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Stabilized Terphenyl-Substituted Digermene Derivatives of Simple Organic Groups and Their Halide Precursors: Preference for Symmetrically Bonded Structures

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The reaction of 1 equiv of MeMgBr, EtMgBr, or LiPh with Ge(Cl)C_6H_3-2,6-$Trip_2$ (**1**; Trip = C_6H_2-2,4,6-*i*-Pr_3) in diethyl ether solution afforded the dimers {Ge(R)C_6H_3-2,6-$Trip_2$}$_2$ (R = Me (**2**), Et (**3**), Ph (**4**)), which have trans-bent Ge−Ge-bonded structures that are maintained in solution. The compounds **2** and **3** are rare examples of "digermene" species having alkyl substituents. The previously described halide precursor **1** was found to crystallize simultaneously as both a V-shaped monomer and weakly Ge−Ge-bonded dimer {Ge(Cl)C_6H_3-2,6-$Trip_2$}$_2$ (**5**), which dissociated readily to monomers in hydrocarbon solution. This species reacted readily with pyridine (py) to form the monomeric 1:1 adduct py·Ge(Cl)C_6H_3-2,6-$Trip_2$ (**7**), which has pyramidal coordination at germanium. The dimeric structures found for **2**−**4** were in sharp contrast with recently published results for their tin and lead analogues, which displayed either unsymmetric dimeric structures as in 2,6-$Trip_2H_3C_6(Me)_2Sn\ddot{S}nC_6H_3$-2,6-$Trip_2$ or monomeric structures as in Pb(Me)C_6H_3-2,6-$Trip_2$. The chloro derivatives {Ge(Cl)C_6H_3-2,6-$Trip_2$}$_n$ (*n* = 1, 2; i.e. **1** and **5**) also differed from their tin congeners in that the corresponding tin dimer is associated through chloride bridging, whereas **5**, and the related dimer {Ge(Cl)C_6H_3-2,6-Mes_2}$_2$ (**6**), are associated through weak element−element bonding. The experimental results are in general agreement with earlier theoretical data on the hypothetical M_2H_4 (M = Ge, Sn, Pb) model compounds which predicted a stable, symmetric, dimeric, Ge−Ge-bonded structure for germanium but an unsymmetric methylmethylene analogue structure for tin.

Introduction

Sterically encumbered terphenyl element(II) halide derivatives of the heavier group 14 elements (i.e., M(X)-Ar: M = Ge,[1,2] Sn,[1−4] Pb;[5] X = halide; Ar = terphenyl) have proven to be useful starting materials for several new classes of compounds.[6] The latter were generally synthesized by reduction of the terphenyl element halide precursors by a variety of routes which yielded stable radical species such as $(GeC_6H_3\text{-}2,6\text{-}Mes_2)_3^{\bullet}$ (Mes = C_6H_2−2,4,6-Me_3)[7] or $[(SnC_6H_3\text{-}2,6\text{-}Trip_2)_2]^-$ (Trip = C_6H_3-2,4,6-i-Pr_3),[3] the doubly bonded dianions $[(MC_6H_3\text{-}2,6\text{-}Trip_2)_2]^{2-}$ (M = Ge, Sn),[8] or the neutral alkyne valence isomer $(PbC_6H_3\text{-}2,6\text{-}Trip_2)_2$.[9] In addition, the reactions of terphenyl element(II) halides with organotransition-metal anions have led to species with the first stable triple bonds to germanium, as in (η^5-C_5H_5)-$(CO)_2M{\equiv}Ge{-}Ar$ (M = Cr, Mo, W).[10] In contrast, their reactions with Grignard, organolithium, and related reagents are expected to yield the more straightforward, but relatively rare, diorgano compounds of the formula M(R)Ar (R = organic or related substituent). This has proven to be the case for the reactions of Pb(Br)C_6H_3-2,6-$Trip_2$ with MeMgBr, MeLi, PhLi, or t-BuLi, which afforded the simple monomeric species Pb(R)C_6H_3-2,6-$Trip_2$ (R = Me, Ph, t-Bu) in good yields.[5] However, the corresponding reactions of MeLi or PhLi with Sn(Cl)-C_6H_3-2,6-$Trip_2$ yield a variety of different and unexpected products, among which are the lithium salts LiSn(Me)ArSn$(Me)_2$Ar[11] and the distannylstannanediyl species Sn{Sn$(Ph)_2$Ar}$_2$ (Ar = C_6H_3-2,6-$Trip_2$),[12] as well as an unsymmetric methylmethylene valence isomer

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analogue of an alkene, Ar(Me)$_2$Sn$\ddot{\mathrm{S}}$nAr.[11] The isolation of the latter species, in particular, instead of its symmetric alkene-like isomer Ar(Me)SnSn(Me)Ar, has prompted the investigation of the corresponding reactions of the organogermanium(II) halide Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$[2] with a variety of small organolithium or Grignard reagents. The results of these investigations are now presented, and it is shown that in accordance with theoretical calculations[13−15] on the simple species M$_2$H$_4$ (M = Ge, Sn), the compounds formed for the germanium and tin species differ fundamentally in their bonding and structure.

Experimental Section

General Procedures. All manipulations were carried out by 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 prior to use. The compounds Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$[2] (**1**) and LiPh[16] were synthesized according to literature procedures. Pyridine (py) was dried by distillation from CaH$_2$. CH$_3$MgBr in ether solution was purchased commercially and used as received. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Varian 400 MHz spectrometer at 399.77 and 100.53 MHz, respectively, and referenced to deuterated solvent.

{Ge(Me)C$_6$H$_3$-2,6-Trip$_2$}$_2$ (2). A diethyl ether solution of CH$_3$MgBr (3 M, 0.77 mL, 2.31 mmol) was added to a solution of Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ (1.37 g, 2.32 mmol) in hexane (80 mL) at ca. 0 °C with constant stirring. The reaction mixture, which had assumed a yellow-orange color, was stirred until the ice bath had thawed to room temperature. The solvent was then removed under reduced pressure, and the yellow residue was extracted with toluene (50 mL). After the orange solution was filtered through Celite, its volume was reduced to incipient crystallization, and storage in a ca. −20 °C freezer gave **2** as yellow crystals: yield 0.51 g, 39%; mp 215−217 °C dec. Anal. Calcd for C$_{37}$H$_{52}$Ge: C, 78.04; H, 9.21. Found: C, 77.69; H, 9.46. ^{1}H NMR (C$_6$D$_6$): δ −0.16 (s, 3H, Ge−CH_3); 1.19 (d, 12H, *o*-CH(CH_3)$_2$), ^3J = 6.8 Hz; 1.28 (d, 12H, *o*-CH(CH_3)), ^3J = 6.8 Hz; 1.35 (d, 12H, *p*-CH(CH_3)$_2$), ^3J = 6.8 Hz; 2.87 (sept, 2H, *p*-CH(CH$_3$)$_2$), ^3J = 6.8 Hz; 2.94 (sept, 4H, *o*-CH(CH$_3$)$_2$), ^3J = 6.8 Hz; 7.15 (s, *m*-Trip); 7.1−7.2 (m, *o*- and *p*-C$_6$H$_3$). ^{13}C{^{1}H} NMR: δ −2.1 (Ge−CH$_3$); 22.64 (*o*-CH$_3$(CH$_3$)$_2$); 24.13 (*o*-CH(CH$_3$)$_2$); 25.78 (*p*-CH(CH$_3$)$_2$); 30.81 (*p*-CH(CH$_3$)$_2$); 34.63 (*o*-CH(CH$_3$)$_2$); 120.5 (*m*-Trip); 137.65 (*p*-C$_6$H$_3$); 138.61 (*m*-C$_6$H$_3$); 143.74 (*o*-C$_6$H$_3$); 146.65 (*i*-Trip); 147.1 (*p*-Trip); 148.63 (*o*-Trip).

{Ge(Et)C$_6$H$_3$-2,6-Trip$_2$}$_2$ (3). A diethyl ether solution of EtMgBr, which was generated from the addition of CH$_3$CH$_2$-Br (0.08 mL, 1.05 mmol) to Mg (0.027 g, 1.11 mmol) in Et$_2$O (10 mL), was added to a solution of Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ (0.62 g, 1.05 mmol) in hexane (80 mL) at ca. 25 °C with constant stirring. The reaction mixture, which had assumed a yellow color, was stirred for a further 16 h at room temperature. The solvent was removed under reduced pressure, and the yellow residue was extracted with benzene (30 mL). After the red solution was filtered through Celite, its volume was reduced to incipient crystallization. Storage in a ca. 4 °C refrigerator afforded **3**·2C$_6$H$_6$ as yellow crystals: yield of **3** 0.37 g, 52%; mp 234−237 °C (darkens at ca. 210 °C). Anal. Calcd for C$_{38}$H$_{54}$Ge: C, 78.23; H, 9.33. Found: C, 79.10; H, 9.68. ^{1}H NMR (C$_6$D$_6$): δ 0.63 (q, 2H, CH_2CH$_3$), ^3J = 8.0 Hz; 0.84 (t, 3H, CH$_2$CH_3), ^3J = 8.0 Hz; 1.07 (d, 12H, *o*-CH(CH_3)$_2$), ^3J = 6.9 Hz; 1.21 (d, 12H, *o*-CH(CH$_3$)$_2$), ^3J = 6.9 Hz; 1.39 (d, 12H, *p*-CH(CH_3)$_2$), ^3J = 6.9 Hz; 2.88 (sept, 2H, *o*-CH(CH$_3$)$_2$), ^3J = 6.9 Hz; 2.95 (sept, 1H, *p*-CH(CH$_3$)$_2$), ^3J = 6.9 Hz. ^{13}C{^{1}H} NMR: δ 6.50 (Ge−CH$_2$CH$_3$); 11.58 (Ge−CH$_2$$CH_3$); 22.75 (*o*-CH($CH_3$)$_2$); 24.55 (*o*-CH($CH_3$)$_2$); 25.92 (*p*-CH($CH_3$)$_2$); 31.05 (*p*-$C$H(CH$_3$)$_2$); 34.29 (*o*-$C$H(CH$_3$)$_2$); 121.18, 122.03, 127.28, 128.00, 130.02, 137.33, 146.80, 148.08, 150.13 (Ar, C's).

{Ge(Ph)C$_6$H$_3$-2,6-Trip$_2$}$_2$ (4). A solution of LiPh·Et$_2$O[17] (0.18 g, 1.12 mmol) in hexane/diethyl ether (1:1, 30 mL) was added to a rapidly stirred solution of Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ (0.66 g, 1.12 mmol) in hexane (20 mL) at room temperature. The reaction mixture underwent little color change, and it was stirred for a further 1 h at room temperature. The solvent was removed under reduced pressure, and the orange residue was extracted with benzene (35 mL). The orange benzene solution was stirred for 16 h at room temperature. After filtration through Celite, the filtrate was reduced to incipient crystallization and stored in a ca. 4 °C refrigerator to give **4** as yellow crystals: yield 0.31 g, 44%; mp 221−225 °C (darkens at ca. 155 °C). Anal. Calcd for C$_{42}$H$_{55}$Ge: C, 79.76; H, 8.77. Found: C, 80.12; H, 8.99. ^{1}H NMR (C$_6$D$_6$): δ 0.91 (d, 12H, *o*-CH(CH_3)$_2$), ^3J = 6.8 Hz; 1.05 (d, 12H, *o*-CH(CH_3)), ^3J = 6.8 Hz; 1.27 (d, 12H, *p*-CH(CH_3)$_2$), ^3J = 6.8 Hz; 2.70 (sept, 2H, *p*-CH(CH$_3$)), ^3J = 6.8 Hz; 3.05 (sept, 4H, *o*-CH(CH$_3$)$_2$), ^3J = 6.8 Hz; 6.8−7.25 (m, Ar H). ^{13}C{^{1}H} NMR: δ 22.74 (*o*-CH(CH$_3$)$_2$); 24.41 (*o*-CH(CH$_3$)$_2$); 26.1 (*p*-CH(CH$_3$)$_2$); 30.9 (*p*-CH(CH$_3$)$_2$); 31.2 (*o*-CH(CH$_3$)$_2$); 121.1, 124.1, 126.5, 128.5, 128.6, 130.9, 136.1, 137.18, 138.8, 146.6, 146.9 (Ar, C's).

py·Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ (7). Pyridine (0.23 mL, 2.84 mmol) was added dropwise via syringe to an orange solution of Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ (1.64 g, 2.78 mmol) in hexane (80 mL) at ca. 25 °C with constant stirring. The solution, which had turned yellow, was stirred at ca. 25 °C for 1 h. The volume of the solution was then reduced to incipient crystallization and stored in a refrigerator at ca. 4 °C to give the product **1** as yellow crystals: yield 1.45 g, 80.1%; mp 160−161 °C dec. Anal. Calcd for C$_{41}$H$_{54}$ClGeN: C, 73.62; H, 8.14; N, 2.09. Found: C, 74.01; H, 8.15; N, 1.99. ^{1}H NMR (C$_6$D$_6$): δ 1.08 (d, 12H, *p*-CH(CH_3)$_2$), ^3J = 6.7 Hz; 1.21 (d, 12H, *o*-CH(CH_3)$_2$), ^3J = 6.7 Hz; 1.41 (d, 12H, *o*-CH(CH_3)$_2$), ^3J = 6.7 Hz; 2.74 (sept, 2H, *p*-CH(CH$_3$)$_2$), ^3J = 6.7 Hz; 3.34 (sept, 4H, *o*-CH(CH$_3$)$_2$), ^3J = 6.7 Hz; 6.26 (2H, *m*-py); 6.59 (1H, *p*-py); 7.19 (s, 4H, *m*-Trip); 7.26 (1H, *p*-C$_6$$H_3$); 7.93 (2H, *m*-C$_6H_3$); 7.98 (2H, *o*-py). ^{13}C{^{1}H} NMR: δ 22.94 (*o*-CH(CH$_3$)$_2$); 24.37 (*o*-CH(CH$_3$)$_2$); 26.33 (*p*-CH(CH$_3$)$_2$); 31.24 (*p*-CH(CH$_3$)$_2$); 34.53 (*o*-CH(CH$_3$)$_2$); 121.16 (*m*-Trip); 123.94 (*m*-py); 130.32 (*p*-py); 131.25 (*p*-C$_6$H$_3$); 137.10 (*m*-C$_6$H$_3$); 146.60 (*i*-Trip); 147.40 (*p*-Trip); 148.58 (*o*-py); 148.61 (*o*-C$_6$H$_3$); 148.62 (*o*-Trip), 159.51 (*i*-C$_6$H$_3$). UV−vis (hexane): λ_{max} = 380, ϵ = 800 L mol^{-1}cm^{-1}.

X-ray Crystallographic Studies. The crystals of **2**−**5** and **7** were removed from the Schlenk tube under a stream of N$_2$ and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[18] All data were collected near 130 K using Bruker SMART 1000 (Mo Kα radiation and a CCD area detector) equipment. The SHELXTL version 5.03 program package was used for structure solutions and refinements.[19] Absorption corrections were applied using the SADABS program.[20] The structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refine-

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(15) A reviewer suggested that the observation of the unsymmetric methyl isomer in the case of tin[11] may be due to the lower barrier to rearrangement in the tin system. Calculations for the process H$_2$GeGeH$_2$ → H$_3$GeGeH indicate a barrier of 12−14 kcal mol^{-1}: Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489. Significantly higher barriers are expected for the methyl-substituted analogue. The barrier for the corresponding methyl−tin system is currently unknown.

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(19) SHELXTL version 5.03; Bruker AXS, Madison, WI, 1998.

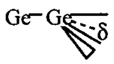
(20) SADABS is an empirical absorption correction program that is part of the SAINT Plus NT version 5.0 package: Bruker AXS, Madison, WI, 1998.

Table 1. Crystallographic Data for Compounds 2–5 and 7

	2	**3**·$2C_6H_6$	**4**	**5**	**7**
formula	$C_{37}H_{52}Ge$	$C_{88}H_{120}Ge_2$	$C_{42}H_{55}Ge$	$C_{72}H_{98}Cl_2Ge_2$	$C_{41}H_{54}ClGeN$
fw	569.38	1323.02	632.45	1179.58	668.89
color, habit	yellow-green, cube	yellow parallelepiped	orange, block	orange, block	yellow, parallelepiped
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	13.8080(6)	14.1210(7)	12.4506(8)	14.003(1)	12.7657(4)
b, Å	16.0161(7)	15.9066(8)	12.6854(9)	15.9072(1)	17.6140(5)
c, Å	17.5669(8)	18.1521(9)	22.626(2)	18.003(1)	16.9179(5)
β, deg	108.771(1)	110.814(1)	94.482(1)	109.817(2)	105.204(1)
V (Å^3)	3678.3(3)	3811.2(3)	3562.6(4)	3772.9(5)	3670.9(2)
Z	4	2	4	2	4
d_{calcd} (Mg/m^3)	1.028	1.153	1.179	1.038	1.210
θ range, deg	1.77–31.51	1.54–25.00	1.81–35.51	1.76–31.53	1.70–31.5
μ (mm^{-1})	0.852	0.832	0.887	0.901	0.935
no. of obsd data, $I > 2\sigma(I)$	8473	3411	6718	4105	9359
R1	0.0398	0.0486	0.0542	0.1194	0.0341
wR2	0.0973	0.1110	0.1481	0.3083	0.0982

Table 2. Selected Structural Parameters for Compounds 1–7

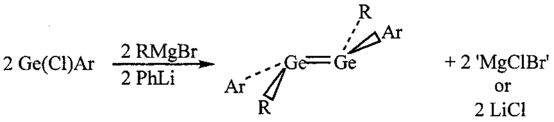
	Ge–Ge (Å)	Ge–C_6H_3-2,6-Trip$_2$ (Å)	Ge–L (Å)	C–Ge–L (deg)	Σ(Ge) (deg)[d]	δ (deg)[e]
Ge(Cl)C_6H_3-2,6-Trip$_2$ (**1**)		1.989(5)[a]	2.2026(19)[b]	101.31(15)		
{Ge(Me)C_6H_3-2,6-Trip$_2$}$_2$ (**2**)	2.3173(3)	1.9705(15)[a]	1.9836(17)[a]	111.77(7)	342.89	39.7
{Ge(Et)C_6H_3-2,6-Trip$_2$}$_2$ (**3**)	2.347(3)	1.995(3)[a]	1.913(5)[a]	106.8(2)	342.98	37.9
{Ge(Ph)C_6H_3-2,6-Trip$_2$} (**4**)	2.3183(5)	1.997(2)[a]	1.950(3)[a]	116.08(10)	348.35	33.7
{Ge(Cl)C_6H_3-2,6-Trip$_2$}$_2$ (**5**)	2.363(2)	1.973(7)[a]	2.209(2)[b]	118.03(19)	346.59	36.8
{Ge(Cl)C_6H_3-2,6-Mes$_2$}$_2$ (**6**)	2.443(2)	2.000(6)[a]	2.120(2)[b]	109.1(2)	332.49	39.0
py·Ge(Cl)C_6H_3-2,6-Trip$_2$ (**7**)		2.0476(12)[a]	2.3021(4)[c] 2.1403(1)[b]	93.24(3)	290.65	

[a] Ge–C bond. [b] Ge–Cl bond. [c] Ge–N bond. [d] Sum of angles at Ge. [e] Out-of-plane angle defined by 

ment at calculated positions using a riding model in the SHELXTL program. The ethyl derivative **3** crystallized from benzene as the solvate **3**·$2C_6H_6$. Some details of the data collection and refinement are given in Table 1. Selected bond distances and angles are given in Table 2. Further details are provided in the Supporting Information.

Results and Discussion

The reaction of 1 equiv of MeMgBr, EtMgBr, or LiPh with Ge(Cl)C_6H_3-2,6-Trip$_2$ in diethyl ether solution afforded the alkyl derivatives **2** and **3** and the aryl species **4**, in moderate yield in accordance with eq 1.

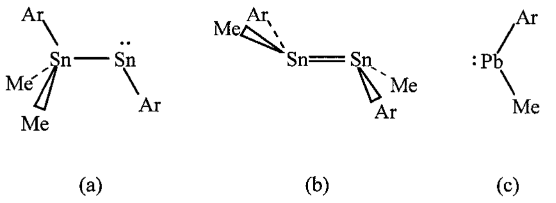


(1)

Ar = C_6H_3-2,6-Trip$_2$

2, R = Me
3, R = Et
4, R - Ph

The symmetric, Ge–Ge-bonded, dimeric formulas of these compounds are in sharp contrast to those observed for their tin[11] and lead[4] methyl analogues, which have either the unsymmetric structure (a), (rather than the symmetric structure (b)) or the monomeric structure (c). For tin it is believed that (a) is preferred over (b), owing to the weakness of the Sn–Sn "double" bond, which is composed of two relatively weak[21] polar–dative interactions,[22] in comparison to the relatively strong (usually ca. 40 kcal mol^{-1}) Sn–Sn covalent single bond.[23] Trinquier has shown, in calculations[13,14] on the hypothetical hydrogen derivatives M_2H_4 (M = Si, Ge,[15] Sn, Pb), that the unsymmetric structure $H_3M\ddot{M}H$ is more stable than the trans-bent symmetric structure H_2MMH_2 for M = Sn, Pb but vice versa for M = Si, Ge. With the crowding R substituents normally required for stability, a symmetric structure similar to (b) is invariably observed for the Sn_2R_4 species, since an unsymmetric $R_3Sn\ddot{S}nR$ structure similar to (a) is disfavored, owing to the steric conflict of the three large R groups at one of the tins. However, the C_6H_3-2,6-Trip$_2$ substituent allows structures such as (a) to be isolated with methyl groups as coligands since two methyl ligands and one terphenyl ligand do not unduly crowd the tin environment.



(a) (b) (c)

Ar = -C_6H_3-2,6-Trip$_2$

In contrast, the monomeric structure depicted in (c) is probably a result of the overall weakness of the Pb–Pb interaction in comparison to the Sn–Sn and Ge–Ge bonds. A similar picture emerges from the synthesis of phenyl derivative **4**, whose symmetric formulation,

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(21) For example: Zilm, K. W.; Lawless, G. A.; Merrill, R. M.; Millar, J. M.; Webb, G. *J. Am. Chem. Soc.* **1987**, *109*, 7236.

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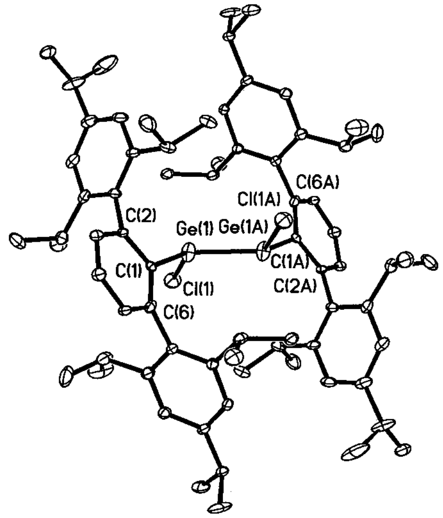

Figure 1. Schematic drawing of the arylgermanium chloride dimer **5**. Selected bond distances and angles are given in Table 2.

similar to those seen for **2** and **3**, differs from the products obtained[12] for the tin and lead derivatives (d) and (e).

$$\underset{(d)}{(THF)LiSnPh_2Ar} \qquad \underset{(e)}{:Pb(Ph)Ar}$$

$$Ar = -C_6H_3\text{-}2,6\text{-}Trip_2$$

It is clear that the sizes of the group 14 element and its organic substituents, the stability of the lone pair, as well as the strength of the M−M (M = Ge, Sn, Pb) interaction play a crucial role in the type of product obtained. This effect is also seen in the aryl element halide precursors **1**, **5**, and **6**, which show a tendency to form element−element-bonded dimers in the case of germanium (see below) but are observed as halide-bridged dimers with no metal−metal bonding for tin and lead.[1,5] However, this should not obscure the fact that the Ge−Ge bonding in the arylgermanium halide dimers **5** and **6** is quite weak, as evidenced by the simultaneous crystallization of $Ge(Cl)C_6H_3$-2,6-$Trip_2$ as the monomer **1**[2] or as the dimer **5**. It is also notable that either **1** or **5** reacts readily with pyridine to give the 1:1 adduct **7**, which is also in keeping with the weakness of the Ge−Ge interaction. Solution ^1H NMR spectroscopic studies of **1** or **5** do not show the existence of a monomer−dimer equilibrium at room temperature. In addition, ^1H NMR spectra of solutions of **2**−**4** also support the existence of only one isomer in solution.

X-ray Crystal Structures. The structures **2**−**5** and **7** were determined by single-crystal X-ray diffraction. The structures of the monomer $Ge(Cl)C_6H_3$-2,6-$Trip_2$ (**1**)[2] and the Ge−Ge bonded dimer $\{Ge(Cl)C_6H_3\text{-}2,6\text{-}Mes_2\}_2$ (**6**)[1] have already been described elsewhere. Key structural data for the series of compounds **1**−**7** are listed in Table 2. The X-ray data for **1** and **5** show that Ge(Cl)-C_6H_3-2,6-$Trip_2$ can exist in the solid state in either the monomeric or the dimeric form. The two structures observed for **1** and **5** (Figure 1) in the crystalline phase parallel recent findings[4] for the corresponding tin monomer and dimers $Sn(Cl)C_6H_3$-2,6-$Trip_2$ and $\{Sn(\mu\text{-}Cl)C_6H_3\text{-}2,6\text{-}Trip_2\}_2$, which also crystallized simultaneously from solution. However, the tin species is dimerized through chloride bridging with no Sn−Sn bonding. The different structures seen for the germanium and tin dimers reflect the weaker metal−metal bonding of tin.

The monomeric structure observed for **1**[2] was originally accounted for on the basis of the large size of $-C_6H_3$-2,6-$Trip_2$ substituent, which prevented association.[24] This steric explanation appeared plausible since, with the less bulky $-C_6H_3$-2,6-Mes_2 substituent, weak association occurred to afford the Ge−Ge-bonded dimer **6**.[1] However, the isolation of the analogous $-C_6H_3$-2,6-$Trip_2$-substituted dimer **5**, whose Ge−Ge bond distance is significantly shorter than that in **6**, essentially vitiates this explanation. The longer Ge−Ge bond in the apparently less crowded **6** can be rationalized on the basis of secondary interactions between the germanium and one of the *o*-mesityl rings, which effectively increase its coordination number and weaken the Ge−Ge interaction (see Figure 5 of ref 1). In the bulkier $-C_6H_3$-2,6-$Trip_2$ analogue **5**, however, significant interactions of this type do not occur. This permits a shorter Ge−Ge bond in **5** despite the larger size of the organic substituent. Nonetheless, the Ge−Ge bond in **5** is quite weak, since the compound is dissociated to the monomer **1** in solution. Closer examination of the monomeric structure of **1** also shows that there exists close intra- and intermolecular contracts between the germanium and various C−H moieties of the isopropyl substituents of $-C_6H_3$-2,6-$Trip_2$ groups. The closest Ge···H approaches are in the range 2.86−3.32 Å. The corresponding interactions in **5** are all greater than 3.4 Å, however. Thus, the key factors in determining the different structures of **1** and **5** are the weak Ge−Ge, Ge−C, and C−H···Ge interactions. The weakness of the Ge−Ge bonding in the structure of **5** is also supported by the absence of significant changes in the Ge−C and Ge−Cl distances upon dissociation to monomers.

The trans-bent geometries of **5** and **6** and the relatively long Ge−Ge "double bond" distances are indicative of weak bonding which can be rationalized in terms of the mixing of the Ge−Ge σ^* and π orbitals,[25] which weakens the bond strength and produces lone pair electronic character and pyramidal geometry at the germaniums. In the case of **5** and **6** this interaction is weakened further by the presence of electronegative chloro substituents which enhance such mixing.[22] The dimeric structures of the tetraorganodigermanium compounds **2**−**4** resemble those of the chloro derivatives **5** and **6** in that they all exist in the trans-bent *E* stereoisomeric form. This finding may be contrasted with the solid-state structure of $\{Ge(Mes)(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)\}_2$, which exists as the *Z* isomer.[26] In solution, however, it is in equilibrium with its *E* isomer. This type of equilibrium is not observed for **2**−**4**. It seems probable that the large size of the $-C_6H_3$-2,6-$Trip_2$ substituent does not favor the formation of the *Z* isomer for steric reasons. The Ge−Ge distances in **2**−**4** lie about midway between the shortest (ca. 2.21 Å) and longest (ca. 2.46

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(24) Other crowded organogermanium(II) chloride species such as $Ge(Cl)C_5Me_5$ and $Ge(Cl)C_6H_2$-2,4,6-t-Bu_3 have also been synthesized: Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1987**, *329*, C17. Jutzi, P.; Leue, C. *Organometallics* **1994**, *13*, 2898.

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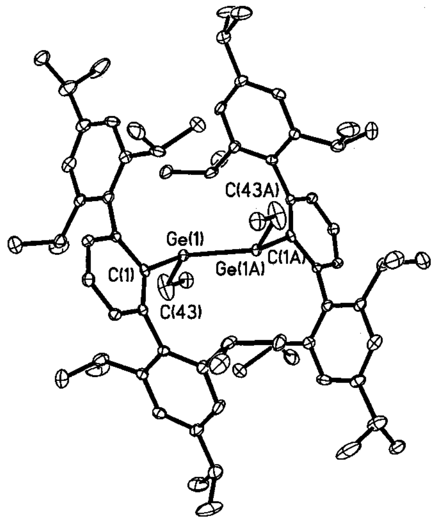

Figure 2. Schematic drawing of $\{Ge(Et)C_6H_3\text{-}2,6\text{-}Trip_2\}_2$ (**3**). Selected bond distances and angles are given in Table 2.

Å) bonds observed for R_2GeGeR_2 species.[27] The Ge−Ge bond lengths in **2** (2.3173(3) Å) and **4** (2.3183(5) Å) resemble the 2.301(1) Å found in $\{Ge(Mes)(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)\}_2$. The out of plane angles 39.7° (**2**) and 33.7° (**4**) bracket the 36° observed for $\{Ge(Mes)(C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)\}_2$. A somewhat longer Ge−Ge bond is observed for the ethyl-substituted **3** (see the structure in Figure 2), although the out-of-plane angle is less than that in **2**. The out-of-plane angles observed in **2**−**4** are at the high end of the scale for tetraorganodigermanium compounds.[27] However, it is apparent from Table 2 that there is no correlation between this parameter and the Ge−Ge bond lengths. Finally, it is notable that the methyl and ethyl derivatives **2** and **3** are rare examples of digermenes with alkyl substituents, the only previous example being the tetraalkyl $[Ge\{CH(SiMe_3)_2\}_2]_2$.[28]

Treatment of solutions of **1** or **5** with pyridine readily affords the 1:1 pyridine complex **7**. The structure of this species (Figure 3) resembles those of its tin[4] and lead[5] analogues, in which the pyridine is coordinated through the "empty" p orbital lying perpendicular to the M, Cl, C(ipso) plane. This results in a pyramidal coordination at germanium (sum of angles at Ge 290.65°). The Ge−N distance is 2.3021(4) Å, which is much greater than the sum of atomic radii of germanium and nitrogen (ca. 1.95 Å).[29] It is only 0.067 Å shorter than the 2.369(4) Å Sn−N distance observed in the corresponding tin species py·$Sn(Cl)C_6H_3\text{-}2,6\text{-}Trip_2$, whereas the difference in covalent radii between these two elements is ca. 0.18 Å.[29] The unusual elongation of the Ge−N bond thus suggests considerable steric crowding in this molecule. The congestion is also reflected in a deviation of the Ge(1)−N(1) vector by 15.5° from an idealized 90° with respect to the C(1)−Ge(1)−Cl(1) plane. The plane of the pyridine ring is also tilted by 12.6° from the Ge(1)−N(1) line. In addition, the Ge(1)−C(1)−C(2) (132.49(9)°) and Ge(1)−C(1)−C(2) (109.05(8)°) angles differ by over 23°, the wider angle being associated with the pyridine-coordinated side of the C(1), Ge(1), Cl(1) plane. The corresponding angular differences in **2**−**6** are in the range 11−14°, and the two angles are identical in the structure of the uncomplexed precursor **1**.

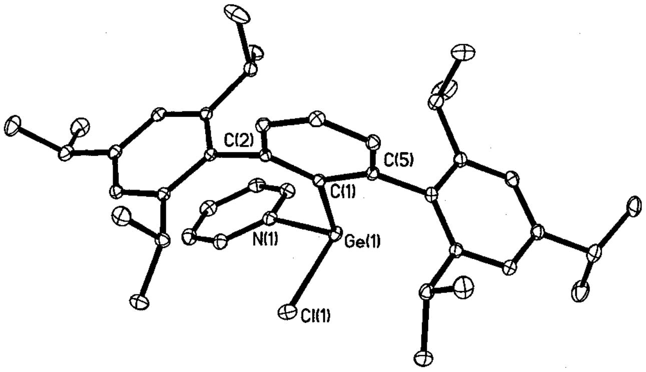

Figure 3. Schematic drawing of py·$Ge(Cl)C_6H_3\text{-}2,6\text{-}Trip_2$ (**7**). Selected bond distances and angles are given in Table 2.

Conclusion. The germanium derivatives **2**−**4** display a different bonding pattern from the corresponding tin and lead species owing to stronger Ge−Ge multiple bonds in comparison to those of tin and lead. The cocrystallization of the halides **1** and **5** show that weak Ge−C, Ge−H interactions play a role in determining the strength of Ge−Ge bonding.

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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 **2**−**5** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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