# Synthesis and Characterization of the Monomeric Sterically Encumbered Diaryls $E\{C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)_2\}_2$ (E = Ge, Sn, or Pb)

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Received December 22<sup>nd</sup>, 2005.

Dedicated to Professor Hansgeorg Schnöckel on the Occasion of his 65th Birthday

**Abstract.** The reaction of two equivalents of LiC<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>)<sub>2</sub> with GeCl<sub>2</sub> dioxane, SnCl<sub>2</sub> or PbBr<sub>2</sub> in a diethyl ether solution resulted in the isolation of the monomeric  $\sigma$ -bonded diaryl tetrylene series E{C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>)<sub>2</sub>}<sub>2</sub> (E = Ge (1), Sn (2), or Pb(3)). Compounds 1-3 are highly sterically congested blue crystalline solids, which possess V-shaped structures and wide interligand bond angles. The solid state structures of 1-3 were determined by single-crystal X-ray methods while their solution structures were investigated by UV spectroscopy and in the cases of 2 and 3, respectively, by <sup>119</sup>Sn and <sup>207</sup>Pb NMR spectroscopy. The series 1-3 constitutes the most sterically crowded examples of  $\sigma$ -bonded diorgano group 14 derivatives yet isolated and, in contrast to previously reported :ER<sub>2</sub> species, the C-E-C angles increase with increasing atomic number.

Keywords: Germanium; Tin; Lead; Tetrylenes; Steric effects

## Introduction

The development of sterically encumbering ligands to stabilize heavier low-valent group 14 element alkylidene, alkene and alkyne analogues has been a major theme in main group organometallic chemistry over the past three decades. The first series of stable  $\sigma$ -bonded metallane divis, the dialkyls  $E\{CH(SiMe_3)_2\}_2$  (E = Ge, Sn or Pb), were reported by Lappert and co-workers beginning in 1973 [1-4]. The germanium [2], tin [1] and lead [5] derivatives were dimeric, with weak E-E interactions in the solid state, but their chemistry proved to be consistent with their formulation as bent singlet : $ER_2$  species in solution [6]. A small increase in steric congestion due to further silvl substitution, as in  $Ge\{CH(SiMe_3)_2\}C(SiMe_3)_3$ , or structural rigidity as in the cyclic species  $EC(SiMe_3)_2(CH_2)_2C(SiMe_3)_2(E = Ge, Sn)$  led to the isolation and structural characterisation of monomers in the crystalline phase [7-9].

Similar complexes, stabilized by bulky diaryl ligands have demonstrated a tendency for further metal-ligand interactions. The well characterized GeMes\*<sub>2</sub> (Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-Bu<sup>t</sup><sub>3</sub>) species [10, 11] undergoes a C-H insertion reaction below room temperature while the equivalent tin species SnMes\*<sub>2</sub> has been shown to rearrange to the arylalkylstannylene species SnMes\*(CH<sub>2</sub>CMe<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-2,5-Bu<sup>t</sup><sub>2</sub>) in solution [12, 13] Trifluoromethyl aryl derivatives are

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thought to be stabilized in solution by intramolecular F...E interactions [14–16] while dimethylamine substituted aryl species are stabilized by a secondary metal-amine interaction in the solid state [17, 18]. However, the use of bulky terphenyls, which act as unidentate ligands without lone pairs on the ligating atom, has been shown to avoid these secondary interactions [19]. Our group has previously employed the very bulky terphenyl ligand Ar' (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>)<sub>2</sub>) to stabilise the synthesis and structural characterization of the alkyne analogues of germanium [20, 21] and tin [22] Ar'EEAr' (E = Ge, Sn) and the alkene analogue Ar'(H)GeGe(H)Ar' [23, 24]. Here we report the synthesis and characterization of the heavier tetrylene series  $E\{C_6H_3$ -2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>)<sub>2</sub>\}\_2 (E = Ge (1), Sn (2), or Pb(3)).

## **Experimental Section**

All operations were carried out by using modified Schlenk techniques under an atmosphere of dry argon or nitrogen. Solvents were dried over an alumina column and degassed prior to use. The chemicals used in this study were purchased from Aldrich or Acros and used as received. GeCl<sub>2</sub>.dioxane [3] and Ar'Li (Ar' = C<sub>6</sub>H<sub>3</sub>-2,6(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>)<sub>2</sub>) [25] were prepared as described in the literature. <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>207</sup>Pb NMR spectroscopic data were recorded on Varian INOVA 400 MHz and 300 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to the deuterated solvent, <sup>119</sup>Sn NMR externally to SnMe<sub>4</sub>/C<sub>6</sub>D<sub>6</sub> and <sup>207</sup>Pb NMR externally to PbMe<sub>4</sub>/C<sub>6</sub>D<sub>6</sub>. UV-vis data were recorded on a Hitachi-1200 spectrometer.

## **Preparation of :**Ge(Ar')<sub>2</sub>, (1)

To a slurry of GeCl<sub>2</sub>·dioxane(0.70 g, 3.00 mmol) in Et<sub>2</sub>O (20 mL) was added a solution of Ar'Li (3.00 g, 7.43 mmol) (Ar' =  $C_6H_3$ -



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2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sup>i</sup><sub>2</sub>)<sub>2</sub> in Et<sub>2</sub>O (100 mL) at ambient temperature. The resultant green solution was stirred at room temperature for 24 h. Removal of the solvent *in vacuo* followed by hexane extraction, concentration to incipient crystallisation and storage at *ca.* –18 °C yielded **1** as air and moisture sensitive blue crystals, (yield 0.91 g, 1.05 mmol, 35 %). Mp: 159-161 °C.

<sup>1</sup>**H** NMR (C<sub>7</sub>D<sub>8</sub>, 300.08 MHz, 90 °C): δ 0.76 (m, 24H), 0.97 (m, 24H, CH*M*e<sub>2</sub>), 2.96 (m, 8H, C*HM*e<sub>2</sub>), 6.74 (m, 4H, Ar-H), 6.9-7.18 (m, 14H, Ar-H). <sup>13</sup>**C** NMR (C<sub>7</sub>D<sub>8</sub>, 75.45 MHz, 90 °C): δ 24.2 (CH*M*e<sub>2</sub>), 26.2 (CH*M*e<sub>2</sub>), 31.5 (CHMe<sub>2</sub>), 124.1, 127.2, 127.5, 133.7, 137.3, 139.7, 145.4, 175.0 (unsaturated carbon atom). UV-Vis (*n*-hexane): 608 nm ( $\varepsilon = 1320$ ).

## Preparation of $:Sn(Ar')_2, (2)$

In a similar manner SnCl<sub>2</sub> (0.57 g, 3.00 mmol) was reacted with Ar'Li (3.00 g, 7.43 mmol) to yield **2** as a blue, air and moisture sensitive, powder, yield 1.70 g, 1.86 mmol, 62 %). Mp: 128 °C (decomp.).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400.08 MHz, 25 °C): 0.93 (m, 12H, CH*Me*<sub>2</sub>), 1.03 (d, 12H, J = 6.9 Hz, CH*Me*<sub>2</sub>), 1.13 (m, 18H, CH*Me*<sub>2</sub>), 1.37 (d, 6H, J = 6.9 Hz, CH*Me*<sub>2</sub>), 2.87 (sept, 4H, J = 6.6 Hz, CH*Me*<sub>2</sub>), 3.09 (m, 4H, CH*Me*<sub>2</sub>), 6.97-7.32 (m, 18H, Ar-H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 75.45 MHz, 25 °C):  $\delta$  24.4 (CH*Me*<sub>2</sub>), 24.5 (CH*Me*<sub>2</sub>), 24.9 (CH*Me*<sub>2</sub>), 25.9 (CH*Me*<sub>2</sub>), 30.2 (CHM*e*<sub>2</sub>), 30.8 (CH*Me*<sub>2</sub>), 31.8 (CHM*e*<sub>2</sub>), 121.1, 121.5, 122.9, 123.0, 127.6, 128.2, 130.0, 138.3, 139.7, 145.5, 145.7, 146.1, 147.1, 197.9, 199.2 (unsaturated carbon). <sup>119</sup>Sn {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 149.00 MHz, 25 °C):  $\delta$  2235. UV-Vis (*n*-hexane): 600 nm ( $\varepsilon = 1430$ ).

Blue crystals of **2** suitable for X-ray crystallography were obtained by dissolving the blue powder in toluene (10 mL) reducing the volume to about 4 ml, and cooling in a freezer for 1 day at *ca.* -18 °C.

## *Preparation of* :Pb(Ar')<sub>2</sub>, (3)

In a similar manner  $PbBr_2$  (1.10 g, 3.00 mmol) with Ar'Li (3.00 g, 7.43 mmol) yielded **3** as, air and moisture sensitive, blue crystals, (yield 1.74 g, 1.74 mmol, 58 %). Mp: 90 °C (decomp.).

<sup>1</sup>**H** NMR (C<sub>6</sub>D<sub>6</sub>, 400.08 MHz, 25 °C): 0.91 (d, 6H, J = 6.9 Hz, CH $Me_2$ ), 1.01 (d, 6H, J = 6.9 Hz, CH $Me_2$ ), 1.09 (d, 6H, J = 6.9 Hz, CH $Me_2$ ), 1.18 (d, 12H, J = 6.9 Hz, CH $Me_2$ ), 1.25 (d, 12H, J = 6.9 Hz, CH $Me_2$ ), 1.36 (d, 6H, J = 6.9 Hz, CH $Me_2$ ), 2.76 (sept, 4H, J = 6.6 Hz, CH $Me_2$ ), 2.90 (sept, 2H, J = 6.6 Hz, CH $Me_2$ ), 3.01 (sept, 2H, J = 6.6 Hz, CH $Me_2$ ), 7.12-7.27 (m, 14H, Ar-H), 7.71 (d, 4H, Ar-H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100.52 MHz, 25 °C): δ 24.4 (CH $Me_2$ ), 24.5 (CH $Me_2$ ), 24.6 (CH $Me_2$ ), 24.7 (CH $Me_2$ ), 24.8 (CH $Me_2$ ), 25.7 (CH $Me_2$ ), 30.1 (CH $Me_2$ ), 30.8 (CH $Me_2$ ), 31.2 (CH $Me_2$ ), 122.6, 122.9, 123.0, 124.6, 126.3, 128.6, 139.7, 141.1, 143.3, 146.2, 146.9, 147.0, 147.1 (unsaturated carbon atom). <sup>207</sup>Pb NMR {<sup>1</sup>H} (C<sub>6</sub>C<sub>6</sub>, 62.77 MHz, 25 °C): δ 9430. UV-Vis (*n*-hexane): 586 nm (ε = 1490).

## X-ray Crystalllographic Studies

The crystals were removed from the Schlenk tube under a rapid flow of argon and immediately submerged in hydrocarbon oil. A suitable crystal was selected, mounted on a glass fiber attached to a copper pin, and rapidly placed in the cold stream of N<sub>2</sub> of the diffractometer for data collection. Data for **1**, **2** and **3** were collected on a Bruker SMART 1000 with use of MoK<sub> $\alpha$ </sub> ( $\lambda =$ 0.71073 Å) radiation and a CCD area detector. Empirical absorption corrections were applied using SADABS [26]. The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL [27]. Non-hydrogen atoms were refined anisotropically while hydrogens were placed at calculated positions and included in the refinement using a riding model. Some details of data collection and refinement are provided given in Table 1.

Table 1Selected X-ray Crystallographic Data for Compounds 1,2 and 3.

| compound                            | :Ge(Ar') <sub>2</sub> , (1)  | :Sn(Ar') <sub>2</sub> , (2) | :Pb(Ar') <sub>2</sub> , (3)        |
|-------------------------------------|--|-----------------------------|------------------------------------|
| formula                             | C <sub>60</sub> H <sub>74</sub> Ge.0.5C <sub>6</sub> H <sub>14</sub> | C60H74Sn.C7H8               | C <sub>60</sub> H <sub>74</sub> Pb |
| fw                                  | 910.81   | 1006.02                     | 1002.38                            |
| color, habit                        | blue block   | blue cube                   | blue block                         |
| cryst syst                          | triclinic  | orthorhombic                | monoclinic                         |
| space group                         | PĪ   | Fddd                        | $P2_1/c$                           |
| a /Å                                | 11.3595(5)   | 25.1923(7)                  | 19.7729(19)                        |
| b /Å                                | 12.7280(5)   | 26.6369(7)                  | 11.6855(11)                        |
| c /Å                                | 19.5446(8)   | 32.6326(8)                  | 21.704(2)                          |
| $\alpha$ /deg                       | 82.655(1)  | 90                          | 90                                 |
| β/deg                               | 87.907(1)  | 90                          | 96.847(2)                          |
| γ /deg                              | 69.292(1)  | 90                          | 90                                 |
| $V/Å^3$                             | 2621.46(19)  | 21897.9(1)                  | 4979.2(8)                          |
| Ζ                                   | 2  | 16                          | 4                                  |
| cryst dims, mm                      | 0.48 x 0.24 x 0.09   | 0.35 x 0.28 x 0.12          | 0.25 x 0.09 x 0.07                 |
| $d_{\text{calc}}, /(\text{g/cm}^3)$ | 1.099  | 1.221                       | 1.337                              |
| $\mu$ /mm <sup>-1</sup>             | 0.619  | 0.506                       | 3.425                              |
| no. of reflns                       | 34331  | 45805                       | 35651                              |
| no. of obsd reflns                  | 10903  | 6305                        | 9262                               |
| R, obsd reflns                      | 0.0496   | 0.0310                      | 0.0572                             |
| wR2, all                            | 0.1695   | 0.0865                      | 0.1438                             |

Further details are in the Supporting Information: Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre. CCDC 293514–293516. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

#### **Results and Discussion**

The compounds  $E\{C_6H_3-2,6-(C_6H_3-2,6-Pr_2^i)_2\}_2$  (E = Ge (1), Sn (2), or Pb(3)) were obtained in moderate yields of 35 %, 62 % and 58 %, respectively, by the reaction of two equivalents  $\text{LiC}_6H_3-2,6-(C_6H_3-2,6-Pr_2^i)_2$  with the corresponding metal dihalide in diethyl ether. Removal of the solvent *in vacuo* followed by extraction with *n*-hexane provided samples of 1-3 for spectroscopic analysis. X-ray quality blue crystals of 1 and 3 were obtained by recrystallization from *n*-hexane and of 2 by recrystallization from toluene. Crystals of 1 possess considerable thermal stability with a melting point of 159–161 °C while those of 2 and 3 decompose in the solid state at 128 °C and 98 °C, respectively.

The products 1-3 were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. At ambient temperature (25 °C) **1** demonstrated a highly complicated <sup>1</sup>H NMR spectrum with broad peaks corresponding to a number of inequivalent isopropyl environments with restricted rotation indicative of a highly congested steric environment. At elevated temperatures (90 °C) in solutions of d<sup>8</sup>-toluene the broad peaks sharpened and two regions could be observed corresponding to the isopropyl CH*Me*<sub>2</sub> protons however no coupling information could be resolved. The <sup>1</sup>H NMR spectra of **2** and **3** at ambient temperature did not show the same degree of inequivalency. However in both cases three isopropyl environments indicated by three isopropyl hydrogen and six overlapping diastereotopic methyl resonances were discernable in the ratio 2:2:4 indicating some restricted rotation.

|  | $\lambda_{max}$ /nm | C-Ge-C /°       | Ref.      |
|--|---------------------|-----------------|-----------|
| $\frac{1}{\text{Ge}\{C_6H_3-2,6-(C_6H_3-2,6-\text{Pr}^i_2)_2\}_2(1)}$          | 608                 | 112.8           | this work |
| $Ge(C_6H_2-2,4,6-Pr^i_3)(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)$                       | 580                 | unknown         | [31]      |
| $Ge\{C_6H_3-2, 6-Mes_2\}_2$  | 578                 | 114.4           | [19]      |
| $\overline{\text{GeC}(\text{SiMe}_3)_2(\text{CH}_2)_2}$ C(SiMe_3) <sub>2</sub> | 450                 | 91              | [8]       |
| GeMes*2  | 430                 | 108             | [10]      |
| $Ge\{CH(SiMe_3)_2\}_2$   | 414                 | 107 (gas phase) | [1, 3]    |
| $Ge\{C_6H_2-2,4,6-(CF_3)_3\}_2$  | 374                 | 100.0           | [32]      |
| $Ge(C_6H_3-2,6-(1-naphthyl)_2)_2$  | Orange              | 102.7           | [29]      |
| $Ge\{CH(SiMe_3)_2\}\{C(SiMe_3)_3\}$  | Red/Orange          | 111.3           | [7]       |
| $Ge\{C_6H_3-2,6-(NMe_2)_2\}_2$   | Orange              | 105.1           | [17, 18]  |

Table 2 UV-Vis data and C-Ge-C angles /° for selected compounds with two-coordinated divalent germanium atoms.

Table 3  $^{119}$ Sn chemical shifts, UV-Vis data and C-Sn-C angles /° for selected compounds With divalent two-coordinate tin atoms.

|   | $\lambda_{max}$ /nm | <sup>119</sup> Sn /ppm | C-Sn-C /°      | Ref.      |
|---|---------------------|------------------------|----------------|-----------|
| $Sn\{C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)_2\}_2$ (2)  | 600                 | 2235                   | 117.6          | this work |
| $Sn(C_6H_2-2,4,6-Pr^i_3)(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)$  | 561                 | 2208                   | unknown        | [33]      |
| $Sn\{C_6H_3-2,6-Mes_2\}_2$  | 553                 | 1971                   | 114.7          | [19, 34]  |
| SnC(SiMe <sub>3</sub> ) <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> SiMe <sub>2</sub> C(SiMe <sub>3</sub> ) <sub>2</sub> | 546                 | 2299                   | 117.6          | [35]      |
| $Sn{CH(SiMe_3)_2}_2$  | 495                 | 2328                   | 97 (gas phase) | [1, 36]   |
| $SnC(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$  | 484                 | 2323                   | 86.7           | [9]       |
| SnMes*2   | 476                 | 980                    | 103.6          | [12]      |
| $Sn\{C_6H_2-2,4,6-(CF_3)_3\}_2$   | 345                 | 723                    | 98.3           | [14]      |
| $Sn\{C_6H_3-2,6-(NMe_2)_2\}_2$  | Red                 | 442                    | 105.6          | [17]      |
| Sn(C <sub>6</sub> H <sub>2</sub> -2,4,6-Pr <sup>i</sup> <sub>3</sub> )C(N <sub>2</sub> )SiPr <sup>i</sup> <sub>3</sub>      | Red                 | 1323                   | 99.2           | [37]      |
| SnC <sub>6</sub> H <sub>2</sub> -2,4,-Pr <sup>i</sup> <sub>2</sub> -6-C(Me)CH <sub>2</sub> CSiPr <sup>i</sup> <sub>3</sub>  | Red                 | 1426                   | 94.4           | [37]      |

tation of the flanking phenyl rings in solution.Similar inequivalence was observed in the corresponding <sup>13</sup>C NMR spectra. This is in marked contrast to the previously isolated series  $E\{C_6H_3-2,6-Mes_2\}_2$  (E = Ge, Sn, or Pb, Mes =  $C_6H_2-2,4,6-Me_3$ ) where in all cases only one ortho-methyl environment was observed and no dynamic character was observed in the range -90 to 80 °C [19].

In addition, compounds 1-3 were studied by UV-vis spectroscopy. Absorption maxima were observed at 608, 600 and 586 nm, respectively. Heavier tetrylenes :  $ER_2$  (E = Ge, Sn, Pb) exist in a singlet ground state with the lone pair on E in a mainly s-type orbital and an empty formally nonbonding p-orbital.  $\lambda_{max}$  corresponds to the singlet-triplet gap, which can be correlated within limits to the solution C-E-C bond angle [28]. In cases of extreme sterical congestion at the metal atom, widening of the C-E-C bond angle with a corresponding lengthening of the E-C bonds is observed. This lowers the energy of the p-orbital and raises the energy of the n-orbital thereby decreasing the HOMO-LUMO gap [19]. However other factors including the electronic properties of the ligand and the presence of secondary element-ligand interactions clearly play a role [28]. For example, the correlation between  $\lambda_{\text{max}}$  and the interligand angle does not provide a full explanation for a blue-shift observed for GeMes<sup>\*</sup><sub>2</sub> ( $\lambda_{max} = 430 \text{ nm}$ ) [11] in comparison to SnMes<sup>\*</sup><sub>2</sub> ( $\lambda_{max} = 476$  nm) [12] suggesting that metal porbital /  $\pi$  or  $\pi^*$  interactions from geometrically distorted aryl groups are possible. Nonetheless, an increasing singlettriplet gap is observed in the sequence Ge < Sn < Pb together with a corresponding decrease in  $\lambda_{max}$  [28]. Comparison of the above maxima with those of the less crowded series  $E\{C_6H_3-2,6-Mes_2\}_2$  [19] (E = Ge, Sn, or Pb) ( $\lambda_{max}$  = 578, 553 and 526 nm) demonstrates the expected higher values for  $\lambda_{max}$  caused by the increased size of Ar' in comparison to  $C_6H_3$ -2,6-Mes<sub>2</sub> (Tables 2, 3 and 4). Wider C-E-C bond angles are therefore expected for **1**, **2** and **3** (see below). The recently synthesized and structurally characterized diarylgermylenes Ge(triph)<sub>2</sub> (triph =  $C_6H_2$ -2,4,6-Ph<sub>3</sub>) and Ge(bisnap)<sub>2</sub> (bisnap =  $C_6H_3$ -2,6-(1-naphthyl)<sub>2</sub>), which were reported as 'strain-free' germylenes with little steric congestion, were not analysed by UV-vis spectroscopy but were reported as orange solids which suggests a much lower  $\lambda_{max}$  and consequently a higher HOMO-LUMO gap [29].

The <sup>119</sup>Sn NMR chemical shift of **2** (2235 ppm) is in the range previously observed for monomeric species 2328-1971 ppm (Table 3) but is shifted down-field in comparison to SnMes\*<sub>2</sub> (980 ppm) [12] and the trifluoromethyl aryl derivative Sn{C<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>}<sub>2</sub> (723 ppm) [14]. This can be rationalized from the general expectation of low shielding due to the low coordination environment at the tin atoms with the latter examples stabilized by further metal-ligand interactions in solution. It is not possible however to rationalize the <sup>119</sup>Sn NMR chemical shifts on the basis of the  $\sigma$ -electron donor characteristics of the ligands since the shift values tend to be dominated by the paramagnetic contributions [30]. A wider interligand angle is expected to increase such contributions and this is consistent with the

| Table 4 | <sup>207</sup> Pb NMR | chemical shifts, | UV-Vis d | lata and C | C-Pb-C | angles / | for select | ed compounds | s with ty | wo-coordinate | divalent | lead atoms. |
|---------|-----------------------|------------------|----------|------------|--------|----------|------------|--------------|-----------|---------------|----------|-------------|
|---------|-----------------------|------------------|----------|------------|--------|----------|------------|--------------|-----------|---------------|----------|-------------|

|   | $\lambda_{max}$ /nm | <sup>207</sup> Pb /ppm | C-Pb-C /° | Ref.      |
|---|---------------------|------------------------|-----------|-----------|
| PbC(SiMe <sub>3</sub> ) <sub>2</sub> SiMe <sub>2</sub> CH <sub>2</sub> SiMe <sub>2</sub> C(SiMe <sub>3</sub> ) <sub>2</sub>   | 610                 | 10050                  | 117.1     | [38]      |
| $Pb\{(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)\}_2$   | 610                 | 9751                   | 116.3     | [39]      |
| $Pb\{C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)_2\}_2(3)$   | 586                 | 9430                   | 121.5     | this work |
| $Pb(C_6H_2-2,4,6-(CH_2SiMe_3)_3)$   |                     |                        |           |           |
| $(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)$   | 560                 | 8873                   | unknown   | [39]      |
| Pb{C <sub>6</sub> H <sub>3</sub> -2,6-(C <sub>6</sub> H <sub>2</sub> -2,4,6-Pr <sup>i</sup> <sub>3</sub> ) <sub>2</sub> }CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -4-Pr <sup>i</sup> | 556                 | 8858                   | 97.6      | [41]      |
| $Pb(C_6H_2-2,4,6-Pr^i_3)(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)$  | 550                 | 8888                   | unknown   | [39]      |
| $Pb{CH(SiMe_3)_2}(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)$   | 531                 | 8884                   | unknown   | [39]      |
| $Pb\{C_6H_3-2, 6-Mes_2\}_2$   | 526                 | 8844                   | 114.5     | [19, 40]  |
| $Pb\{C_6H_3-2, 6-(C_6H_2-2, 6-Pr_1^i_2)_2\}Bu^t$  | 520                 | 8275                   | 102.5     | [41]      |
| $Pb\{C_{6}H_{3}-2,6-(C_{6}H_{2}-2,6-Pr^{i}_{2})_{2}\}C_{6}H_{4}-4-Bu^{t}$   | 462                 | 7275                   | 94.5      | [41]      |
| $Pb\{C_{6}H_{3}-2,6-(C_{6}H_{2}-2,4,6-Pr^{i}_{3})_{2}\}Bu^{t}$  | 470                 | 7853                   | 100.5     | [40]      |
| $Pb\{C_6H_3-2,6-(C_6H_3-2,6-Pr_2)_2\}Me$  | 470                 | 8738                   | 91.8      | [41]      |
| $Pb\{C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)_2\}Me$  | 466                 | 7420                   | 101.4     | [40]      |
| $Pb\{C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)_2\}Ph$  | 460                 | 6657                   | 95.6      | [40]      |
| PbMes*(CH <sub>2</sub> CMe <sub>2</sub> C <sub>6</sub> H <sub>2</sub> -2,5-Bu <sup>t</sup> ) <sub>2</sub>   | 406                 | 5067                   | 94.8      | [5]       |
| $Pb\{CH(SiMe_3)_2\}_2$  | Purple              | 9112                   | unknown   | [42]      |
| $Pb(C_6H_2-2,4,6-Pr^i_3)(C_6H_2-2,4,6-(CH(SiMe_3)_2)_3)$  | Purple              | 8888                   | unknown   | [39]      |
| $Pb\{C_6H_2-2,4,6-(CF_3)_3\}_2$   | Yellow              | 4878                   | 94.5      | [16]      |

266 ppm downfield chemical shift of **2** (C-Sn-C = 117.6°) in comparison to Sn{C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>}<sub>2</sub> (C-Sn-C = 114.7°) [19]. Similarly the <sup>207</sup>Pb NMR chemical shift of **3** (9430 ppm) is in the range previously observed (10050-7420 ppm) (Table 4) but downfield of Pb{C<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>}<sub>2</sub> (4878 ppm) [16]. In addition the chemical shift of **3** is almost 600 ppm further downfield than that of Pb{C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>}<sub>2</sub> which is consistent with the wider C-Pb-C angle (121.5° vs 114.5°) [19].

### X-ray Crystal Structures

Crystals of 1-3 were studied by X-ray diffraction and thermal ellipsoid plots are shown in Figures 1, 2 and 3, respectively. They exist as V-shaped, discrete monomers with the closest E-E (E = Ge, Sn, Pb) distances being 10.245 Å, 11.648 Å and 9.777 Å, respectively. The E-C bond lengths are 2.033(2) Å and 2.048(2) Å for 1, 2.255(2) Å for 2 and 2.379(9) Å and 2.390(8) Å for 3 with any further metal-ligand interactions being longer than 3.0 A. These values are similar to those seen in previously reported  $\sigma$ -bonded divalent organometallic species although for 3 a lengthening of the Pb-C bonds of 0.03-0.04 Å is observed in comparison to Pb{C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>}<sub>2</sub> (2.334(12) Å). However the C-E-C bond angles vary from 112.77(9)° for Ge to 121.5(3)° for Pb whereas for  $E\{C_6H_3-2, 6-Mes_2\}_2$  (E = Ge, Sn, Pb) they were essentially invariant having values of 114.4(2)°, 114.7(2)° and 114.5(6)°, respectively [19]. The large C-Ge-C angles in 1 and  $Ge\{C_6H_3-2,6-Mes_2\}_2$  may also be compared with those experimentally observed in  $Ge(C_6H_3-2,6 (1-naphthyl)_2)_2$   $(102.72(9)^\circ)$  and calculated for GePh<sub>2</sub> (101.6°) [29]. In the solid state the crowded nature of  $Ge\{C_6H_3-2, 6-(C_6H_3-2, 6-Pr_2)_2\}_2$  (1) leads to significant distortions in the terphenyl substituents. The flanking rings of one terphenyl substituent are tilted by the angles 15.89° and 8.68° from the C-C vectors (i.e. C(32)-C(37) and C(36)-C(49)) through which they are attached to the central phe-



Figure 1 Thermal ellipsoid of 1 with 50 % probability. Hydrogen atoms are not shown. Selected bond distances /Å and angles /°:

nyl ring and the central phenyl ring is tilted  $27.6^{\circ}$  from the Ge(1)-C(31) vector (Fig. 4). In contrast for **2** the flanking rings of the terphenyl substituents are tilted by  $8.30^{\circ}$  and  $1.35^{\circ}$  and the central phenyl ring is only tilted by  $14.1^{\circ}$  from the Sn(1)-C(1) vector whilst for **3** the terphenyl sustituents are tilted by  $9.77-4.94^{\circ}$  and the central phenyl rings are tilted by  $14.07^{\circ}$  and  $14.54^{\circ}$ . For **2** and **3** the C-E-C (E = Sn, Pb) bond angles are wider than those in previously reported species which is consistent with the steric bulk of Ar'. The highly red shifted UV-vis absorption maxima observed for



Figure 2 Thermal ellipsoid of 2 with 50 % probability. Hydrogen atoms are not shown. Selected bond distances /Å and angles  $/^\circ$ :

Sn(1)-C(1) 2.255(2), C(1)-C(2) 1.412(2), C(1)-C(6) 1.421(2); C(1)'-Sn(1)-C(1) 117.56(8), C(2)-C(1)-C(6) 117.3(2), C(2)-C(1)-Sn(1) 125.30(12), C(6)-C(1)-Sn(1) 114.72(11).



Figure 3 Thermal ellipsoid of 3 with 50 % probability. Hydrogen atoms are not shown. Selected bond distances /Å and angles /°:

1 and 2 suggest a relaxation to an even wider angle in solution than those observed in the solid state [41].

### Conclusion

The characterization of a series of three new diaryl germanium, tin and lead derivatives of the very bulky terphenyl ligand Ar' show that they possess the widest cur-



**Figure 4** Thermal ellipsoid plot with 50 % probability illustrating the distortions of one of the terphenyl substituents in **1**.

rently known C-E-C (E = Ge, Sn or Pb) angles for :ER<sub>2</sub> species in the case of tin and lead and the second widest in the case of germanium. Examination of their UV-Vis spectra show that they display the longest wavelength n - p, HOMO-LUMO, transitions of all known diorgano derivatives of Ge<sup>II</sup>, Sn<sup>II</sup> and Pb<sup>II</sup>. The red shift to > 600 nm in the case of the germanium and tin derivatives 1 and 2 led us to speculate that the C-E-C angles may be even wider in solution than they are in the solid state. This is consistent with the experimentally determined angular sequence C-Pb-C (121.5°) > C-Sn-C (117.6°)> C-Ge-C (112.8°) found in the solid state which is opposite to that normally expected on steric grounds (*cf.* C-E-C in E{C<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, E = Ge (100.0°) [32], Sn (98.3°) [14], Pb (94.5°) [16].

Acknowledgements. We would like to acknowledge the National Science Foundation for funding this work and *Dr. A. F. Richards* and *M. Jarosh* for their help in solving the crystal structure of **2**.

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