). Compound **6** reacts with 2,6-diphenylphenol to yield [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_3$(Me)] (**7**), while **3**–**5** do not. The X-ray crystal structures of **3**–**5** and **7** were determined, and **3**–**5** represent the first structurally characterized germanium(IV) species having germanium bound to both oxygen and iodine.

## 1. Introduction

Germanium aryloxides are an interesting class of compounds that exhibit a diverse array of possible structures [1–36], and have also recently been shown to serve as well-defined precursors for the preparation of germanium(0) nanomaterials. In particular, the morphology of the nanomaterials obtained has been shown to depend on the substituent pattern of the ligands in the precursors that contain germanium in either the divalent or tetravalent oxidation state [2,8]. Germanium aryloxides contain germanium attached to one or more phenolic oxygen atom and the aromatic rings can have varying substitution patterns at the *ortho*-, *meta*-, and/or *para*-positions. Both monomeric and dimeric complexes containing simple aryloxide ligands are known [2,8,33], and some germanium aryloxides containing calix[*n*]arene [10–12,19,34,35] or binaphthoxide ligands [31,36], as well as cluster-type materials [9], have also been reported.

The monomeric germanium(II) aryloxide [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$] has been shown to yield the germanium(IV) aryloxide complex [Ge(OC$_6$HPh$_4$-2,3,5,6)$_2$(Me)(I)] via the oxidative addition of the germanium(II) center into the C–I bond of methyl iodide [33]. However, the X-ray crystal structure of this compound was not obtained, and crystallographically characterized compounds containing a germanium–iodine bond are rare. A search of the CCDC database in April 2010 provided data for only 48 such species [37–71]. Furthermore, the only compound containing germanium bound to both oxygen and iodine was the acetylacetonate complex (Acac)GeI [48], and no examples of germanium(IV)-containing species have been reported.

We have prepared and structurally characterized the germanium(IV) binaphthoxide compounds (*S*)-[Ge{O$_2$C$_{20}$H$_{10}$-(SiMe$_2$Ph)$_2$-3,3′}{R}{I}] (R = Bu$^t$ or Me) and the aryloxide [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$-(Bu$^t$)(I)], each of which has a Ge–I bond. We have also prepared [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$(Me)(I)], that was converted to the tri(aryloxide) complex [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_3$(Me)] upon reaction of the iodo compound with 2,6-diphenylphenol. The ligands in the two binaphthoxide complexes are chelating and each contain a GeO$_2$C$_4$ seven-membered ring. The size of the organic substituent R has a measurable effect on the size of the chiral pocket in these ligands, and the aryloxide species [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$(R)(I)] (R = Bu$^t$ or Me) exhibit different reactivity toward 2,6-diphenylphenol due to the steric attributes of the organic substituent at germanium.

## 2. Results and discussion

The germanium(II) aryloxides (*S*)-[Ge{O$_2$C$_{20}$H$_{10}$-(SiMe$_2$Ph)$_2$-3,3′}{NH$_3$}] (**1**) [36] and [Ge(OC$_6$H$_3$Ph$_2$-2,6)$_2$] (**2**) [33] were synthesized from Ge[N(SiMe$_3$)$_2$]$_2$ and (HO)$_2$C$_{20}$H$_{10}$-(SiMe$_2$Ph)$_2$-3,3′ or HOC$_6$H$_3$Ph$_2$-2,6 (respectively). Compound **1** was converted to the

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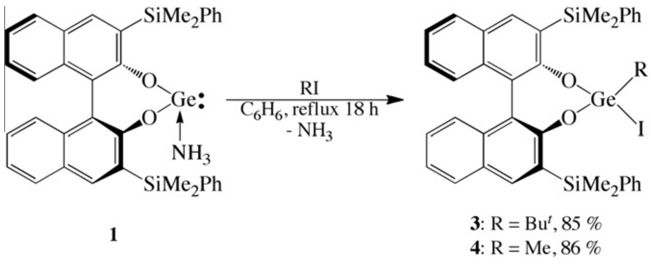
germanium(IV) binaphthoxide derivatives (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{Bu$^t$}{I}] (**3**) and (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{Me}{I}] (**4**) in yields of 85% and 86% via insertion of the germylene **1** into the C–I bond of the corresponding alkyl iodide (Scheme 1), which also involves liberation of the coordinated ammonia molecule from **1**.

The conversion of **1** to **3** and **4** is evident in the $^1$H NMR spectrum of the products. The spectrum of **1** exhibits a singlet for the 4,4′-protons at $\delta$ 8.18 ppm, indicating that they are magnetically equivalent, and two closely spaced resonances for the methyl protons of the 3,3′-$SiMe_2Ph$ groups at $\delta$ 0.75 and 0.68 ppm were also observed [36]. In the $^1$H NMR spectra of both **3** and **4** two resonances at $\delta$ 8.16 and 8.10 ppm for **3** and $\delta$ 8.20 and 8.13 for **4** were observed for the 4,4′-protons. This indicates that the two 4,4′-protons are no longer magnetically equivalent in **3** and **4** due to the absence of a $C_2$-axis in these compounds as a result of the attachment of an organic substituent and an iodine atom to the germanium center. Similarly, a singlet was observed for each of the four methyl groups of the –$SiMe_2Ph$ substituents in the $^1$H NMR spectra of **3** and **4**. For compound **3** these peaks appear at $\delta$ 0.88, 0.84, 0.80, and 0.66 ppm, while for **4** the resonances were observed at $\delta$ 0.82, 0.79, 0.71, and 0.63 ppm. A singlet corresponding to the protons of the *tert*-butyl group of **3** was observed at $\delta$ 0.70 ppm, and the methyl group in **4** results in the appearance of an upfield singlet at $\delta$ 0.12 ppm.

Compounds **3** and **4** are sparingly soluble in hydrocarbon solvents. However, X-ray quality crystals of **3** and **4** were obtained by dissolving the compound in an aliquot of hot benzene that was slowly cooled to room temperature, and ORTEP diagrams of **3** and **4** are shown in Figs. 1 and 2 while and selected bond distances and angles are collected in Tables 1 and 2 (respectively). The germanium centers in the starting material **1** and the products **3** and **4** are incorporated into a seven-membered $GeO_2C_4$ ring that includes the interannular C–C bond of the binaphthoxide ligand. The $GeO_2C_4$ ring in the *tert*-butyl substituted species **3** has Ge–O bond distances that differ from one another in length by 0.017(3) Å and have an average value of 1.789(3) Å. The Ge–O bond lengths in the methyl-substituted derivative **4** are shorter than those in **3** and have an average value of 1.734(4) Å, and they also differ significantly from one another by 0.12(4) Å. The Ge–O bond distances in the germylene **1** have an average value of 1.875(3) Å, and the shorter Ge–O bond lengths in both **3** and **4** are a result of the higher oxidation state of germanium in these two complexes. The Ge–O bond distances in **3** and **4** are similar to other germanium(IV) aryloxides, including that in the chelate complexe [{2,2-CH($CH_3)_2$($CH_2$Bu$^t$)}$_2C_6H_2O_2$]Ge($CH_3)_2$ (1.770(2) Å), [20] which contains a seven-membered $GeO_2C_4$ ring.

The Ge–C bond distance in **3** is 1.972(5) Å and is typical for a germanium–carbon single bond, and the Ge–I bond length that measures 2.5141(7) Å is similar to the average Ge–I bond lengths in the organogermanium iodides ($C_5Me_5$)$GeI_3$, ($C_6Cl_5)_2GeI_2$, [(2-MeO–5-Bu$^t$$C_6H_3)_3$C]$GeI_3$, and $MeGeI_3$ which are 2.5335(9) Å [37], 2.509(2) Å [61], 2.5180(8) Å [68], and 2.498(2) Å [38] (respectively). The only crystallographically characterized complex containing germanium bound to both oxygen and iodine is (acac)-GeI (acac = acetylacetonato), which has a Ge–I bond length of 2.7360(3) Å [48]. However, this species contains a divalent germanium atom and therefore would be expected to have a longer Ge–I bond than **3**.



**Scheme 1.**

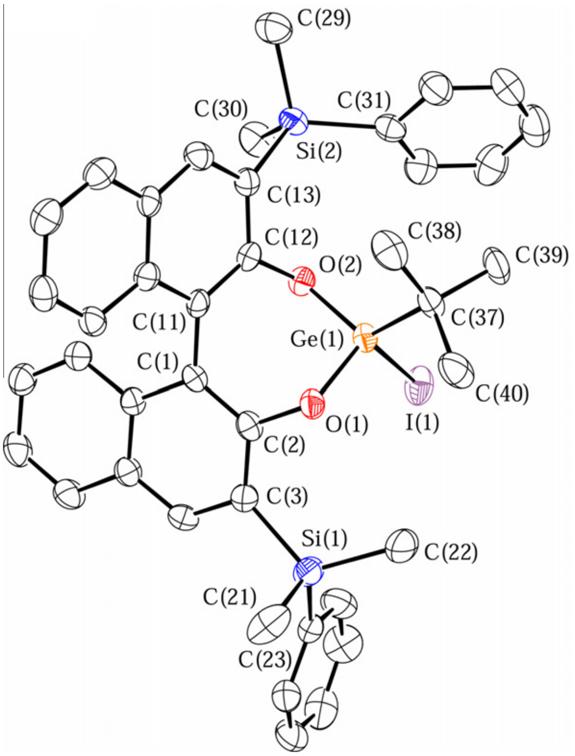


**Fig. 1.** ORTEP diagram of (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{Bu$^t$}{I}] (**3**). Thermal ellipsoids are drawn at 50% probability.

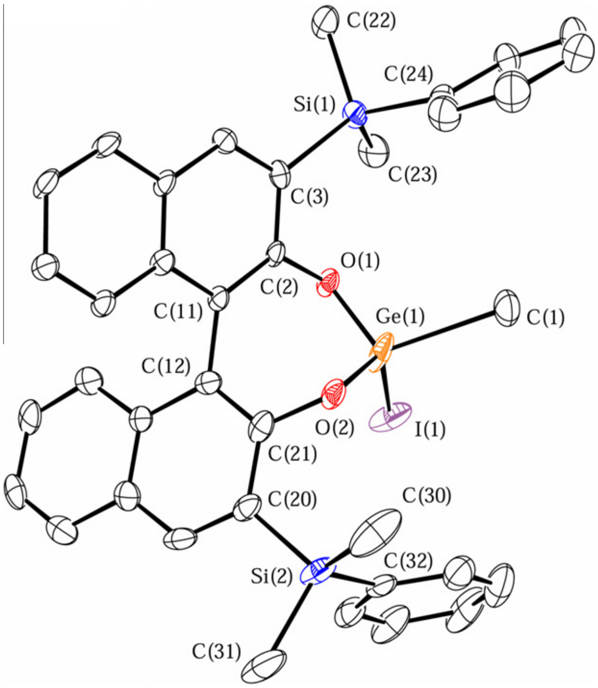


**Fig. 2.** ORTEP diagram of (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{Me}{I}] (**4**). Thermal ellipsoids are drawn at 50% probability.

**Table 1**
Selected bond distances (Å) and angles (°) for (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{But}{I}] (**3**).

| | |
|---|---|
| Ge(1)–O(1) | 1.780(3) |
| Ge(1)–O(2) | 1.797(3) |
| Ge(1)–I(1) | 2.5141(7) |
| Ge(1)–C(37) | 1.972(5) |
| O(1)–C(2) | 1.377(5) |
| O(2)–C(12) | 1.383(4) |
| C(1)–C(11) | 1.484(6) |
| C(3)–Si(1) | 1.886(4) |
| C(13)–Si(2) | 1.879(4) |
| O(1)–Ge(1)–O(2) | 103.7(1) |
| O(1)–Ge(1)–I(1) | 111.1(1) |
| O(1)–Ge(1)–C(37) | 103.8(2) |
| O(2)–Ge(1)–I(1) | 99.38(9) |
| O(2)–Ge(1)–C(37) | 121.1(2) |
| I(1)–Ge(1)–C(37) | 117.2(1) |

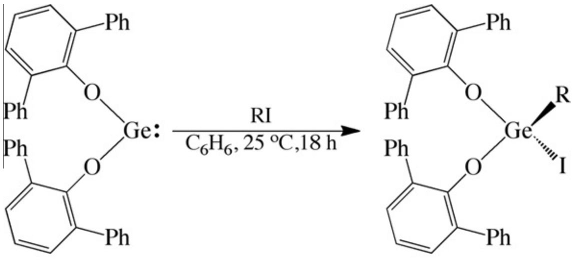
**Table 2**
Selected bond distances (Å) and angles (°) for (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{Me}{I}] (**4**).

| | |
|---|---|
| Ge(1)–O(1) | 1.674(3) |
| Ge(1)–O(2) | 1.794(4) |
| Ge(1)–I(1) | 2.508(1) |
| Ge(1)–C(1) | 2.351(1) |
| O(1)–C(2) | 1.280(5) |
| O(2)–C(21) | 1.458(7) |
| C(11)–C(12) | 1.486(7) |
| C(3)–Si(1) | 1.889(5) |
| C(20)–Si(2) | 1.799(5) |
| O(1)–Ge(1)–O(2) | 109.0(2) |
| O(1)–Ge(1)–I(1) | 113.9(1) |
| O(1)–Ge(1)–C(1) | 96.1(1) |
| O(2)–Ge(1)–I(1) | 101.5(1) |
| O(2)–Ge(1)–C(1) | 121.4(1) |
| I(1)–Ge(1)–C(1) | 115.32(4) |

The germanium atom in **3** is present in a *pseudo*-tetrahedral environment which is distorted due to the presence of the sterically encumbering *tert*-butyl group. The O(1)–Ge(1)–O(2) and O(1)–Ge(1)–C(37) bond angles are 103.7(1)° and 103.8(1)° (respectively) and approach the idealized tetrahedral value of 104.5°. However, the O(2)–Ge(1)–C(37) bond angle measures 121.1(2)° and is significantly distorted due to the steric interaction of the –$SiMe_2Ph$ group attached to C(13) with the *tert*-butyl substituent at germanium. The disposition of the *tert*-butyl group relative to the oxygen atoms in **3** due to its steric interactions with the 3,3′-substituents also results in a distortion of the O–Ge–I bond angles from the ideal value, as the O(1)–Ge(1)–I(1) bond angle measures 111.1(1)° while the O(2)–Ge(1)–I(1) bond angle is 99.38(9)°.

The carbon atom of the methyl group and the iodine atom in **4** are disordered with one another, with relative occupancies for the carbon atoms of 0.623(2) and 0.377(2) over the two sites. The ORTEP diagram shown in Fig. 2 is drawn with the iodine atom located on the more distant site from the germanium atom. The Ge–I distance in **4** measures 2.508(1) Å, and is consistent with the germanium–iodine distances in 28 other crystallographically characterized compounds containing a Ge–I bond [37–71]. However, the germanium–carbon bond distance in **4** is 2.351(1) Å, which is elongated relative to the usual Ge–C bond distance of ca. 1.94 Å [72] as a result of the dominance of the heavy iodine atom versus the smaller carbon. The actual Ge–C bond distance in **4** is likely in the range of 1.94–1.97 Å. As found for the *tert*-butyl substituted species **3**, the germanium atom in **4** is also in a distorted tetrahedral environment. The O(1)–Ge(1)–O(2) bond angle measures 109.0(2)° while the O(1)–Ge(1)–I(1) and O(2)–Ge(1)–I(1) bond angles are 113.9(1) and 101.5(1)°. The O(1)–Ge(1)–C(1), O(2)–Ge(1)–C(1) and I(1)–Ge(1)–C(1) bond angles each deviate from the idealized tetrahedral value, and measure 96.1(1)°, 121.4(1)°, and 115.32(4)° (respectively).

The dihedral angle between the two naphthalene rings is 64.78° in **4** while that in the *tert*-butyl substituted compound **3** measures 65.97°. These values can be compared with that in the germanium(II) complex **1** which is 70.14° [36]. The trend in the acuteness of the dihedral angles in **1**, **3**, and **4** correlates with the Ge–O bond lengths in these three compounds, which average 1.875(3) [36], 1.789(3), and 1.734(4) Å (respectively). Thus, the steric attributes of the substituents at germanium affects the Ge–O bond distances, which in turn affects the dihedral angle between the naphthyl rings. The lengths of the interannular C–C bonds in these compounds also correlate with the dihedral angles. Compound **4** which has the most acute dihedral angle has an C–C bond distance of 1.486(7) Å, while **1** has the most obtuse dihedral angle and has a C–C bond length of 1.380(5) Å. The C–C bond distance in **3** is 1.383(5) Å, which is intermediate between those of **1** and **4**.



**2**

**5**: R = $Bu^t$, 34 %
**6**: R = Me, 86 %

**Scheme 2.**

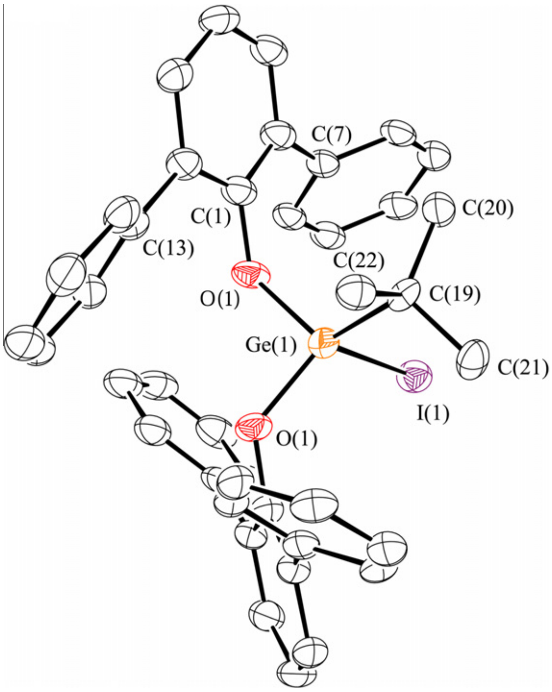


**Fig. 3.** ORTEP diagram of [Ge($OC_6H_3Ph_2$-2,6$)_2$($Bu^t$) (I)] (**5**). Thermal ellipsoids are drawn at 50% probability.

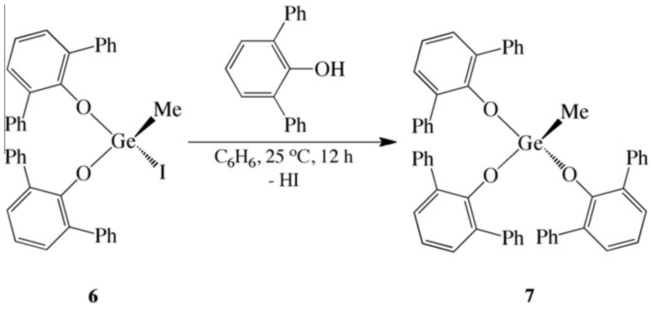
**Table 3**
Selected bond distances (Å) and angles (°) for $[Ge(OC_6H_3Ph_2\text{-}2,6)_2(Bu^t)(I)]$ (**5**) and $[Ge(OC_6H_3Ph_2\text{-}2,6)_3(Me)]\cdot C_6H_6$ (**7**·$C_6H_6$).

| **5** | | **7**·$C_6H_6$ | |
|---|---|---|---|
| Ge(1)–O(1) | 1.763(4) | Ge(1)–O(1) | 1.771(2) |
| Ge(1)–I(1) | 2.641(1) | Ge(1)–C(19) | 1.914(6) |
| Ge(1)–C(19) | 1.92(1) | O(1)–C(1) | 1.374(4) |
| O(1)–C(1) | 1.392(7) | O(1)–Ge(1)–O(1′) | 100.8(1) |
| O(1)–Ge(1)–O(1′) | 96.2(3) | O(1)–Ge(1)–C(19) | 117.15(8) |
| O(1)–Ge(1)–I(1) | 107.8(1) | | |
| O(1)–Ge(1)–C(19) | 128.5(3) | | |
| I(1)–Ge(1)–C(19) | 103.0(3) | | |

The reaction of the 2,6-diphenylphenoxy-substituted germylene $[Ge(OC_6H_3Ph_2\text{-}2,6)_2]$ (**2**) with $Bu^tI$ generates the germanium(IV) species $[Ge(OC_6H_3Ph_2\text{-}2,6)_2(Bu^t)(I)]$ (**5**) (Scheme 2). The $^1H$ NMR spectrum of **5** contains a resonance at $\delta$ 0.32 ppm corresponding to the nine methyl protons of the *tert*-butyl group. Crystals of **5** suitable for X-ray diffraction were obtained by the slow evaporation of a benzene solution of this material, and an ORTEP diagram of **5** is shown in Fig. 3 and selected bond distances and angles are collected in Table 3. The iodine atom and the carbon atoms of the *tert*-butyl group are disordered with one another and were refined with occupancies of 0.5. As a result, there is a crystallographic $C_2$-axis in **5** that renders both oxygen atoms equivalent. The Ge–O bond distance is 1.763(4) Å and is similar to those in **3** and **4**, while the Ge–I bond length is 2.641(1) Å and is consistent with other compounds containing a germanium–iodine bond [37–71]. Despite the disorder in **5**, the Ge–C bond length is normal for a germanium(IV)–oxygen bond distance and measures 1.918(1) Å. The O(1)–Ge(1)–O(1′) bond angle is extremely acute and measures 96.2(3)°, the O(1)–Ge(1)–I(1) bond angle is 107.8(1)° and approaches the idealized tetrahedral angle, and the C(19)–Ge(1)–I(1) bond angle measures 103.0(3)°.

The reaction of **2** with iodomethane yields the complex $[Ge(OC_6H_3Ph_2\text{-}2,6)_2(Me)(I)]$ (**6**) in 86% yield (Scheme 2). In order to successfully prepare **6**, the iodomethane was meticulously dried over magnesium sulfate and activated molecular sieves immediately before use to prevent hydrolysis and subsequent reaction of **6** with the liberated 2,6-diphenylphenol (*vide infra*). The $^1H$ NMR spectrum of **6** contains a resonance at $\delta$ −0.49 ppm corresponding to the protons of the methyl group. Despite several attempts, we were not able to obtain X-ray quality crystals of this material, but the composition of **6** was further confirmed by elemental analysis and mass spectrometry. The mass spectrum of **6** exhibits a peak at $m/z = 706$ amu with the expected isotope pattern, as well as peaks corresponding to fragmentation of the molecule at $m/z = 579$ amu ($M^+ - I$) and $m/z = 461$ amu ($M^+ - OC_6H_3Ph_2$).

Compound **6** can be converted to the tri(aryloxo)-species $[Ge(OC_6H_3Ph_2\text{-}2,6)_3(Me)]$ (**7**) upon reaction with additional 2,6-diphenylphenol (Scheme 3). The formation of **7** was initially discovered serendipitously upon reaction of **6** with adventitious 2,6-diphenylphenol formed via hydrolysis of **6** by water present in the iodomethane reagent. The conversion of **6** to **7** indicates that the iodide ligand in **6** is sufficiently labile to react with the acidic phenolic proton of 2,6-diphenylphenol, and **7** was subsequently prepared directly by the reaction of **6** with one equiv. of 2,6-diphenylphenol in 77% yield. Compound **7** is virtually insoluble in hydrocarbon solvents, but a $^1H$ NMR spectrum of **7** was obtained and exhibits a resonance for the methyl group at $\delta$ – 0.12 ppm that is shifted downfield from that for the methyl protons in **6** due to the presence of the additional Ge–O bond.



**Scheme 3.**

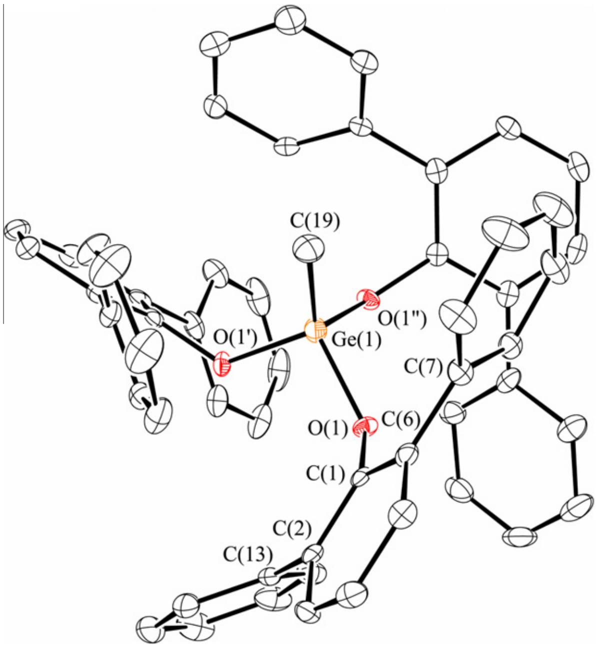


**Fig. 4.** ORTEP diagram of $[Ge(OC_6H_3Ph_2\text{-}2,6)_3(Me)]\cdot C_6H_6$ (**7**·$C_6H_6$). Thermal ellipsoids are drawn at 50% probability.

X-ray quality crystals of **7** were obtained from the slow cooling of a hot dilute benzene solution of **7**, and an ORTEP diagram of **7** is shown in Fig. 4. There is a $C_3$-axis present in **7** located along the Ge(1)–C(19) bond that renders all three aryloxo ligands equivalent. The three Ge–O bonds in **7** measure 1.771(2) Å, which is similar to the Ge–O bond distances in **3**–**5**, while the Ge(1)–C(19) bond length is 1.914(6) Å. The three O–Ge–O bond angles are 100.8(1)° while the O(1)–Ge(1)–C(19) bond angles each measure 117.15(8)°. The *ortho*-phenyl rings in **7** are each rotated about the C–C bonds to C(2) and C(6) relative to the plane of the phenolic phenyl ring due to steric effects arising from the presence of three bulky 2,6-diphenylphenolate ligands at the germanium center. The angle about the C(2)–C(13) bond is 48.5(1)° and the angle about the C(6)–C(7) bond is 42.0(1)°, and the 2,6-diphenylphenolate ligands interlock in a gear-like fashion in **7**.

Curiously, treatment of **5** with an additional equivalent of 2,6-diphenylphenol did not provide the tri(aryloxo)-compound $[Ge(OC_6H_3Ph_2\text{-}2,6)_3(Bu^t)]$. Although the iodide ligand in **5** would also be expected to be reactive toward protonolysis, no evidence for the formation of $[Ge(OC_6H_3Ph_2\text{-}2,6)_3(Bu^t)]$ was found even if the reaction mixture was heated for 7 days at 85 °C. Therefore, the formation of **7** from **6** appears to be possible due to the presence of the less sterically encumbering methyl group in **6** versus the large *tert*-butyl group in **5**. Similarly, compounds **3** and **4** were not found to react with 2,6-diphenylphenol which is likely a result of the sterically congested environment at the germanium atoms in these species arising from the bulky 3,3′-$SiMe_2Ph$ substituents.

## 3. Conclusions

The germylenes (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{$NH_3$}] (**1**) and [Ge($OC_6H_3Ph_2$-2,6$)_2$] (**2**) have been shown to react with iodomethane and 2-iodo-2-methylpropane ($Bu^tI$) to yield the germanium(IV) complexes (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{$Bu^t$}{I}] (**3**), (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{Me}{I}] (**4**), [Ge($OC_6H_3Ph_2$-2,6$)_2$($Bu^t$)(I)] (**5**), and [Ge($OC_6H_3Ph_2$-2,6$)_2$(Me)(I)] (**6**). The X-ray crystal structures of **3**–**5** were determined and compounds **3** and **4** were shown to be chelates that each contain a seven-membered $GeO_2C_4$ ring, and the size of the organic group attached to the germanium atom in **3** and **4** affects the size of the chiral pocket in the attached binaphthoxide ligand. The 2,6-diphenylphenolate species **5** was crystallographically characterized, and compound **6** was found to react with one equiv. of 2,6-diphenylphenol to yield the tri(aryloxo)-species [Ge($OC_6H_3Ph_2$-2,6$)_3$(Me)] (**7**). However, similar reactivity was not observed for compounds **3**–**5**. The structure of **7** contains a $C_3$-axis of rotation about the central Ge–$CH_3$ bond and the three aryloxide ligands in **7** are arranged in an interlocking gear-like fashion about the central germanium atom.

## 4. Experimental

### 4.1. General considerations

All manipulations were carried out using standard Schlenk, syringe, and glovebox techniques [73]. Solvents were purified using a Glass Contour solvent purification system. The starting materials (*S*)-[Ge{$O_2C_{20}H_{10}$-($SiMe_2Ph)_2$-3,3′}{$NH_3$}] (**1**) [36] and [Ge($OC_6H_3Ph_2$-2,6$)_2$] (**2**) [33] were prepared according to published procedures. The reagents 2,6-diphenylphenol, iodomethane and 2-iodo-2-methylpropane ($Bu^tI$) were purchased from Aldrich and the iodo compounds were dried over anhydrous $MgSO_4$ followed by activated molecular sieves immediately prior to use. Proton NMR spectra were run at 25 °C in benzene-$d_6$ on a Varian Gemini 2000 spectrometer at 300 MHz and were referenced to residual protio solvent. Carbon-13 NMR spectra were not acquired due to the low solubility of these compounds in benzene-$d_6$ and their instability in more polar solvents including chloroform-*d* and acetonitrile-$d_3$. Mass spectra were acquired via direct injection using a Shimadzu LCMS-2010 equipped with an ACPI ionization source. Elemental analyses were conducted by Desert Analytics (Tucson, AZ).

### 4.2. Synthesis of 3

To a solution of **1** (0.200 g, 0.312 mmol) in benzene (20 mL) was added a solution of $Bu^tI$ (0.070 g, 0.380 mmol) in benzene (5 mL). The reaction mixture was stirred at reflux for 12 h and the volatiles were removed *in vacuo* to yield **3** (0.215 g, 85%) as white crystals. $^1$H NMR: $\delta$ 8.16 (s, 1H, 4,4′-H), 8.10 (s, 1H, 4,4′-H), 7.70–7.52 (m, 8H, aromatics), 7.29–7.25 (m, 4H, aromatics), 7.12–7.04 (m, 8H, aromatics), 6.99–6.84 (m, 2H, aromatics), 0.88 (s, 3H, Si($CH_3)_2$Ph), 0.84 (s, 3H, Si($CH_3)_2$Ph), 0.80 (s, 3H, Si($CH_3)_2$Ph), 0.70 (s, 9H, GeC($CH_3)_3$), 0.67 (s, 3H, Si($CH_3)_2$Ph), ppm. *Anal.* Calcd. for $C_{40}H_{41}GeIO_2Si_2$: C, 59.35; H, 5.11. Found: C, 58.98; H, 5.21%.

### 4.3. Synthesis of 4

To a solution of **1** (0.145 g, 0.226 mmol) in benzene (20 mL) was added neat iodomethane (0.160 g, 1.13 mmol). The reaction

**Table 4**
Crystallographic data for compounds **3**–**5** and **7**·$C_6H_6$.

| | **3** | **4** | **5** | **7**·$C_6H_6$ |
|---|---|---|---|---|
| Empirical formula | $C_{40}H_{41}GeIO_2Si_2$ | $C_{37}H_{35}GeIO_2Si_2$ | $C_{40}H_{35}GeIO_2$ | $C_{61}H_{46}GeO_3$ |
| Formula weight (g/mol) | 809.40 | 767.32 | 747.17 | 899.57 |
| *T* (K) | 209(2) | 100(2) | 100(2) | 100(2) |
| Wavelength (Å) | 0.71073 (Mo Kα) | 0.71073 (Mo Kα) | 0.71073 (Mo Kα) | 0.71073 (Mo Kα) |
| Crystal system | orthorhombic | monoclinic | monoclinic | rhombohedral |
| Space group | $P2_12_12_1$ | $P2_1$ | $C2/c$ | $R3$ |
| *a* (Å) | 7.470(3) | 9.052(1) | 14.466(4) | 15.8640(5) |
| *b* (Å) | 12.560(4) | 10.631(2) | 13.592(4) | 15.8640(5) |
| *c* (Å) | 38.94(1) | 17.652(3) | 17.452(6) | 15.736(1) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 95.623(2) | 100.712(7) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 | 120 |
| *V* ($Å^3$) | 3653(2) | 1690.6(5) | 3372(2) | 3429.6(3) |
| *Z* | 4 | 2 | 4 | 3 |
| Density ($g/cm^3$) | 1.472 | 1.507 | 1.472 | 1.307 |
| Absorption coefficient ($mm^{-1}$) | 1.783 | 1.921 | 1.857 | 0.718 |
| *F* (0 0 0) | 1640 | 772.1 | 1504 | 1404 |
| Crystal size (mm) | 0.33 × 0.08 × 0.05 | 0.20 × 0.15 × 0.15 | 0.36 × 0.31 × 0.31 | 0.44 × 0.36 × 0.30 |
| $\theta$ Range for data collection (°) | 1.70–28.21 | 2.24–28.28 | 2.07–28.18 | 1.97–25.32 |
| Index ranges | $-5 \leqslant h \leqslant 9$ | $-11 \leqslant h \leqslant 11$ | $-18 \leqslant h \leqslant 19$ | $-18 \leqslant h \leqslant 18$ |
| | $-16 \leqslant k \leqslant 16$ | $-13 \leqslant k \leqslant 13$ | $-13 \leqslant k \leqslant 17$ | $-19 \leqslant k \leqslant 19$ |
| | $-41 \leqslant l \leqslant 49$ | $-23 \leqslant l \leqslant 22$ | $-22 \leqslant l \leqslant 22$ | $-18 \leqslant l \leqslant 16$ |
| Reflections collected | 18 942 | 14 200 | 14 144 | 8305 |
| Independent reflections | 8464 ($R_{int} = 0.0414$) | 7263 ($R_{int} = 0.0803$) | 3800 ($R_{int} = 0.0479$) | 2492 ($R_{int} = 0.0293$) |
| Completeness to $\theta$ = 25.00° | 99.9% | 99.8% | 97.3% | 100.0% |
| Absorption correction | multi-scan (SADABS) | semi-empirical from equivalents | multi-scan (SADABS) | multi-scan (SADABS) |
| Maximum and minimum transmission | 0.9162 and 0.5908 | 0.7615 and 0.6999 | 0.5967 and 0.5544 | 0.8134–0.7429 |
| Refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 8464/0/415 | 7263/1/395 | 3800/0/213 | 2492/1/199 |
| Goodness-of-fit (GOF) on $F^2$ | 1.006 | 1.121 | 1.187 | 1.052 |
| Final *R* indices ($I > 2\sigma(I)$) | $R_1 = 0.0453$ | $R_1 = 0.0545$ | $R_1 = 0.0697$ | $R_1 = 0.0407$ |
| | $wR_2 = 0.0746$ | $wR_2 = 0.1290$ | $wR_2 = 0.1557$ | $wR_2 = 0.1090$ |
| *R* indices (all data) | $R_1 = 0.0604$ | $R_1 = 0.0594$ | $R_1 = 0.0892$ | $R_1 = 0.0415$ |
| | $wR_2 = 0.0799$ | $wR_2 = 0.1314$ | $wR_2 = 0.1630$ | $wR_2 = 0.1099$ |
| Largest difference peak and hole (e $Å^{-3}$) | 0.991 and −0.417 | 1.338 and −0.906 | 0.677 and −1.363 | 1.189 and −0.299 |

mixture was stirred at reflux for 18 h and the volatiles were removed *in vacuo* to yield **4** (0.148 g, 86%) as white crystals. $^1$H NMR: $\delta$ 8.20 (s, 1H, 4,4′-H), 8.13 (s, 1H, 4,4′-H), 7.73–7.55 (m, 8H, aromatics), 7.24–7.00 (m, 12H, aromatics), 6.86–6.78 (m, 2H, aromatics), 0.82 (s, 3H, Si(C$H_3$)$_2$Ph), 0.79 (s, 3H, Si(C$H_3$)$_2$Ph), 0.71 (s, 3H, Si(C$H_3$)$_2$Ph), 0.63 (s, 3H, Si(C$H_3$)$_2$Ph), 0.12 (s, 3H, GeC$H_3$) ppm. *Anal.* Calcd. for $C_{37}H_{35}GeIO_2Si_2$: C, 57.91; H, 4.60. Found: C, 57.64; H, 4.45%.

### 4.4. Synthesis of **5**

To a solution of **2** (0.100 g, 0.178 mmol) in benzene (10 mL) was added a solution of Bu$^t$I (0.040 g, 0.218 mmol) in benzene (5 mL). The reaction mixture was stirred at room temperature for 8 h and the volatiles were removed *in vacuo* to yield **5** (0.045 g, 34%) as colorless crystals. $^1$H NMR: $\delta$ 7.43 (d, $J$ = 8.1 Hz, 4H, *m*-$C_6H_3Ph_2$), 7.24–7.13 (m, 20H, *o*- and *p*-$C_6H_3(C_6H_5)_2$), 6.89 (t, $J$ = 8.1 Hz, 2H, *p*-$C_6H_3Ph_2$), 0.32 (s, 9H, –C(C$H_3$)$_3$) ppm. *Anal.* Calcd. for $C_{40}H_{35}GeIO_2$: C, 64.27; H, 4.72. Found: C, 64.11; H, 4.59%.

### 4.5. Synthesis of **6**

To a solution of **2** (0.383 g, 0.680 mmol) in benzene (25 mL) was added neat MeI (0.105 g, 0.740 mmol). The reaction mixture was stirred at room temperature for 8 h and the volatiles were removed *in vacuo* to yield **6** (0.412 g, 86%) as a colorless powder. $^1$H NMR: $\delta$ 7.48 (d, $J$ = 7.5 Hz, 4H, *m*-$C_6H_3Ph_2$), 7.28–7.10 (m, 20H, –$C_6H_3(C_6H_5)_2$), 6.92 (t, $J$ = 7.5 Hz, 2H, *p*-$C_6H_3Ph_2$), −0.49 (s, 3H, –C$H_3$) ppm. MS: $m/z$ = 706 amu ($M^+$), 579 ($M^+$–I), 461 ($M^+$–$OC_6H_3Ph_2$) amu. *Anal.* Calcd. for $C_{37}H_{29}GeIO_2$: C, 63.00; H, 4.15. Found: C, 62.87; H, 4.27%.

### 4.6. Synthesis of **7**

To a solution of **6** (0.292 g, 0.414 mmol) in benzene (25 mL) was added a solution of 2,6-diphenylphenol (0.102 g, 0.414 mmol) in benzene (10 mL). The reaction mixture was stirred at room temperature for 12 h after which time a white precipitate had formed. The reaction mixture was filtered, washed with benzene (3 × 5 ml) and hexane (3 × 5 mL) and the solid was dried *in vacuo* to yield **7** (0.262 g, 77%) as a colorless powder. $^1$H NMR: $\delta$ 7.64 (d, $J$ = 7.7 Hz, 6H, *m*-$C_6H_3Ph_2$), 7.40–7.28 (m, 24H, *o*- and *m*-$C_6H_3(C_6H_5)_2$), 7.07 (t, $J$ = 7.7 Hz, 3H, *p*-$C_6H_3Ph_2$), 7.00 (t, $J$ = 7.5 Hz, 6H, *p*-$C_6H_3(C_6H_5)$), −0.12 (s, 3H, –C$H_3$) ppm. *Anal.* Calcd. for $C_{61}H_{48}GeO_3$ (**7**·$C_6H_6$): C, 81.24; H, 5.37. Found: C, 81.52; H, 5.31%.

### 4.7. Single crystal X-ray crystallography

Samples were mounted on a Cryoloop with Paratone-*N* oil under a stream of nitrogen gas at −173 °C. Data was collected on an APEX2 CCD system and then processed using the APEX2 software for preliminary determination of the unit cell. Diffraction intensity data were collected with a Siemens P4/CCD diffractometer. Crystallographic data and details are shown in Table 4. Absorption corrections were applied for all data using SADABS. The structures were solved using direct methods, completed by difference Fourier syntheses, and refined on full-matrix least-squares procedures on $F^2$. All ordered non-hydrogen atoms were refined with anisotroptic displacement coefficients and hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHEXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI). ORTEP diagrams were drawn using the ORTEP3 program (L.J. Farrugia, Glasgow).

## Appendix A. Supplementary material

CCDC 774956, 774957, 774958, and 774959 contain the supplementary crystallographic data for **3**, **4**, **5**, and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.06.060.

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