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Synthesis and Characterization of the Monomeric Diaryls $M\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (M = Ge, Sn, or Pb; Mes = $2,4,6\text{-}Me_3C_6H_2-$) and Dimeric Aryl−Metal Chlorides $[M(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ (M = Ge or Sn)

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The reaction of 2 equiv of $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2-$) with $GeCl_2\cdot$dioxane, $SnCl_2$, or $PbCl_2$ in ether solution has resulted in the isolation of rare examples of monomeric, σ-bonded, diaryl derivatives $M\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (M = Ge (**1**), Sn (**2**), or Pb (**3**)). The compounds **1**−**3** are thermally stable, purple, crystalline solids with V-shaped geometries and remarkably wide (*ca.* 114.5°) interligand bond angles. The monoaryl metal chloride derivatives $[M(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ (M = Ge (**4**) or Sn (**5**)) were isolated by treatment of the appropriate dichlorides with either 1 equiv of $LiC_6H_3\text{-}2,6\text{-}Mes_2$ or 1 equiv of the diaryls **1** or **2**. The orange germanium compound **4** has a dimeric structure in which the monomers are linked by a relatively weak, 2.443(2) Å, Ge−Ge interaction. In sharp contrast, its yellow tin analogue **5** has a dimeric structure in which three-coordinate tin centers are associated by asymmetrically bridging chlorides. The compounds **1**−**3** constitute a unique, structurally characterized diaryl series for Ge, Sn, and Pb and display evidence of steric crowding that is significantly greater than that observed in previously known σ-bonded diorgano group 14 derivatives. The compounds **4** and **5** are the first fully structurally characterized organometal halide derivatives of Ge or Sn in which the organic ligand is monodentate, purely σ-bonded, and nonchelating.

Introduction

The chemistry of stable, σ-bonded,[1] divalent organic derivatives of the heavier main group 14 elements (i.e., MR_2, M = Ge, Sn, or Pb; R = monodentate alkyl or aryl group) has been a major research theme in main group organometallic chemistry for over 20 years. The first examples of such compounds were the dialkyls $M\{CH(SiMe_3)_2\}_2$ (M = Ge, Sn, or Pb) which were reported by Lappert and co-workers.[2] The germanium and tin derivatives had M−M bonded dimeric structures in the solid state, but they were shown to be monomeric in solution. Moreover, their chemistry proved to be consistent with their formulation as bent, singlet $:MR_2$ species that were essentially heavier analogues of carbenes.[3] Subsequent work has extended the range of monomeric alkyls to include the structurally characterized compounds $Ge\{CH(SiMe_3)_2\}C(SiMe_3)_3$[4] and $SnC(SiMe_3)_2(CH_2)_2C(SiMe_3)_2$.[5] In addition, there are closely related silyl derivatives $[Sn\{Si(SiMe_3)_3\}_2]_2$[6] (dimeric in the solid state, with Sn−Sn = 2.8247(6) Å), $Pb\{Si(SiMe_3)_3\}_2$[6] (monomer, Si−Pb−Si = 113.56(10)°), and the dimeric germanium compounds $Ge_2[Si\{SiMe(i\text{-}Pr)_2\}_3]_4$[7] and $Ge_2[Si\{Si(i\text{-}Pr)_3\}_3]_4$ (Ge−Ge distances = 2.267(1) Å average).[7] Parallel work on diaryls has afforded the well-characterized species $\{Ge(C_6H_3\text{-}2,6\text{-}Et_2)_2\}_2$,[8] $\{GeMes(C_6H_3\text{-}2,6\text{-}(i\text{-}Pr)_2)_2\}_2$,[9] $MMes^*_2$ (M = Ge[10] or Sn;[11] Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2-$), $M\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$ (M = Sn[12] or Pb[13]), the solid $Sn\{C_6H_3\text{-}2,6\text{-}(CF_3)_2\}_2$[14] (characterized by Mössbauer spectroscopy), and the solution species $M(C_6H_2\text{-}2,4,6\text{-}(i\text{-}Pr)_3)\ [C_6H_2\text{-}2,4,6\text{-}\{CH(SiMe_3)_2\}_3]$ (M = Ge,[15] Sn,[16a] or Pb[16b]). The $GeMes^*_2$ species, however, undergoes a C−H insertion reaction by the germanium center below room temperature,[10] and its tin analogue[11]

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is accessible only through use of the amide precursor $Sn\{N(SiMe_3)_2\}_2$.[17] The trifluoromethyl aryl derivatives may owe their stability to intramolecular−F···M (M = Sn or Pb) interactions.[12,13]

The use of the above range of monodentate alkyl or aryl ligands has resulted in the isolation of only two monosubstituted compounds of formula M(X)R (M = Ge, Sn, or Pb; X = halide; R = monodentate, σ-bound, alkyl or aryl ligand) to date, i.e., the species Ge(Cl)Mes* which was described as a monomer in both the solution and solid phases, although no other structural details were given.[18] The related lithium halide adduct $(Me_3Si)_3CGeCl{\cdot}LiCl{\cdot}3THF$[19] has also been reported, and some of its chemistry has been explored although no structural details have been published.

We are anxious to develop the chemistry of M(X)R species (where R is a unidentate[20] ligand without lone pairs on the ligating atom) in order to explore the use of stable M(X)R compounds as precursors to species in which the MR fragment could behave in a multiply-bonded fashion. In this paper, we report the facile synthesis and characterization of the thermally stable diaryl compounds $M\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (M = Ge (**1**), Sn (**2**), or Pb (**3**), Mes = $2,4,6\text{-}Me_3C_6H_2-$) and the dimeric monoaryl metal halides $[M(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ (M = Ge (**4**) or Sn (**5**)).

Experimental Section

General Procedures. All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from Na/K alloy and degassed twice immediately before use. The compounds $LiC_6H_3\text{-}2,6\text{-}Mes_2$[21] and $GeCl_2{\cdot}dioxane$[2d] were prepared according to literature procedures. Anhydrous $SnCl_2$ and $PbCl_2$ were purchased commercially and used as received. ^1H, ^{13}C, ^{117}Sn, ^{119}Sn, and ^{207}Pb NMR data were recorded on a Bruker 300 MHz instrument and referenced to the deuterated solvent in the case of the ^1H and ^{13}C NMR spectra. The Sn and Pb NMR spectra were referenced to $SnMe_3$ or $Pb(OAc)_4$. Infrared data were recorded on a Perkin PE-1430 instrument. UV−vis data were recorded on a Hitachi-1200 instrument.

$Ge\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (1). $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (0.96 g, 3.0 mmol) in Et_2O (20 mL) was added to $GeCl_2{\cdot}dioxane$ (0.35 g, 1.5 mmol) in Et_2O (20 mL) at *ca.* 0 °C with rapid stirring. The solution, which became an intense purple color, was stirred at *ca.* 0 °C for 30 min and then stirred for a further 4 h at room temperature. The volatile materials were removed under reduced pressure, and the residue was extracted with warm toluene (40 mL). After filtration through Celite, the solution was reduced to incipient crystallization and stored in a *ca.* −20 °C freezer for 30 h to give **1** as purple crystals. Yield: 0.45 g, 43%; dec 185 °C. Anal. Calcd for $C_{48}H_{50}Ge$: C, 82.42; H, 7.20. Found: 82.12; H, 7.31. ^1H NMR (C_6D_6): δ 1.88 (s, 12H, *o*-CH_3), 2.20 (s, 6H, *p*-CH_3), 6.71 (d, 2H, J_{HH} = 7.5 Hz, *m*-C_6H_3), 6.76 (s, 4H, *m*-Mes), 7.05 (tr, 1H, J_{HH} = 7.89 Hz, *p*-C_6H_3). ^{13}C {^1H} NMR (C_6D_6): δ 21.20 (*p*-CH_3), 22.01 (*o*-CH_3), 129.01 (*m*-Mes), 129.59 (*p*-C_6H_3), 129.83 (*m*-C_6H_3), 136.64 (*p*-Mes), 136.64 (*o*-Mes), 139.41 (*i*-Mes), 145.08 (*o*-C_6H_3), 169.58 (*i*-C_6H_3). UV−vis (ethyl ether): λ_{max} 578 nm. IR (Nujol, cm^{-1}): 3070 (sh), 3020 (sh), 2910 (vs), 1720 (w), 1601 (s), 1560 (m), 1550 (m), 1260 (m), 1210 (w), 1170 (w), 1110 (m), 1080 (m), 1030 (m), 850 (s), 800 (s), 770 (w), 740 (m), 660 (w), 610 (vw), 580 (vw), 480 (vw), 370 (vw), 255 (vw), 245 (vw).

$Sn\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (2). Compound **2** was synthesized in a manner similar to **1** by adding $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (1.22 g, 3.8 mmol) in Et_2O (20 mL) to $SnCl_2$ (0.36 g, 1.9 mmol) in Et_2O (20 mL) at *ca.* 0 °C with rapid stirring. A similar work-up procedure afforded **2** as purple crystals. Yield: 0.66 g, 46.5%; dec 175 °C. Anal. Calcd for $C_{48}H_{50}Sn$: C, 77.33; H, 6.76. Found: C, 77.82; H, 6.98. ^1H NMR (C_6D_6): δ 1.90 (s, 12H, *o*-CH_3), 2.21 (s, 6H, *p*-CH_3), 6.77 (s, 4H, *m*-Mes), 6.80 (d, 2H, J_{HH} = 7.5 Hz, *m*-C_6H_3), 7.12 (tr, 1H, J_{HH} = 7.8 Hz, *p*-C_6H_3). ^{13}C {^1H} NMR (C_6D_6): δ 21.21 (*p*-CH_3), 21.61 (*o*-CH_3), 128.68 (*p*-C_6H_3), 129.12 (*m*-Mes), 130.44 (*m*-C_6H_3), 136.75 (*p*-Mes), 136.87 (*o*-Mes), 139.54 (*i*-Mes), 147.38 (*o*-C_6H_3). ^{117}Sn {^1H} NMR (C_6D_6): δ 645. ^{119}Sn {^1H} NMR: δ 635. UV−vis (ethyl ether): λ_{max} 553 nm. IR (Nujol, cm^{-1}): 3080 (sh), 3030 (sh), 2920 (vs), 1601 (m), 1260 (m), 1210 (vw), 1175 (vw), 1100 (m), 1020 (m), 850 (m), 800 (m), 730 (m), 570 (vw), 475 (vw), 360, 250 (m).

$Pb\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (3). This compound was synthesized from $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (1.24 g, 3.86 mmol) in Et_2O/hexane (3:1, 20 mL) and $PbCl_2$ (0.54 g, 1.94 mmol) in Et_2O/hexane (3:1, 20 mL) and purified in a manner identical to **1** to afford the product **3** as purple crystals. Yield: 0.98 g, 60.7%; dec 197−199 °C. Anal. Calcd for $C_{48}H_{50}Pb$: C, 69.12; H, 6.05. Found: C, 68.96; H, 6.00. ^1H NMR (C_6D_6): δ 1.92 (s, 12H, *o*-CH_3), 2.21 (s, 6H, *p*-CH_3), 6.80 (s, 4H, *m*-Mes), 7.26 (tr, 1H, J_{HH} = 7.8 Hz, *p*-C_6H_3), 7.47 (d, 2H, J_{HH} = 7.5 Hz, *m*-C_6H_3). ^{13}C NMR (C_6D_6): δ 21.20 (*p*-CH_3), 21.32 (*o*-CH_3), 126.66 (*p*-C_6H_3), 129.01 (*m*-Mes), 136.45 (*p*-Mes), 136.48 (*o*-Mes), 137.46 (*m*-C_6H_3), 139.91 (*i*-Mes), 149.34 (*o*-C_6H_3). ^{207}Pb {^1H} NMR (C_6D_6): δ 3870. UV−vis (ethyl ether): λ_{max} 526 nm. IR (Nujol, cm^{-1}): 3070 (sh), 3020 (sh), 2900 (vs), 2720 (w), 1605 (m), 1555 (w), 1530 (w), 1255 (w), 1210 (w), 1080 (m), 1005 (m), 1030 (m), 1005 (m), 880 (w), 845 (s), 795 (s), 735 (m), 725 (s), 710 (w), 565 (w), 455 (w), 405 (w), 370 (m), 305 (m), 280 (w), 243 (m).

$[Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2$ (4). Method A. With rapid stirring and cooling to *ca.* −78 °C, $2,6\text{-}Mes_2C_6H_3Li$ (0.8 g, 2.5 mmol) in THF (20 mL) was added dropwise to $GeCl_2{\cdot}dioxane$ (0.6 g, 2.5 mmol in THF (20 mL). After the solution was stirred for 2 h, the solution was warmed to room temperature and all of the volatile materials were removed under reduced pressure. The dark red residual material was extracted with hexane (40 mL), and the solution was filtered and concentrated to incipient crystallization. Storage at *ca.* −20 °C for 1 day gave the product **4** as orange crystals. Yield: 0.41 g, 0.98 mmol, 39.0%.

Method B. $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (2.0 g, 6.23 mmol) in THF (20 mL) was added to a solution of $GeCl_2{\cdot}dioxane$ (0.72 g, 3.12 mmol) in THF (10 mL) at *ca.* −78 °C with rapid stirring. The solution immediately turned purple and was stirred for an additional 1 h before being introduced via cannula to $GeCl_2{\cdot}dioxane$ (0.72 g, 3.12 mmol) in THF (10 mL) at *ca* −78 °C with rapid stirring. After 2 h at *ca.* −78 °C, the solution had turned a magenta color. It was warmed to −10 °C, and the volatile materials were removed under reduced pressure. The residual solid was extracted with hexane (40 mL), filtered through Celite, and concentrated to incipient crystallization. Storage in a *ca.* −20 °C freezer for 2 days gave the product **4** as orange crystals. Yield: 0.95 g, 2.25 mmol, 36.2%; mp 185−190 °C.

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Table 1. Experimental Details for Data Collection, Reduction, and Refinement for Compounds 1–5

	1	2	3	4	5
formula	$C_{48}H_{50}Ge$	$C_{48}H_{50}Sn$	$C_{48}H_{50}Pb$	$C_{24}H_{25}ClGe$	$C_{24}H_{25}ClSn$
fw	699.47	745.57	834.07	421.48	467.58
cryst dimens, mm	0.20 × 0.07 × 0.04	0.68 × 0.24 × 0.14	0.5 × 0.1 × 0.1	0.40 × 0.40 × 0.30	0.4 × 0.4 × 0.4
color	violet-magneta dichroic	purple	purple	orange	yellow
cryst syst	orthorhombic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	*Fdd*2	*Fdd*2	*Fdd*2	*C*2/*m*	$P\bar{1}$
a (Å)	20.676(3)	20.991(10)	21.078(4)	10.024(2)	8.360(2)
b (Å)	42.255(5)	42.44(2)	42.546(9)	22.667(5)	11.595(2)
c (Å)	8.4089(9)	8.392(3)	8.388(2)	9.012(2)	12.061(2)
α (deg)					75.67(3)
β (deg)				99.64(3)	71.28(3)
γ (deg)					82.86(3)
V (Å^3)	7347(2)	7476(6)	7522(3)	2018.7(8)	1071.5(4)
Z	8	8	8	4	2
d_{calc} (Mg/m^3)	1.265	1.325	1.473	1.387	1.449
μ (mm^{-1})	1.365	0.716	1.372	3.290	1.321
GOF	1.038	1.118	1.012	0.897	0.591
R1 (obsd data)	0.0298	0.0375	0.0403	0.0659	0.0391
wR2 (all data)	0.0684	0.1099	0.0887	0.1748	0.1046
largest diff peak (e Å^{-3})	0.191	1.734	0.695	1.361	0.609

Anal. Calcd for $C_{24}H_{25}ClGe$: C, 68.39; H, 5.98. Found: C, 68.71; H, 6.04. ^1H NMR (C_6D_6): δ 2.12 (s, 12H, *o*-CH_3), 2.23 (s, 6H, *p*-CH_3), 6.81 (s, 4H, *m*-Mes), 6.85 (d, 2H, J_{HH} = 7.20 Hz, *m*-C_6H_3), 7.11 (tr, 1H, J_{HH} = 7.20 Hz, *p*-C_6H_3). ^{13}C NMR (C_6D_6): δ 21.33 (*p*-CH_3), 21.56 (*o*-CH_3), 128.77 (*o*-Mes), 129.27 (*m*-Mes), 130.64 (*o*-C_6H_3), 137.07 (*m*-C_6H_3), 137.45 (*p*-C_6H_3), 137.99 (*p*-Mes), 146.38 (*i*-Mes), 153.93 (*i*-C_6H_3). IR (Nujol cm^{-1}): 2910 (s), 1620 (w), 1560 (w), 1300 (w), 1260 (m), 1109 (m), 1092 (m), 1030 (w), 870 (m), 850 (m), 805 (m), 395 (w), 350 (m), 320 (m), 250 (m).

[Sn(Cl){C_6H_3-2,6-Mes$_2$}]$_2$ (5). Method A. LiC_6H_3-2,6-Mes$_2$ (1.87 g, 5.8 mmol) in toluene (30 mL) was added to a solution of $SnCl_2$ (1.10 g, 5.8 mmol) in toluene (30 mL) at room temperature with rapid stirring, which was continued for a further 2 h. The solution was diluted with 10 mL of hexane, filtered, and stored in a *ca.* −20 °C freezer for 1 day to give the product **5** as yellow crystals. Yield: 1.82 g, 3.89 mmol, 67%; mp 186 °C.

Method B. 3 (0.35 g, 0.5 mmol) in toluene (20 mL) was added to a suspension of $SnCl_2$ (0.1 g, 0.525 mmol) in toluene (10 mL) and stirred at room temperature for 4 h. The solution was diluted with hexane (*ca.* 7–8 mL) and filtered through Celite. Storage in a −20 °C freezer for 30 h afforded **5** as yellow crystals. Yield 0.21 g (45%). Anal. Calcd for $C_{24}H_{25}ClSn$: C, 61.65; H, 5.39. Found C, 61.15; H, 5.62. ^1H NMR (C_6D_6): δ 2.14 (s, 12H, *o*-CH_3), 2.22 (s, 6H, *p*-CH_3), 6.81 (s, 4H, *m*-Mes), 6.98 (d, 2H, J_{HH} = 7.80 Hz, *m*-C_6H_3), 7.20 (tr, 1H, J_{HH} = 7.80 Hz, *p*-C_6H_3). ^{13}C {^1H} NMR (C_6D_6): δ 21.29 (*p*-CH_3), 21.70 (*o*-CH_3), 129.13 (*m*-Mes), 129.19 (*o*-C_6H_3), 129.29 (*m*-C_6H_3), 136.79 (*p*-C_6H_3), 137.17 (*p*-Mes), 138.12 (*i*-Mes), 147.60 (*o*-Mes), 177.54 (*i*-C_6H_3). ^{117}Sn {^1H} NMR (C_6D_6): δ 572. ^{119}Sn {^1H} NMR (C_6D_6): δ 562. IR (Nujol, cm^{-1}): 2920 (s), 1601 (w), 1090 (w), 1030 (w), 1010 (w), 850 (m), 800 (m), 690 (w), 570 (m), 330 (m).

X-ray Crystallography. Sample preparation consisted of coating the crystal with hydrocarbon oil, mounting it on a glass fiber, and placing it under a cold stream of N_2 on the diffractometer.[22] X-ray data for **1** and **4** were collected at 130 K on Siemens P4 and Siemens P2$_1$ diffractometers using Cu Kα (λ = 1.541 78 Å) radiation. The diffractometers were each equipped with a low-temperature device and a nickel or graphite monochromator. X-ray data for **2**, **3**, and **5** were collected at 130 K on a Siemens R3 m/v diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Unit cell parameters were obtained from a least-squares fit of at least 20 well-centered reflections with 25 ≤ 2θ ≤ 30° for **2**, **3**, and **5** and 50 ≤ 2θ ≤ 60° for **1** and **4**. Additional experimental details for all compounds are given in Table 1. The structure of all compounds were solved by direct methods.[23] The phenyl and methyl hydrogen atoms were placed in idealized positions using a riding model and C–H distances of 0.96 and 0.97 Å, respectively. An absorption correction was applied using the program XABS2[24] for **1**, **3**, **4**, and **5** and by the method of ψ-scans for **2**. All compounds were refined to convergence by using anisotropic thermal parameters for all non-hydrogen atoms. For **4**, a 50/50 conformational disorder was modeled by computing the occupancy of the Ge atom at 0.5.

Results and Discussion

Syntheses and Spectroscopy. The compounds M{C_6H_3-2,6-Mes$_2$}$_2$ (M = Ge (**1**), Sn (**2**), Pb (**3**)) were obtained in moderate, purified yields of 43%, 47%, and 61%, respectively, by the reaction of 2 equiv of LiC_6H_3-2,6-Mes$_2$ with MCl_2 in ether (Scheme 1). Crystallization from toluene provided samples of **1**–**3** as X-ray quality, purple crystals, which were stable in the absence of air and moisture. They also possess considerable thermal stability with melting points in the range 175–199 °C (dec)).

The monoaryl derivatives **4** and **5** were also prepared in moderate yields (47% and 45%, respectively), either by the reaction of 1 equiv of LiC_6H_3-2,6-Mes$_2$ with the appropriate dichloride or in comparable yields by the reaction of the dichloride with **1** or **2**. Compounds **4** and **5** are stable at room temperature in toluene or hexane solutions and in the solid state (mp = 191–195 and 186 °C, respectively). Several attempts to isolate the corresponding monoaryl lead compound according to Scheme 1 were unsuccessful. Instead, 1,3-Mes$_2C_6H_4$ was the only pure compound to be isolated. The products **1**–**5** were also characterized by ^1H and ^{13}C NMR spectroscopy. No dynamic character was observed in the range from −90 to 80 °C. In addition, compounds **1**–**3** were studied by UV–vis spectroscopy. Absorption maxima were observed at 578, 553, and 526 nm, respectively. The wavelength of the maximum absorption seen for **1** (i.e., 578 nm) may be contrasted with the value of 430 nm reported for GeMes*$_2$.[10b] The blue shift seen for the latter was attributed[10b] to the absence of coplanarity of

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[22] This method is described by Hope, H. A Practicum in Synthesis and Characterization. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

[23] *SHELXTL, A Program for Crystal Structure Determinations*, Version 5.03; Siemens Analytical Instruments: Madison, WI, 1994.

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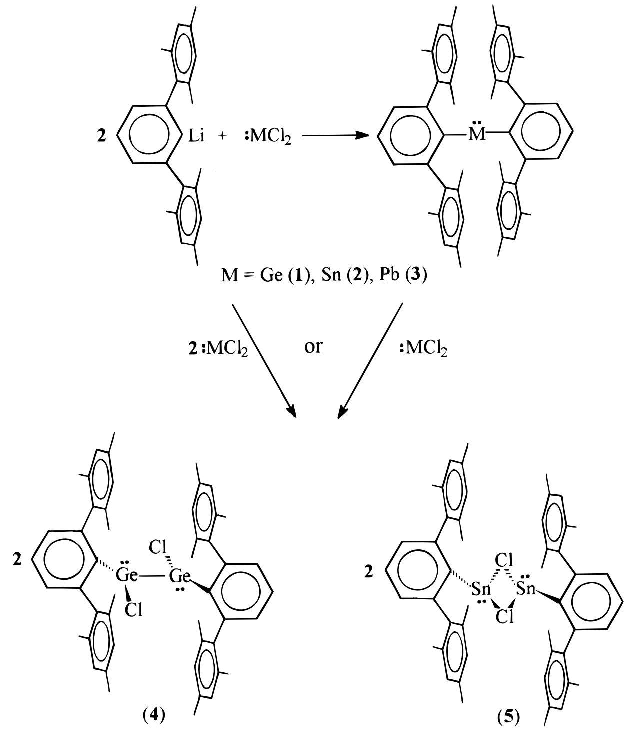
Scheme 1



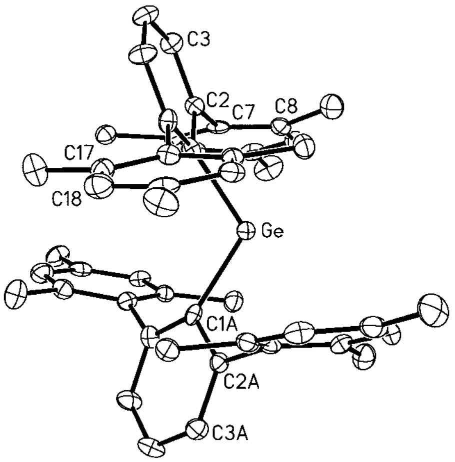


Figure 1. Thermal ellipsoid plot of **1**. H atoms are not shown for clarity.

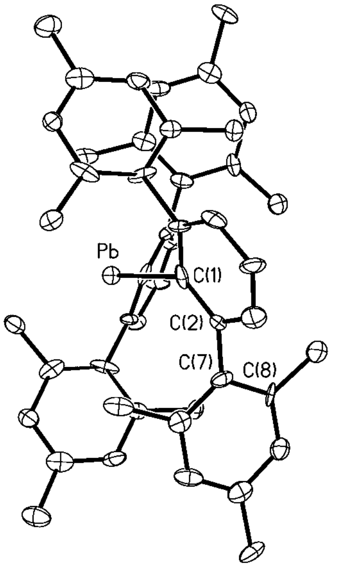


Figure 2. Thermal ellipsoid plot of **3**. H atoms are not shown for clarity.

the aryl rings (for steric reasons), which also permitted the C−Ge−C bond angle to decrease to 108.0(2)°. This raises the energy of the p-orbital and lowers the energy of the n-orbital, thereby increasing the HOMO−LUMO gap. The larger λ_{max} observed for **1** is consistent with the wider interligand angle observed (*ca.* 114.5° vide infra). However, it may be noted that the λ_{max} value for SnMes*$_2$ is 476 nm[11] (*cf.* 553 nm for **2** or 561 nm in Sn(C_6H_2-2,4,6-(*i*-Pr)$_3$)(C_6H_2-2,4,6-{CH(SiMe$_3$)$_2$}$_3$)) whereas the C−Sn−C angle is 103.6(1)°[11] vs the 114.5° angle observed in **2**. Thus, it appears that the correlation between the λ_{max} and the interligand angle is not a full explanation of the blue shift seen in GeMes*$_2$. It is possible that the large shift has its origin in an interaction between the germanium p-orbital and a π or π^*-orbital from a very geometrically distorted Mes* group. The high thermal stability of the compounds **1**−**5** is also notable. For instance, **1** is considerably more thermally robust than the diaryl germylene GeMes*$_2$, which is stable at *ca.* −30 °C but decomposes at room temperature via an intramolecular C−H bond activation or an ortho-*tert*-butyl group to give a germaindane.[10a] The tin analogue SnMes*$_2$[11] and the compound Sn{C_6H_2-2,4,6-(CF_3)$_3$}$_2$ are stable[12] at room temperature in solution and in the solid state (mp 125−130 °C and 73 °C, respectively). The only structurally characterized diaryl plumbylene is Pb{C_6H_2-2,4,6-(CF_3)$_3$}$_2$.[13] It is stable in the solid state with a melting point of 58 °C, however, it decomposes in solution. In contrast to GeMes*$_2$, the monoaryl compound Ge(Cl)Mes* is stable in solution up to 80 °C and has a melting point of 56 °C.[18] Presumably, it is sufficiently sterically relaxed compared to GeMes*$_2$ such that C−H activation does not occur.

The ^{119}Sn NMR chemical shift of **2** (635 ppm) is relatively close to that observed for the monomers Sn{N(SiMe$_3$)$_2$}$_2$ (δ = 776)[25] and Sn{C_6H_2-2,4,6-(CF_3)$_3$}$_2$ (δ = 723)[12] but differs significantly from the shift (980 ppm) observed for SnMes$_2$* and differs greatly from the values reported for Sn{CH(SiMe$_3$)$_2$}$_2$ (2272 ppm at 345 K),[26] SnC(SiMe$_3$)$_2$CH$_2$CH$_2$C(SiMe$_3$)$_2$ (2323 ppm), and Sn(C_6H_2-2,4,6-(*i*-Pr)$_3$)(C_6H_2-2,4,6-{CH(SiMe$_3$)$_2$}$_3$ (2208 ppm).[16] Similarly, the ^{207}Pb NMR chemical shift of **3** (3870 ppm) is well upfield of the value (4878 ppm) observed for Pb{C_6H_2-2,4,6-(CF_3)$_3$}$_2$.[13]

X-ray Crystal Structures. Crystals of **1**−**3** were studied by X-ray diffraction, and the thermal ellipsoid plots of the germanium and lead compounds are shown in Figures 1 and 2. Selected bond distances and angles are given in Table 2. In the solid state, compounds **1**−**3** are isomorphous and essentially isostructural. They exist as V-shaped, discrete monomers with the closest M−M (M = Ge, Sn, or Pb) distances being 8.409(1), 8.392(3), and 8.388(1) Å, respectively. The M−C (M = Ge, Sn, or Pb) bond lengths are 2.033(4), 2.225(5), and 2.334(12) Å, with any further metal−ligand interaction being longer than 3.0 Å. The C(1)−M−C(1A) (M = Ge, Sn, or Pb) bond angles are essentially invariant, having

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1−5

	Compound **1**		
Ge−C(1)	2.033(4)	C(3)−C(4)	1.372(6)
C(1)−C(6)	1.406(6)	C(4)−C(5)	1.382(5)
C(1)−C(2)	1.419(6)	C(5)−C(6)	1.393(5)
C(2)−C(3)	1.387(6)		
C(1)−Ge−C(1A)	114.4(2)	Ge−C(1)−C(6)	128.2(3)
Ge−C(1)−C(2)	112.7(3)		
	Compound **2**		
Sn−C(1)	2.225(5)	C(3)−C(4)	1.383(8)
C(1)−C(6)	1.408(6)	C(4)−C(5)	1.387(6)
C(1)−C(2)	1.420(6)	C(5)−C(6)	1.397(6)
C(2)−C(3)	1.401(7)		
C(1)−Sn−C(1A)	114.7(2)	Sn−C(1)−C(6)	129.6(3)
Sn−C(1)−C(2)	111.6(3)		
	Compound **3**		
Pb−C(1)	2.334(12)	C(2)−C(3)	1.39(2)
C(1)−C(6)	1.41(2)	C(3)−C(4)	1.39(2)
C(1)−C(2)	1.41(2)	C(4)−C(5)	1.38(2)
C(1)−Pb−C(1A)	114.5(6)	Pb−C(1)−C(6)	129.7(9)
Pb−C(1)−C(2)	110.6(9)		
	Compound **4**		
Ge−C(1)	2.000(6)	C(2)−C(3)	1.387(6)
Ge−Cl	2.120(2)	C(3)−C(4)	1.387(6)
Ge−Ge(A)	2.443(2)	C(4)−C(3A)	1.388(6)
C(1)−C(2)	1.403(5)		
C(1)−Ge−Cl	109.1(2)	C(2A)−C(1)−Ge	133.9(3)
Ge−Ge(A)−Cl	107.49(8)	C(1)−Ge−Ge(B)	113.7(2)
Ge−Ge(A)−C(1)	115.9(2)	Cl−Ge−Ge(B)	111.03(7)
C(4)−C(1)−Ge	161.0	fold angle	39.0
C(2)−C(1)−Ge	105.0(2)		
	Compound **5**		
Sn−C(1)	2.222(5)	C(2)−C(3)	1.390(8)
Sn−Cl	2.600(2)	C(3)−C(4)	1.383(9)
Sn−Cl(A)	2.685(2)	C(4)−C(5)	1.384(9)
C(1)−C(6)	1.407(8)	C(5)−C(6)	1.392(8)
C(1)−C(2)	1.406(8)		
C(1)−Sn−Cl	102.11(14)	C(4)−C(1)−Sn	166.0(4)
Sn−Cl−Sn(A)	98.28(6)	C(2)−C(1)−Sn	130.64(4)
Cl−Sn−Cl(A)	81.72(6)	C(6)−C(1)−Sn	111.1(4)
C(1)−Sn−Cl(A)	92.35(14)		

values of 114.4(2)°, 114.7(2)°, and 114.5(6)°, respectively. The M−C (M = Ge, Sn, Pb) bond distances are close to the values seen in previously reported σ-bonded, divalent organometallics species;[3−13] however, the C−M−C bond angles are the widest[27] for any σ-bonded MR_2 (M = Ge, Sn, or Pb) organometallic derivative with monodentate ligands. The angles can be compared to those in the sterically crowded species $GeMes*_2$ (108.0(2)°)[10b] and $SnMes*_2$ (103.6(1)°)[11] and the fluorinated mesityl derivatives $Sn\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$ (98.3(1)°)[12] and $Pb\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$ (94.5(1)°).[13] Oddly, the interligand angles observed in **1**−**3** are only approached by the Si−Pb−Si angle (113.56(10)°) observed in $Pb\{Si(SiMe_3)_3\}_2$.[6] Perhaps in this case, the more electropositive silyl substituents give rise to a wider angle in accordance with Walsh/Bent rules.[28] The essentially invariant nature of the C−M−C bond angles in **1**−**3** is surprising, owing to the fact that steric crowding decreases (as the radius of the group 14 element increases) in the order Ge > Sn > Pb. This should have given rise to a similar decrease in the bond angle.

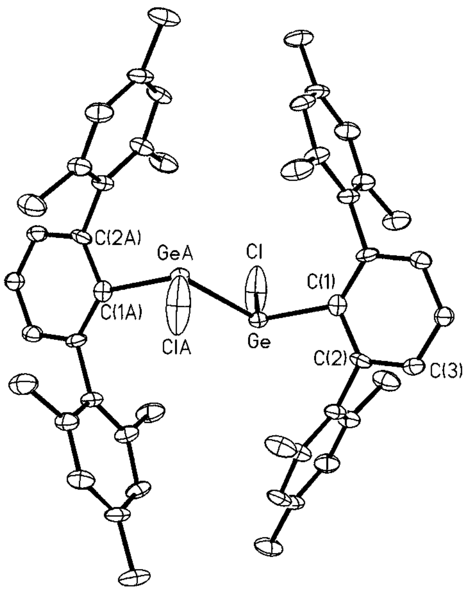

Figure 3. Thermal ellipsoid plot of **4**. H atoms are not shown for clarity.

The aryl metal halide compound **4** crystallizes as a dimer, and its structure is illustrated in Figure 3. Selected bond distances and angles are given in Table 2. The dimeric Ge−Ge bonded arrangement in **4** may be contrasted with the monomeric formula reported for the closely related species Ge(Cl)Mes*.[10b] The difference in structure may be attributed to the difference in the steric properties of the Mes* and $-C_6H_3\text{-}2,6\text{-}Mes_2$ ligands, which has been discussed elsewhere.[29] The Ge−C(1) and Ge−Cl bond distances of 2.000(6) and 2.120(2) Å are in the normal range and approximately equal to the sum of their respective covalent radii,[30] with correction for ionic effects.[31] The C−Ge−Cl bond angle is 109.1(2)° which is smaller than the C−Ge−C angles seen in $Ge_2\{CH(SiMe_3)_2\}_4$ (112.5(5)°)[2c] and $Ge_2\{C_6H_3\text{-}2,6\text{-}Et_2\}_4$ (115.4(2)°).[8] Most probably, the decreased interligand angle is a consequence of the substitution by one chloride at each germanium and consequent lowering of steric crowding. The most striking structural feature of **4**, however, is the Ge−Ge bond distance of 2.443(2) Å, which is long in comparison to other structurally characterized digermylenes; e.g., 2.213(2) Å in $Ge_2\{C_6H_3\text{-}2,6\text{-}Et_2\}_4$,[8] 2.347(2) Å in $Ge_2\{CH(SiMe_3)_2\}_4$,[2c] 2.267(1) Å in $Ge_2[Si\{SiMe(i\text{-}Pr)_2\}_3]_4$,[7] and 2.298(11) Å in $Ge_2[Si\{Si(i\text{-}Pr)_3\}_3]_4$.[7] The Ge−Ge distance is in fact more consistent with Ge−Ge single bonding (Ge−Ge = 2.44 Å). Also, **4** has a fold angle of 39°, which is much larger than the 5.9−32° range reported for the above digermylenes.[2c,7,8]

Compound **5** crystallizes as a centrosymmetric dimer, and its structure is shown in Figure 4. The dimeric units are associated through bridging chlorides and the Sn···Sn separation is 3.997(1) Å. A notable feature of the structure is the asymmetry of the bridging Sn−Cl

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(27) They are not as wide, however, as the 118.9° angle observed in $Ge\{C(SiMe_3)_3\}(\eta^2\text{-}C_5Me_5)$. In this case, the germanium is three-coordinate, having strong interactions with two of the carbons in the C_5Me_5 ring. See: Jutzi, P.; Becker, C.; Leue, C.; Stammler, G.; Neumann, B.; Hursthouse, M. B.; Karulov, M. B. *Organometallics* **1991**, *10*, 3838.

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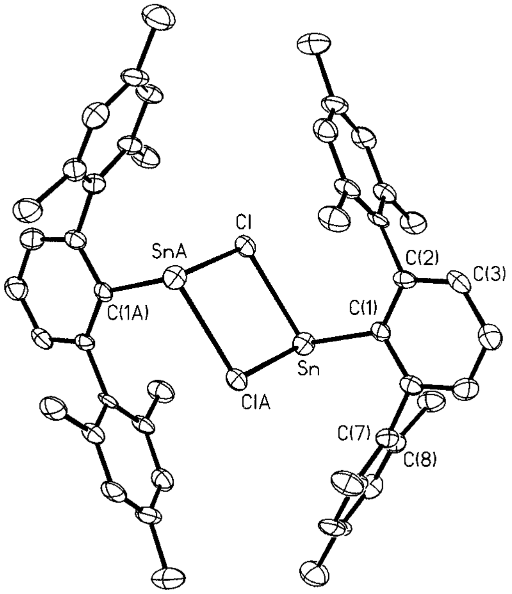

Figure 4. Thermal ellipsoid plot of **5**. H atoms are not shown for clarity.

distances (2.600(2) and 2.685(2) Å), which suggests that there may be a tendency to dissociate to monomers. The organo groups are arranged in the trans configuration, presumably for steric reasons. Although the structure of the germanium compound **4** is unprecedented for a Ge(Cl)R species, the structure of **5** is related to those observed for the amido derivatives $\{Sn(Cl)N(SiMe_3)_2\}_2$[32] and $\{Sn(Cl)TMP\}_2$[32] (TMP = 2,2,6,6-tetramethylpiperidino), which adopt trans and cis chloro-bridged structures, respectively. Although cis,trans isomerization could be observed for $\{Sn(Cl)TMP\}_2$, no such process could be detected for $\{Sn(Cl)N(SiMe_3)_2\}_2$ or **5**.

A notable feature of the structures of **1**−**5** is that some of the structural parameters show deviation from idealized values. For the most part, these deviations have their origin in steric effects. Thus, in **1**−**3**, it is notable that the closest C···C approach involving mesityl rings from the pairs of terphenyl substituents are quite short with values of 3.226 (**1**), 3.221 (**2**), and 3.228 Å (**3**). To relieve this intramolecular crowding, the planes of the neighboring pairs of mesityl rings are tilted by the angles 14.9°/5.2° (**1**), 14.2°/5.2° (**2**), and 13.4°/4.0° (**3**) from the C−C vectors (i.e., C(2)−C(7) and C(6)−C(16)) through which they are attached to the central phenyl ring. In the sterically less crowded **4** and **5**, the corresponding deformation is essentially negligible. A further deformation in **1**−**3** relates to the angles formed by the C(4)−C(1) and the M−C(1) vectors which have values of 165.8 (**1**), 166.0° (**2**), and 161.0° (**3**) instead of the expected 180°. In **4**, there is a deformation of the Ge−C(1) bond toward the C(5) mesityl ring (Figure 5) that results in a close approach of the germanium center, as evidenced by the Ge···C(5), C(6), and C(7) distances of 2.823, 3.330, and 3.418 Å.

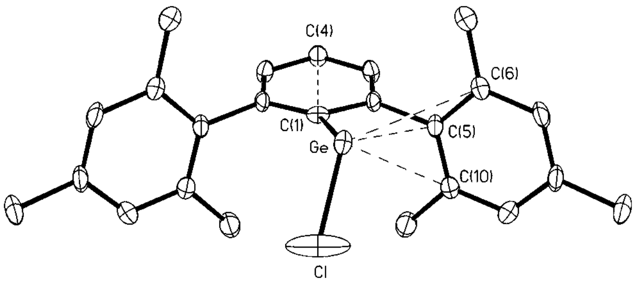

Figure 5. Drawing of half of molecule **4**, illustrating some of the geometrical distortions.

Conclusion

The structures of **1**−**5** highlight the difference in steric properties between the Mes* and $-C_6H_3$-2,6-Mes_2 ligands. Where one of these aryl substituents is present, the Mes* moiety appears to be the most crowded[29] of the two; cf. the dimeric structure of **4** versus the monomeric structure of Ge(Cl)Mes*. When two of these aryl groups are present, however, the $-C_6H_3$-2,6-Mes_2 appears to produce the most crowded environment, as reflected in the wider interligand angles in **1** and **2** in comparison to the corresponding angles in $GeMes^*_2$ and $SnMes^*_2$.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Supporting Information Available: Tables giving full details of the crystallographic data and data collection parameters, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates for **1**−**5** (41 pages). Ordering information is given on any current masthead page.

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