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Catenated Group 14 Compounds. Synthesis, Structural and Spectral Characterization, and Chemistry of the Chains $Me_3CSiMe_2GeMe_2SnR_3$ (R = Me, Ph)

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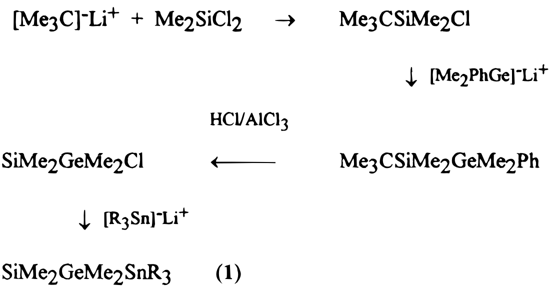
The permethylated catenated group 14 compound with the periodic chain C−Si−Ge−Sn is reported, **1a**, together with the triphenyltin analog, **1b**. Complete spectral characterization, including multinuclear NMR, is provided. The single-crystal structure of **1b** is reported: the bond lengths $C_{t\text{-Bu}}$−Si, Si−Ge, and Ge−Sn, 1.900(9), 2.386(2), and 2.608(1) Å, respectively, are all in the normal range. Bond angle measurements indicate that the *tert*-butyl group dominates the structure resulting in significant distortions about the Ge atom. Photochemical treatment of **1a** resulted in elimination of Me_2Ge and Me_2Sn, with a small amount of direct Ge−Sn cleavage. Treatment of **1a** with *n*-butyllithium resulted in the predominant formation of $Me_3CSiMe_2GeMe_2Li$ and $Me_3Sn(n\text{-Bu})$. Both the photochemical and *n*-BuLi reactions of **1a** also produced $(Me_3CSiMe_2GeMe_2)_2$ as a significant byproduct.

Introduction

The chemistry of group 14 elements is distinguished by their capacity to form catenate chains. Thus hydrocarbons, polysilanes, and polygermanes are well-established and well-studied systems, and Sn−Sn and Pb−Pb systems are known but less prevalent.[1] The polysilanes and -germanes have received more attention by virtue of their potential technological value as photoresists, preceramics, free radical polymerization initiators, and related uses.[2,3] Their properties derive from the special characteristics of the metalloid−metalloid bond such as electron delocalization, the ability of group exchange between elements, formation of silylenes and germylenes upon photochemical or thermal excitation,[4] and various molecular rearrangements,[5] some of which are catalyzed by transition metals.[6]

We are interested in the synthesis of intragroup 14 catenated systems and recently published the first solid-state structural analyses of the Si−Ge bond[7] and the Ge−Sn bond.[8] In the case of transition metal derivatives, we have also studied their photochemical properties which led to novel molecular rearrangements.[9] The extension to more complex chains containing more than 2 or 3 of the elements poses some interesting synthetic problems and would open new areas of chemistry. We have briefly described the formation of new materials containing the extended, and periodically correct, linkage C−Si−Ge−Sn,[10] and now report the complete synthesis, structural analysis, and photochemistry of $Me_3CSiMe_2GeMe_2SnR_3$ (R = Me(**1a**), Ph(**1b**)).

Scheme 1[a]



[a] R = Me (**1a**), Ph(**1b**).

Discussion

Synthesis and Spectral Characterization. The reaction sequence for the formation of the title compounds involving sequential salt-elimination reactions is illustrated in Scheme 1.

Each step is a moderate- to high-yield reaction, and all spectroscopic details, recorded in Table 1, are in accord with the structural assignments. An important key reaction is that involving the replacement of the Ge−Ph linkage by Ge−Cl. The reactivity of Si(Ge)−C(sp^2) bonds compared to the related Si(Ge)−C(sp^3) bonds is an important synthetic strategy for function-

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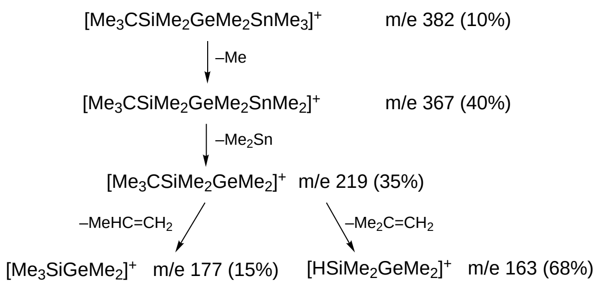
Table 1. Analytical and Spectral Data for Compounds[a]

$Me_3CSiMe_2GeMe_2Ph$	
^1H	0.068 (6H, s, $SiMe_2$); 0.49 (s, 6H, $GeMe_2$); 0.88 (s, 9H, CMe_3); 7.15−7.22, 7.42−7.46 (m, 5H, Ph)
^{13}C	−5.40 ($SiMe_2$); −2.86 ($GeMe_2$); 18.33 ($\mathit{C}Me_3$); 27.47 ($C\mathit{Me_3}$), 128.2, 128.4, 133.8, 142.8 (Ph)
^{29}Si	0.83
MS	296 $[M]^+$, 8; 281 $[M - Me]^+$, 5; 239 $[PhGeMe_2SiMe_3]^+$, 12; 177 $[GeMe_2SiMe_3]^+$, 10; 166 $[PhGeMe]^+$, 8; 151 $[PhGe]^+$, 9; 135 $[PhSiMe_2]^+$, 100; 89 $[GeMe]^+$, 3; 73 $[SiMe_3]^+$, 80; 57 $[CMe_3]^+$, 5
$Me_3CSiMe_2GeMe_2Cl$	
^1H	0.11 (6H, s, $SiMe_2$); 0.62 (6H, s, $GeMe_2$); 0.85 (9H, s, CMe_3)
^{13}C	−6.25($SiMe_2$); 5.28 ($GeMe_2$); 18.12 ($\mathit{C}Me_3$); 27.14 ($C\mathit{Me_3}$)
^{29}Si	6.10
MS	254 $[M]^+$, 3; 239 $[M - Me]^+$, 2; 219 $[M - Cl]^+$, 3; 197 $[M - CMe_3]^+$, 15; 115 $[CMe_3SiMe_2]^+$, 8; 89 $[GeMe]^+$, 5; 73 $[SiMe_3]^+$, 100
$Me_3CSiMe_2GeMe_2H$	
anal.	C, 43.88 (calcd), 44.57 (fnd); H, 10.12 (calcd), 9.52 (fnd)
^1H	0.07 (6H, s, $SiMe_2$); 0.29 (6H, d, $J = 4.3$ Hz, $GeMe_2$); 0.93 (9H, s, CMe_3); 3.66 (1H, m, $J = 4.3$ Hz, Ge−H)
^{13}C	−6.25 ($SiMe_2$); −5.43 ($GeMe_2$); 17.84 ($\mathit{C}Me_3$); 27.15 ($C\mathit{Me_3}$)
^{29}Si	1.66
IR	ν(Ge−H) 2000.7
MS	220 $[M]^+$, 4; 204 $[M - 16]^+$, 2; 163 $[SiMe_2GeMe_2H]^+$, 6; 115 $[CMe_3SiMe_2]^+$, 10; 89 $[GeMe]^+$, 8; 73 $[SiMe_3]^+$, 100; 59 $[SiMe_2H]^+$, 7
Me_3CSiMe_3	
^1H	0.50 (9H, s, $SiMe_3$); 0.97 (9H, s, CMe_3)
^{13}C	−4.43 ($SiMe_3$); 16.38 ($\mathit{C}Me_3$) 26.41 ($C\mathit{Me_3}$)
^{29}Si	8.04
MS	130 $[M]^+$, 3; 115 $[CMe_3SiMe_2]^+$, 1; 73 $[SiMe_3]^+$, 100; 57 $[CMe_3]^+$, 40
$Me_3CSiMe_2GeMe_3$	
anal.	C, 46.40 (calcd), 46.12 (fnd); H, 10.38 (calcd), 10.16 (fnd)
^1H	0.15 (6H, s, $SiMe_2$); 0.35 (9H, s, $GeMe_3$); 1.03 (9H, s, CMe_3)
^{13}C	−5.66 ($SiMe_2$); −1.61($GeMe_3$); 18.2 ($\mathit{C}Me_3$); 27.5 ($C\mathit{Me_3}$)
^{29}Si	0.42
UV (hexane)	215
MS	234 $[M]^+$, 4; 219 $[M\text{-}Me]^+$, 4; 177 $[SiMe_3GeMe_2]^+$, 6; 163 $[SiMe_2GeMe_2H]^+$, 10; 115 $[CMe_3SiMe_2]^+$, 12; 104 $[GeMe_2]^+$, 2; 89 $[GeMe]^+$, 12; 73 $[SiMe_3]^+$, 100; 59 $[SiMe_2H]^+$, 6
$Me_3CSiMe_2SnMe_3$	
anal.	C, 38.73 (calcd), 39.61 (fnd); H, 8.67 (calcd), 8.84 (fnd)
^1H	0.13 (6H, s, $SiMe_2$); 0.21 (9H, s, $^2J(Sn-H) = 44$ Hz, $SnMe_3$); 0.92 (9H, s, CMe_3)
^{13}C	−10.92 ($SnMe_3$); −3.71 ($SiMe_2$); 18.62 ($\mathit{C}Me_3$); 27.40 ($C\mathit{Me_3}$)
^{29}Si	5.30 ($^1J(^{117}Sn-^{29}Si) = 602$ Hz; $^1J(^{119}Sn-^{29}Si) = 630$ Hz)
^{119}Sn	−126.4
UV (hexane)	214
MS	280 $[M]^+$, 5; 265 $[M - Me]^+$, 80; 165 $[Me_3Sn]^+$, 5; 150 $[Me_2Sn]^+$, 8; 135 $[MeSn]^+$, 60; 120 $[Sn]^+$, 5; 73 $[Me_3Si]^+$, 100; 58 $[SiMe_2]^+$, 4
$Me_3CSiMe_2GeMe_2SnMe_3$, 1a	
anal.	C, 34.60 (calcd), 35.27 (fnd); H, 7.92 (calcd), 7.54 (fnd)
^1H	0.08 (6H, s, $SiMe_2$); 0.23 (9H, s, $^2J(Sn-H) = 46$ Hz, $SnMe_3$); 0.42 (6H, s, $^3J(Sn-H) = 34$ Hz, $GeMe_2$); 0.92 (9H, s, CMe_3)
^{13}C	−10.43 ($SnMe_3$); −4.52 ($SiMe_2$); −4.03 ($GeMe_2$); 18.77 ($\mathit{C}Me_3$); 27.59 ($C\mathit{Me_3}$)
^{29}Si	5.48 ($^2J(^{119}Sn-^{29}Si) = 70$ Hz)
^{119}Sn	−81.8
UV (*c*-hexane)	228 ($\epsilon = 15, 120$)
MS	382 $[M]^+$, 10; 367 $[M - Me]^+$, 40; 219 $[CMe_3SiMe_2GeMe_2]^+$, 35; 177 $[Me_3SiGeMe_2]^+$, 15; 163 $[Me_3SiGeMeH]^+$, 68; 135 $[SnMe]^+$, 30; 119 $[Me_3Ge]^+$, 32; 89 $[MeGe]^+$, 8; 73 $[Me_3Si]^+$, 100; 59 $[SiMe_2H]^+$, 5
$Me_3CSiMe_2GeMe_2SnPh_3$, 1b	
anal.	C, 54.98 (calcd), 55.00 (fnd); H, 6.39 (calcd), 6.66 (fnd)
^1H	0.065 (6H, s, $SiMe_2$); 0.66 (6H, s, $GeMe_2$); 0.85 (9H, s, CMe_3); 7.18, 7.67 (m, 15H, Ph)
^{13}C	−4.37 ($SiMe_2$), −2.41 ($GeMe_2$); 19.07 ($\mathit{C}Me_3$); 27.46 ($C\mathit{Me_3}$); 128.5, 128.7, 137.8, 140.8 (Ph)
^{29}Si	6.41 ($^2J(^{119}Sn-^{29}Si) = 72$ Hz)
^{119}Sn	−137.9
MS	553 $[M - Me]^+$, 15; 351 $[Ph_3Sn]^+$, 25; 281 $[CMe_3SiMe_2GeMePh]^+$, 20; 239 $[Me_3SiGeMePh]^+$, 10; 197 $[PhSn]^+$, 50; 163 $[Me_3SiGeMeH]^+$, 25; 135 $[PhMeSi]^+$, 45; 89 $[MeGe]^+$, 6; 73 $[Me_3Si]^+$, 100
$(Me_3CSiMe_2GeMe_2)_2$	
anal.	C, 43.88 (calcd), H, 9.66 (calcd); C, 44.31 (fnd), H, 9.97 (fnd)
^1H	0.16 (12H, s, $SiMe_2$); 0.46 (12H, s, $GeMe_2$); 0.97 (18H, s, CMe_3)
^{13}C	−3.90 ($SiMe_2$); −3.51 ($GeMe_2$); 19.0 ($\mathit{C}Me_3$); 27.7 ($C\mathit{Me_3}$)
^{29}Si	4.60
UV (hexane)	229
MS	436 $[M]^+$, 10; 421 $[M - 15]^+$, 4; 219 $[Me_3CMe_2SiMe_2Ge]^+$, 30; 163, $[HMe_2SiMe_2Ge]^+$, 32; 119 $[Me_3Ge]^+$, 8; 73 $[Me_3Si]^+$, 100; 59 $[HMe_2Si]^+$, 6
$Me_3CSiMe_2GeMe_2SiMe_2CMe_3$	
^1H	0.15 (12 H, s, $SiMe_2$); 0.40 (6H, s, $GeMe_2$); 0.98 (18H, s, CMe_3)
^{29}Si	2.94
MS	334 $[M]^+$, 5; 319 $[M - 15]^+$, 3; 277 $[M - Bu]^+$, 3; 219 $[Me_3CMe_2SiMe_2Ge]^+$, 7; 163 $[HSiMe_2Me_2Ge]^+$, 15; 130 $[Me_3CSiMe_3]^+$, 7; 115 $[Me_3CSiMe_2]^+$, 8; 89 $[MeGe]^+$, 6, 73 $[Me_3Si]^+$, 100; 59 $[HSiMe_2]^+$, 11

[a] NMR data in δ; IR (hexane) in cm^{-1}; MS in m/z; UV (λ_{max}) in nm.

Scheme 2



alizing silicon and germanium compounds.[11] Therefore, the use of the reagent $[Me_2PhGe]^-Li^+$ for the purpose of later removing the Ph group by taking advantage of this enhanced reactivity provides a very convenient entry into substituted Ge compounds. The final step in Scheme 1, the salt-elimination reaction between $Me_3CSiMe_2GeMe_2Cl$ and $[R_3Sn]^-Li^+$, may be substituted by an amine elimination reaction which has been previously used for synthesizing metal–metal bonds.[12] Thus, the reaction between the tin amide, Me_3SnNEt_2, and the germanium hydride, $Me_3CSiMe_2GeMe_2H$ (formed by LAH reduction of $Me_3CSiMe_2GeMe_2Cl$), is a useful alternative method for the formation of the Ge–Sn bond, eq 1.

$$Me_3CSiMe_2GeMe_2Cl \xrightarrow{LAH} Me_3CSiMe_2GeMe_2H \xrightarrow{Me_3SnNEt_2} Me_3CSiMe_2GeMe_2SnMe_3 + Et_2NH \quad (1)$$

The amine-elimination reaction may be a more general and preferred route since it imparts more flexibility with respect to the other groups coordinated to the tin atom. Compounds **1a,b** are air and thermally stable materials, and **1a** may be purified by distillation. Compound **1b** is a solid, and recrystallization yielded crystals suitable for analysis by single-crystal X-ray diffractometry; *vide infra*. All the nuclei comprising **1a,b** have a nuclear spin, and we have used multinuclear NMR to characterize the chains. Overall the data are in accord with expectations based upon the limited data available on simple binary Si–Ge and Ge–Sn compounds.[9]

Mass spectral analysis of **1a** illustrated several of the reported aspects of the fragmentation patterns of individual Si–Ge and Ge–Sn compounds,[13–15] including ligand exchange, butylene/propylene expulsion, and simple element–element bond cleavage. The pattern is outlined in Scheme 2. In addition to the ions in Scheme 2, $[Me_3Si]^+$, *m/e* 73 (100%), and $[Me_3Ge]^+$, *m/e* 119 (32%), were observed resulting from expected methyl migration reactions.

The mass spectral fragmentation pattern of **1b** exhibits similar characteristic properties, plus the migration of the phenyl group, *via* a series of 1,2-shifts, down the group 14 chain from Sn, *via* Ge, to Si, to form ions $[Me_2PhSi]^+$, *m/e* 135 (45%), and $[Me_2PhGe]^+$, *m/e* 181 (20%).

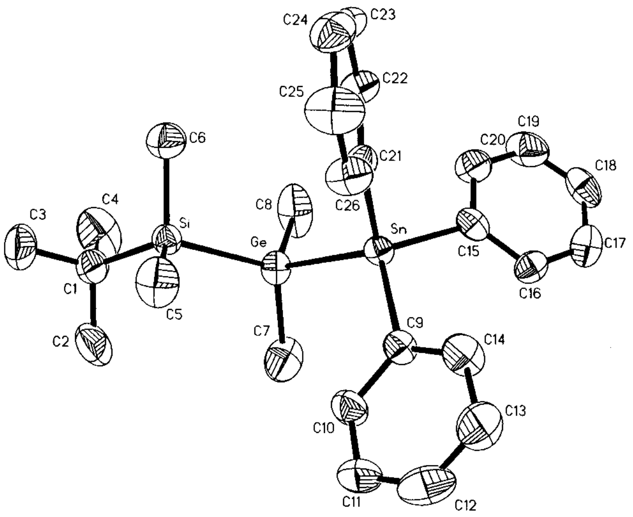


Figure 1. Structure of **1b**.

Structure of 1b. The structure of **1b** is illustrated in Figure 1. Pertinent crystal, collection, and refinement data are presented in Table 2, and the atomic coordinates are listed in Table 3. The bond lengths and angles are recorded in Tables 4 and 5, respectively. The bonds $C_{t\text{-Bu}}$–Si = 1.900(9) Å (marginally longer than the C_{Me}–Si lengths of 1.87(1) and 1.88(1) Å), Si–Ge = 2.386(2) Å, and Ge–Sn = 2.608(1) Å are all close to the expected mean distances. For example, the limited Si–Ge bond distances reported range from 2.384(1) to 2.405(2) Å,[7] and the recently reported $Me_3GeSnPh_3$, $Ph_3GeSnMe_3$, and $[(Me_3Si)_3Ge]_2SnCl_2$ bond lengths range from 2.602(1) to 2.631(1) Å.[8,16] Any strain along the chain is principally reflected by the bond angles of the ancillary groups attached to the Si, Ge, and Sn atoms. Thus, while the C_{Me}–Si–C_{Me} and C_{Me}–Ge–C_{Me} bond angles are reduced from the tetrahedral angle, 107.0(5) and 106.2(5)°, respectively, the chain angle C–Si–Ge is larger, 112.5(3)°. The germanium group bond angles are those affected to the largest extent, and it is the *tert*-butyldimethylsilyl group that is responsible; while the two Sn–Ge–C bond angles are 106.5(3) and 107.5(3)°, the corresponding Si–Ge–C angles are considerably increased to 112.4(4) and 116.2(3)°. Figure 1 suggests that the close proximity of the *tert*-butyl group plays a major role in this deformation. A Newman projection about the Si–Ge bond shows that the bulky *tert*-butyl and triphenylstannyl groups are *trans* to each other as expected, Figure 2.

Photochemistry of 1a. Since the photochemistry of oligosilanes and germanes has proved to be a fruitful area of research, we initially investigated the photochemical properties of **1a**. The compound has a λ_{max} (hexane) at 228 nm, close to that reported for octamethyltrisilane, $Me_3SiSiMe_2SiMe_3$, 215 nm,[2,4] suggesting that the three group 14 elements behave in a manner similar to the equivalent homoelement compounds with respect to electronic excitations. Irradiation of a benzene solution of **1a** in a quartz tube with a 450 W medium-pressure mercury lamp resulted in the slow formation of an array of compounds that may be

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Table 2. Structure Determination Summary

	Crystal Data
empirical formula	$C_{26}H_{36}GeSiSn$
color; habit	colorless plate (sealed in epoxy glue)
cryst size	0.50 × 0.50 × 0.16 mm
cryst system	monoclinic
space group	$P2_1$
unit cell dimens	$a = 8.704(3)$ Å $b = 8.195(2)$ Å $c = 19.299(6)$ Å $\beta = 99.39(3)°$
V	1358.1(7) Å^3
Z	2
fw	567.9
D(calcd)	1.389 Mg/m^3
abs coeff	2.067 mm^{-1}
F(000)	576
	Data Collection
diffractometer used	Siemens R3m/V
radiation	Mo Kα ($\lambda = 0.710\,73$ Å)
temp (K)	210
monochromator	highly oriented graphite crystal
2θ range	3.5−50.0°
scan type	ω
scan speed	variable; 3.00−20.00°/min in ω
scan range (ω)	1.20°
bckg meast	stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of tot. scan time
std rflcns	3 measd every 97 reflcns
index ranges	$0 \le h \le 10$, $0 \le k \le 9$, $-22 \le l \le 22$
reflcns collcd	4412
indpdt rflcns	3578 ($R_{\mathrm{int}} = 1.97\%$)
obsd reflcns	3578 ($F > 0.0\sigma(F)$)
abs corr	N/A
	Solution and Refinement
system used	Siemens SHELXTL PLUS (PC Version)
solution	direct methods
refinement method	full-matrix least-squares
quantity mimimized	$\sum w(F_o - F_c)^2$
absolute struct	$\eta = 0.81(5)$
extinction corr	$\chi = 0.00000(15)$, where $F^* = F[1 + 0.002\chi F^2/(\sin(2\theta))]^{-1/4}$
H atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
no. of params refined	265
final R indices (obsd data)	$R = 4.22\%$, w$R = 5.26\%$
R indices (all data)	$R = 4.22\%$, w$R = 5.26\%$
goodness-of-fit	1.62
largest and mean Δ/σ	0.009, 0.001
data-to-param ratio	13.5:1
largest diff peak	2.91 e Å^{-3}
largest diff hole	−1.89 e Å^{-3}

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)[a]
Sn	2339(1)	0	2000(1)	30(1)
Ge	3802(1)	1610(1)	3075(1)	36(1)
Si	6179(2)	204(3)	3481(1)	36(1)
C(1)	7186(11)	971(13)	4369(4)	51(3)
C(2)	6130(14)	688(17)	4923(5)	76(5)
C(3)	8690(12)	−36(23)	4588(5)	85(4)
C(4)	7578(18)	2742(15)	4336(6)	89(5)
C(5)	5797(14)	−2036(12)	3530(6)	68(4)
C(6)	7459(12)	497(13)	2797(5)	58(4)
C(7)	2363(13)	1854(16)	3756(5)	70(4)
C(8)	4146(15)	3796(12)	2740(6)	78(5)
C(9)	953(9)	−1934(9)	2317(4)	36(2)
C(10)	1053(11)	−2375(11)	3025(4)	49(3)
C(11)	230(13)	−3663(14)	3233(5)	62(4)
C(12)	−754(14)	−4533(12)	2727(6)	72(4)
C(13)	−902(14)	−4158(13)	2046(6)	68(4)
C(14)	−8(13)	−2856(11)	1840(5)	53(3)
C(15)	884(10)	1617(10)	1283(4)	38(2)
C(16)	−736(9)	1470(10)	1150(4)	40(3)
C(17)	−1592(12)	2505(11)	665(5)	52(3)
C(18)	−894(13)	3690(12)	325(4)	54(3)
C(19)	664(13)	3862(12)	478(5)	62(4)
C(20)	1543(11)	2832(11)	945(5)	49(3)
C(21)	3872(9)	−1188(9)	1396(4)	34(2)
C(22)	4788(10)	−355(8)	985(4)	40(3)
C(23)	5777(11)	−1142(12)	615(5)	51(3)
C(24)	5903(12)	−2821(12)	635(5)	55(3)
C(25)	5015(14)	−3693(11)	1030(6)	66(4)
C(26)	4006(11)	−2899(10)	1414(5)	50(3)

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

Table 4. Bond Lengths (Å)

Sn−Ge	2.608(1)	Sn−C(9)	2.140(8)
Sn−C(15)	2.169(8)	Sn−C(21)	2.145(8)
Ge−Si	2.386(2)	Ge−C(7)	1.967(11)
Ge−C(8)	1.944(11)	Si−C(1)	1.900(9)
Si−C(5)	1.871(11)	Si−C(6)	1.876(11)
C(1)−C(2)	1.538(15)	C(1)−C(3)	1.547(16)
C(1)−C(4)	1.494(16)	C(9)−C(10)	1.402(11)
C(9)−C(14)	1.366(12)	C(10)−C(11)	1.372(15)
C(11)−C(12)	1.387(15)	C(12)−C(13)	1.336(17)
C(13)−C(14)	1.415(15)	C(15)−C(16)	1.397(12)
C(15)−C(20)	1.367(13)	C(16)−C(17)	1.386(12)
C(17)−C(18)	1.369(14)	C(18)−C(19)	1.347(16)
C(19)−C(20)	1.374(13)	C(21)−C(22)	1.392(12)
C(21)−C(26)	1.406(11)	C(22)−C(23)	1.367(13)
C(23)−C(24)	1.380(14)	C(24)−C(25)	1.371(16)
C(25)−C(26)	1.399(16)		

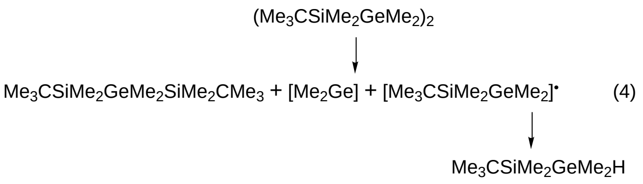
completely understood in terms of three basic reactions: (a) photoelimination of the elements of dimethylgermylene, eq 2a; (b) photoelimination of the elements of dimethylstannylene, eq 2b; (c) cleavage of the Ge−Sn bond to form radicals, eq 2c.

$$\begin{array}{llr} & \longrightarrow \mathrm{Me_3CSiMe_2SnMe_3 + [Me_2Ge]} & (2a) \\ \mathrm{Me_3CSiMe_2GeMe_2SnMe_3} & \longrightarrow \mathrm{Me_3CSiMe_2GeMe_3 + [Me_2Sn]} & (2b) \\ & \longrightarrow \mathrm{[Me_3CSiMe_2GeMe_2]^{\bullet} + [Me_3Sn]^{\bullet}} & (2c) \\ & \qquad\qquad\downarrow & \\ & \mathrm{Me_3CMe_2SiMe_2GeH + (Me_3Sn)_2} & \end{array}$$

All the compounds were identified by comparison of their spectral and GC/MS properties with those of authentic samples, some of which were previously unknown and were independently synthesized for the first time. All synthetic and spectral details are reported in the Experimental Section. The results indicate that, to a large extent, **1a** behaves in a manner similar to octamethyl- and related trisilanes which photoeject silylenes,[4] with the added features that the relatively weak Sn−C and Ge−Sn bonds are also prone to cleavage resulting in the chemistry noted in eq 2b,2c. Significant amounts (10%) of $\mathrm{(Me_3CSiMe_2GeMe_2)_2}$ were observed in the GC/MS resulting from the dimerization of the germyl radicals formed in eq 2c. We have independently synthesized this compound via the coupling reaction noted in eq 3.

$$\mathrm{2Me_3CSiMe_2GeMe_2Cl + Li \rightarrow (Me_3CSiMe_2GeMe_2)_2} \quad (3)$$

In separate experiments we have shown that the new compound $\mathrm{(Me_3CSiMe_2GeMe_2)_2}$ is also prone to photochemical transformation, eq 4. Irradiation resulted in the formation of the GeMe$_2$ elimination product $\mathrm{(Me_3CSiMe_2)_2GeMe_2}$ in high yield (synthesized indepen-

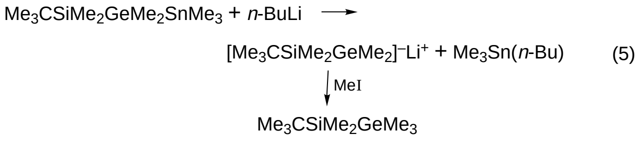


$$\begin{array}{c} (Me_3CSiMe_2GeMe_2)_2 \\ \downarrow \\ Me_3CSiMe_2GeMe_2SiMe_2CMe_3 + [Me_2Ge] + [Me_3CSiMe_2GeMe_2]^{\bullet} \\ \downarrow \\ Me_3CSiMe_2GeMe_2H \end{array} \tag{4}$$

dently) along with significant amounts of $Me_3CSiMe_2GeMe_2H$ presumably formed by radical cleavage of the Ge−Ge bond.

We have made many attempts to trap the various germylene and stannylene fragments with the usual agents, i.e. Ph_3GeH, Et_3SiH, Me_3GeH, *n*-Bu_3SnH, 2,3-dimethyl-1,3-butadiene, and dimethyl disulfide. From all the various reactions we have not observed any trapping! The product distributions from the photolysis of **1** did not change appreciably from that observed in the absence of traps with the exception of the reaction with dimethyl-1,3-butadiene. In this latter case we did not observe any of the radical process products derived from the chemistry described in eq 2c. We conclude that the presence of both ER_2 and radical generation interferes with the ability of the traps to efficiently react with the germylene/stannylene photoproducts. A similar inability to trap R_2Ge species was recently reported by Walsh and co-workers, and the work of Egorov and Gaspar suggests that such intermediates are capable of electron-transfer ion-based chemistry that often precludes their ready trapping.[22]

Reaction of 1a with MeLi. The cleavage of group 14 element−element bonds by alkali metals and alkyllithiums is a well-established route for the formation of $[R_3E]^-Li^+$ salts which are important synthons.[17] Treatment of **1a** with alkyllithium species could involve several different processes in much the same manner that the photochemistry above resulted in several distinct pathways. The reaction between **1a** and *n*-butyllithium resulted in cleavage of the Ge−Sn bond as noted in eq 5. The formation of the germyllithium



$$\begin{array}{c} Me_3CSiMe_2GeMe_2SnMe_3 + n\text{-}BuLi \longrightarrow \\ [Me_3CSiMe_2GeMe_2]^-Li^+ + Me_3Sn(n\text{-}Bu) \\ \downarrow \text{MeI} \\ Me_3CSiMe_2GeMe_3 \end{array} \tag{5}$$

was confirmed by quenching the reagent with methyl iodide; however, in THF a significant amount of halogen−metal exchange occurred with MeI to produce $(Me_3CSiMe_2GeMe_2)_2$. Minor products, Me_4Sn and $Me_2Sn(n\text{-}Bu)_2$, were also observed by both ^{119}Sn NMR and GC/mass spectral analysis of the crude product mixture.

Conclusions

A rational synthetic pathway has been used to develop group 14 compounds containing the periodic connectivity C−Si−Ge−Sn. All the products from these reactions were synthesized by independent routes for complete characterization. X-ray analysis shows the chain to arrange itself such that the bulky *t*-Bu− and Ph_3Sn− groups are *trans* to each other about the central Si−Ge bond. All bond lengths C−Si, Si−Ge, and Ge−Sn are in the limited ranges expected, and the *tert*-butyl group forces the methyl groups on Ge to be displaced away from the C end of the chain. The compounds are thermally and oxidatively stable but are photochemically labile with respect to elimination of R_2Ge and R_2Sn and cleavage of the Ge−Sn bond. Alkyllithium reagents produces cleavage of the Ge−Sn bond and formation of the corresponding germyllithium reagent. We are currently examining the chemistry of the new compounds in detail including reactivity with transition metal complexes and wavelength-dependent photochemistry.

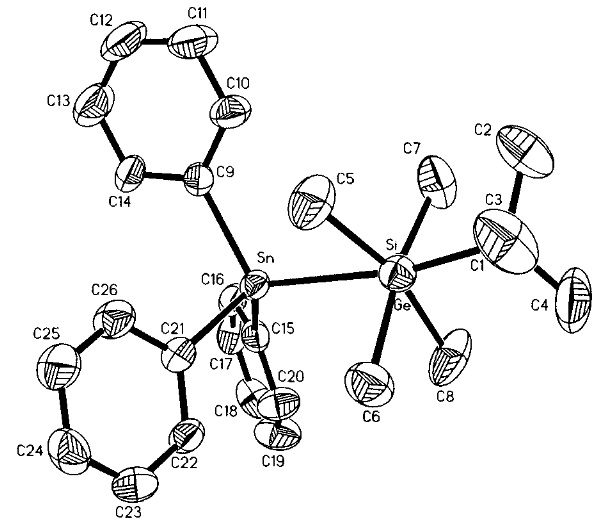


Figure 2. Newman projection of **1b** along the Si−Ge bond.

Table 5. Bond Angles (deg)

Ge−Sn−C(9)	111.9(2)	Ge−Sn−C(15)	110.9(2)
C(9)−Sn−C(15)	109.7(3)	Ge−Sn−C(21)	113.3(2)
C(9)−Sn−C(21)	104.4(3)	C(15)−Sn−C(21)	106.3(3)
Sn−Ge−Si	107.5(1)	Sn−Ge−C(7)	107.5(3)
Si−Ge−C(7)	116.2(3)	Sn−Ge−C(8)	106.5(3)
Si−Ge−C(8)	112.4(4)	C(7)−Ge−C(8)	106.2(5)
Ge−Si−C(1)	112.6(3)	Ge−Si−C(5)	109.8(4)
C(1)−Si−C(5)	109.8(5)	Ge−Si−C(6)	106.9(3)
C(1)−Si−C(6)	110.6(4)	C(5)−Si−C(6)	107.0(5)
Si−C(1)−C(2)	109.7(7)	Si−C(1)−C(3)	108.4(7)
C(2)−C(1)−C(3)	107.7(8)	Si−C(1)−C(4)	111.0(7)
C(2)−C(1)−C(4)	110.0(10)	C(3)−C(1)−C(4)	109.9(10)
Sn−C(9)−C(10)	121.4(6)	Sn−C(9)−C(14)	121.9(6)
C(10)−C(9)−C(14)	116.6(8)	C(9)−C(10)−C(11)	122.1(8)
C(10)−C(11)−C(12)	118.8(9)	C(11)−C(12)−C(13)	121.6(11)
C(12)−C(13)−C(14)	118.7(10)	C(9)−C(14)−C(13)	122.1(9)
Sn−C(15)−C(16)	122.1(6)	Sn−C(15)−C(20)	120.2(6)
C(16)−C(15)−C(20)	117.7(7)	C(15)−C(16)−C(17)	119.1(8)
C(1)−C(17)−C(18)	121.7(9)	C(17)−C(18)−C(19)	118.6(9)
C(18)−C(19)−C(20)	120.8(10)	C(15)−C(20)−C(19)	121.9(9)
Sn−C(21)−C(22)	123.5(5)	Sn−C(21)−C(26)	119.7(6)
C(22)−C(21)−C(26)	116.8(8)	C(21)−C(22)−C(23)	122.3(7)
C(22)−C(23)−C(24)	120.6(9)	C(23)−C(24)−C(25)	119.1(10)
C(24)−C(25)−C(26)	120.7(9)	C(21)−C(26)−C(25)	120.5(9)

Experimental Section

All manipulations were carried out under an argon atmosphere. Purchased reagents, *t*-$BuSiMe_2Cl$ (Hüls America), Me_3GeBr (Gelest), Me_3SnCl, and Ph_3SnCl (Aldrich), were used as supplied. Other reagents were synthesized using literature procedures: Me_2GeCl_2,[18] Me_3GeLi,[19] and Me_3SnNEt_2.[20]

^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded in C_6D_6 on a Bruker NR 200 MHz spectrometer; electron-impact mass

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spectra were recorded on a Hewlett Packard 5890/5971 GC/mass spectrometer; elemental analyses were performed by Galbraith Laboratories, and all data are recorded in Table 1.

Synthesis of $Me_3CSiMe_2GeMe_2Ph$. A 250 mL three-necked flask equipped with magnetic stirring bar and an addition funnel was charged with *t*-$BuSiMe_2Cl$ (3.08 g, 20.4 mmol) in 30 mL of THF. The solution was cooled to −25 °C. In a separate 100 mL Schlenk flask $PhMe_2GeLi$ was prepared from $PhMe_2GeCl$ (4.4 g, 20.4 mmol) and lithium metal (0.56 g) in 70 mL of THF. The green solution of $PhMe_2GeLi$ was transferred via a cannula to the addition funnel and added dropwise to the cooled solution of *t*-$BuSiMe_2Cl$. Upon complete addition, the reaction mixture was stirred at low temperature for 30 min, and then the solution was permitted to warm to room temperature and stirred for an additional 15 h. The solvent was removed on a rotary evaporator, 150 mL of hexane was added, and the resultant slurry was stirred for 15 min. The solution was filtered, hexane was removed on a rotary evaporator, and the residue was distilled at 148−150 °C at 20 mmHg to yield 4.3 g, 14.6 mmol (71%), of $Me_3CSiMe_2GeMe_2Ph$ as a colorless liquid.

Synthesis of $Me_3CSiMe_2GeMe_2Cl$. In a 250 mL Schlenk flask at room temperature hydrogen chloride was bubbled slowly into a 50 mL benzene solution of $Me_3CSiMe_2GeMe_2Ph$ (4.0 g, 13.5 mmol) and 100 mg of $AlCl_3$. The reaction flask became slightly warm, and the progress of chlorination was followed by GC and ^1H NMR spectroscopy. After 20 min, when the chlorination was complete, 5 mL of acetone was added to deactivate the catalyst. The solution was filtered and solvents were distilled at 50 mmHg. Finally, distillation at 118−119 °C at 61 mmHg yielded $Me_3CSiMe_2GeMe_2Cl$, 2.4 g (9.48 mmol, 70%).

Synthesis of $(Me_3CSiMe_2GeMe_2)_2$. A flame-dried 250 mL Schlenk flask was charged with 3.93 g (15.5 mmol) of $Me_3CSiMe_2GeMe_2Cl$ and 0.1 g of finely cut lithium metal in 60 mL of THF. The reaction mixture was vigorously stirred at room temperature. After 30 min the mixture became a gray slurry, and monitoring of the reaction *via* GC/mass spectrometry indicated that the coupled product was being formed. Continued stirring for 2 h resulted in the complete disappearance of the starting material and formation of the desired product, together with 5% of a material whose mass spectral properties indicated it was $Me_3CSiMe_2GeMe_2SiMe_2CMe_3$. Excess lithium was removed by filtration, the solvent was removed *in vacuo*, and the residue was extracted with 150 mL of hexane. Subsequent to filtration of this solution, and removal of the solvent, the residue was distilled at 88−99 °C/0.05 mmHg to yield 1.55 g (3.56 mmol, 46%) of $(Me_3CSiMe_2GeMe_2)_2$.

Synthesis of $Me_3CSiMe_2GeMe_2H$. To a slurry of 0.15 g (3.95 mmol) of lithium aluminium hydride in 10 mL of THF was added slowly via a syringe 1.0 g (3.95 mmol) of $Me_3CSiMe_2GeMe_2Cl$ in 20 mL of THF at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 30 min. The solution was filtered and quenched with 50 mL of cold water containing a few drops of HCl. The organic layer was extracted twice with hexane and washed with water and dried over $MgSO_4$. After the organic layer was filtered, and the solvent removed, distillation at 82 °C/61 mmHg yielded 0.32 g (1.46 mmol, 37%) of $Me_3CSiMe_2GeMe_2H$.

Synthesis of $Me_3CSiMe_2GeMe_3$. A flame-dried three-necked flask equipped with stirring bar and dropping funnel was charged with 2.29 g (15.2 mmol) of *t*-$BuMe_2SiCl$ in 20 mL of THF and cooled to −78 °C. To this cooled solution was added a solution of Me_3GeLi (prepared from 3.0 g, 15.2 mmol, of Me_3GeBr and 0.45 g of lithium metal in a mixture of HMPA (6 mL) and THF (15 mL)). The addition was conducted over a period of 45 min. The mixture was stirred at low temperature for 1 h and then further stirred for 16 h at room temperature. The reaction was quenched with cold water and extracted with hexane. The organic layer was repeatedly washed with water and dried over $MgSO_4$. After filtration, hexane was distilled off at 70 mmHg and the residue was distilled at 68 °C/20 mmHg to yield 1.8 g (7.74 mmol, 51%) of $Me_3CSiMe_2GeMe_3$.

Synthesis of $Me_3CSiMe_2SnMe_3$. Into a 250 mL three-necked-flask was placed 3.02 g (20.0 mmol) of *t*-$BuSiMe_2Cl$ in 30 mL of THF. To this solution was added slowly a solution of Me_3SnLi (prepared from 4.0 g (20.0 mmol) of Me_3SnCl and 1 g of lithium in 60 mL of THF) at −78 °C. The reaction mixture was stirred at low temperature for 1 h and then permitted to warm to room temperature and stirred for 16 h. THF was removed on a rotary evaporator, and 200 mL of hexane was added and stirred for 15 min. LiCl was removed by filtration, and hexane was removed at 60 mmHg. The residue was distilled at 86−88 °C/20 mmHg (lit.[21] 72−73.5 °C/11 mmHg) to yield 2.4 g (8.6 mmol, 43%) of $Me_3CSiMe_2SnMe_3$ as a colorless liquid.

Synthesis of $Me_3CSiMe_2GeMe_2SnMe_3$. A flame-dried 250 mL three-necked-flask equipped with stirring bar and addition funnel was charged with 12.5 g (49.4 mmol) of $Me_3CSiMe_2GeMe_2Cl$ in 100 mL of THF. To this solution was added dropwise a solution of Me_3SnLi (prepared from 9.84 g (49.4 mmol) of Me_3SnCl and 1.0 g of finely divided lithium metal in 100 mL of THF) at −78 °C. The addition was conducted over a period of 1 h. After complete addition of Me_3SnLi the reaction mixture was stirred at low temperature for 45 min and then stirred for 16 h at room temperature. THF was removed on a rotary evaporator, and the residue was extracted with 200 mL of hexane and filtered to remove LiCl. Hexane was removed and the residue was distilled through a small vigroux column at 96 °C/2 mmHg to yield 8.54 g (22.4 mmol, 45%) of $Me_3CSiMe_2GeMe_2SnMe_3$ as a colorless liquid.

Alternative Method for the Synthesis of $Me_3CSiMe_2GeMe_2SnMe_3$. Reaction of $Me_3CSiMe_2GeMe_2H$ with Me_3SnNEt_2. A flame-dried 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stirring bar was charged with 0.6 g (2.71 mmol) of $Me_3CSiMe_2GeMe_2H$ and 0.64 g (2.71 mmol) of Me_3SnNEt_2 in 15 mL of benzene. The reaction mixture was heated at reflux, and the formation of Et_2NH in the reaction was checked by IR spectroscopy. After 1 h evaporation of the solvent yielded 0.35 g (0.92 mmol, 34%) of crude $Me_3CSiMe_2GeMe_2SnMe_3$.

Synthesis of $Me_3CSiMe_2GeMe_2SnPh_3$. A 100 mL three-necked flask equipped with magnetic stirring bar and an addition funnel was charged with 1.0 g (3.95 mmol) of $Me_3CSiMe_2GeMe_2Cl$ in 20 mL of THF. To this solution at 0 °C was added a dark gray solution of Ph_3SnLi (prepared from 1.52 g (3.95 mmol) of Ph_3SnCl and 0.11 g of Li metal in 30 mL of THF). Upon complete addition, the mixture was stirred at 0 °C for 30 min, and then the solution was allowed to warm to room temperature and further stirred for 20 h. The solvent was removed on a rotary evaporator, and the residue was extracted with 50 mL of hexane and filtered. Removal of hexane yielded 1.42 g (2.50 mmol, 63%) of $Me_3CSiMe_2GeMe_2SnPh_3$ as a white crystalline solid. It was purified by sublimation at 70−75 °C/0.04 mmHg, mp 53 °C.

Photolysis of $Me_3CSiMe_2GeMe_2SnMe_3$. A quartz tube was charged with 0.1 g (0.26 mmol) of $Me_3CSiMe_2GeMe_2SnMe_3$ in 10 mL of degassed benzene. The solution was irradiated with a 450-W medium-pressure Hg lamp at a distance of 6 cm. The progress of the reaction was periodically monitored by GC/mass spectroscopy. Photolysis after 14 h showed formation of traces of $Me_3CSiMe_2GeMe_2H$ and $Me_3SnSnMe_3$, and the color of the solution changed to orange. After 38 h of photolysis, the color of the solution changed to orange-yellow and the solution became slightly turbid. The GC/mass spectra

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recorded at this time showed an increase in concentration of $Me_3CSiMe_2GeMe_2H$ and $Me_3SnSnMe_3$ along with the formation $Me_3CSiMe_2GeMe_3$, $Me_3CSiMe_2SnMe_3$, and $(Me_3CSiMe_2GeMe_2)_2$. The photolysis was stopped after 110 h when about 50% of the starting material had been consumed and the solution became colorless with the precipitation of a white solid. The solution was filtered, and 12 mg of a white solid was obtained which was found to be insoluble in common organic solvents. GC/mass spectral analysis of the solution showed the following compounds to be present: $Me_3CSiMe_2GeMe_2H$ (6%); $Me_3CSiMe_2GeMe_3$ (16%); $Me_3CSiMe_2SnMe_3$ (14%); $Me_3SnSnMe_3$ (4%); $(Me_3CSiMe_2GeMe_2)_2$ (10%). The formation of these photoproducts was also confirmed by ^{29}Si and ^{119}Sn NMR spectroscopy.

Reaction of $Me_3CSiMe_2GeMe_2SnMe_3$ with *n*-BuLi. A 100 mL Schlenk flask was charged with 0.16 g (0.42 mmol) of $Me_3CSiMe_2GeMe_2SnMe_3$ in 20 mL of THF. To this solution was added 0.3 mL of 1.6 M *n*-BuLi solution in hexane at −78 °C. No color change was observed, and the mixture was stirred at low temperature for 30 min and then at room temperature for 30 min. The mixture was cooled again to −78 °C, an excess of MeI was added, and the mixture stirred at low temperature for 5 min and then brought to room temperature for 10 min. After removal of the solvent 10 mL of hexane was added and LiI was removed by filtration. GC/mass spectroscopic analysis showed the formation of the following: Me_4Sn (14%); n-$BuSnMe_3$ (18%); $Me_3CSiMe_2GeMe_3$ (35%); $(n\text{-}Bu)_2SnMe_2$ (17%); $(Me_3CSiMe_2GeMe_2)_2$ (16%). The formation of these products was also confirmed by ^{29}Si and ^{119}Sn NMR spectroscopy.

Photolysis of $(Me_3CSiMe_2GeMe_2)_2$. A quartz tube was charged with 0.05 g (0.11 mmol) of $(Me_3CSiMe_2GeMe_2)_2$ in 8 mL of benzene. The solution was irrardiated as described above and the progress of the reaction monitored by GC/MS. After 26 h the solution was pale yellow and >91% of the starting material had been consumed. Analysis of the resulting solution showed that it contained the following products: $Me_3CSiMe_2GeMe_2H$ (25%); $(Me_3CSiMe_2)_2GeMe_2$ (75%); $Me_3CSiMe_2GeMe_3$ (trace); Me_3CSiMe_2Ph (trace), the latter incorporating the solvent presumably *via* a free radical process.

X-ray Analysis of 1 b, $Me_3CSiMe_2GeMe_2SnPh_3$. Data Collection. Intensity data were collected from a colorless plate crystal 0.50 × 0.50 × 0.16 mm encapsulated in epoxy glue, on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation. A preliminary data collection, structure determination, and refinement was carried out at room temperature. Because of the low melting point of the crystal (53 °C) high thermal motion was observed for most of the atoms; therefore, we repeated the measurement at 210 K. The strongest 4283 reflections (including the set of Friedel opposites to eliminate polar dispersion errors) in the 2θ range 3.5−50° plus another 129 indexed reflections predicted from the calculated (using the data of the structure determination at room temperature) powder diagram between 50 and 60° were measured at low temperature from the same crystal. The ω scan technique was applied with a variable scan speed (3.00−19.50°/min) and a scan range of 1.20°. The background measurement was performed using a stationary crystal and stationary counter at the beginning and end of each scan, each for 25.0% of the total scan time. Three standard reflections were measured every 97 reflections, and the intensities of these remained constant during the data collection. A total of 4412 reflections were collected (index ranges $0 \leq h \leq 10$, $0 \leq k \leq 9$, $-22 \leq l \leq 22$) of which 3578 were independent ($R_{int} = 1.97\%$). The data were corrected for Lorentz and polarization effects but not for absorption because the crystal was encapsulated in epoxy glue and a semiempirical absorption correction might not be accurate.

Solution and Refinement. Space groups $P2_1$ and $P2_1/m$ were possible with intensity distribution favoring the former. Attempts to solve the structure in $P2_1/m$ failed, but it was solved by direct methods and subsequent difference Fourier syntheses from the room-temperature data. The structure was finally refined by full-matrix least-squares using all 4412 reflections collected at low temperature (210 K). The quantity minimized was $\sum w(F_o - F_c{}^2$, where w is the weighting scheme ($w^{-1} = \sigma^2(F) + 0.0008F^2$). Hydrogen atoms were included as riding atoms and common isotropic U's were refined for the methyl (0.105 Å^2) and the phenyl hydrogen atoms (0.069 Å^2). A total of 265 parameters were refined, including Roger's parameter, $\eta = 0.81$, to establish the absolute configuration. The data to parameter ratio was 13.5:1, and the largest shift/esd was 0.001 in the final cycle. The final R indices are $R = 4.22\%$, w$R = 5.26\%$, and goodness-of-fit = 1.62. The largest difference peak and largest difference hole in the final Fourier map were 2.91 and −1.89 e Å^{-3}, respectively. The Siemens SHELXTL PLUS (PC version) software package was used for all calculations.

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Supporting Information Available: Tables of anisotropic thermal parameters and hydrogen positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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