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Dispersion Forces and Counterintuitive Steric Effects in
Main Group Molecules: Heavier Group 14 (Si-Pb)
Dichalcogenolate Carbene Analogues with Sub-90°
Interligand Bond Angles

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Abstract

The synthesis, spectroscopic and structural characterization of an extensive series of acyclic, monomeric tetrylene dichalcogenolates of formula $M(\text{ChAr})_2$ ($M = \text{Si, Ge, Sn, Pb}$; $\text{Ch} = \text{O, S, or Se}$; $\text{Ar} =$ bulky *m*-terphenyl ligand) are described. They were found to possess several unusual features—the most notable of which is their strong tendency to display acute interligand, Ch-M-Ch, bond angles that are often well below 90°.

Furthermore, and contrary to normal steric expectations, the interligand angles were

found to become narrower as the size of the ligand was increased. Experimental and structural data in conjunction with high-level DFT calculations, including corrections for dispersion effects, led to the conclusion that dispersion forces play a key role in stabilizing their acute interligand angles.

Introduction

The use of sterically crowding substituents to influence chemical reactivity, to protect reactive sites, and to stabilize molecules with unusual bonding or low coordination numbers is a well-established and powerful technique in molecular chemistry. Such ligands have been crucial for the synthesis of numerous new molecular classes throughout the periodic table.¹ It is no exaggeration to say that a considerable portion of modern main group chemistry is sustained by their use to isolate compounds with previously unknown oxidation states or bonding by blocking decomposition routes that often involve disproportionation or polymerization.² The crowded environments produced by the ligands introduce some degree of steric strain due to overlapping electron clouds. The presence of strain is usually manifested in the distortion of structural parameters, and may result in bond lengthening and the widening of interligand angles to reduce the congestion.³ The distortions can, in extreme cases, lead to bond cleavage or dissociation,⁴ or molecular rearrangement.⁵ In such cases, the cause and effect relationship between the strain and geometrical distortion appears to be intuitively obvious. However, in this paper we will describe the synthesis and characterization of a series of compounds where such trends are apparently reversed, so that increasing the size of the ligand leads to a decrease, rather than an increase, in the interligand angles.

The bis-chalcogenolate derivatives of the heavier group 14 elements form part of a wider class of stable, monomeric heavier group 14 element derivatives (metallylenes) of formula MR_2 ($M = Si, Ge, Sn, \text{ or } Pb$; $R = \text{alkyl, aryl, silyl, amido, phosphide, alkoxo, etc.}$) which are analogous to carbenes and for which more than two hundred and fifty stable examples are currently known.⁶ They possess V-shaped geometries with interligand angles that are usually well below 120° , but generally greater than 90° . The angles decrease with increasing atomic number of the group 14 element and increasing electronegativity of the ligand in accordance with Bent's rule.⁷ In isolated cases, interligand angles below the expected lower limit of 90° (on the basis of the orthogonality of the valence p-orbitals) have been observed, as in $Sn(OC_6H_2-2,6-Bu^t_2-4-Me)_2$ ($O-Sn-O = 88.8(2)^\circ$),⁸ $Sn(SMes^*)_2$ ($Mes^* = C_6H_2-2,4,6-Bu^t_3$; $S-Sn-S = 85.4(1)^\circ$),⁹ or the bis primary amides $M\{N(H)Ar^{Me_6}\}_2$ ($N-M-N = 88.6(2)^\circ$, Ge ; $87.07(8)^\circ$, Sn ; $87.47(9)^\circ$, Pb ; $Ar^{Me_6} = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)_2$).¹⁰ Recently, we demonstrated that the terphenyl chalcogenolate ligands, $-OAr^{Pri_4}$ and $-SAr^{Pri_4}$ ($Ar^{Pri_4} = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)_2$) produced very different interligand angles in their divalent lead derivatives $Pb(OAr^{Pri_4})_2$ ($O-Pb-O = 99(1)^\circ$ average value) and $Pb(SAr^{Pri_4})_2$ ($S-Pb-S = 77.21(4)^\circ$).¹¹ The latter angle was the narrowest reported for a group 14 element metallylene derivative. We also showed that the use of the somewhat less crowding chalcogenolate ligand $-SAr^{Me_6}$ ($Ar^{Me_6} = C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)_2$) stabilized an acyclic silylene, $Si(SAr^{Me_6})_2$,¹² (reported essentially simultaneously to the acyclic silylene, $\overline{\hspace{10em}}$) $Si\{N(SiMe_3)(Dipp)\}\{BN(Dipp)CHCHN(Dipp)\}$ ($Dipp = C_6H_3-2,6-Pr^i_2$) by Aldridge and Jones)¹³ which possesses a relatively narrow interligand angle $90.52(2)^\circ$ in an acyclic silylene.^{1,14} These unusual angular variations suggested that a more extensive study on a

larger range of compounds was warranted to explain their origin. We now describe our experimental and computational studies of an extensive series (a total of twenty compounds, of which fourteen are newly-described, including two new acyclic silylenes) of low-valent dichalcogenolate, ChAr ($\text{Ch} = \text{O}, \text{S}, \text{Se}$; $\text{Ar} = \text{terphenyl}$), derivatives of Si , Ge , Sn , and Pb , including two new acyclic silylenes. The data show that interligand angles as low as $73.09(2)^\circ$ can be obtained and that the Ch-M-Ch angle depends on a variety of factors, including steric interactions across the two-fold axis bisecting the ChMCh bond. DFT calculations employing a correction for dispersion effects provide further insight to bonding, and show that attractive dispersion forces between the alkyl substituents of the terphenyl ligands play a key role in narrowing the interligand angles. All of the compounds are stabilized by chalcogenolate ligands bearing the terphenyl substituents illustrated in Figure 1.

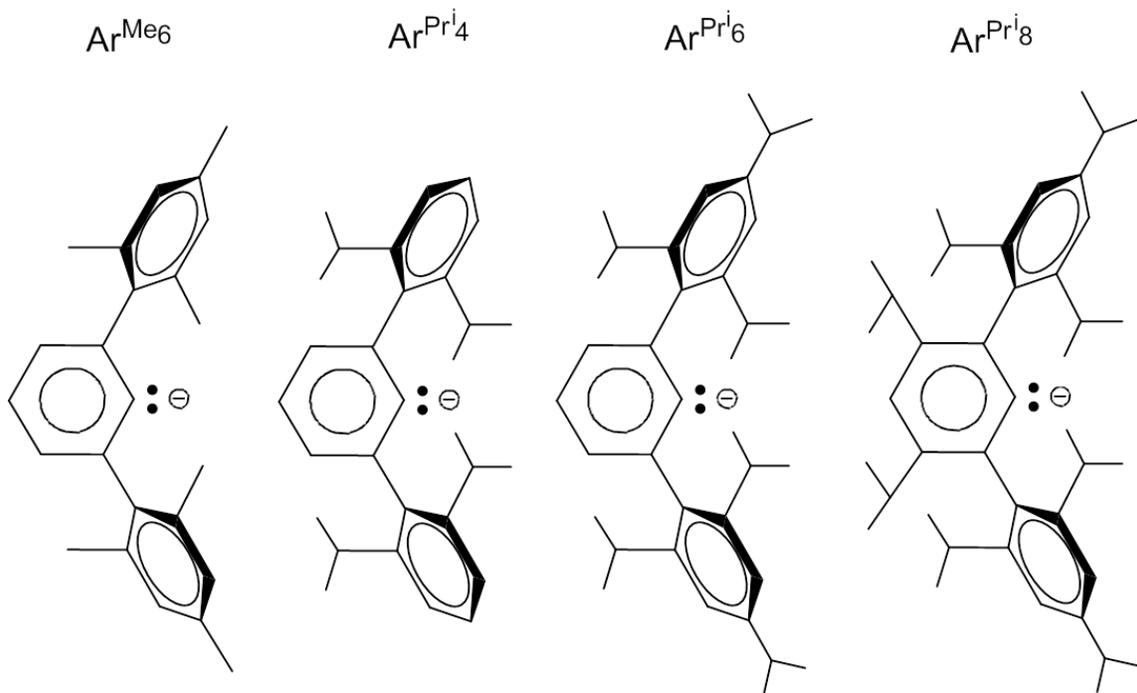


Figure 1. The terphenyl group substituent anions display increasing bulk moving from left to right. The *ipso* carbon is bonded to O, S, or Se.

Experimental

General Procedures

All manipulations were performed with the use of modified Schlenk techniques under an N₂ atmosphere or in a Vacuum Atmospheres drybox under N₂ except the magnesium reductions, which were performed under argon. Solvents were distilled over a sodium mirror and degassed immediately prior to use via freeze-pump-thaw cycles. Unless otherwise noted, all chemicals were obtained from commercial sources and used without further purification. Rieke's magnesium,^{15, 16} and the thiols Ar^{Me}₆SH, Ar^{Pri}₄SH, and Ar^{Pri}₆SH, were prepared by literature procedures.¹⁷ The thiol, Ar^{Pri}₈SH (see below, **28**), was prepared by reaction of Ar^{Pri}₈Li(OEt₂)¹⁸ with sulfur employing the same synthetic procedure as used for Ar^{Pri}₆SH.^{17c} The MSeAr^{Pri}₄ (M = Li, K) salts were prepared by addition of either LiBuⁿ or K metal to the air-stable triselenine, Se(SeAr^{Pri}₄)₂ (see Supporting Information).¹⁹ ¹H and ¹³C NMR spectra were recorded on either a Varian 300 MHz, 400 MHz or a 600 MHz instrument and referenced internally to either protio benzene or trace silicone grease ($\delta = 0.29$ in C₆D₆). ²⁹Si NMR spectra were acquired on a Varian 600 MHz (operating at 119.14 MHz) instruments referenced to an external standard of SiMe₄ (TMS) ($\delta = 0$) in C₆D₆. ⁷⁷Se NMR spectra were acquired on a Varian 600 MHz (operating at 114.4 MHz) instrument and were externally referenced to a saturated solution of selenous acid in D₂O ($\delta = 1300$). ¹¹⁹Sn (223.63 MHz) and ²⁰⁷Pb (125.53 MHz) NMR spectra were acquired on a Varian 600 MHz instrument and were referenced to SnBuⁿ₄ in C₆D₆ ($\delta = -11.7$) or PbMe₄ in C₆D₆ ($\delta = 0$). IR spectra were

recorded as Nujol mulls between KBr or CsI plates on a Perkin-Elmer 1430 spectrophotometer. UV-visible spectra were recorded as dilute hexanes solutions in 3.5 mL quartz cuvettes using a HP 8452 diode-array spectrophotometer. Melting points were determined on a Meltemp II apparatus using glass capillaries sealed with vacuum grease and are uncorrected.

Si(SAr^{Prⁱ4})₂ (2). Si(Br)₂(SAr^{Prⁱ4})₂ (1.698 g, 1.62 mmol — see Supporting Information) was dissolved in THF (45 mL) and added over 10 min with cooling to *ca.* 0°C. Rieke's magnesium (0.0493 g, 2.03 mmol), freshly prepared in 40 mL of THF, sonicated with a catalytic amount of anthracene for 3 hours. The solution became red, and after 30 min., was allowed to warm to ambient temperature and stirred for a further 5 days. All the volatile components were removed under reduced pressure, and *ca.* 60 mL of hexanes and *ca.* 12 mL of 1,4-dioxane were added. The resultant solution was stirred for 24 h and filtered to give a clear, red solution. All of the volatile components were removed under reduced pressure, and the residue was redissolved in hexanes (12 mL), which were concentrated to *ca.* 3 mL storage in a *ca.* -18° C refrigerator. This afforded small yellow needles of **2** after 1 week. Repeated attempts to obtain X-ray quality crystals of **2** using various solvents (single and mixtures) proved unsuccessful. Yield: (0.243 g, 0.27 mmol, 16.9 %); m.p. 203-207° C. Calcd. for C₆H₇₄S₂Si: C, 81.2; H, 8.41. Found: C, 80.4; H, 8.23. ¹H NMR (399.8 MHz, C₆D₆, 295 K): δ = 1.07 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.80 Hz), 1.19 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 7.20 Hz), 2.69 (m, 8H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.80 Hz), 6.97 (t, 2H, *p*-C₆H₃, ³J_{H,H} = 6.80 Hz), 7.05 (d, 4H, *m*-C₆H₃, ³J_{H,H} = 7.2 Hz), 7.10 (d, 8H, *m*-C₆H₃Prⁱ₂, ³J_{HH} = 6.80 Hz), 7.20 (t, 4H, *p*-C₆H₃Prⁱ₂, ³J_{HH} = 7.20 Hz); ¹³C {¹H}

NMR (100.5 MHz, C₆D₆, 296 K): δ = 23.34 (*o*-CH(CH₃)₂), 25.39 (*o*-CH(CH₃)₂), 31.23 (*o*-CH(CH₃)₂), 123.55 (*m*-C₆H₃Prⁱ₂), 125.41 (*p*-C₆H₃), 128.97 (*m*-C₆H₃), 129.78 (*o*-C₆H₃), 137.38 (*p*-C₆H₃Prⁱ₂), 138.87 (*o*-C₆H₃Prⁱ₂), 141.85 (*i*-C₆H₂Prⁱ₂), 147.05 (*i*-C₆H₃Prⁱ₂); ²⁹Si NMR (119.1 MHz, C₆D₆, 295 K): δ = 270.4; UV-Vis: [λ , nm (ϵ , M⁻¹cm⁻¹)] 405 (3700), 318 (7400), 290 (11 200). IR (cm⁻¹): Si-S tentatively assigned to a band at 648. A small portion of the silylene (0.05 g) was mixed with the potassium thiolate, K₂(SAr^{Prⁱ₄)₂ (see supporting information), and dissolved in a mixture of 1,4-dioxane (*ca.* 2 mL) and hexanes (*ca.* 2 mL) and placed in a *ca.* 7° C refrigerator to yield X-ray quality crystals of **2** after 3 days.}

Si(SAr^{Prⁱ₆)₂ (3).} Si(Br)₂(SAr^{Prⁱ₆)₂ (1.141 g, 0.94 mmol) was dissolved in THF (45 mL) and added over 10 min to a suspension of Rieke's magnesium (0.0285 g 1.17 mmol), freshly prepared in 40 mL of THF, and sonicated with a catalytic amount of anthracene for 3 hours prior to use. The solution became red, and was allowed to warm to ambient temperature and stirred for a further 3 days. All the volatile components were removed under reduced pressure, and hexanes (*ca.* 65 mL) and 1,4-dioxane (*ca.* 8 mL) were added and stirred for 24 h. Filtration yielded a clear, red solution which was concentrated to *ca.* 8 mL and placed in a *ca.* 7° C refrigerator. Small yellow crystalline blocks of **3** (0.201 g) were obtained and isolated after 3 days. The supernatant liquid was evaporated to dryness, and the yellow residue was redissolved in toluene (*ca.* 15 mL), which was concentrated to *ca.* 8 mL under reduced pressure and placed in a *ca.* 7° C refrigerator to yield X-ray quality crystals of **3**. Yield: (0.422 g total weight, 0.400 mmol, 42.6 %); m.p.: 254-257° C. Calcd. for C₇₂H₉₈S₂Si: C, 81.91; H, 9.36. Found: C, 81.01; H, 9.08. ¹H}

NMR (599.7 MHz, C₆D₆, 295 K): δ = 1.12 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.99 Hz), 1.25 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.99 Hz), 1.33 (d, 24H, *p*-CH(CH₃)₂, ³J_{H,H} = 7.00 Hz), 2.75 (m, 8H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.99 Hz), 2.89 (m, 4H, *p*-CH(CH₃)₂, ³J_{H,H} = 6.99 Hz), 6.93 (t, 2H, *p*-C₆H₃, ³J_{H,H} = 7.63 Hz), 7.05 (d, 4H, *m*-C₆H₃, ³J_{H,H} = 7.63 Hz), 7.12 (s, 8H, *m*-C₆H₂Prⁱ₃); ¹³C{¹H} NMR (C₆D₆, 150.8 MHz, 295 K): δ = 23.62 (*o*-CH(CH₃)₂), 24.50 (*o*-CH(CH₃)₂), 25.56 (*o*-CH(CH₃)₂), 31.28 (*p*-CH(CH₃)₂), 34.81 (*p*-CH(CH₃)₂), 121.48 (*p*-C₆H₃), 125.36 (*m*-C₆H₂Prⁱ₃), 130.11 (*m*-C₆H₃), 136.87 (*o*-C₆H₃), 138.04 (*o*-C₆H₂Prⁱ₃), 141.66 (*p*-C₆H₂Prⁱ₃), 146.84 (*i*-C₆H₂Prⁱ₃), 148.92 (*i*-C₆H₃); ²⁹Si NMR (119.1 MHz, C₆D₆, 295 K): δ = 270.9; UV-Vis: [λ , nm (ϵ , M⁻¹cm⁻¹)] 411 (4400), 331 (7500), 290 (10 500). IR (cm⁻¹): Si-S stretching band tentatively assigned to an absorption at 645 cm⁻¹.

Ge(SAr^{Prⁱ4})₂ (5). A slurry of LiSAr^{Prⁱ4} (1.253 g, 2.87 mmol) in diethyl ether (60 mL) was added dropwise over 45 min to a diethyl ether slurry (5 mL) of GeCl₂(1,4-dioxane) (0.332 g, 1.43 mmol) cooled to *ca.* 0° C. The solution became yellow and, after 30 minutes, was allowed to warm to ambient temperature and stirred for a further 12h. All volatile components were removed and the residue was extracted with hexanes (50 mL) and filtered. The solution was concentrated to *ca.* 4 mL, and cooled to -17° C to give **5** as a microcrystalline, threadlike solid. A small amount of **5** (*ca.* 0.04 g) was dissolved in a concentrated THF solution and stored at -17° C for 3 days to yield X-ray quality crystals of **5**. Yield: (0.943 g, 1.01 mmol, 70.5 %). m.p. 203-206° C. ¹H NMR (399.8 MHz, C₆D₆, 294 K): δ = 1.07 (d, 24H, CH(CH)₂, ³J_{HH} = 6.83 Hz), 1.20 (d, 24H, CH(CH)₂, ³J_{HH} = 6.83 Hz), 2.72 (m, 8H, CH(CH)₂, ³J_{HH} = 6.83 Hz), 6.94 (t, 2H, *p*-C₆H₃, ³J_{HH} = 7.51 Hz), 7.04 (d, *m*-C₆H₃, 4H, ³J_{HH} = 7.41 Hz), 7.10 (d, 8H, *m*-C₆H₃Prⁱ₂, ³J_{HH} =

7.41 Hz), 7.20 (t, 4H, *p*-C₆H₃Prⁱ₂, ³J_{HH} = 6.84 Hz); ¹³C {¹H} NMR (100.5 MHz, C₆D₆, 296 K): δ = 23.46 (*o*-CH(CH₃)₂), 25.23 (*o*-CH(CH₃)₂), 31.16 (*o*-CH(CH₃)₂), 123.81 (*m*-C₆H₂Prⁱ₃), 124.64 (*p*-C₆H₃), 128.89 (*m*-C₆H₃), 129.44 (*o*-C₆H₃), 139.39 (*p*-C₆H₂Prⁱ₂), 139.97 (*o*-C₆H₂Prⁱ₂), 141.12 (*i*-C₆H₂Prⁱ₂), 147.12 (*i*-C₆H₃); UV-Vis: [λ, nm (ε, M⁻¹cm⁻¹)] 410 (3110), 330 (3640), 278 (5550).

Ge(SAr^{Prⁱ6})₂ (6). A flask, charged with LiSAr^{Prⁱ6} (1.518 g, 2.91 mmol) and GeCl₂(1,4-dioxane) (0.338 g, 1.43 mmol), was cooled to *ca.* -78° C. Diethyl ether (65 mL) was added slowly over 20 min to afford a solution which, after 2 hours, was allowed to warm to ambient temperature and stirring was continued for 24h. All volatile components were removed under reduced pressure and the residue was extracted with toluene (40 mL) and filtered. The solution was concentrated to *ca.* 4 mL, and cooled to *ca.* -17° C to give **6** as a microcrystalline solid. Crystals of **6** suitable for X-ray diffraction were obtained by cooling their hexane solutions at *ca.* -17°C. Yield: 0.836 g (0.76 mmol, 52.0 %); m.p. 273-276° C; ¹H NMR (599.7 MHz, C₆D₆, 295 K): δ = 1.12 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 7.04 Hz), 1.27 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 7.04 Hz), 1.32 (d, 24H, *p*-CH(CH₃)₂, ³J_{H,H} = 7.04 Hz), 2.78 (m, 8H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.75 Hz), 2.90 (m, 4H, *p*-CH(CH₃)₂, ³J_{H,H} = 7.04 Hz), 6.91 (t, 2H, *p*-C₆H₃, ³J_{H,H} = 7.49 Hz), 7.04 (d, 4H, *m*-C₆H₃, ³J_{H,H} = 7.63 Hz), 7.12 (s, 8H, *m*-C₆H₂Prⁱ₃); ¹³C {¹H} NMR (C₆D₆, 150.8 MHz, 295 K): δ = 23.69 (*o*-CH(CH₃)₂), 24.47 (*o*-CH(CH₃)₂), 25.50 (*o*-CH(CH₃)₂), 31.23 (*p*-CH(CH₃)₂), 34.75 (*p*-CH(CH₃)₂), 121.59 (*p*-C₆H₃), 124.64 (*m*-C₆H₂Prⁱ₃), 129.90 (*m*-C₆H₃), 137.25 (*o*-C₆H₃), 138.82 (*o*-C₆H₂Prⁱ₃), 141.19 (*p*-C₆H₂Prⁱ₃), 146.99 (*i*-C₆H₂Prⁱ₃), 148.91 (*i*-C₆H₃); UV-Vis:

[λ , nm (ϵ , M⁻¹cm⁻¹)] 414 (3600), 338 (3700), 286 (4100); IR (cm⁻¹): Ge-S tentatively assigned to an absorption at 438 cm⁻¹.

The germylenes Ge(SAr^{Me6})₂ (**4**) and Ge(SAr^{Pris})₂ (**7**) were prepared by a similar method to **5**; see Supporting Information for details.

Sn(SAr^{Me6})₂ (8**)**. LiSAr^{Me6} (1.120 g, 3.18 mmol) was dissolved in *ca.* 60 mL of diethyl ether and added dropwise over 30 min. to a diethyl ether (5 mL) slurry of SnCl₂ (0.301 g, 1.59 mmol) cooled to *ca.* -78° C. The solution immediately became yellow and was stirred at *ca.* -78° C for a further 30 min and then allowed to warm slowly to a room temperature. The solution was stirred for 24 h to give a yellow solution and a white precipitate. All the volatile components were removed under reduced pressure. Toluene (50mL) was added and filtration afforded a clear, yellow solution. The filtrate was concentrated under reduced pressure to a *ca.* 12 mL and placed in a *ca.* -17° C freezer to afford X-ray quality crystals of **8** as pale yellow blocks after 3 days. Yield: 0.404 g (0.50 mmol, 31.4 %); m.p. 194-196° C. ¹H NMR (300.1 MHz, C₆D₆, 298 K): δ = 2.06 (s, 24H, *o*-CH₃), 2.17 (s, 12H, *p*-CH₃), 6.78 (s, 8H, C₆H₂Me₃), 6.85 (d, 4H, *m*-C₆H₃, ³J_{H,H} = 7.50 Hz), 7.00 (t, 2H, *p*-C₆H₃, ³J_{H,H} = 7.50 Hz); ¹³C {¹H} NMR (C₆D₆, 75.45 MHz, 298 K): δ = 20.27 (*p*-CH₃), 21.23 (*o*-CH₃) 124.78 (*p*-C₆H₃), 125.46 (*m*-C₆H₂Me₃), 129.35(*m*-C₆H₃), 136.31 (*o*-C₆H₃), 137.11 (*o*-C₆H₂Me₃), 137.47 (*p*-C₆H₂Me₃), 140.03 (*i*-C₆H₂Me₃), 142.58 (*i*-C₆H₃); ¹¹⁹Sn NMR (223.6 MHz, C₆D₆, 295 K): δ = 763.8; UV-Vis: [λ , nm (ϵ , M⁻¹cm⁻¹)] 400 (1100), 298 (5300), 292 (5300); IR (cm⁻¹): Sn-S stretching band tentatively assigned to an absorption at 393 cm⁻¹.

The stannylenes, Sn(SAr^{Pr4})₂ (**9**), Sn(SAr^{Pr6})₂ (**10**), and Sn(SAr^{Pr8})₂ (**11**) were prepared by a similar method as **8**, see Supporting Information for details.

Pb(SAr^{Pr8})₂ (14**)**. LiSAr^{Pr8} (0.952 g, 1.557 mmol) and PbBr₂ (0.289 g, 0.79 mmol) were placed in a flask and cooled to *ca.* -78 ° C. Diethyl ether (60mL), cooled to *ca.* -78° C, was added. The resulting solution was stirred at *ca.* -78° C for 2 h and allowed to warm to a *ca.* 25° C. It was stirred for a further 24 h to give an orange-red solution and a white precipitate. All of the volatile components were removed under reduced pressure. The product was extracted with pentane (100mL) and filtered. The filtrate was concentrated under reduced pressure to a *ca.* 20 mL and placed in a *ca.* -17° C freezer, which afforded a small quantity of X-ray quality crystals of the disulfide, (SAr^{Pr8})₂ as yellow rods after 3 days. The supernatant liquid was decanted and further concentrated to 8 mL and placed in a *ca.* -17° C freezer for 2 weeks to afford X-ray quality crystals of **14** as orange rods.

Yield: 0.450 g (0.321 mmol 40.8%); m.p. 246-249° C; ¹H NMR (599.7 MHz, C₆D₆, 295 K): δ = 1.14 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.63 Hz), 1.25 (d, 24H, *m*-CH(CH₃)₂, ³J_{H,H} = 6.96 Hz), 1.34 (d, 24H, *p*-CH(CH₃)₂, ³J_{H,H} = 6.97 Hz), 1.41 (d, 24H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.63 Hz), 2.60 (m, 8H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.64 Hz), 2.88 (m, 8H, *p*-CH(CH₃)₂, ³J_{H,H} = 6.97 Hz), 2.90 (m, 8H, *o*-CH(CH₃)₂, ³J_{H,H} = 6.63 Hz), 7.18 (s, 2H, *p*-C₆H₃), 7.24 (s, 8H, *m*-C₆H₃); ¹³C {¹H} NMR (C₆D₆, 150.8 MHz, 295 K): δ = 24.29 (CH(CH₃)₂), 24.42 (CH(CH₃)₂), 24.83 (CH(CH₃)₂), 25.07 (CH(CH₃)₂), 26.43 (CH(CH₃)₂), 26.55 (CH(CH₃)₂), 31.21 (CH(CH₃)₂), 121.89 (*p*-C₆HPrⁱ₂), 122.12 (*m*-C₆H₂Prⁱ₃), 136.94 (*m*-C₆HPrⁱ₂), 140.29 (*o*-C₆HPrⁱ₂), 141.30 (*p*-C₆H₂Prⁱ₃), 146.69 (*o*-C₆H₂Prⁱ₃), 147.73 (*i*-

$C_6H_2Pr^i_3$), 149.13 ($i-C_6HPr^i_2$); $^{207}Pb\{^1H\}$ NMR (125.53 MHz, C_6D_6 , 295 K): $\delta = 4335$; UV-Vis: [λ , nm (ϵ , $M^{-1}cm^{-1}$)] 446 (4200), 372 (2500), 292 (6600); IR (cm^{-1}): Pb-S stretching band tentatively assigned to an absorption at $302\ cm^{-1}$.

$Pb(SAr^{Pr^i_6})_2$ (**13**) was prepared by a similar method to **14**, see Supporting Information for details.

Ge(SeAr^{Prⁱ4})₂ (15). $LiSeAr^{Pr^i_4}$ (1.21 g, 2.50 mmol) in diethyl ether (40 mL) was added dropwise over 15 minutes to a diethyl ether slurry (5 mL) of $GeCl_2(1,4-dioxane)$ (0.290 g, 1.25 mmol) cooled to $-72^\circ\ C$. The solution became a bright orange immediately and, after 1 hour, the solution was allowed to warm to ambient temperature and was stirred overnight. All the volatile components were removed under reduced pressure and the residue was extracted with n-pentane (50 mL) and filtered. The solution was concentrated to *ca.* 3 mL, warmed gently, and allowed to sit at ambient temperature overnight to produce X-ray quality crystals of **15**. Yield: 0.710 g (0.690 mmol, 53.7 %); m.p. $205-207^\circ\ C$; 1H NMR (599.7 MHz, C_6D_6 , 295 K): $\delta = 1.05$ (d, 24H, $o-CH(CH_3)_2$, $^3J_{H,H} = 6.75$ Hz), 1.22 (d, 24H, $o-CH(CH_3)_2$, $^3J_{H,H} = 6.75$ Hz), 2.77 (m, 8H, $o-CH(CH_3)_2$, $^3J_{H,H} = 7.04$ Hz), 6.99 (t, 2H, $p-C_6H_3$, $^3J_{H,H} = 8.22$ Hz), 7.02 (d, 4H, $m-C_6H_3$, $^3J_{H,H} = 7.92$ Hz), 7.09 (d, 8H, $m-C_6H_2Pr^i_2$, $^3J_{H,H} = 7.63$ Hz), 7.19 (t, 4H, $p-C_6H_2Pr^i_2$, $^3J_{H,H} = 7.63$ Hz); $^{13}C\{^1H\}$ NMR (C_6D_6 , 150.8 MHz, 295 K): $\delta = 23.73$ ($o-CH(CH_3)_2$), 25.16 ($o-CH(CH_3)_2$), 31.15 ($o-CH(CH_3)_2$), 123.92, ($m-C_6H_2Pr^i_3$), 125.36 ($p-C_6H_3$), 129.02 ($m-C_6H_3$), 129.47 ($o-C_6H_3$), 138.38 ($p-C_6H_2Pr^i_2$), 140.43 ($o-C_6H_2Pr^i_2$), 142.77 ($i-C_6H_2Pr^i_2$),

146.74 (*i*-C₆H₃); ⁷⁷Se NMR (114.4 MHz, C₆D₆, 295 K): δ = 657.5; UV-Vis: [λ, nm (ε, M⁻¹cm⁻¹)] 435 (7700), 358 (9000), 303 (8900).

Sn(SeAr^{Pr})₂ (16). Stannylene **16** was prepared by a similar method to **15** except that potassium selenolate was used instead of the lithium selenolate, see Supporting Information for details.

X-ray Crystallography

Crystals of **2**, **7-11**, **13-16**, **25**, **26**, and **28-33** were removed from a Schlenk tube under N₂ and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and quickly placed in low temperature N₂ stream. The data for **2-11**, **13-16**, **25**, **26**, and **28-33** were collected at ca. 90 K on a Bruker APEX II CCD or Bruker DUO APEX II CCD diffractometers with Mo Kα (λ = 0.71073 Å) radiation or Cu Kα (λ = 1.5418 Å). The crystal structures were solved by direct methods using SHELX version 6.1 program package.^{20,21} All non hydrogen atoms were refined anisotropically.

Absorption corrections were applied using SADABS program (*SADABS*, an empirical absorption correction programs, part of the SAINTPlus NT version 5.0 package; Bruker AXS: Madison, WI 1998). All crystallographic calculations were performed on an iMac with 2.80GHz i7 quad core processor and 8GB of memory. Data collected were corrected for Lorentz and polarization effects and absorption using Blessing's method and merged as incorporated into the program Twinabs. Structures were drawn using the program OLEX2.^{22a} Details of the data collections and refinements are given in the

Supporting Information. For **2**, the potassium thiolate salt $(\text{KSAr}^{\text{Pr}^i4})_2$ (**29**) was used for cocrystallization with the silicon dithiolate $\text{Si}(\text{SAr}^{\text{Pr}^i4})_2$ (**2**). The structure of the potassium salt (**29**) was also determined from an independently-synthesized sample, as was the structure of the $\text{Si}(\text{Br})_2(\text{SAr}^{\text{Pr}^i4})_2$ (**25**), which was a 5 % contaminant. X-ray data for the Ar^{Pr^i6} substituted thiolate derivatives **3** and **6** were also obtained. The data refinement for these two structures could not be performed to low residual values, although the key structural parameters for the core atoms could be obtained without difficulty. It is noteworthy that the Ar^{Pr^i6} terphenyl substituent has also been associated with difficulties in the refinement of X-ray data for other systems.^{22b} Some key structural data for the core atoms in these structures are given in Table 2, where it can be seen that their structural parameters conform to the pattern established by the structures of the other compounds in the series.

Mössbauer Spectroscopy

Experimental samples were shipped in sealed ampoules, transferred (*ca.* 45 seconds) to O-ring-sealed sample holders in an inert atmosphere glove box, and quenched to liquid nitrogen temperature prior to mounting in the pre-cooled cryostat. They were examined in transmission geometry using a 10 mCi CaSnO_3 source at room temperature as previously described as was the spectrometer calibration.²³ The Mössbauer effect (ME) data were collected over the temperature range $\sim 90 < T < 220$ K. Sample temperature was

monitored using the Daswin program (ref.) and the transmission data were monitored (to insure no sample loss) before and after each temperature data point acquisition.

Computational Details

All calculations and orbital visualizations were performed with Turbomole 6.3^{24a} and gOpenMol program packages, respectively.^{24b} The geometries of R-Ch-M-Ch-R, where M = Si, Ge, Sn, Pb; Ch = O, S, Se; and R = H, Ph, C₆H₃-2,6-Ph₂, Ar^{Pr_i8} were optimized with the hybrid PBE1PBE density functional²⁵ in combination with the TZVP basis sets.²⁶ Due to the size of the systems in question, frequency calculations were performed only for R = H, Ph derivatives to assess the nature of stationary points found. The structures with R = Ar^{Pr_i8} substituents were also optimized using Grimme's empirical dispersion correction scheme (DFT-D3).²⁷

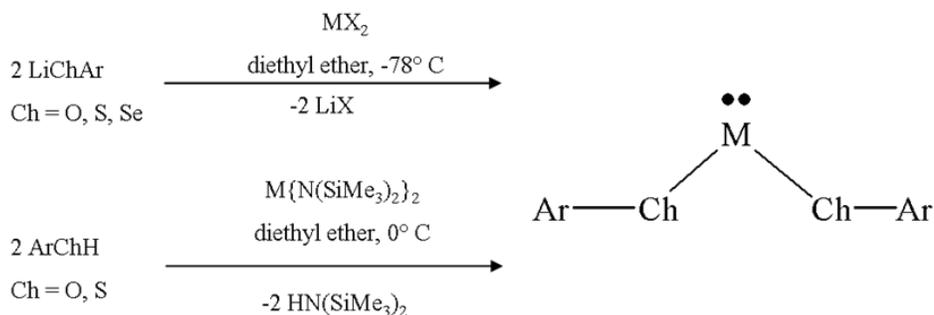
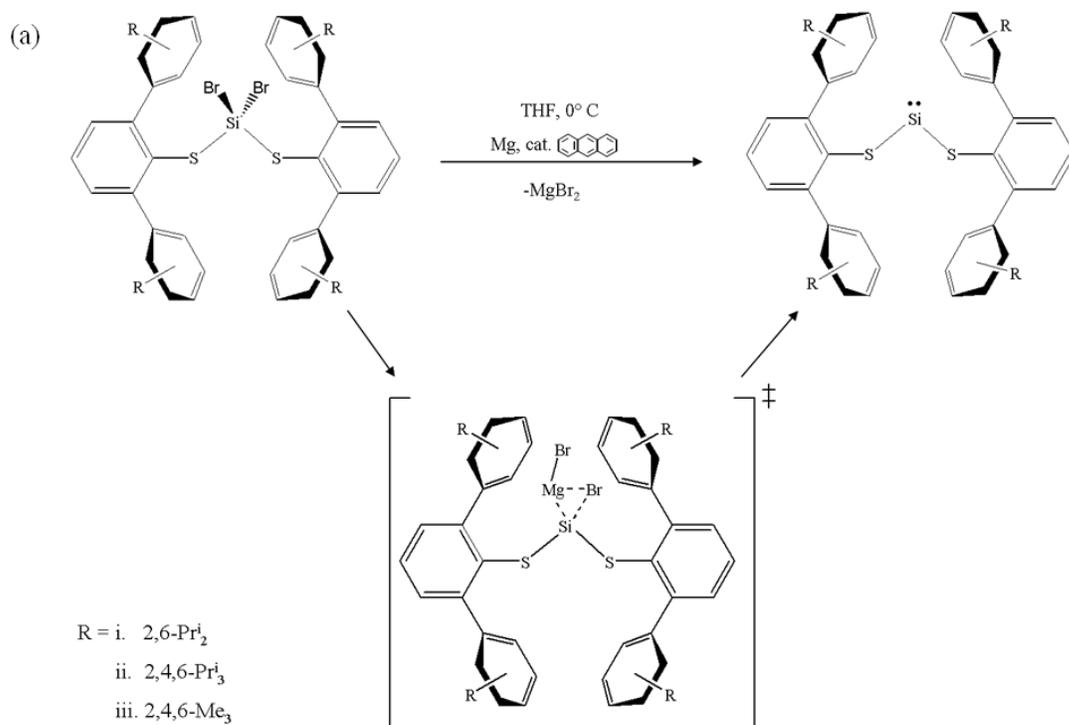
Results and Discussion

Synthesis

As recently shown, the silylene, Si(SAr^{Me6})₂ (**1**) was synthesized by reduction of Br₂Si(SAr^{Me6})₂ with (IMesMg)₂ (IMes = [(2,4,6-trimethylphenyl)NC(CH₃)₂CH]).¹² However, attempts to extend this method to the more sterically crowded silylenes Si(SAr^{Pr_i4})₂ (**2**) and Si(SAr^{Pr_i6})₂ (**3**) were unsuccessful. This is likely due to the increased steric hindrance of the bulkier terphenyl ligands. Instead, the dibromo-bisthiolato Si(IV) precursors, Br₂Si(SAr^{Pr_i4})₂ and Br₂Si(SAr^{Pr_i6})₂, were reduced using magnesium (as

prepared by Rieke)¹⁵ with a catalytic amount of anthracene to yield silylenes, Si(SAr^{Pri4})₂ (**2**) and Si(SAr^{Pri6})₂ (**3**). Attempts to synthesize Si(SAr^{Me6})₂, by reduction using only Rieke's magnesium, were unsuccessful. Based on ²⁹Si NMR evidence ($\delta = 50.5$), we believe that a magnesium bromide-bisthiolato-bromosilylenoid, SiBr(MgBr)(SAr^{Me6})₂, was formed instead.^{12,28,29} A previously reported magnesium silylenoid, SiBr(Mes)(Tsi)(MgBr) (Mes = 2,4,6-C₆H₂-Me₃, Tsi = C(SiMe₃)₃) has a shift of $\delta = 140.5$ in the ²⁹Si NMR spectrum.³⁰ The upfield shift of SiBr(MgBr)(SAr^{Me6})₂ is probably due to the more electronegative thiolate substituents. The silylenoid is likely an intermediate in the synthesis of silylenes **2** and **3**; however, in those systems, the MgBr₂ is apparently eliminated, possibly due to increased steric crowding of the bulkier ligands (Supporting Information).

The syntheses of the Ge-Pb aryloxo and arylthiolato complexes were primarily carried out by a salt metathesis of the lithium or potassium chalcogenolates with the corresponding metal dihalide. An exchange reaction using Sn{N(SiMe₃)₂}₂ with two equivalents of the corresponding thiol was also used as an alternative synthetic route to Sn(SAr^{Pri8})₂. Previous work by Clyburne to determine a structure for the complex Ge(OAr^{Me6})₂ proved unsuccessful due to poor crystallinity although a structure of Sn(OAr^{Me6})₂ was obtained.³¹ An overview of the synthesis of **2-20** is given in Scheme 1.



Scheme 1. (a) Reduction of dibromo-bisthiolato-silanes with magnesium anthracene gives the silylene analogues (i, ii). Reduction is believed to proceed through a magnesium silylenoid intermediate. (b) A general overview of the synthetic routes for the synthesis of very bulky germylene, stannylene, and plumbylene dichalcogenolates.

During the synthesis of M(SAr^{Pr}₈)₂ or M(SeAr^{Pr}₄)₂, (M = Sn, Pb) small amounts of the disulfide (Ar^{Pr}₈S)₂ and diselenide (Ar^{Pr}₄Se)₂ were observed as coproducts. Furthermore,

solutions of $\text{Sn}(\text{SAr}^{\text{Pri}8})_2$ deposit tin metal and the disulfide $(\text{SAr}^{\text{Pri}8})_2$ upon standing at *ca.* 25° C over a period of several months. This is similar to reports of other group 14 dithiolate oligomers that have been shown to decompose over time; although, those resulted in the formation of the metal sulfide and diaryl sulfide.³² The decomposition pathways may differ because of the greater steric hindrance associated with the terphenyl ligands.

Structures

Dithiolates

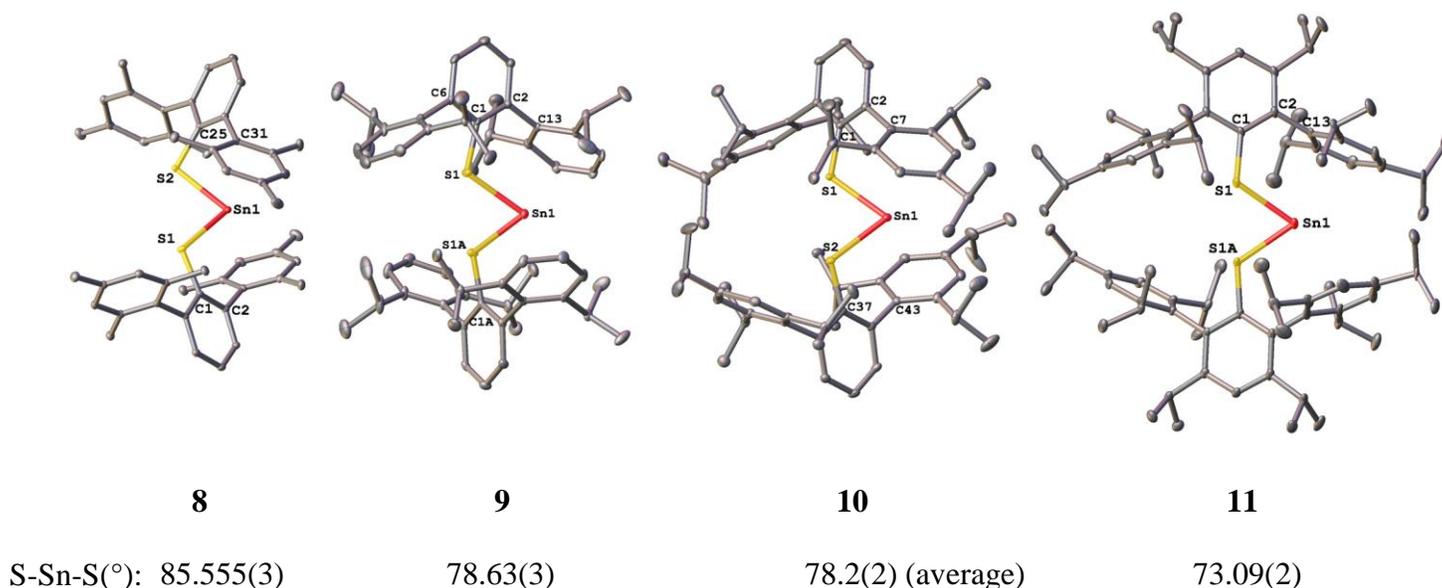
The most numerous of the divalent derivatives discussed in this paper are the dithiolates of Si, Ge, Sn and Pb, **1-14**, and their structures are described first. Important structural data for **1-14** are given in Table 1 which also includes data for the stannylene, $\text{Sn}(\text{SMes}^*)_2$, (**24**) for comparison.⁹ The most notable feature of the structures is that with the exception of $\text{Si}(\text{SAr}^{\text{Me}6})_2$, ($\text{S-Si-S} = 90.52(2)^\circ$), they all possess interligand bond angles below 90°. Furthermore, and in contrast to the usual expectation,^{6,33} as the bulk of the aryl substituents increases in the silicon, germanium and tin dithiolates, the S-M-S bond angle *decreases*. In contrast, the S-Pb-S angles change little when the size of the substituents is varied. The structures of the compounds of the thiolate series are illustrated by the tin derivatives shown in Figure 2, as well as the silylenes $\text{Si}(\text{SAr}^{\text{Me}6})_2$ and $\text{Si}(\text{SAr}^{\text{Pri}4})_2$ in Figure 3.

Table 1. Selected distances (Å) and angles (°), for M(SAr)₂ (M = Si, Ge, Sn, Pb) compounds.

Compound	S-M	S-M-S	C-S-M	M-S-C-C	C-S	M-Centroid	S---S	Reference
(1) Si(SAr ^{Me} ₆) ₂	2.158(3)*	90.52(2)	102.93(6)*	44.9(1)*	1.791(2)*	3.431*	3.0666(4)	25
(2) Si(SAr ^{Pri} ₄) ₂	2.137(1)	85.08(5)	113.80(9)	38.2(2)	1.775(2)	3.249	2.8903(9)	This Work
(3) Si(SAr ^{Pri} ₆) ₂ ^a	2.089(9)*	84.8(1)*	118.(1)*	29(7)*	1.77(1)	3.31(6)*	2.817(3)*	This Work
(4) Ge(SAr ^{Me} ₆) ₂	2.265(1)*	88.68(2)	103(3)*	40(6)*	1.785(1)*	3.28(5)*	3.1656(6)	This Work
(5) Ge(SAr ^{Pri} ₄) ₂	2.284(4)	81.26(2)	113.58(5)	32.3(1)	1.778(1)	3.094	2.9749(6)	This Work
(6) Ge(SAr ^{Pri} ₆) ₂ ^a	2.24(4)*	79.6(2)	114(1)*	27(7)*	1.79(3)*	3.3(1)*	2.867(7)	This Work
(7) Ge(SAr ^{Pri} ₈) ₂	2.2940(6)	77.01(2)	119.42(6)	3.6(2)	1.782(2)*	3.302	2.8566(6)	This Work
(24) Sn(SMes*) ₂	2.4356(3)	85.4(1)	101.64	86.34	1.8087(2)	4.383	3.3034(5)	23
(8) Sn(SAr ^{Me} ₆) ₂	2.479(5)*	85.555(3)	104(5)*	38(10)*	1.7815(9)*	3.22(9)	3.3677(4)	This Work
(9) Sn(SAr ^{Pri} ₄) ₂	2.470(1)	78.63(3)	113.8(1)*	31.2(3)*	1.778(4)*	3.082*	3.130(1)	This Work
(10) Sn(SAr ^{Pri} ₆) ₂	2.46(6)*	78.2(2)*	113(1)*	34(6)*	1.774(2)*	3.3(2)*	3.10(2)*	This Work
(11) Sn(SAr ^{Pri} ₈) ₂	2.5009(6)	73.09(2)	119.15(8)	3.8(2)	1.776(2)	3.220	2.9783(8)	This Work
(12) Pb(SAr ^{Pri} ₄) ₂	2.5656(9)	77.21(4)	113.42(11)	31.0(1)	1.771(3)	3.046	3.202(1)	26
(13) Pb(SAr ^{Pri} ₆) ₂	2.579(5)*	77.27(2)	114.9(7)*	28(8)*	1.772(2)*	3.12(5)*	3.2207(7)	This Work
(14) Pb(SAr ^{Pri} ₈) ₂	2.587(7)*	80.07(2)	117.4(9)*	29(4)*	1.782(1)*	3.08(2)*	3.3281(7)	This Work

* = Averaged Values

a. Data for these two structures could not be refined to a low residual value.

**Figure 2.** X-ray structures of tin dithiolates **8-11** (30% probability ellipsoids) without hydrogen atoms, for the Sn(II) derivatives of the SAr^{Me}₆, SAr^{Pri}₄, SAr^{Pri}₆, and SAr^{Pri}₈

narrower (*ca.* 89-77°) than those of Jutzi's bithiolatogermylene chromium complex, Cr(CO)₅Ge(SC₆H₂-2,4,6-Me₃)₂ that has Ge-S distances of 2.181(4) and 2.192(6) Å and a S-Ge-S angle of 102.4(2)°. ³⁵ The S-Sn-S angle in Sn(SAr^{Me6})₂ (**8**, 85.553(3)°) is similar to that in Sn(SMes*)₂ (**24**)⁹ (85.4(1)°, but the interligand angles become narrower in the bulkier stannylenes **9** (78.63(3)°), **10** (78.2(2)°), and **11** (73.09(2)°). In contrast to the silylene, germylene and stannylene derivatives, the plumbylene dithiolates displayed only minor variation (*ca.* 2.9°) in their S-M-S angles regardless of terphenyl substituent size. The M-S-C-C torsion angles, of the lead thiolates, also remain relatively constant at *ca.* 29°. We attribute the lower angular/ substituent dependence to the larger size of lead in comparison to the lighter elements. In the Pb derivatives, the Pb-S bonds lengthen slightly with increasing substituent size and in all cases,¹¹ the Pb-S distances in plumbylenes **12-14** are longer than the Pb-S distance found in Tokitoh's monothiolato plumbylene, Pb(Tbt)(STbt), (Tbt = C₆H₂-2,4,6-(CH(SiMe₃)₂)₃) (2.498(10) Å).³⁶ The C-S bond lengths are very similar to those for the lighter analogues with an almost negligible average decrease of about 0.01 Å upon descending the group.³⁷

As mentioned in points 1 and 4 above, the most striking features of the structural data are the decreasing interligand Ch-M-Ch and M-Ch-C-C angles with terphenyl substituent size for the Si, Ge, and Sn derivatives. These trends are counterintuitive from the point of view of purely steric considerations. Clearly, other factors influence the structures and these will be discussed below.

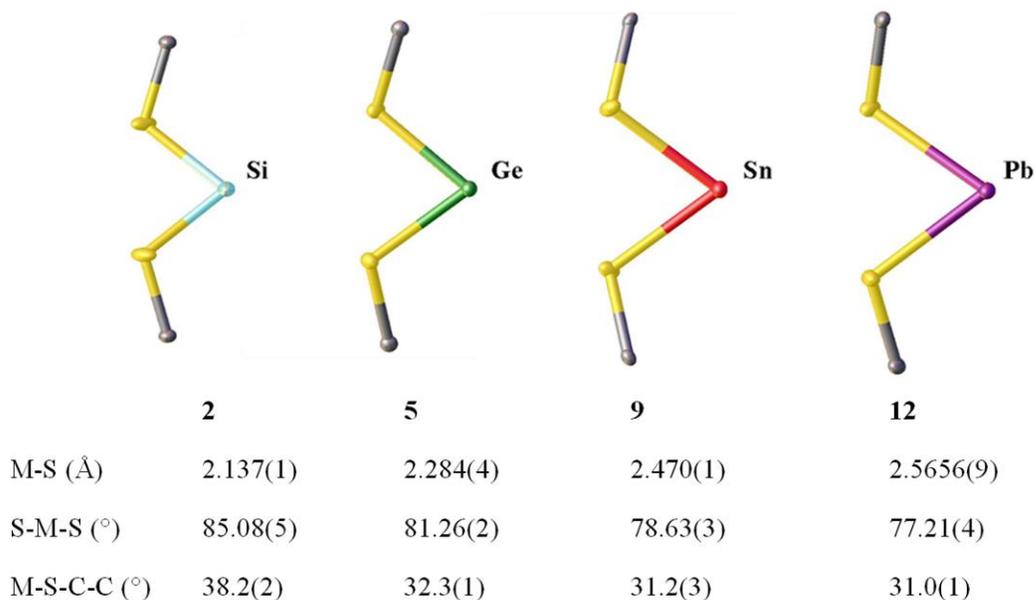


Figure 4. Drawings of the core atoms in the bithiolato tetrylenes $M(\text{SAr}^{\text{Pri}4})_2$ ($M = \text{Si}$, **2**; Ge , **5**; Sn , **9**; Pb , **12**). (30% probability ellipsoids) derivatives with identical $\text{SAr}^{\text{Pri}4}$ ligands showing that the S-M-S angle becomes narrower with increasing atomic number.

Although not all of the structures of the compounds of the thiolate series are currently known, the structural data clearly display patterns that can be summarized as follows:

1. The S-M-S interligand angles for $M = \text{Si}$, Ge and Sn derivatives decrease as the bulk of the terphenyl substituents increases.
2. The S-M-S interligand angles decrease in the order $M = \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$ (Figure 4).
3. The M-S-C_(ipso) bending angles of the thiolate ligands increase as the size of the terphenyl substituents increases for all compounds including those of lead.
4. The M-S-C-C torsion angles decrease with increasing size of the terphenyl substituents except in the lead derivatives where it changes little. This results in

- the opposition of flanking ring iso-propyl substituents from the two terphenyl substituents across the axis of the molecule, contrary to steric expectations.
5. The M-S bond lengths for each element display only minor variation with terphenyl substituent size.
 6. The C_(ipso)-S bond lengths vary little throughout the series.

Aryloxo and Selenolato Derivatives

Selected structural data for aryloxo and selenolato derivatives are given in Tables 2 and

3. The tetrylenes, Ge(SeAr^{Pri4})₂ (**15**) and Sn(SeAr^{Pri4})₂ (**16**), are the first structurally characterized Ge(II) and Sn(II) selenolates and rare examples of two-coordinate metallylenes stabilized by ligands bonded through 4th row elements.^{6, 38}

The structural data for the selenolates is necessarily limited because of their lower stability in comparison to the aryloxides or thiolates which is presumably a result of the decreased M-Si bond strengths.³⁹ The compounds, Ge(SeAr^{Pri4})₂ and Sn(SeAr^{Pri4})₂, have group 14 element-selenium bonds that are 0.11 and 0.12 Å longer than their thiolate counterparts. The increase corresponds roughly to the 0.13 Å difference in single bond covalent radii of S and Se.³⁷ The Se-Ge-Se angle in Ge(SeAr^{Pri4})₂ is about 3.5° wider than the S-Ge-S angle in Ge(SAr^{Pri4})₂ and the Ge-Se-C angle is about 4.8° narrower. In the tin complexes, Sn(SAr^{Pri4})₂ and Sn(SeAr^{Pri4})₂, the Ch-Sn-Ch and Sn-C-Ch angles are very similar (78.63(3) and 31.2(3) for SAr^{Pri4} vs. 78.60(3) and 26(7)°).

In Table 2, it can be seen that the aryloxo derivatives are characterized by O-M-O angles that are significantly wider than the corresponding S-M-S and Se-M-Se angles.^{8,31,40}

Table 4 gives structural details of all the available divalent, group 14 element aryloxo, thiolate and selenolato metallylenes that carry a common terphenyl substituent (i.e. Ar^{Pri}₄, a similar range of structural data is not currently available for the other terphenyl substituents). The Ch-M-Ch angles for the terphenyloxo complexes are wider than those of the thiolato and selenolato derivatives by *ca.* 11.28° for germanium, by *ca.* 1.77-13.55° for tin and *ca.* 22° for lead complexes. The deviation of the Ch-M-Ch angle from 90° is largest for S and Se derivatives, whereas on average, the most electronegative aryloxide derivatives might be expected to afford interligand angles that are closest to 90°, in accordance with Bent's rule.⁷

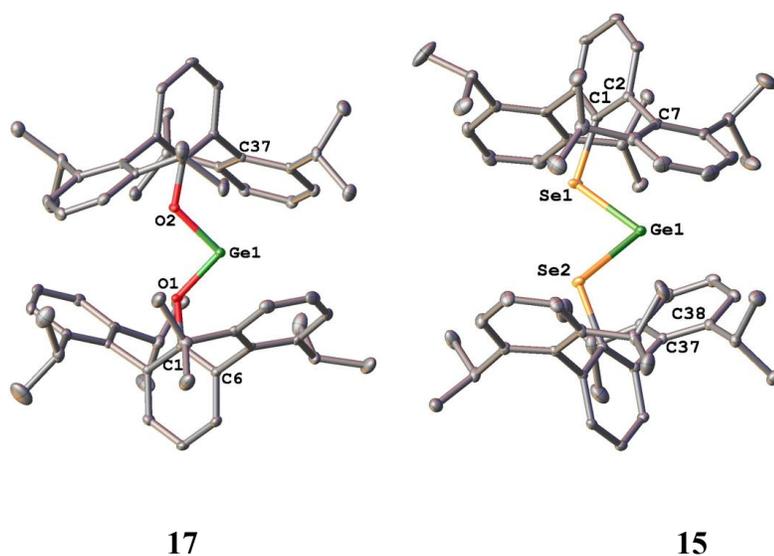


Figure 5. X-ray structures of the bisphenoxo and bis-selenolato germynes **17** and **15** (30% probability ellipsoids) without hydrogen atoms. The O1-Ge1-O2 = 92.54(6)°; Se1-Ge1-Se2 = 84.75(1)°. Other structural data are given in Table 4.

Table 2. Selected distances (Å) and angles (°) for compounds M(OAr)₂, M = Ge, Sn, Pb

Compound	O-M	O-M-O	C-O-M	M-O-C-C	C-O	M-Centroid	O---O	Reference
(17) Ge(OAr ^{Prⁱ4}) ₂	1.8271(16)*	92.54(6)	128.03(13)*	36.9(4)*	1.378(3)*	3.377*	2.640(2)	40
(18) Sn(OAr ^{Me6}) ₂	2.041(3)*	87.32(11)	126.7(3)*	30.0*	1.343(6)*	2.961*	2.818(5)	31
(19) Sn(OAr ^{Prⁱ4}) ₂	2.0472(17)*	92.18(6)	129.25(15)*	30.6*	1.360(3)*	3.163*	3.13	40
(20) Pb(OAr ^{Prⁱ4}) ₂	2.216(8)*	99(1)*	127(2)*	26(5)	1.354(2)*	2.95(3)*	3.38(3)*	11
(21) Ge(OAr*Me) ₂	1.807(9)*	92.0(4)	124.7(7)*		1.44(2)*			8a
(22) Sn(OAr*Me) ₂	2.009(5)*	88.8(2)	125.2(5)*		1.371(7)*			8a
(23) Pb(OAr*Me) ₂	2.14(2)*	86.2(4)	124(2)*		1.36(1)*			8b

* = Average Value

Ar*Me = C₆H₂Bu^t₂-2,6-Me-4**Table 3.** Selected distances (Å) and angles (°) for compounds M(SeAr)₂, M = Ge, Sn

Compound	Se-M	Se-M-Se	C-Se-M	M-Se-C-C	C-Se	M-Centroid	Se---Se	Reference
(15) Ge(SeAr ^{Prⁱ4}) ₂	2.396(5)*	84.715(1)	108.8(5)*	36(1)*	1.939(4)*	3.17(3)*	3.2301(6)	This Work
(16) Sn(SeAr ^{Prⁱ4}) ₂	2.594(3)*	78.60(3)	112.1(3)*	26(7)*	1.935(9)*	3.17(7)*	3.286(1)	This Work

* = Average Value

Table 4. Selected distances (Å) and angles (°) for ChAr^{Prⁱ4} substituted derivatives, M = Ge, Sn, Pb

		OAr ^{Prⁱ4}	SAr ^{Prⁱ4}	SeAr ^{Prⁱ4}
Ge	Ge-Ch	(17) 1.827(16)	(5) 2.284(4)	(15) 2.396(5)
	Ch-Ge-Ch	(17) 92.54(6)	(5) 81.26(2)	(15) 84.75(1)
	Ge-Ch-C	(17) 128.03(13)	(5) 113.58(5)	(15) 108.8(5)
Sn	Sn-Ch	(19) 2.0472(17)	(9) 2.470(1)	(16) 2.594(3)
	Ch-Sn-Ch	(19) 92.18(6)	(9) 78.63(3)	(16) 78.60(3)
	Sn-Ch-C	(19) 129.25(15)	(9) 113.8(1)	(16) 112.1(3)
Pb	Pb-Ch	(20) 2.216(8)	(12) 2.5656(9)	
	Ch-Pb-Ch	(20) 99(1)	(12) 77.21(4)	
	Pb-Ch-C	(20) 127(2)	(12) 113.42(11)	

Finally, we draw attention to the fact that the structure of Sn(SAr^{Prⁱ6})₂ (10) is worthy of further comment. It contains two molecules in the asymmetric unit possessing similar S-Sn-S angles of 78.27(1)° and 78.1(2)° and Sn-S-C-C torsion angles of 30(2)° and 36(7)°, respectively. However, one of the molecules in the asymmetric unit has two tin sites, A

and B, with 71/29 % occupancy. The main difference in the two sites is the disparity of the S-Sn bond lengths. For site A, the S-Sn bond lengths are 2.4919(6) Å and 2.4114(6) Å whereas for site B, the lengths are 2.3530(12) Å and 2.5235(12) Å. The Sn-centroid distances for site A are 3.160 Å (centroid 1) and 3.492 Å (centroid 2). For site B, the distances between the centroids are similar at 3.498 Å (centroid 1) and 3.151 Å (centroid 2). The shorter Sn-centroid distances in the mixed occupancy molecule are comparable to the Sn-centroid distances in the other molecule in the asymmetric unit at 3.126 Å and 3.155 Å.

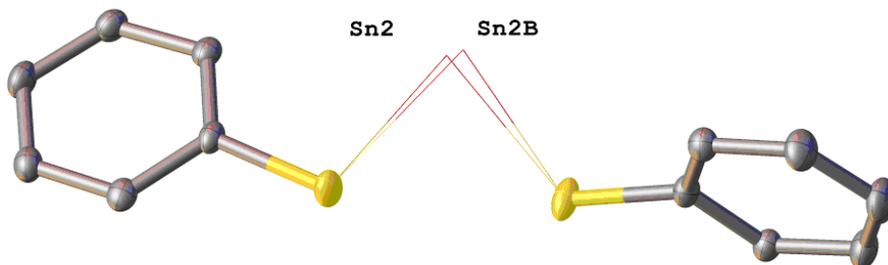


Figure 6. X-ray crystal structure of one of the molecules of $\text{Sn}(\text{SAr}^{\text{Pri}6})_2$ in the asymmetric unit. For clarity, flanking arene rings are not shown.

A possible explanation of the two different tin sites in $\text{Sn}(\text{SAr}^{\text{Pri}6})_2$ (**10**) (Figure 6) observed by X-ray crystallography and Mössbauer spectroscopy (see below) is that at low temperatures the structures, which are related by the asymmetric b_2 vibration of the SnS_2 moiety, are close in energy and are stabilized by steric, dispersion, and packing forces. When the crystals are dissolved at ambient temperature, only one ^{119}Sn NMR signal is observed; indicating that the structures are indistinguishable by the slower time scale of

the NMR technique, or that there is only one structure. Although this complex displays some of the characteristics of bond-stretch isomerism,⁴¹ an extensive attempt to model the two environments resulted in only one (symmetric) minimum on the potential energy surface corresponding to a symmetric S-Sn-S moiety.

²⁹Si, ⁷⁷Se, ¹¹⁹Sn, and ²⁰⁷Pb NMR Spectroscopy

The ²⁹Si spectrum of Si(SAr^{Me6})₂ features a downfield singlet at $\delta = 285.5$.¹² Signals for the bulkier silylenes Si(SAr^{Pr4})₂ and Si(SAr^{Pr6})₂ were located at similar chemical shifts but slightly upfield at $\delta = 270.4$ and 270.9 , respectively. The very similar shifts obtained for the silylenes show that the angular changes at silicon have only a minor effect on the chemical shift of the thiolate derivatives.

Table 5. ²⁹Si, ⁷⁷Se, ¹¹⁹Sn, and ²⁰⁷Pb Heteronuclear NMR chemical shifts for tetrylene dichalcogenolates

	δ : ²⁹ Si	δ : ⁷⁷ Se	δ : ¹¹⁹ Sn	δ : ²⁰⁷ Pb
(1) Si(SAr ^{Me6}) ₂	285.5			
(2) Si(SAr ^{Pr4}) ₂	270.4			
(3) Si(SAr ^{Pr6}) ₂	270.9			
(8) Sn(SAr ^{Me6}) ₂			763.8	
(9) Sn(SAr ^{Pr4}) ₂			814.8	
(10) Sn(SAr ^{Pr6}) ₂			827.4	
(11) Sn(SAr ^{Pr8}) ₂			919.4	
(12) Pb(SAr ^{Pr4}) ₂				4283
(13) Pb(SAr ^{Pr6}) ₂				4299
(14) Pb(SAr ^{Pr4}) ₈				4335
(15) Ge(SeAr ^{Pr4}) ₂		657.5		
(16) Sn(SeAr ^{Pr4}) ₂		526.9*	1148	
(18) Sn(OAr ^{Me6}) ₂			-344	
(19) Sn(OAr ^{Pr4}) ₂			-289.7	
(20) Pb(OAr ^{Pr4}) ₂				1070

* ¹J_{SeSn} = 516 Hz

The ^{119}Sn NMR spectra indicate a progressive downfield shift as the interligand angle decreases.⁴² $\text{Sn}(\text{SAr}^{\text{Me}_6})_2$ has a signal at $\delta = 763.8$ whereas $\text{Sn}(\text{SAr}^{\text{Pri}_4})_2$ and $\text{Sn}(\text{SAr}^{\text{Pri}_6})_2$ display signals $\delta = 814.8$ and 827.4 , respectively, and the signal of $\text{Sn}(\text{SAr}^{\text{Pri}_8})_2$ has the furthest downfield shift at $\delta = 919.4$. The ^{119}Sn NMR chemical shifts of $\text{Sn}(\text{SAr}^{\text{Pri}_4})_2$ ($\delta = 814.8$), $\text{Sn}(\text{SeAr}^{\text{Pri}_4})_2$ ($\delta = 1148.1$), and the previously reported $\text{Sn}(\text{OAr}^{\text{Pri}_4})_2$ ($\delta = -289.7$)⁴⁰ clearly illustrate the very large effects on the ^{119}Sn chemical shift of different substituents. The trend is opposite of what one would expect based on σ -inductive effects; however, the more electropositive substituents decrease the HOMO-LUMO gap, and as a result, increase the paramagnetic deshielding which augments the applied field and causes a downfield chemical shift on the ^{119}Sn NMR signal.^{43,44}

A comparison of the chemical shifts for stannylene dichalcogenolates with other two coordinate stannylenes show their ^{119}Sn NMR signal to be downfield of stannylene diamides, such as $\text{Sn}\{\text{N}(\text{SiMe}_3)\}_2$ ($\delta = 746$),⁴⁴ and upfield of dialkyl or diaryl stannylenes, such as $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2$ ($\delta = 2328$)⁴⁵ and $\text{Sn}(\text{Ar}^{\text{Me}_6})_2$ ($\delta = 1971$).⁴⁶ The signals of $\text{Sn}(\text{SAr}^{\text{Pri}_8})_2$ and $\text{Sn}(\text{SeAr}^{\text{Pri}_4})_2$ are close to that observed for the diarylstannylene $\text{Sn}(\text{Mes}^*)_2$ ($\delta = 980$) ($\text{Mes}^* = \text{C}_6\text{H}_2\text{-}2,4,6\text{-Bu}^t_3$).³

The ^{207}Pb NMR spectra of the lead thiolates demonstrated only small shift differences upon varying the thiolate ligands (in comparison to the very wide range of ^{207}Pb NMR shifts.⁴⁷). Plumbylenes $\text{Pb}(\text{SAr}^{\text{Pri}_4})_2$, $\text{Pb}(\text{SAr}^{\text{Pri}_6})_2$, and $\text{Pb}(\text{SAr}^{\text{Pri}_8})_2$ have signals in the narrow range of 4283-4335 ppm. These are comparable to other monomeric plumbylenes such as $\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2$ which has a chemical shift at $\delta = 4916$,⁴⁷ though they are much further downfield of the previously reported $\text{Pb}\{\text{N}(\text{H})\text{Ar}^{\text{Me}_6}\}_2$ ($\delta = 2871$).¹⁰ The difference between these two amido plumbylenes is

believed to be due to the interaction of flanking aryl rings of $\text{Pb}\{\text{N}(\text{H})\text{Ar}^{\text{Me}_6}\}_2$ with the lead atom.

The ^{77}Se NMR spectra for $\text{Ge}(\text{SeAr}^{\text{Pri}_4})_2$ and $\text{Sn}(\text{SeAr}^{\text{Pri}_4})_2$ display signals that have a greater downfield shift for the germylene ($\delta = 657.5$) in comparison to the stannylene analogue ($\delta = 526.9$). The difference is likely due to an inductive effect since germanium is more electronegative than tin. The region of ^{77}Se NMR shifts for both metals are characteristic of organic selenides.⁴⁸ The $^1J_{\text{SeSn}}$ coupling observed in the ^{77}Se NMR spectrum of $\text{Sn}(\text{SeAr}^{\text{Pri}_4})_2$ is 516 Hz, which represents an average of the ^{119}Sn or ^{117}Sn couplings due to broad signals. This is similar to the $^1J_{\text{SeSn}}$ coupling observed in the triselenolato Sn(II) complex, $\text{NaSn}(\text{SePh})_3$ ($^1J_{\text{SeSn}} \approx 400$ Hz) (no reported structure), which has a chemical shift ($\delta = 164$) significantly upfield of **15** and **16**.⁴⁹ A weak signal corresponding to the diselenide, $(\text{SeAr}^{\text{Pri}_4})_2$, was also located at $\delta = 480.2$. Chemical shifts for the ^{29}Si , ^{77}Se , ^{119}Sn , and ^{207}Pb NMR spectra are shown in Table 5.

^{119}Sn Mössbauer Spectroscopy

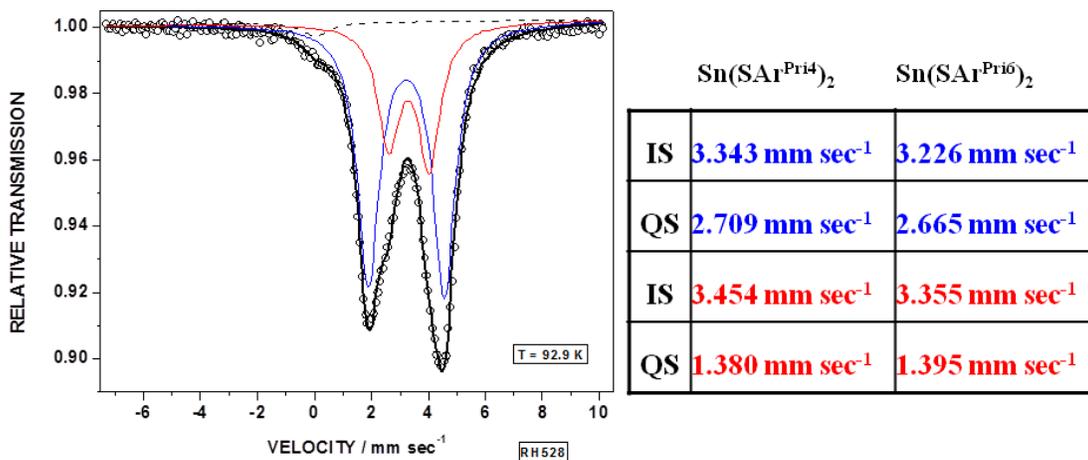


Figure 7. Mössbauer spectrum for $\text{Sn}(\text{SAr}^{\text{Pri}_4})_2$ (**9**) at 93 K, with tabular data for

$\text{Sn}(\text{SAr}^{\text{Pri}6})_2$ (**10**) also included. Two signals, in an almost identical ratio, are also observed for $\text{Sn}(\text{SAr}^{\text{Pri}6})_2$. Only one tin site is observed for compounds $\text{Sn}(\text{SAr}^{\text{Me}6})_2$ and $\text{Sn}(\text{SAr}^{\text{Pri}8})_2$.

The isomer shifts of stannylenes $\text{Sn}(\text{SAr}^{\text{Me}6})_2$ (**8**), $\text{Sn}(\text{SAr}^{\text{Pri}4})_2$ (**9**), $\text{Sn}(\text{SAr}^{\text{Pri}6})_2$ (**10**), $\text{Sn}(\text{SAr}^{\text{Pri}8})_2$ (**11**), $\text{Sn}(\text{SeAr}^{\text{Pri}4})_2$ (**16**) and $\text{Sn}(\text{OAr}^{\text{Pri}4})_2$ (**19**) all appear above 2.65 mm/s, so clearly all of these correspond to Sn(II).⁵⁰ For the stannylenes $\text{Sn}(\text{SAr}^{\text{Pri}4})_2$ (**9**) and $\text{Sn}(\text{SAr}^{\text{Pri}6})_2$ (**10**), two tin sites are present, both in approximately a 2:1 ratio at 90 K. While the isomer shift difference between the two sites is relatively small, the quadrupolar splitting is significantly different. The two signals can be assigned to a change in the geometry of the tin sites leading to a large difference in the electric field gradient tensor at the metal site. As mentioned earlier, in the X-ray crystal structure, one of the two molecules of **10** at 90 K reveals two tin sites with occupancies of 71 to 29 %. While this ratio does not match that seen in the ME (Mössbauer Effect) spectra (is *ca.* 50 % of the ratio) it does show that two tin sites with similar electronic but different geometric structures can coexist in the solid state. All of the ^{119}Sn ME data are summarized in Table 6, in which the hyperfine parameters (IS and QS) are those observed at 90 K. The IS values are reported with respect to a room temperature absorber spectrum of BaSnO_3 . The data relating to the mean-square amplitude-of-vibration (msav) of the tin atoms in the various compounds are noteworthy. The msav is most readily expressed in terms of the parameter $F = -k^2 \langle x^2 \rangle k^2$. This parameter can be evaluated from the ^{119}Sn ME data ($F_{X,T}$) as well as the U_{ij} values determined in the X-ray studies ($F_{X,T}$) all at temperature T.⁵¹ The ^{119}Sn ME F parameters were calculated from the temperature

dependence of the logarithm of the recoil-free fraction, which in turn, for an optically thin absorber, is equal to the temperature dependence of the logarithm of the area under the resonance curve. An assumption underlying this calculation is that $f \rightarrow 1$ as $T \rightarrow 0$; that is that the zero point vibration is negligibly small compared to the $m\Delta v$ in the cited temperature regime. The F_M values are smaller than the F_X values, the ratios ranging from 0.59 to 0.76. As has been shown in a number of recent studies involving iron and/or tin containing organometallics, the difference in the F factors is especially large when the metal atom (in this case Sn) is ligated to its nearest neighbor environment by single σ - rather than multiple - bonds.⁵² Such ligated atoms are sensitive to low frequency rotational/ librational motions which are recorded in the X-ray determination, but not in the ^{119}Sn Mössbauer data. This bonding feature is clearly evident in the structures of compound **8** and **11**.

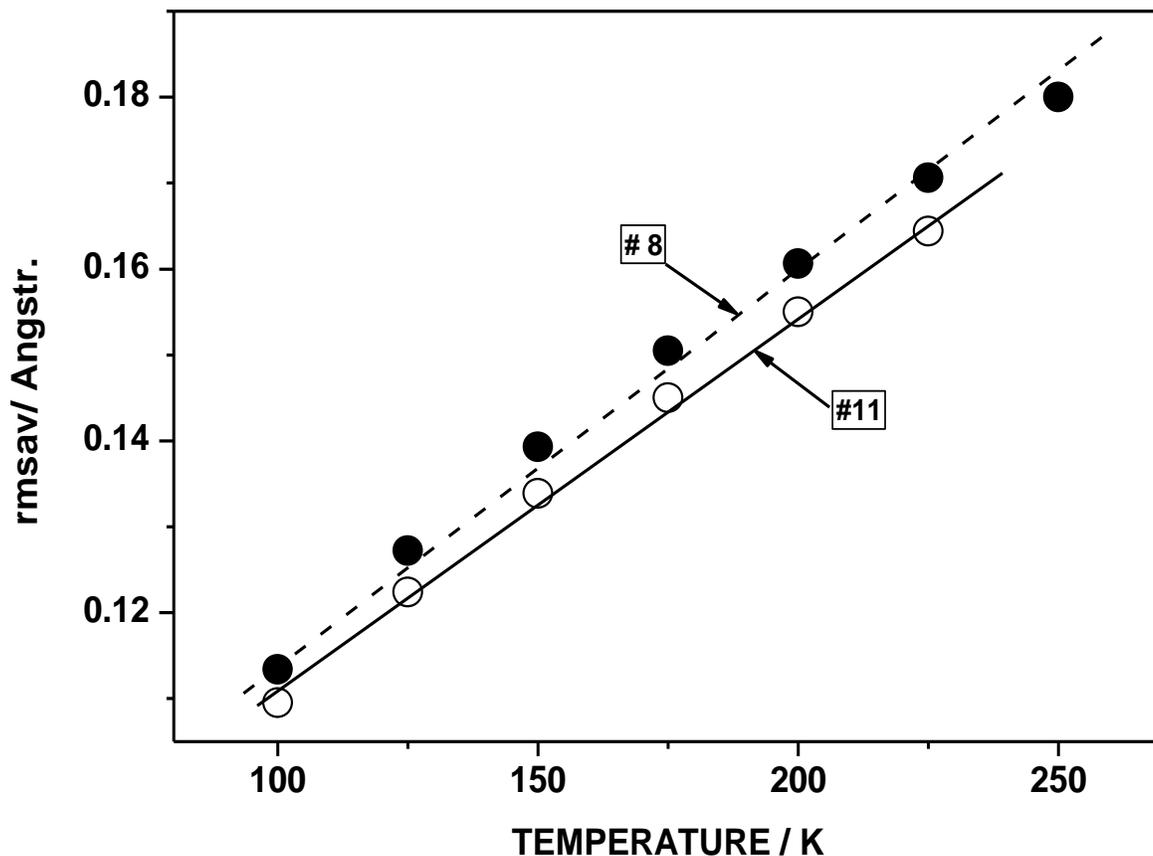


Figure 8. The root-mean-square-amplitude-of-vibration of the Sn atoms in two of the compounds discussed in the text, calculated from the temperature-dependent ^{119}Sn Mössbauer data.

The temperature dependence of the logarithm of the recoil-free fraction, $-\text{d} \ln f / \text{d}T$, for both **8** and **11**, *inter alia*, are well fitted by a linear regression and thus the F parameter permits the evaluation of the rmsav of the tin atoms over the range $90 < T < 225$ K in the two structures. These rmsav values are summarized graphically in Figure 8, from which it is seen that the vibrational amplitudes in **8** are somewhat larger than in **11**. Finally, it is worth noting that the temperature dependence of the recoil-free fraction in **9** and **16** are

essentially identical, implying that replacing S (in **9**) by Se (in **16**) has little effect on the metal atom dynamics in the two compounds.

The X-ray crystal data for **10** suggest that the main difference in the two sites is the change of the S-Sn bond lengths. For the higher occupancy tin site, the two S-Sn bond lengths differ slightly at 2.4919(6) Å and 2.4114(6) Å, whereas in the low occupancy site the lengths are 2.3530(12) and 2.5235(12) Å. The QS of 2.665 mm sec⁻¹ appears to

Table 6. Summary of the ¹¹⁹Sn Mössbauer effect results cited in the text. The parenthetical values are the experimental errors in the last significant figure(s). The subscripts on the cited F parameters indicate M for the Mössbauer experiment results and X for the X-ray derived values.

	8	9	10	11	16	19	Units
IS ₁ (90)	3.08(1)	3.34(1)	3.23(1)	3.34(1)	3.30(2)	3.15(1)	mm/sec
QS ₁ (90)	2.03(1)	2.71(1)	2.67(1)	2.60(1)	2.59(2)	2.10(1)	mm/sec
IS ₂ (90)		3.45(1)	3.36(1)				mm/sec
QS ₂ (90)		1.38(1)	1.40(1)				mm/sec
-dIS ₁ /dT		~indep	1.4(3)	~4.6(1)			mm/sec/K x10 ⁻⁴
-dIS ₂ /dT		~indep	~indep				mm/sec/K x10 ⁻⁴
-dQS ₁ /dT		~indep	3.4(3)	~8.(1)	2.2(4)		mm/sec/K x10 ⁻⁴
-dQS ₂ /dT		~indep	~indep				mm/sec/K x10 ⁻⁴
-d ln A ₁ /dT	18.94(21)	25.13(16)	24.93(9)	17.55(41)	25.7(21)		K ⁻¹ x10 ⁻³
-d ln A ₂ /dT		21.31(16)	19.53(9)				K ⁻¹ x10 ⁻³
k ₁ ² <x _{ave} ² > _{M,88}	1.68(8)	2.22(6)	2.19(5)	1.55(13)	2.27(9)	1.83(4)	
k ₁ ² <x _{ave} ² > _{X,88}	2.77(4)	2.99(6)	2.86(9)	2.63(2)	3.94(2)	2.79(1)	
k ₂ ² <x _{ave} ² > _{M,88}		1.89(6)					
ME/X-RAY	0.61	0.74	0.76	0.59	0.58	0.66	

correlate with the more symmetric tin site with the smaller QS of 1.395 mm sec⁻¹

corresponding with the asymmetric tin site.

Electronic Spectra

The electronic spectra of the divalent chalcogenolates (wavelengths and intensities are given in Table 7) are all characterized by transitions in the UV-visible and near-UV regions for the thiolates and selenolates and in the near UV for most of the aryloxo

complexes.^{12,33} We have recently shown that the experimental UV-Vis spectrum of **1** can

be interpreted with the help of TD-DFT calculations which showed the first low-energy transition at 382 nm to be of tetrylene n (HOMO) → tetrylene p (LUMO) type. However, as the orbital analysis in Figure 9 demonstrates, the exact bonding characteristics of the frontier orbitals in divalent chalcogenolates depend on the Ch-M-Ch bond angle and no statements on the type of transitions observed in the electronic spectra of **2-16** can therefore be made based on the data available for **1**. The exact assignment of each experimental spectrum would require explicit TD-DFT calculations to be carried out for the specific molecule in question, which would be a very time-consuming undertaking. However, some general comments of trends in the experimental spectra can still be given.

Table 7. Experimental data for the electronic spectra of **1-16, 20**.Transition energy and intensities (in parentheses) given in nm and $M^{-1}cm^{-1}$.

(1) Si(SAr ^{Me6}) ₂	(2) Si(SAr ^{Pri4}) ₂	(3) Si(SAr ^{Pri6}) ₂		
382 (8300)	405 (3700)	411 (4400)		
318 (23 000)	318 (7400)	331 (7500)		
291 (20 000)	290 (11 200)	290 (10 500)		
269 (25 000)				
(4) Ge(SAr ^{Me6}) ₂	(5) Ge(SAr ^{Pri4}) ₂	(6) Ge(SAr ^{Pri6}) ₂	(7) Ge(SAr ^{Pri8}) ₂	
396 (3000)	410 (3100)	414 (3600)	430 (7200)	
276 (7700)	330 (3600)	338 (3700)	362 (6100)	
	278 (5600)	286 (4100)	282 (10 400)	
(8) Sn(SAr ^{Me6}) ₂	(9) Sn(SAr ^{Pri4}) ₂	(10) Sn(SAr ^{Pri6}) ₂	(11) Sn(SAr ^{Pri8}) ₂	
400 (1100)	406 (1300)	414 (1400)	430 (2400)	
298 (5300)	330 (1500)	342 (1700)	366 (2500)	
292 (5300)	276 (3700)	276 (4900)	286 (4900)	
	(12) Pb(SAr ^{Pri4}) ₂	(13) Pb(SAr ^{Pri6}) ₂	(14) Pb(SAr ^{Pri8}) ₂	
	422 (1300)	427 (1800)	446 (4200)	
	354 (1100)	365 (1600)	372 (2500)	
	292 (5800)	316 (2200)	292 (6600)	
	(15) Ge(SeAr ^{Pri4}) ₂			
	435 (7700)			
	358 (9000)			
	303 (8900)			
	(16) Sn(SeAr ^{Pri4}) ₂			
	434 (5800)			
	368 (6900)			
	305 (9500)			
	296 (12 900)			
	(20) Pb(OAr ^{Pri4}) ₂			
	370 (860)			
	300 (3000)			
	293 (3200)			

As shown in Table 8, the lowest energy transition in **1-16** moves to longer wavelengths on descending group 14. Also, more electronegative group 16 substituents more effectively stabilize the tetrylene lone pair via an electron withdrawing effect and

increase the energy difference between the lone pair and the empty p orbital.² The energy of the transition also decreases with increasing ligand bulk. As the lowest energy transition is presumably of HOMO → LUMO type in all systems studied, the above trends can be correlated to accompanying changes in the key structural parameters, that is, the Ch-M-Ch and M-Ch-C bond angles, which directly affect the energy of the HOMO orbital (see Figure 9) and therefore the electronic spectra.

The data from electronic spectra indicate that the heavier tetrylenes have a smaller HOMO-LUMO gap than their lighter congeners. Although similar trends have been observed previously,^{6,10} this result is opposite of what is expected on the basis of a comparison with transient dialkyl or diaryl species,^{6,53-56} and stable diaryl tetrylene complexes, such as $M(\text{Ar}^{\text{Me}_6})_2$ and $M(\text{Ar}^{\text{Pri}_4})_2$ ($M = \text{Ge-Pb}$).^{6,57} These predict the transition energy should become higher descending the group based on the inert pair effect—which loosely states that frontier s electrons become progressively lower in energy upon descending the periodic table.⁵⁸ However, the contradiction is only superficial since the tetrylene lone pair orbital does in fact decrease in energy on descending group 14. Also, because of the acute bond angles, there are other high energy orbitals present in these systems (see Figure 9). Consequently, the low energy transitions observed in the experimental spectra of tin and lead derivatives are presumably of HOMO → LUMO character but they most likely originate from the π -type lone pairs on the chalcogen atoms and not from the tetrylene lone pair. Our recent analysis of the electronic spectrum of the silicon derivative **1** showed these transitions to reside only

slightly higher in energy (around 60 nm in (the experimental spectrum) compared to the transition with silylene $n \rightarrow p$ character.¹²

Orbital Analysis

The major factor producing the acute bond angles in tetrylenes **2-16**, as well as in other similar compounds, involves a combination of repulsive steric interactions and attractive dispersion forces between the bulky substituents across the axis that bisects the MCh_2 angle. For the terphenyls, the greatest repulsion comes from the *ortho*-substituents of the flanking arene rings on the lone pair side of the group 14 atom. The dispersion interactions occur both on the group 14 element lone pair side and the side of chalcogenolate ligands, and may be visualized to best advantage in the illustration of the structure of **11** (Figure 2), where these *ortho*-isopropyl groups (and also the *para*-isopropyl groups) are brought into close approach. The interligand interactions cause the C-Ch-M bond angles to widen in order to relieve strain, which also cause the Ch-M-Ch angles to contract to sub-90° angles. There appears to be little direct interaction of the flanking arene rings with the metal based on heteronuclear NMR and ¹¹⁹Sn Mössbauer spectroscopy and no significant distortions within the crystal structures.

To further investigate the structural trends in dichalcogenolate tetrylenes, a series of calculations was carried out using density functional theory (DFT). In particular, the role of electronic and steric effects in determining the Ch-M-Ch angle was analyzed by carrying out geometry optimizations for R-Ch-M-Ch-R, where M = Si, Ge, Sn, Pb; Ch = O, S, Se; and R = H, Ph, Tph, Ar^{Prⁱ8} (Tph = C₆H₃-2,6-Ph₂). However, before discussing

the results of these calculations, we begin by concentrating on an orbital-type analysis of bonding in dichalocogenolate tetrylenes and inspect the Kohn-Sham MOs of the parent molecular framework.

The valence MOs of the model species H-Ch-M-Ch-H have C_{2v} symmetry and their relative energy levels are shown in Figure 9 (center) for Ch = S and M = Ge combination. As already seen, the HOMO (a_1) corresponds to the tetrylene lone pair and the HOMO-1 (a_2) and HOMO-2 (b_1) are π -type bonding and non-bonding combinations of the p_z AOs at Ch and M; the LUMO (b_1) is the third π -type combination which is anti-bonding. By visual inspection of the orbitals, it becomes immediately evident that there is a net bonding contribution from two σ -type orbitals within the Ch-M-Ch moiety, which correspond to two single bonds. Furthermore, there is also a π -type bonding orbital, HOMO-2, but its contribution to Ch-M bonding is likely to be of less importance for systems with sterically encumbered substituents as these have non-planar R-Ch-M-Ch moieties and, consequently, a lower symmetry C_2 point group.

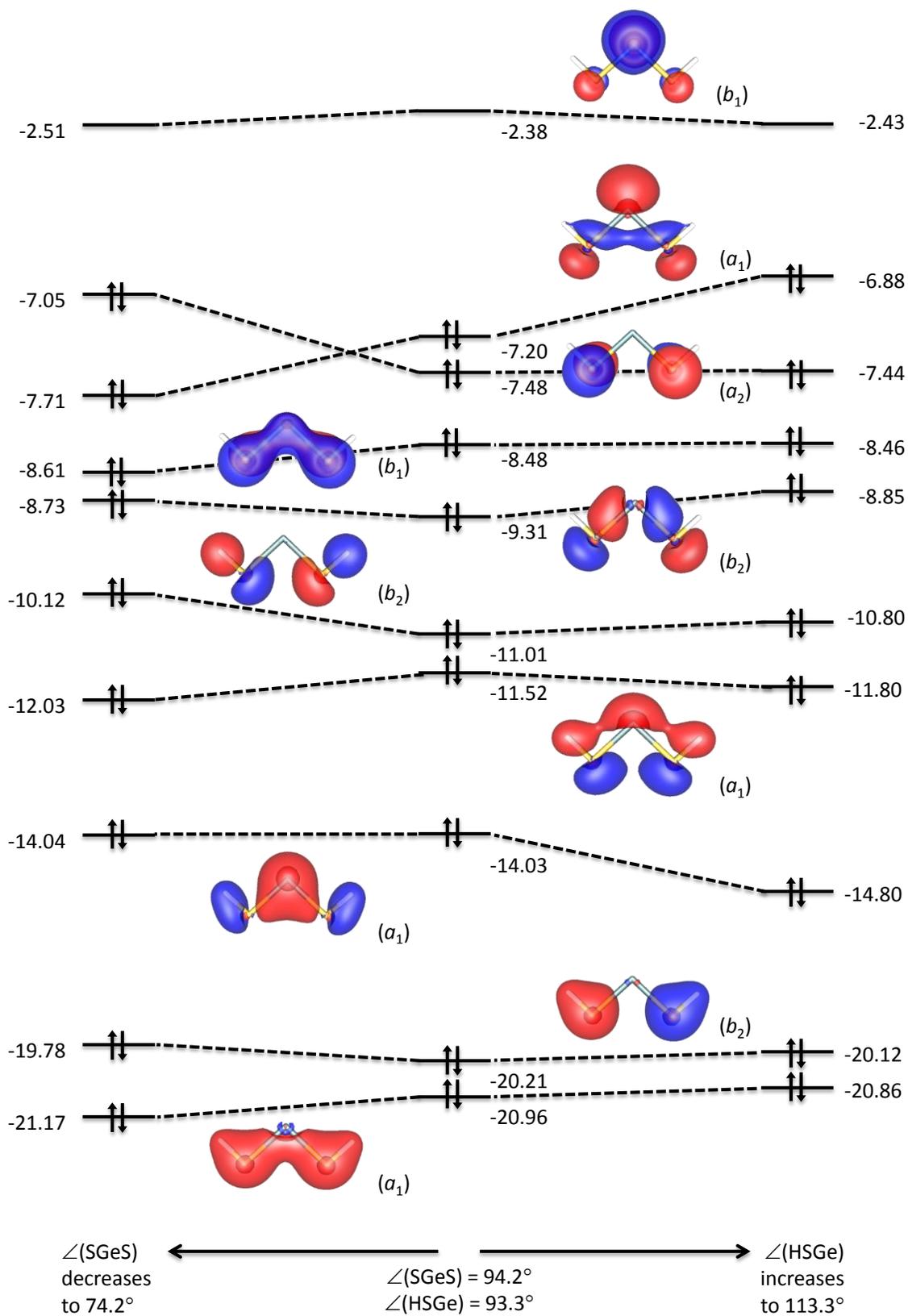


Figure 9. Valence Kohn-Sham MOs of H-S-Ge-S-H and their energies [eV].

Figure 9 also shows the changes in the valence MOs due to a 20° decrease in the Ch-M-Ch angle (left) or a 20° increase in the R-Ch-M angle (right) from the calculated lowest energy value near 94.2°. What is most notable is that both perturbations induce major changes in the energies and shapes of only a few orbitals. Specifically, when the Ch-M-Ch angle decreases, the energy of the lone pair a_1 HOMO decreases as the orbital attains more Ch···Ch bonding character. This is supported by the ^{119}Sn Mössbauer spectra of stannylenes, **8-11**, where the isomer shift becomes more positive from **8** (3.08 mm sec⁻¹) to **12** (3.34 mm sec⁻¹) indicating an increase of electron density at the tin nucleus. At the same time, the energy of the π -type non-bonding orbital (a_2) increases as it gradually becomes more and more Ch···Ch anti-bonding. Consequently, at some point, these MOs will cross and the nature of the HOMO will change. We note that with realistic substituents, the molecular point group is lowered to C_2 in which both HOMO and HOMO-1 transform according to the same irreducible representation, with the result that the orbital levels will not cross and there will be an avoided crossing. In contrast to the above, widening the R-Ch-M angle in R-Ch-M-Ch-R increases the energy of the HOMO as it loses its Ch···Ch bonding character and becomes more M-Ch anti-bonding. Again, this change is counterbalanced by a decrease in the energy of one of the orbitals which attains more M-Ch bonding character upon increasing the R-Ch-M angle. However, in this case there is no associated change in the relative ordering of the orbitals as the two MOs are well separated in energy.

Figure 9 raises two important points. First, the relative ordering of the frontier MOs in dichalcogenolate tetrylenes is dependent on the key geometrical parameters which in

turn depend heavily on the identity of the M and Ch atoms and the steric bulk of the aromatic substituent employed. Consequently, trends in e.g. electronic spectra are not expected to correlate with X-ray structural parameters in any straightforward manner (see above). Second, the potential energy surface of dichalcogenolate tetrylenes can, at least to some extent, adapt to changes in the geometrical parameters through changes in the nature of key orbital interactions. For example, the potential energy surface for the bonding of the Ch-M-Ch angle in parent dichalcogenolate tetrylenes is calculated to be particularly shallow, with energy increasing only around 1 kJ mol^{-1} per successive 1° decrease in the bond angle. This is in good agreement with the range of R-Ch-M-Ch-R systems that can be synthesized experimentally and the straightforward nature of the synthetic procedure used to obtain even the bulkiest derivatives (metathesis).

Optimized Structures

The results from geometry optimizations of R-Ch-M-Ch-R with different R groups (Supporting Information) show that electronic effects of the organic substituent have very little impact on the key geometrical parameters of the system. For example, the Ch-M-Ch angle hardly changes at all when comparing data for R = H systems to that of the corresponding R = Ph species. Accordingly, there is very little substituent induced change in the calculated atomic charge for the group 14 element. What is also notable from the calculated structures is that the Bent's rule is in general obeyed in both R = H and Ph series,^{7,59} and the smallest Ch-M-Ch angles are found in bisphenoxides. This strongly suggests that the counterintuitive results obtained experimentally do not arise from electronic effects but instead predominantly from steric and dispersion factors.

Furthermore, in all systems studied the Ch-M-Ch angle spans a relatively modest range from 89.6° to 96.9° with the largest values obtained when M = Si (most s-p hybridization) and the smallest when M = Sn and Pb (least s-p hybridization).

The bonding in dichalocogenolate tetrylenes does not change markedly from that described above even when using the parent terphenyl ligand (Tph = C₆H₃-2,6-Ph₂) as a substituent. The calculated Ch-M bond lengths change somewhat only in the case of the most crowded Ch = O derivatives but the differences are at most 0.05 Å. Also, the range of optimized Ch-M-Ch bond angles is only slightly narrower than that calculated for R = Ph species, from 87.4° to 93.5°, indicating very little changes in the electronic structure of the Ch-M-Ch moiety. Clearly the parent terphenyl ligand (Tph) is not sterically encumbered enough to alter the key bonding characteristics of these systems to any significant degree. This is also apparent from the calculated C-Ch-M bond angles which are between 95° and 100° for all sulfur and selenium derivatives i.e. significantly less than that observed experimentally. We therefore turned our attention to the analysis of the

Table 8. Selected bond lengths [Å] and bond angles [°] for calculated structures of formulae Ar^{Prig}-Ch-M-Ch-Ar^{Prig}, where M = Si-Pb and Ch = O-Se.

	Ch\M	PBE0/TZVP				disp. corr. PBE0/TZVP			
		Si	Ge	Sn	Pb	Si	Ge	Sn	Pb
$r(\text{ChM})$	O	1.772	1.874	2.123	2.248	1.759	1.869	2.109	2.228
	S	2.210	2.322	2.553	2.647	2.203	2.315	2.539	2.631
	Se	2.354	2.442	2.663	2.751	2.348	2.435	2.649	2.736
$\angle\text{MChM}$	O	99.1	96.2	96.0	97.3	96.4	93.0	92.3	93.0
	S	84.4	81.8	78.3	79.0	82.2	77.8	74.1	73.6
	Se	81.5	80.3	76.7	77.4	79.4	78.1	72.1	72.3
$\angle\text{CChM}$	O	136.6	136.7	136.1	136.2	136.7	133.4	134.6	134.6
	S	117.2	117.6	117.9	118.1	116.4	117.6	119.0	119.8
	Se	115.5	115.2	115.2	115.5	114.6	114.0	117.8	117.5

more crowded structures for which X-ray data allows direct comparison between theory and experiment.

The calculated key metrical parameters for the $R = Ar^{Pr^i8}$ series are summarized in Table 8. A comparison with the available experimental data (Table 1) shows the two sets of numbers to be in reasonable agreement with each other: the calculated Ch-M bond lengths are accurate to less than 0.05 Å and the optimized Ch-M-Ch are only around 5° wider than those found experimentally. However, what is most notable is that the calculated structures reproduce the “inverse” of Bent’s rule that has been observed experimentally—the widest Ch-M-Ch angles are found for Ch = O, around 100°, and the narrowest for Ch = Se, in which case angles close to 75° are seen. Consequently, for the bisphenoxide tetrylenes, there is too much steric repulsion, as well as interelectronic repulsion between the O-M bonding pairs, to permit acute interligand bond angles to occur. This is mainly due to their short C-O distances as compared to C-S and C-Se bonds in corresponding thiolato and selenolato derivatives. The calculations also accurately reproduce the increase in the R-Ch-M bond angle upon increasing the steric bulk of the substituent employed.

It would be reasonable to assume that the remaining discrepancies between the data in Tables 1 and 8 are attributable to packing effects generated by the large terphenyl substituents as these are not modeled in calculations. However, as has recently been shown⁶⁰ for the quintuple bonded complex, $Ar^{Pr^i4}CrCrAr^{Pr^i4}$,⁶¹ dispersion forces can play an important role as secondary bonding interactions capable of stabilizing compounds with exotic bonding environments and bulky substituents. To this end, we tested the

effect of empirical dispersion correction (Grimme's DFT-D3)⁶² on the geometry optimization of the studied $R = \text{Ar}^{\text{Pri}8}$ series (see Table 8). The results show that dispersion has the largest impact on the Ch-M-Ch bond angle which decreases by 2-5° throughout the series, therefore improving the agreement between theoretical and experimental structures. The Pb-S derivative, $\text{Pb}(\text{SAr}^{\text{Pri}8})_2$ (**14**), makes an interesting exception to the above: calculations predict it to have a similar geometry to its lighter group 14 congeners, that is also seen with the less sterically crowded plumbynes, $\text{Pb}(\text{SAr}^{\text{Pri}4})_2$ (**12**) and $\text{Pb}(\text{SAr}^{\text{Pri}6})_2$ (**13**), whereas the experimental structure of $\text{Pb}(\text{SAr}^{\text{Pri}8})_2$ (**14**) shows a surprisingly wide S-Pb-S angle (80.07(2)°) accompanied by a significant twist in the relative orientation of the two terphenyl groups. However, the two S-Pb bond lengths are essentially equivalent in the experimental structure and comparable to the calculated values, indicating that the discrepancy in the bond angles could simply be a packing effect since there are four solvent molecules in the crystal structure of **14**, while there are none in those of **7**, **11**, or in the theoretically calculated $\text{Si}(\text{SAr}^{\text{Pri}8})_2$.

The acute Ch-M-Ch bond angles in dichalcogenolate tetrylenes are in many cases accompanied by intramolecular Ch...Ch distances that are well below the sum of van der Waals radii for the respective elements (see Tables 1-3). This raises the important question if the chalcogen atoms share an orbital-type (covalent) bonding interaction between them. A visual inspection of the valence Kohn-Sham orbitals for H-S-Ge-S-H (Figure 9) shows that there is a net Ch...Ch bonding contribution from one MO which is the tetrylene lone pair.^{63,64} As the Ch-M-Ch angle becomes more acute, the energy of this MO is lowered and the Ch...Ch interaction strengthened. However, as previously

discussed, the change is accompanied with an increase in the energy of the π -type HOMO-1 which simultaneously acquires more Ch \cdots Ch anti-bonding character. It is therefore not entirely surprising that an analysis of the theoretically determined total electron densities of dichalcocogenolate tetrylenes with Bader's Quantum Theory of Atoms in Molecules (QTAIM)⁶⁵ failed to locate a bond critical point connecting the chalcogen centers in any of the model systems studied. Consequently, the short intramolecular Ch \cdots Ch distances are mostly a result of geometrical constraints, augmented with dispersion forces as evidenced by a comparison of the two sets of theoretical results for the R = Ar^{Prig} series.

It is interesting to note that the build-up of electron density in between the chalcogen atoms can be seen from the experimentally determined difference electron density maps. For example, examination of the electron density map for Pb(SAr^{Prig})₂ shows electron density centralized within the plane of the S-Pb-S angle (Figure 10). Additionally, the map of Sn(SAr^{Me6})₂ reveals no appreciable electron density in a centralized point within the S-Sn-S system. The difference map of the highly bent stannylene, Sn(SAr^{Prig})₂, reveals yet a different picture where one sees a large buildup of electron density bisecting the Sn-S bonds.

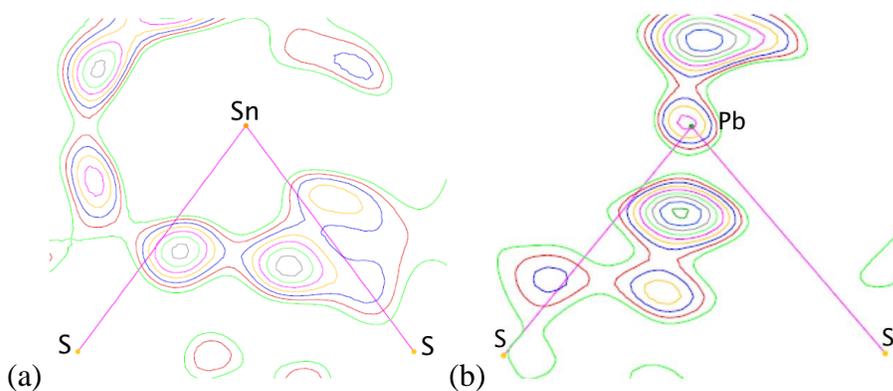


Figure 10. Difference electron density map of (a) $\text{Sn}(\text{SAr}^{\text{Pri}8})_2$ (**11**) shows contours of electron density bisecting the two M-S bonds. (b) $\text{Pb}(\text{SAr}^{\text{Pri}8})_2$ (**14**) shows a buildup of electron density within the S-Pb-S plane. Lines are shown connecting the sulfur and lead nuclei.

Conclusions

- (1) The principal forces leading to the sub- 90° bond angles observed in the chalcogenolato tetrylenes are those of intramolecular steric repulsion and dispersion between the bulky substituents across the molecules.
- (2) Dispersion forces stabilize the acute interligand angles.
- (3) Decreases in the bending angle below 90° for the heavier chalcogenolate derivatives require relatively small changes (*ca.* $1 \text{ kJ mol}^{-1} \text{ deg}^{-1}$) down to Ch-M-Ch angles of *ca.* 70° .
- (4) The size of the chalcogen also has a large effect on the geometry of the tetrylenes. Because of the small radius of oxygen, there is significantly greater interligand and bond pair-bond pair repulsion that prevents closure of the interligand angle much below 90° . The size increase between oxygen (radius = 0.63 \AA) and sulfur (1.03 \AA) or selenium (1.16 \AA) is large, so that bond pair – bond pair repulsion is

diminished.²⁷ This greatly reduces the amount of energy required to close the S(Se)-M-S(Se) angle below 90°. The wider M-O-C angles (*ca.* 10-20° wider than M-S-C angles) also reduce steric repulsion across the molecular axis on the tetrel lone pair side of the molecule which reduces the steric pressure to close the O-M-O angle. Additionally, electronegativity plays a minor role in determining the angles. The high electronegativity of oxygen promotes greater p character in its bonds relative to the more electropositive sulfur and selenium (which are still significantly more electronegative than the central metals) which favors an interligand angle closer to 90°.

Supporting Information

Experimental details for compounds **4**, **7**, **9-11**, **13**, **16**, **25**, **26**, and **28-33**;

Crystallographic Information Files, thermal ellipsoid plots, and tables of crystallographic data for **2**, **4**, **5**, **7-11**, **13-16**, **25**, **26**, and **28-33**; crystallographic data and files for the high residual value structures of **3** and **6**. ²⁹Si NMR spectra for silylenes **2** and **3**; ⁷⁷Se NMR spectra for **15** and **16**; ¹¹⁹Sn NMR spectra for **8-11** and **16**; ²⁰⁷Pb NMR spectra for **13** and **14**; ¹¹⁹Sn Mössbauer spectra for **8-11**, **16**, and **19**; Plot of $k^2\langle x_{ave}^2 \rangle$ as a function of temperature for **19**; Further discussion regarding the effect of ligand bulk on the synthesis of silylenes **1-3**; key structural parameters of calculated model systems and optimized structures (xyz data) of Ar^{Prⁱ8}-Ch-M-Ch-Ar^{Prⁱ8} (M = Si-Pb; Ch = O-Se). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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