(RIST). We also thank Mr. Sang-Yong Lee for his help at the early stage of this work.

Registry No. **1**, 128302-30-7; **2**, 137822-83-4; **3**, 86177-71-1; [Et$_4$N][Fe$_2$OCl$_6$], 87495-23-6.

Supplementary Material Available: Tables of positional and isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles for **2** and **3** (16 pages); tables of structure factors for **2** and **3** (30 pages). Ordering information is given on any current masthead page.

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The Germanium-Tin Bond. Structures of the Isomeric Complexes Me$_3$E-E'Ph$_3$ (E = Ge, E' = Sn; E = Sn, E' = Ge)

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Received July 26, 1991

Introduction

A compound containing a Ge-Sn bond was initially reported in 1927 by Kraus and Foster, Ph$_3$GeSnMe$_3$ (II); much later Gilman and Gerow reported Ph$_3$GeSnPh$_3$, and Creemers and Noltes reported several oligomeric germylstannanes.[1,2] However, there has been limited study on such compounds. Chambers and Glockling determined heats of formation and bond dissociation energies from appearance potential measurements[3] and also studied the mass spectral fragmentation patterns of such compounds in which significant ligand exchange between the two metals was observed.[4] Carey and Clark studied the far-infrared spectra of these compounds and assigned metal-metal stretching frequencies for the Ge-Sn bond in the range 225-235 cm^{-1}.[5] Chemical studies on such bonds by Kraus and Foster showed that II underwent homolytic cleavage of the Ge-Sn bond when reacted with bromine. Optically active Ge-Sn compounds with activity at both Ge and Sn have also been reported.[6]

Whereas much crystallographic data have been published concerning the nature of the homonuclear group 14 bonds, Si-Si,[7,8] Ge-Ge,[9] Sn-Sn,[10] and Pb-Pb,[11] reports concerning heteronuclear intra group 14 bonding are rare, totaling only nine examples, Si-Ge,[12] Si-Sn,[13] Ge-Pb,[14] and Sn-Pb.[14] There are no examples of a Ge-Sn-bonded compound, although Adams and Dräger have published the space group and cell constants of Ph$_3$SnGePh$_2$SnPh$_3$ but were unable to obtain crystals suitable for total structural analysis.[13b] A series of Ph$_3$PbEPh$_3$ complexes (E = Ge, Sn, Pb) have been structurally characterized, but it was not possible to positively distinguish the two different group 14 metal atoms.[14] We recently reported that the isomeric pair of compounds Me$_3$SiGePh$_3$ and Ph$_3$SiGeMe$_3$ possess significantly different bond lengths and suggested that a simple explanation for this difference involved expansion and contraction of valence orbitals by electron-donating or -withdrawing substituents that permitted more energetically favorable overlap.[12b] If correct, this explanation should apply to a general class of inorganic systems containing ligand-exchanged isomers.

We have now structurally characterized the Ge-Sn bonds in the isomeric compounds Me$_3$GeSnPh$_3$ (I) and Ph$_3$GeSnMe$_3$ (II) and wish to report the results of this study to provide first-time values for the Ge-Sn bond length and furthermore to show that the simple ideas promulgated to explain the bond length differences in the isomeric Ge-Si compounds hold for the intermetallic bonds in isomers I and II.

Table I. Structure Determination Summary

	I	II
empirical formula	C$_{21}$H$_{24}$GeSn	C$_{21}$H$_{24}$GeSn
color; habit	colorless; fragment	colorless; prism
cryst size, mm	0.24 × 0.40 × 0.22	0.42 × 0.36 × 0.60
cryst system	orthorhombic	orthorhombic
space group	*Pna*2$_1$	*Pna*2$_1$
unit cell dimens		
a, Å	20.634 (2)	20.395 (4)
b, Å	12.394 (2)	12.412 (2)
c, Å	8.0340 (10)	8.085 (2)
V, Å^3	2054.6 (5)	2046.7 (7)
Z	4	4
fw	467.7	467.7
density (calc), Mg/m^3	1.512	1.518
abs coeff, mm^{-1}	2.662	2.672
F(000)	928	928
no. of reflns collected	1076	1069
no. of indep reflns	1034 (R_{int} = 0.00%)	1027 (R_{int} = 0.00%)
no. of obs reflns	814 ($F > 3.0\sigma(F)$)	869 ($F > 3.0\sigma(F)$)
final *R*, R_w (obs data)	3.02%, 3.95%	2.63%, 3.31%
R, R_w (all data)	4.40%, 4.92%	3.45%, 3.54%

Table II. Selected Bond Lengths (Å) and Angles (deg)

	I	II
Ge-Sn	2.599 (3)	2.652 (2)
Ge-C	1.969 (19) (C19)	1.929 (13) (C1)
	1.973 (19) (C21)	1.940 (12) (C7)
	1.947 (17) (C20)	1.924 (13) (C13)
Sn-C	2.143 (17) (C1)	2.191 (16) (C19)
	2.161 (14) (C7)	2.173 (14) (C21)
	2.162 (17) (C13)	2.137 (17) (C20)

I		II	
C1-Sn-C7	107.2 (6)	C20-Sn-C21	107.5 (6)
C19-Ge-C20	109.0 (9)	C1-Ge-C13	109.4 (6)
Sn-Ge-C19	110.7 (9)	Sn-Ge-C1	109.6 (6)
Ge-Sn-C1	111.1 (7)	Ge-Sn-C20	110.3 (6)

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Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for I

	x	y	z	U(eq)[a]
Sn	1657 (1)	2100 (1)	0	40 (1)
Ge	1644 (1)	2091 (1)	−3235 (3)	45 (1)
C1	2623 (7)	1914 (9)	937 (34)	46 (7)
C2	2792 (8)	1077 (12)	2119 (34)	60 (8)
C3	3389 (7)	979 (12)	2667 (29)	50 (9)
C4	3856 (10)	1708 (14)	2350 (35)	64 (10)
C5	3733 (10)	2498 (16)	1221 (38)	82 (12)
C6	3103 (7)	2609 (12)	600 (26)	55 (9)
C7	1282 (8)	3595 (9)	994 (28)	46 (7)
C8	1658 (8)	4246 (13)	2084 (34)	55 (9)
C9	1389 (10)	5220 (12)	2658 (30)	60 (9)
C10	802 (8)	5525 (13)	2205 (35)	67 (8)
C11	429 (9)	4907 (15)	1223 (46)	71 (11)
C12	675 (7)	3930 (10)	637 (31)	59 (10)
C13	1076 (7)	842 (11)	1121 (35)	53 (7)
C14	559 (9)	1076 (15)	2111 (38)	64 (9)
C15	196 (9)	252 (14)	2820 (35)	67 (11)
C16	376 (10)	−816 (14)	2629 (38)	75 (12)
C17	893 (10)	−1054 (14)	1572 (29)	64 (10)
C18	1226 (7)	−267 (11)	800 (40)	78 (11)
C19	900 (9)	2917 (11)	−4088 (38)	61 (9)
C20	1581 (9)	609 (11)	−4022 (41)	81 (10)
C21	2456 (8)	2750 (12)	−4040 (39)	66 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Experimental Section

Syntheses were performed under a nitrogen atmosphere using dry, oxygen-free solvents; Me_3GeCl and Ph_3GeCl were obtained from Gelest Inc., Bensalem, PA.; Me_3SnCl and Ph_3SnCl were purchased from Aldrich Chemical Co., Milwaukee, WI.; and NMR spectra of the compounds were recorded on an IBM NR/200 FTNMR spectrometer in $CDCl_3$.

Synthesis of (Triphenylstannyl)trimethylgermane (I). A 250-mL Schlenk flask was charged with 0.79 g (5.18 mmol) of trimethylchlorogermane dissolved in 30 mL of THF and maintained at −25 °C. To this was added slowly a THF solution of (triphenylstannyl)lithium (prepared from 2.0 g (5.18 mmol) of triphenyltin chloride and 0.14 g of lithium in 40 mL of THF). The mixture was stirred at low temperature for 0.5 h, permitted to warm to room temperature, and stirred for 12 h. The solvent was removed on a rotary evaporator, and the compound was extracted with 100 mL of hexane; subsequent to removal of LiCl via filtration and hexane by distillation, the crude material was twice recrystallized from hexane to yield 1.36 g (56%) of I, mp 115 °C (lit.[4] 110–111 °C). ^1H NMR ($CDCl_3$), δ: 0.67 (9 H, s, $GeMe_3$); 7.40–7.43, 7.59–7.60 (15 H, m, Ph). ^{13}C NMR ($CDCl_3$), δ: 1.43 ($GeMe_3$); 129.35, 129.43, 137.99, 140.35 (Ph).

Data for (Triphenylgermyl)trimethylstannane (II). Mp: 89 °C (lit.[1] 88 °C). ^1H NMR ($CDCl_3$), δ: 0.33 (9 H, s, $SnMe_3$); 7.33–7.37, 7.43–7.44 (15 H, m, Ph). ^{13}C NMR ($CDCl_3$), δ: −9.24 ($SnMe_3$); 128.74, 128.92, 135.64, 139.42 (Ph).

Crystal Structure Determination. The crystals were mounted on glass fibers and data collected at room temperature on a R3m/V Nicolet four-circle diffractometer with graphite-monochromated Mo Kα radiation; λ(Mo Kα) = 0.71073 Å. Unit cell parameters and estimated standard deviations were obtained by a least-squares fit to 25 reflections randomly distributed in reciprocal space and lying in the 2θ range of 15–30°. Intensity data were collected in the ω-scan mode with scans from 0.75° below Kα_1 to 0.75° above Kα_2. Background counts were taken with a stationary crystal and total background time to scan time ratio of 0.5. Three standard reflections were monitored in each case and showed no significant decay. The data were corrected for Lorentz and polarization effects but not for absorption.

The structures were solved and refined using the SHELEXTL-PLUS software package on a Microvax II computer. The hydrogen atoms were placed at calculated positions with C–H bond distances of 0.96 Å and isotropic temperature factors of $U = 0.08$ Å^2 during refinements. Full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$ was carried out with anisotropic thermal parameters for non-hydrogen atoms. The weighting scheme has the form $w^{-1} = \sigma^2(F) + gF^2$, and the final R factors have the forms $R = \sum|F_o - F_c|/\sum F_o$ and $R_w = [w|F_o - F_c|^2/\sum wF_o^2]^{1/2}$. Relevant crystallographic parameters are given in Table II, while atomic coordinates are presented in Tables III and IV.

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for II

	x	y	z	U(eq)[a]
Sn	1631 (1)	2055 (1)	0	49 (1)
Ge	1649 (1)	2087 (1)	−3279 (2)	42 (1)
C1	1088 (5)	963 (9)	−4126 (27)	54 (6)
C2	1225 (6)	−118 (9)	−3809 (27)	66 (7)
C3	847 (7)	−911 (10)	−4633 (28)	80 (9)
C4	321 (8)	−647 (14)	−5546 (33)	100 (11)
C5	164 (7)	405 (15)	−5804 (34)	101 (12)
C6	559 (6)	1206 (11)	−5116 (26)	59 (6)
C7	1331 (6)	3491 (9)	−3961 (26)	59 (6)
C8	1698 (6)	4109 (8)	−5088 (24)	71 (6)
C9	1458 (7)	5090 (9)	−5695 (25)	71 (7)
C10	840 (7)	5439 (9)	−5151 (32)	87 (8)
C11	477 (7)	4844 (10)	−4085 (32)	87 (8)
C12	731 (6)	3888 (10)	−3491 (24)	67 (8)
C13	2534 (6)	1842 (8)	−4013 (22)	50 (5)
C14	3050 (6)	2511 (11)	−3488 (22)	72 (8)
C15	3676 (6)	2394 (11)	−4117 (29)	70 (8)
C16	3814 (7)	1571 (11)	−5181 (36)	81 (9)
C17	3335 (6)	900 (11)	−5732 (29)	79 (8)
C18	2695 (6)	1033 (8)	−5144 (29)	70 (7)
C19	822 (8)	3006 (10)	1024 (30)	72 (7)
C20	2508 (8)	2759 (11)	961 (28)	75 (7)
C21	1572 (7)	418 (10)	942 (28)	75 (7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

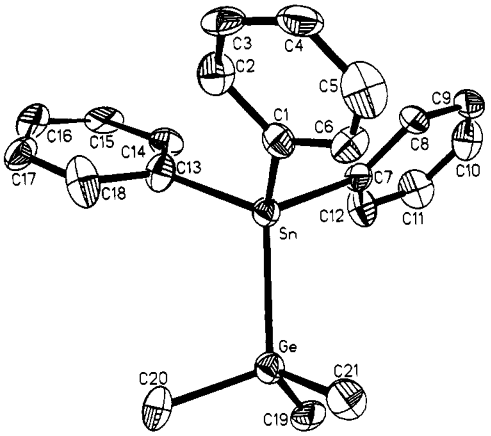

Figure 1. Structure of $Me_3GeSnPh_3$ (I).

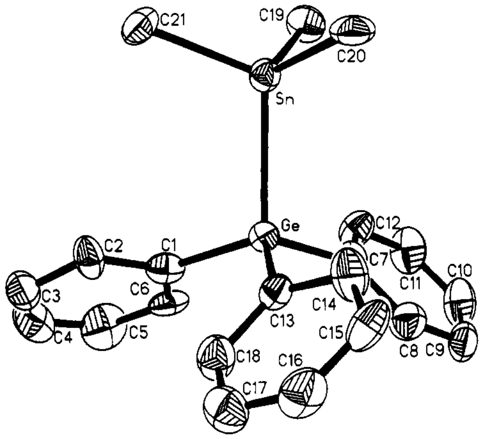

Figure 2. Structure of $Ph_3GeSnMe_3$ (II).

Results and Discussion

The structures of I and II are presented in Figures 1 and 2. The Ge–Sn bond lengths in I and II are significantly different: 2.599 (3) Å (I), 2.652 (2) Å (II). This distinction parallels that

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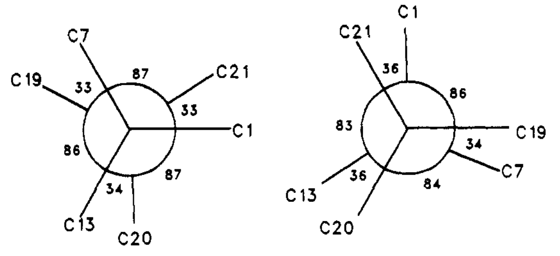

II I

Figure 3. Newman projections of I and II along the Ge–Sn bond.

of the isomeric Ge–Si compounds in exactly the same manner: $Me_3SiGePh_3$, 2.384 (1) Å; $Ph_3SiGeMe_3$, 2.394 (1) Å. When the heavier element is bonded to the electron-withdrawing Ph groups and the lighter element to the electron-releasing methyl groups, contraction of the higher energy valence orbitals, coupled with an increase in energy of the lower energy system, results in a better energy match, which in turn results in a clear contraction of the Ge–Sn and Si–Ge bonds. The effect is much greater for the Ge–Sn bond, 0.051 Å; cf. the Si–Ge bond length difference, which is 0.01 Å. The overall greater polarizability and higher energy of the valence orbitals of the larger Ge–Sn grouping are probably responsible for this result.

The conformations of I and II (Figure 3) are identical and are between the fully staggered and eclipsed forms. These conformations are also identical to those observed in the analogous compounds $Me_3SiSiPh_3$,[8e] $Me_3SiGePh_3$,[12a] and $Ph_3SiGeMe_3$,[12b] which possess a crystallographic 3-fold axis. Since molecules I and II have no crystallographic molecular symmetry, this conformation seems to be a characteristic feature of these molecules.

Acknowledgment. Support of this research by the National Science Foundation under Grant RII-88-02973 for the establishment of a Minority Research Center of Excellence in Materials Science and Grant CHE-91-16934 for USA/East European collaborative research is gratefully acknowledged.

Supplementary Material Available: For complexes I and II, complete listings of crystallographic data, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, and bond distances and angles (12 pages); listings of observed and calculated structure factors for I and II (8 pages). Ordering information is given on any current masthead page.

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Metal Complexes with Tetrapyrrole Ligands. 62.[1] ^{13}C NMR Spectra of Dicerium(III) and Dipraseodymium(III) Tris(octaethylporphyrinate)

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Received April 25, 1991

With the recent synthesis of two new families of lanthanide porphyrins, the double-decker LnP_2 and the triple-decker Ln_2P_3 sandwich compounds,[3-6] opportunities are now present to study molecular properties as a function of lanthanide contraction and concomitant sandwich compression. Recent physical studies have involved cyclic voltammetry,[7] optical and resonance Raman spectroscopy,[8] and ^1H NMR spectroscopy.[9] This note discusses the ^{13}C NMR spectra of the paramagnetic "triple-decker" sandwiches $Ce_2(OEP)_3$ and $Pr_2(OEP)_3$, OEP = octaethylporphyrin, and presents further commentary on the ^1H NMR spectra of the series $Ln_2(OEP)_3$, Ln = Ce, Pr, Nd, Sm, Eu.[9]

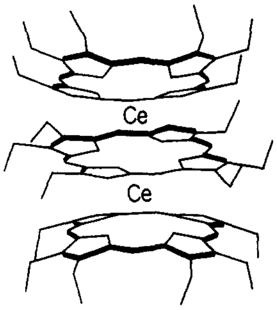

Figure 1. Line drawing of $Ce_2(OEP)_3$, showing doming of the outer OEP rings. Some C_2H_5 groups have been omitted for clarity.

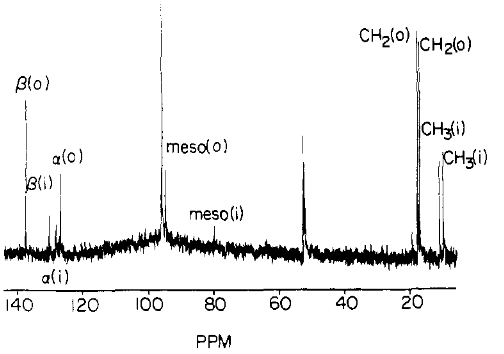

Figure 2. Broadband-decoupled ^{13}C NMR spectrum of $Ce_2(OEP)_3$ in CCl_4/CD_2Cl_2 at 125 MHz and 293 K.

In our previous work we examined in detail the ^1H NMR spectrum of $Ce_2(OEP)_3$ and showed that the observed isotropic shifts (*meso*-H, CH_2, and CH_3) were essentially dipolar in origin, a fact consistent with the literature on lanthanide complexes and shift reagents.[10-12] Also the C_2H_5 outer-ring protons exhibited isotropic shifts consistent only with a solution geometry in which the outer ethyl groups, on average, point upward, away from the inner porphyrin ring. This geometry is illustrated schematically in Figure 1. Although the proton resonances appear to result solely from a dipolar interaction between proton and unpaired electron spin, this does *not* preclude the existence of a covalent interaction between the spin containing cerium orbital and a low-lying (π or π^*) porphyrin molecular orbital. Recent work by McGarvey,[13] for example, shows that uranocene, a $5f^2$ sandwich compound, has substantial ^1H and ^{13}C contact shift contributions. In $Ce_2(OEP)_3$, a lanthanide porphyrin sandwich, the protons in

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