Organometallics 1984, *3*, 255-263 255

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Registry No. 1, 84430-77-3; 2, 84430-78-4; 3, 87902-57-6; 4, 87902-58-7; 5, 87902-59-8; Mo(η^6-PhPMePh)(NCMe)($PMePh_2$)$_2$, 87902-60-1; Mo(η^6-PhPMePh)(PMe_3)($PMePh_2$)$_2$, 87902-61-2; Mo(η^6-PhPMePh)(PMe_2Ph)($PMePh_2$)$_2$, 87902-62-3; Mo(η^6-PhPMePh(CO)$_2$($PMePh_2$), 87902-63-4; molybdenum pentachloride, 10241-05-1; acetylene, 74-86-2.

Supplementary Material Available: Tables VI–X containing bond lengths and bond angles for the phenyl rings, thermal parameters, least-squares mean planes, root-mean-square vibration amplitudes, and final structure amplitudes (23 pages). Ordering information is given on any current masthead page.

Group 4A 9,10-Dihydro-9,10-diheteroanthracenes: Synthesis and Structure

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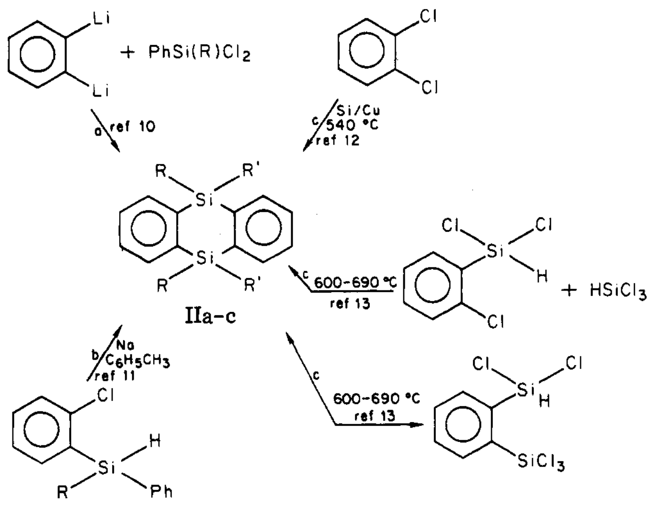
9,10-Dihydro-9,10-diheteroanthracenes are prepared by a ring closure reaction of a dilithio or di-Grignard intermediate prepared from (o-XC_6H_4)$_2$SiMeR (R = H, Me; X = Cl, Br) with $RR'MCl_2$ (R or R′ = H, Me, Ph; M = Si, Ge, Sn, Pb). Compounds that contain a silicon atom with germanium, tin, or lead are a previously unreported class of compounds. The molecular structures of 9,9,10,10-tetramethyl-9,10-dihydro-10-germa-9-silaanthracene, IIIa, and 9,9,10,10-tetramethyl-9,10-dihydro-10-stanna-9-silaanthracene, IIIb, have been determined by X-ray diffraction methods. The crystal data are as follows: compound IIIa, orthorhombic, *Pbca*, a = 9.585 (5) Å, b = 16.200 (12) Å, c = 21.236 (12) Å, Z = 8, 1512 observed data yielded a final R value of 0.043 by least-squares refinement (of a model with disordered silicon and germanium atoms); compound IIIb, monoclinic, $P2_1/n$, a = 18.897 (8) Å, b = 9.093 (6) Å, c = 19.439 (13) Å, β = 95.60°, Z = 8, 3475 observed data yielded a final R value of 0.051 for least-squares refinement. Molecules of compounds IIIa and IIIb exist in a "butterfly" shape with a boat conformation in the central 6-membered diheterocyclic ring. The dihedral angles of the benzo groups in compounds are 153° (IIIa) and 142° and 148° for the two independent molecules of IIIb. This boat conformation gives rise to pseudoaxial and pseudoequatorial geminal methyl groups that are equivalent as determined by both ^{1}H and ^{13}C NMR between room temperature and −95 °C.

Introduction

Dihydroanthracenes that contain group 4A heteroatoms (Si, Ge, Sn) were reported in the early 1970s.[1] An example, dihydrosilaanthracene, I, is illustrated in Figure 1. In the parent class of diheteroanthracenes, II, the only derivatives that contain group 4 heteroatoms in both 9- and 10-positions are those where X = Y = Si[2] and Ge,[3] although the tin derivative has been mentioned with no details.[4] Derivatives where all aromatic hydrogens in II have been replaced by fluorine have also been reported for Si,[5] Ge,[6] and Sn.[7] No diheteroanthracenes of type III have been previously reported. Dihydrosilaanthracenes, I, have been prepared by a route developed by Jutzi[1] and modified by Corey.[8] Bis(o-chlorophenyl)methane, IV, prepared in a multistep sequence, is the precursor to the di-Grignard intermediate used in the ring closure reaction with dichlorosilanes. Another study concluded that IV and not the corresponding bromo and iodo derivative was the precursor of choice to dihydrosilaanthracenes in spite of the difficulty in forming Grignard reagents from aryl chlorides.[9]

Scheme I



IIa, R = R′ = Ph; IIb, R = Ph, R′ = Ph, n-$C_{12}H_{25}$, CH_3; IIc, R = R′ = Cl

Two general routes to diheteroanthracenes have been developed. Gilman and co-workers produced the first disilaanthracene (DSA), II (X = Y = Si), by a coupling reaction of ortho-substituted aromatic derivatives in the presence of sodium or lithium[10,11] (Scheme I). This ap-

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(5) Haiduc, I.; Gilman, H. *J. Organomet. Chem.* **1968**, *11*, 55.

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(10) Gilman, H.; Zeuch, E. A. *J. Am. Chem. Soc.* **1960**, *82*, 3605.

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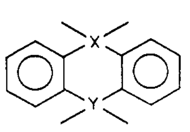


Figure 1. I: X = Si, Y = C; dihydrosilaanthracenes. II: X = Y = Si, Ge; dihydrodiheteroanthracenes. III: X = Si, Y = Ge, Sn, Pb; dihydroheterosilaanthracenes.

proach produced DSAs in low yields (<20%) and could not be used to incorporate selectively a sila functional group at a single silicon center. The precursors, *o*-$ClC_6H_4(Ph)SiRH$, are prepared in a four-step sequence. Alternate approaches of Chernyshev and co-workers[12,13] employ high-temperature reactions including a direct method synthesis to generate DSA where all exocyclic substituents at silicon are chlorine (Scheme I). Low yields, less convenient laboratory conditions, and lack of selective substitution at a silicon center are all disadvantages of this route.

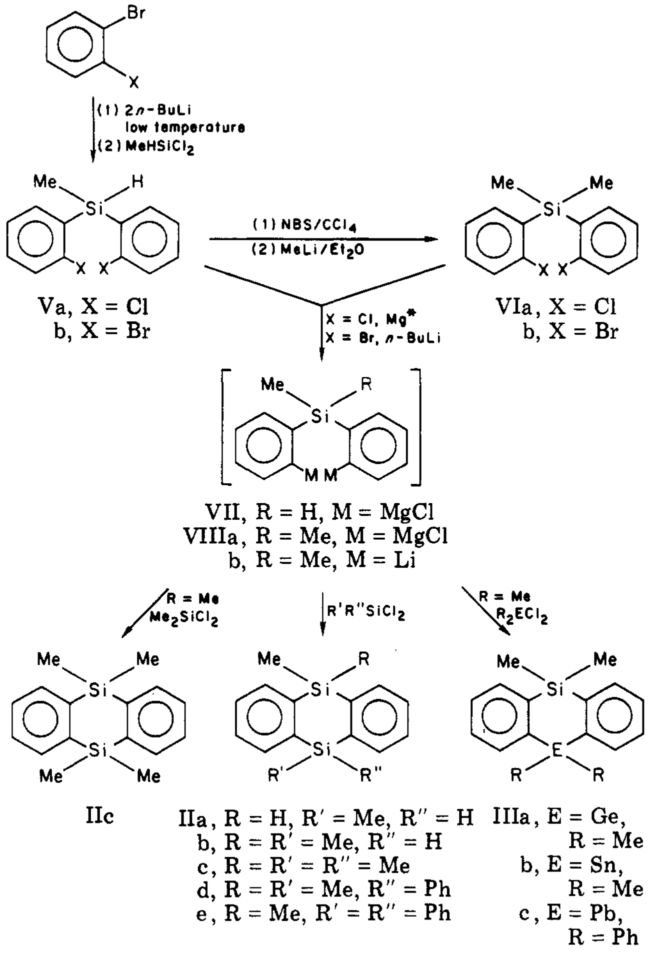
Our continued interest in the chemistry and structure of heteroanthracenes led us to develop a more efficient and versatile route to these ring systems. The key intermediates in this new route are bis(*o*-halophenyl)silanes. The strategy of including the silicon atom prior to a ring closure reaction can provide not only silaanthracenes but also allows incorporation of a variety of additional heteroatoms in the cyclization step to give disilaanthracenes and heterosilaanthracenes. This report addresses specifically the use of bis(*o*-halophenyl)silanes in the preparation of compounds that include silicon and all heavier group 4 atoms, silicon, germanium, tin, and lead.[14] The synthetic approach that has been developed is not limited to the incorporation of group 4 elements but, in principle, may be extended to other metalloid or non-metal atoms as well.

Results and Discussion

Although Gilman and co-workers demonstrated the successful coupling of 2 mol of (*p*-chlorophenyl)lithium to dimethyldichlorosilane to give bis(*p*-chlorophenyl)dimethylsilane in 80% yield,[15] an attempt to couple 2 mol of (*o*-bromophenyl)lithium to dimethyldichlorosilane was unsuccessful.[16] Two moles of (*o*-chlorophenyl)magnesium bromide with dimethyldichlorosilane also produced no bis(*o*-chlorophenyl)dimethylsilane. However, 2 mol of (*o*-halophenyl)lithium will couple to methyldichlorosilane to give bis(*o*-halophenyl)methylsilane [halo = Cl (Va), Br (Vb[16])] in good yield (Scheme II). The (*o*-halophenyl)lithium is prepared from *o*-chlorobromo- or *o*-dibromobenzene by exchange reactions with *n*-BuLi at low temperatures to minimize benzyne formation (−96 and −110 °C for the chlorobromo and dibromo derivatives, respectively). The products Va and Vb contain the appropriate ortho substituents on each phenyl group that are necessary for the preparation of the diorganometallic precursors to ring closure.

The dimethyl derivatives of Va and Vb were obtained by reaction of the hydrosilane with NBS, followed by addition to methyllithium. The bis(*o*-halophenyl)dimethylsilanes [halo = Cl (VIa), Br (VIb)], were formed in high yield. The dimethyl derivatives were prepared to

Scheme II



prevent possible reaction at Si–H when Va and Vb were subjected to the conditions required to prepare the organometallic precursor to ring closure. This precaution was unnecessary. Ring closure was accomplished from the diorganometallic intermediate prepared from the three precursors Va, VIa, and VIb. Lithium exchange of VIb with *n*-BuLi provided the dilithio intermediate. Attempts to prepare a Grignard intermediate from Va and VIa with commercially available granular or powdered magnesium were not successful even with prolonged reflux (1 week, THF as solvent) but successful transformations were possible with magnesium produced by the Reike process.[17] The di-Grignard or dilithium intermediates, (*o*-$ClMgC_6H_4)_2SiMeH$ (VII) and (*o*-$MC_6H_4)SiMe_2$ [M = BrMg (VIIIa), Li (VIIIb)], were reacted with a variety of group 4 dichlorides.

Disilaanthracenes. The feasibility of this synthetic route to II was verified initially by quenching the diorganometallic intermediate VIII with dimethyldichlorosilane to give the known DSA, IIc [X = Y = $SiMe_2$[13] (Scheme II)]. A variety of DSAs were then prepared by quenching with dichlorosilanes such as methyl-, dimethyl-, methylphenyl- and diphenyldichlorosilane. Reaction of VIII with $MeSiHCl_2$ can produce selectively a DSA with only one silicon center that contains a functional group. The same DSA can also be prepared by quenching the diorganometallic VII with dimethyldichlorosilane. These variations demonstrate the potential to direct a sila functional (or heterofunctional) group to a specific location. Another option is ring closure of the intermediate VII with

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[14] The use of ethylformates or carbamates to prepare silaanthracenes will be the subject of a future report.

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[16] Chen, L. S.; Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1980**, *193*, 283.

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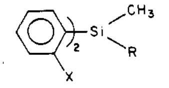
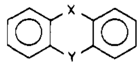
Table I. Spectroscopic Data

compound	no.	X	R	IR, cm^{-1}	60-MHz ^1H NMR,[a] δ SiH	CH$_3$	C_6H_5 (arom)
	Va	Cl	H	2152	5.0 (q)	0.73 (d)	6.9–7.4 (m)
	VIa	Cl	CH_3			0.72 (s)	7.1–7.5 (m)
	Vb	Br	H	2143	5.1 (q)	0.73 (d)	7.0–7.5 (m)
	VIb	Br	CH_3			0.73 (s)	7.0–7.6 (m)

compound	no.	X	Y	IR, cm^{-1}	60-MHz ^1H NMR SiH	CH$_3$	C_6H_5 (arom)
	IIa	CH_3SiH	CH_3SiH	2105[c]	4.9 (q)[d]	0.57 (d)[d]	7.1–7.7[d] (m)
	b	CH_3SiCH_3	CH_3SiH	2110	4.97 (q)	0.58 (d), 0.52 (s), 0.45 (s)	7.3–7.8 (m)
	c	CH_3SiCH_3	CH_3SiCH_3			0.48	7.3–7.8 (m)
	d	CH_3SiCH_3	$CH_3SiC_6H_5$			0.77 (s), 0.52 (s), 0.29 (s)	7.1–7.7 (m)
	e	CH_3SiCH_3	$C_6H_5SiC_6H_5$			0.30	7.2–7.8 (m)
	IIIa	CH_3SiCH_3	CH_3GeCH_3			0.57 (s), 0.46 (s)	7.1–7.9 (m)
	b	CH_3SiCH_3	CH_3SnCH_3			0.50 (0.48 (s), 0.40 (s))[b]	7.2–7.8 (m)
	c	CH_3SiCH_3	$C_6H_5PbC_6H_5$			0.43 (s)	6.9–7.8 (m)

[a] In $CDCl_3$, unless noted, with internal Me_4Si. [b] In C_6D_6. [c] Mixture. [d] Single isomer.

methyldichlorosilane to give 9,10-dimethyl-9,10-disilaanthracene, IIa, which is formed in an *E*/*Z* isomeric mixture and contains an Si–H functional group at both the 9- and 10-positions. Two other DSA derivatives, IId and IIe, were also prepared and illustrate formation of derivatives with different organic substituents at each of the silicon centers (a previously unknown type of DSA).

Throughout the isolation and purification steps minor amounts of side products were observed and identified by comparison with authentic samples. Presence of unreacted organometallic intermediate would give methyldiphenylsilane, $MePh_2SiH$ (from V), or dimethyldiphenylsilane, Me_2SiPh_2 (from VI), upon hydrolysis. Other products that were obtained in variable amounts were 9-methyldibenzosilole and 9,9-dimethyldibenzosilole both of which may result from an intramolecular coupling of (*o*-LiC_6H_4)(*o*-BrC_6H_4)$SiMe_2$ or (*o*-$ClMgC_6H_4$)(*o*-ClC_6H_4)SiMeR. Yields of both the hydrolysis and intramolecular coupling products are estimated to be below 10%. Such products also have been observed in the synthesis of phosphanthrenes from treatment of (*o*-ClC_6H_4)$_2$PR with lithium followed by $RPCl_2$.[18]

Dihydrosilaanthracenes are prepared by this route in higher yields than any previously reported synthesis. In addition, selective incorporation of a sila functional group in the starting diarylsilane and/or the dichlorosilanes used for ring closure is possible, and the reaction sequence contains only two or three steps to the ring-closed products starting form commercially available reagents.

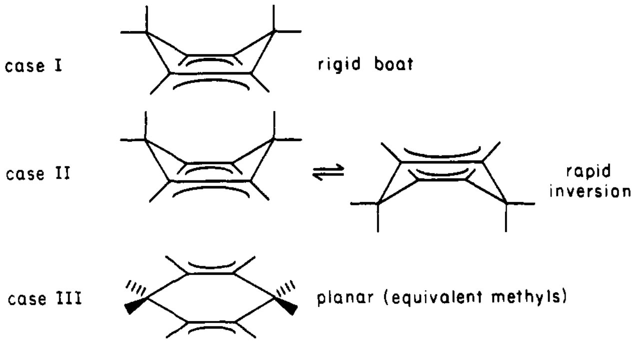
Dihydroheterosilaanthracenes. The additional utility of this synthetic approach is illustrated by the ring closure reaction of VIII with other group 4 dichlorides. From the commercially available reagents Me_2GeCl_2, Me_2SnCl_2 and Ph_2PbCl_2, IIIa, IIIb, and IIIc are obtained (Scheme II). All three compounds are the first examples of dihydrosilaheteroanthracenes where the second heteroatom is from the same group as silicon. Attempts to prepare the lead derivative IIIc from the di-Grignard and Me_2PbCl_2 resulted in the formation of elemental lead. The reaction of VIII with anhydrous $PbCl_2$ followed by MeLi also failed to produce the heterocycle III although this approach was useful in the preparation of a phenoxaplumbin.[19] However, IIIc was synthesized successfully from VIIIb in low yield. The dihydrogermasilaanthracene was prepared from both the di-Grignard and the dilithium precursor with higher yields from the latter precursor.

Table II. 100-MHz NMR Data for IIc and IIIb

compd	nuclei	temp, °C	Me resonance,[a] ppm $C_6D_5CD_3$	CD_2Cl_2
IIc	^1H	25	0.41 (s)	
		−20	0.43 (s)	
		−95	0.43 (s)	
	^{13}C	−95	0.12 (s)	
IIIb	^1H	25	0.44 (s)[b] 0.40 (s)[c]	0.64 (s)
		−95	0.45 (s)[b] 0.45 (s)[c]	0.68 (s)
	^{13}C	25		−0.05 (s)[b] −8.00 (s)[c]
		−95	−0.70 (s)[b] −8.70 (s)[c]	−0.93 (s)[b] −8.24 (s)[c]

[a] Residual solvent resonances were used as internal standards for the reporting of chemical shifts. [b] SiMe. [c] SnMe.

Scheme III



Spectral Data. Room-temperature ^1H NMR and infrared data for II, III, V, and VI are recorded in Table I and low-temperature ^1H and ^{13}C NMR data for IIc and IIIb in Table II. Solid-state structural studies for compounds IIc,[20] IIIa, and IIIb show that the central ring exhibits a folded boat conformation in which each heteroatom has pseudoaxial and pseudoequatorial methyl substituents. If a rigid-boat conformation exists in solution, two different chemical shifts for the methyl resonances in either ^{13}C or ^1H NMR data could be anticipated for these nonequivalent methyl groups. The data in Table

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Table III. Characteristics of the Mass Spectra (m/e) of II and III[a]

	$P^{+\cdot}$	$P - Me^{+\cdot}$		other ions >10%, base peak[b]	source temp, °C
IIa	240 (66)	225 (100)	195 (32)	none	140
IIb	254 (37)	239 (100)	195 (28)	none	108
IIc	268 (12)	252 (100)	195 (62)	none	room temp
IId	330 (21)	315 (100)	195 (31)	257 (21)[c,d]	100
IIe	392 (42)	377 (100)	195 (67)	257 (59)[d,e]	room temp
IIIa	314 (8)	299 (100)	195 (18)	none	70
IIIb	360 (8)	345 (90)	195 (100)	none	75
IIIc	*f*	*g*	195 (37)	285 (57) 208 (67)	170

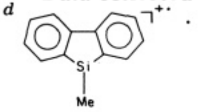
[a] Data collected at 70 eV and given as mass (% of base peak). [b] Ions of mass above m/e 195. [c] $[P - Me - SiMe_2]^{+\cdot}$. [d]  . [e] $[P - Ph - SiMe_2]^{+\cdot}$. [f] Accurate count not possible. [g] $[P - Ph]^{+\cdot}$ cluster (100%).

Table IV. Selected Bond Lengths and Angles for 9,9,10,10-Tetramethyl-9,10-dihydro-10-germa-9-silaanthracene

Bond Lengths (A)

C(1)–C(2)	1.39 (1)	C(6)–C(7)	1.38 (1)	Si,Ge(10)–C(12)	1.902 (7)
C(1)–C(11)	1.40 (1)	C(7)–C(8)	1.37 (1)	Si,Ge(10)–C(13)	1.910 (6)
C(2)–C(3)	1.36 (1)	C(8)–C(14)	1.40 (1)	Si,Ge(10)–C(17)	1.908 (7)
C(3)–C(4)	1.38 (1)	Si,Ge(9)–C(11)	1.917 (7)	Si,Ge(10)–C(18)	1.903 (7)
C(4)–C(12)	1.40 (1)	Si,Ge(9)–C(14)	1.911 (7)	C(11)–C(12)	1.41 (1)
C(5)–C(6)	1.38 (1)	Si,Ge(9)–C(15)	1.913 (7)	C(13)–C(14)	1.40 (1)
C(5)–C(13)	1.40 (1)	Si,Ge(9)–C(16)	1.910 (8)		

Bond Angles (deg)

C(2)–C(1)–C(11)	121 (1)	C(15)–Si,Ge(9)–C(16)	108.4 (4)	C(1)–C(11)–Si,Ge(9)	118.9 (6)
C(1)–C(2)–C(3)	119 (1)	C(12)–Si,Ge(10)–C(13)	109.2 (3)	C(5)–C(13)–C(14)	119 (1)
C(2)–C(3)–C(4)	121 (1)	C(12)–Si,Ge(10)–C(17)	109.7 (3)	Si,Ge(10)–C(13)–C(14)	122.9 (5)
C(3)–C(4)–C(12)	121 (1)	C(12)–Si,Ge(10)–C(18)	110.2 (3)	C(8)–C(14)–Si,Ge(9)	119.3 (5)
C(6)–C(5)–C(13)	122 (1)	C(13)–Si,Ge(10)–C(17)	109.8 (3)	C(8)–C(14)–C(13)	118 (1)
C(14)–Si,Ge(9)–C(15)	108.7 (3)	C(13)–Si,Ge(10)–C(18)	109.2 (3)	Si,Ge(9)–C(14)–C(13)	123.1 (5)
C(14)–Si,Ge(9)–C(16)	111.0 (3)	C(17)–Si,Ge(10)–C(18)	108.6 (4)		

I show that a singlet methyl is observed for IIc and also singlets for each MMe_2 heteroatom unit in IIIa and IIIb and also for Me_2Si in IIIc. Three possible explanations could account for these observations and are summarized in Scheme III. Accidental equivalence in chemical shifts would be required for a rigid boat in solution (case I). A rapid boat to boat equilibrium (case II) would average the pseudoaxial–pseudoequatorial signals. The chemical shifts (in toluene-d_8) for the methyl resonances in IIc and IIIb do not shift appreciably down to −95 °C, and only slight line broadening is observed. Similar results have been reported for 10,10-dimethylphenothiasilin, -germin, and -stannin derivatives down to −150 °C[21] and for 10,10-dimethylphenoxaplumbin down to −90 °C.[19] In both cases a rapid boat to boat inversion was suggested to rationalize the observed data.

A third alternative would occur if the DSAs or heterosilaanthracenes are planar structures in solution in which case geminal methyl groups are magnetically equivalent. This is analogous to a model that has been proposed for 9,10-dihydroanthracene from molecular mechanics and molecular orbital calculations.[22] The ^1H and ^{13}C data for IIc and IIIb in $CDCl_3$, CD_2Cl_2, or $C_6D_5CD_3$ over the temperature range +25 to −96 °C exhibit only a single resonance for geminal methyl groups. These observations would fit a planar structure in solution for IIc and by extension to IIIb.

Other spectral characteristics of II, III, V, and VI are given in Tables I and III. The hydrosilanes Va, VIa and IIa, IIb exhibit a characteristic SiH infrared absorption band at 2150 cm^{-1} for the acyclic derivatives and about 2110 cm^{-1} for the cyclic. The mass spectra of the DSAs are characterized by a base peak (70 eV) that corresponds to $P - Me^+$ as well as a common ion with m/e 195. This latter ion corresponds to loss of SiMeR (R = H, Me, Ph) from the $P - Me^+$ ion (metastable support for this fragmentation). The $P - Me^+$ (or $P - Ph$ for IIIc) ion as well as the ion at m/e 195 are also present in the spectra of III. The lead derivative exhibits intense ions for PbPh and Pb^+. The $P - Me^+$ ion is also the base peak in the spectra of 10,10-dimethylphenothiasilin, -germin, and -stannin derivatives.[23]

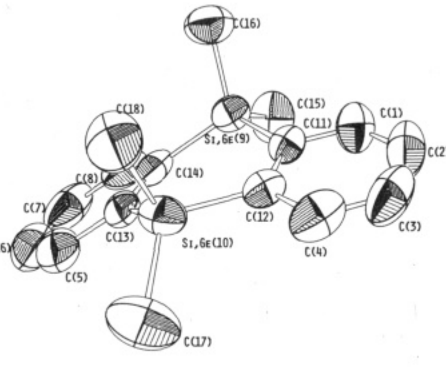


Figure 2. Perspective drawing of IIIa with atom labels.

Structures of IIIa and IIIb. The structures of 9,9,10,10-tetramethyl-9,10-dihydro-10-germa-9-silaanthracene (IIIa) and 9,9,10,10-tetramethyl-9,10-dihydro-10-stanna-9-silaanthracene (IIIb) are molecular solids. The

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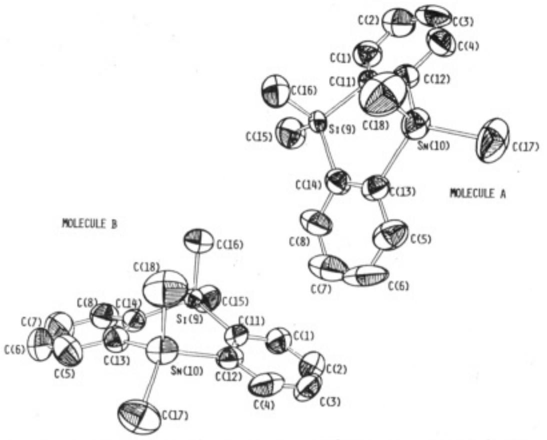


Figure 3. Perspective drawing of IIIb with atom labels.

tricyclic frameworks of both compounds have a butterfly conformation. Figures 2 and 3 are perspective drawings of the molecules with atom labels. Tables IV and V contain values for the bond lengths and angles.

The dihydrogermasilaanthracene (IIIa) is disordered with a 50/50 occupancy by silicon and germanium of the heteroatom sites. The mean C–(Si,Ge) distance of 1.909 Å is intermediate between the accepted X-ray values[24] of 1.88 Å for C–Si and 1.95 Å for C–Ge (mean of 1.91_5 Å). The dihydrostannasilaanthracene (IIIb) has a mean C–Si distance of 1.878 Å (molecule A, 1.882 Å; molecule B, 1.873 Å) and a mean C–Sn distance of 2.138 Å (molecule A, 2.138 Å; molecule B, 2.138 Å); the accepted X-ray value for the C–Sn distance is 2.17 Å.[24]

Table VI is a tabulation of the dihedral angles ("butterfly" angles) for group 4 dihydroheteroanthracenes. Compounds with group 4 atoms at the 9- and 10-positions and with identical exocyclic substituents are included in Table VI. Replacement of the 9- and 10-carbon atoms of dihydroanthracene by identical group 4 atoms increases the butterfly angle (i.e., more planar framework). Replacement of one carbon atom by silicon results in a smaller butterfly angle (i.e., less planar framework); a decrease in butterfly angle is observed also for IIIb (Sn replacement of Si) when compared to dihydrodisilaanthracene. These variations in butterfly angle may result from a balance of interactions that include axial–axial, equatorial peri-proton, van der Waals repulsions of atoms in the 9,10-positions, and packing effects. Insufficient data are available to determine the relative importance of the above factors.

Experimental Section

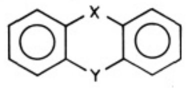
General Data. Organometallic reactions are carried out in oven-dried glassware that is flamed under an inert atmosphere. Activated magnesium preparations are carried out under argon whereas N_2 is used for organolithium and other atmosphere-sensitive reactions.

The organic halides (*o*-chlorobromo)benzene and *o,o′*-dibromobiphenyl are prepared by literature methods.[31,32] Di-

Table V. Selected Bond Lengths and Angles for 9,9,10,10-Tetramethyl-9,10-dihydro-10-stanna-9-silaanthracene

	molecule	
	A	B
Bond Lengths (Å)		
C(1)–C(2)	1.36 (1)	1.37 (1)
C(1)–C(11)	1.36 (1)	1.36 (1)
C(2)–C(3)	1.32 (1)	1.32 (2)
C(3)–C(4)	1.38 (2)	1.40 (2)
C(4)–C(12)	1.43 (1)	1.39 (1)
C(5)–C(6)	1.40 (2)	1.37 (2)
C(5)–C(13)	1.39 (1)	1.39 (1)
C(6)–C(7)	1.38 (2)	1.35 (2)
C(7)–C(8)	1.35 (2)	1.36 (1)
C(8)–C(14)	1.40 (1)	1.41 (1)
Si(9)–C(11)	1.911 (8)	1.883 (8)
Si(9)–C(14)	1.902 (9)	1.909 (8)
Si(9)–C(15)	1.837 (11)	1.840 (9)
Si(9)–C(16)	1.880 (11)	1.859 (9)
Sn(10)–C(12)	2.160 (10)	2.139 (9)
Sn(10)–C(13)	2.153 (9)	2.148 (9)
Sn(10)–C(17)	2.123 (12)	2.151 (11)
Sn(10)–C(18)	2.116 (14)	2.115 (11)
C(11)–C(12)	1.37 (1)	1.41 (1)
C(13)–C(14)	1.41 (1)	1.43 (1)
Interatomic Angles (deg)		
C(2)–C(1)–C(11)	123 (1)	124 (1)
C(1)–C(2)–C(3)	118 (1)	119 (1)
C(2)–C(3)–C(4)	123 (1)	121 (1)
C(3)–C(4)–C(12)	118 (1)	120 (1)
C(6)–C(5)–C(13)	119 (1)	122 (1)
C(5)–C(6)–C(7)	121 (1)	120 (1)
C(6)–C(7)–C(8)	119 (1)	121 (1)
C(7)–C(8)–C(14)	123 (1)	122 (1)
C(11)–Si(9)–C(14)	110.4 (4)	110.7 (4)
C(11)–Si(9)–C(15)	108.1 (4)	109.4 (4)
C(11)–Si(9)–C(16)	108.8 (5)	110.3 (4)
C(14)–Si(9)–C(15)	110.8 (4)	107.4 (4)
C(14)–Si(9)–C(16)	107.5 (5)	108.2 (4)
C(15)–Si(9)–C(16)	111.3 (5)	111.2 (4)
C(12)–Sn(10)–C(13)	102.2 (3)	102.6 (3)
C(12)–Sn(10)–C(17)	110.3 (5)	111.2 (4)
C(12)–Sn(10)–C(18)	113.1 (5)	113.2 (5)
C(13)–Sn(10)–C(17)	111.4 (4)	112.2 (4)
C(13)–Sn(10)–C(18)	108.7 (5)	110.3 (4)
C(17)–Sn(10)–C(18)	110.8 (5)	107.4 (5)
C(1)–C(11)–Si(9)	118.6 (7)	120.0 (7)
C(1)–C(11)–C(12)	119 (1)	117 (1)
Si(9)–C(11)–C(12)	122.3 (7)	122.9 (6)
C(4)–C(12)–Sn(10)	119.6 (8)	120.5 (7)
C(4)–C(12)–C(11)	119 (1)	118 (1)
Sn(10)–C(12)–C(11)	121.8 (6)	121.2 (6)
C(5)–C(13)–Sn(10)	118.8 (7)	120.9 (7)
C(5)–C(13)–C(14)	121 (1)	119 (1)
Sn(10)–C(13)–C(14)	120.2 (6)	120.3 (6)
C(8)–C(14)–Si(9)	119.6 (7)	118.7 (7)
C(8)–C(14)–C(13)	117 (1)	117 (1)
Si(9)–C(14)–C(13)	123.3 (6)	123.9 (6)

Table VI. Dihedral Angles for Group 4 Dihydroanthracenes



X	Y	dihedral angles	ref
CH_2	CH_2	145	25
CH_2	SiH_2	136	26
SiH_2	SiH_2	157	27, 28
$Si(CH_3)_2$	$Si(CH_3)_2$	156	28
$(Si,Ge)(CH_3)_2$	$(Si,Ge)(CH_3)_2$	153	this work
$Ge(CH_3)_2$	$Ge(CH_3)_2$	152	29
$Si(CH_3)_2$	$Sn(CH_3)_2$	142, 148	this work
$Si(C_6H_5)_2$	$Si(C_6H_5)_2$	180	30

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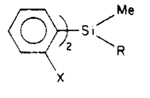
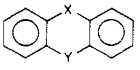
Table VII. Analytical Data

compound	no.	X	R	elemental anal.,[a] % carbon	elemental anal.,[a] % hydrogen	mp,[b] °C bp, °C (mmHg)	yield,[c] %	m/e (parent)
	Va	Cl	H	58.85 (58.43)	4.64 (4.53)	104–108 (0.06)	86	266 (2 ^{35}Cl)
	VIa	Cl	Me	59.85 (59.81)	5.19 (5.02)	48.5–49	85	280 (2 ^{35}Cl)
	VIb	Br	Me	45.48 (45.43)	3.85 (3.81)	64–65	72	370 (^{79}Br, ^{81}Br)

compound	no.	X	Y	elemental anal.,[a] % carbon	elemental anal.,[a] % hydrogen	mp,[b] °C bp, °C (mmHg)	yield,[c] %	m/e (parent)
	IIa	MeSiH	MeSiH	69.76 (69.93)	6.79 (6.71)	40–45[d]	70[d,e]	240
	IIb	MeSiH	MeSiMe	70.95 (70.80)	7.00 (7.13)	92–98 (0.01)	61[e,f]	254
		MeSiH	MeSiMe				56[e,g]	
	IIc	MeSiMe	MeSiMe	. . .	. . .	81–82[h]	44[e,i]	
	IId	MeSiMe	MeSiPh	76.38 (76.30)	6.80 (6.71)	157–158	45[e]	330
	IIe	MeSiMe	PhSiPh	79.43 (79.53)	6.23 (6.16)	125–126.5	61[i]	392
	IIIa	MeSiMe	MeGeMe	61.43 (61.40)	6.39 (6.44)	83–84	74[j]	314 (^{74}Ge)
		MeSiMe	MeGeMe				33[e]	
	IIIb	MeSiMe	MeSnMe	53.69 (53.52)	5.67 (5.61)	65–66	56[e]	360 (^{120}Sn)
	IIIc	MeSiMe	PhPbPh	54.62 (54.68)	4.23 (4.28)	128–129	10[i,j]	

[a] Found (calculated). [b] Uncorrected. [c] Crude yield of distilled product unless otherwise specified. Purity of distilled product estimated to be about 90% in most cases. [d] Mixture of isomers. Isolated isomer, mp 59–61 °C. [e] Prepared from the di-Grignard. [f] Prepared from Va. [g] Prepared from VIa. [h] Lit.[13] mp 79.5 °C. [i] Analytically pure compound. [j] Prepared from dilithio intermediate.

phenylmethylsilane is prepared from phenyllithium and methyldichlorosilane.[33]

Dichlorosilanes, dimethylgermanium dichloride, dimethyltin dichloride, diphenyllead dichloride, NBS, MeLi, *n*-BuLi, and *o*-dibromobenzene are commercial reagents and are used as supplied.

Tetrahydrofuran and ether are purified by distillation from alkali-metal benzophenone ketal followed by distillation from CaH_2. The CCl_4 is dried by distillation from P_2O_5.

Proton NMR data are recorded on a Varian T-60 spectrometer, and a JEOL FX-100 Multinuclear spectrometer is used to obtain the ^1H and ^{13}C variable-temperature data. Mass spectra are collected on an AEI MS-1201B mass spectrometer. Infrared spectra are recorded on a Beckman IR 8 instrument and calibrated with the 2850 cm^{-1} band of polystyrene. Melting points are uncorrected and are obtained on a Thomas-Hoover capillary melting point apparatus.

Analyses were performed by Gailbraith Laboratories, Inc.

Bis(*o*-bromophenyl)methylsilane, Vb. The literature method[16] is used with minor changes. A cooling bath of Et_2O/EtOH is more convenient for maintaining temperatures below −110 °C, and efficient stirring is accomplished with a mechanical stirrer. To a 500-mL flask is added *o*-dibromobenzene (20 g, 85 mmol) in Et_2O/THF (200 mL, 1:1). A 10% excess of *n*-BuLi (59 mL, 1.6 M, 93 mmol) is added at a sufficient rate to maintain the internal temperature below −110 °C and stirred 20 min after addition is complete. A 0.50 mol equiv of methyldichlorosilane (4.9 g, 42 mmol) in Et_2O/THF (100 mL, 1:1) is added and stirring continued for 2 h. The reaction mixture is hydrolyzed with a solution of concentrated HCl (10 mL) in ethanol (25 mL) and poured into 2 M HCl (400 mL). The organic layer is separated and the aqueous layer extracted with ether. The organic layers are dried with $MgSO_4$ and the solvents removed. The crude oil can be used for the methylation of Si–H (preparation of VIb) without further purification or distilled to obtain material suitable for ring closure reactions. Kugelrohr distillation provides 13 g (87%) of crude Vb as a colorless oil, bp 120–160 °C (0.04 mm) [lit.[16] bp 158–159 °C, (0.005 mm)].

Bis(*o*-chlorophenyl)methylsilane, Va. Preparation of bis(*o*-chlorophenyl)methylsilane is similar to the preparation of the bromo derivative. A 500-mL flask fitted with a mechanical stirrer is immersed in a toluene slush bath (−96 °C) and charged with *o*-chlorobromobenzene (38.2 g, 200 mmol) and Et_2O/THF (100 mL, 1:1). To the rapidly stirring solution is added *n*-BuLi (138 mL of 1.6 M, 220 mmol) at a sufficient rate to maintain internal temperature below −96 °C, and the mixture stirred 20 min after addition is complete. Methyldichlorosilane (11.5 g, 100 mmol) in Et_2O/THF (100 mL, 1:1) is added dropwise, and the resultant reaction mixture is stirred for 2 h. The solution is hydrolyzed with concentrated HCl (12 mL) in ethanol (60 mL) and poured into 2 M HCl (900 mL). The organic layer is separated and the aqueous layer extracted with ether. The organic layers are dried over $MgSO_4$ and the solvents removed to produce a crude oil. The oil may be used directly for the methylation of Si–H (preparation of VIa) or otherwise purified by distillation. Kugelrohr distillation produces 22.9 g (86%) of crude Va, bp 90–130 °C (0.05 mm), which is suitable for conversion to the di-Grignard reagent. An analytical sample is obtained by column chromatography [silica gel, hexanes/methylene chloride (4:1), as eluant] and redistillation to give a colorless oil, bp 104–108 °C (0.06 mm). Analytical data for precursors and dihydroheteroanthracenes are given in Table VII.

5-Methyl-5*H*-dibenzosilole. To a slurry of *o,o*′-dibromobiphenyl (6.24 g, 20 mmol) in ether (50 mL) that has been cooled in an ice bath is added *n*-BuLi (1.2 mmol, 42 mL, 1.21 M) dropwise with stirring. After addition is complete, stirring is continued for 1.5 h with cooling and an additional 4 h at room temperature. The *o,o*′-dilithiobiphenyl solution is transferred under N_2 pressure to an addition funnel, and the original flask is charged with $MeHSiCl_2$ (3.2 g, 28 mmol) and ether (50 mL) and heated to reflux before the dropwise addition of the organometallic reagent is begun. The reflux is continued for 20 h before addition of $LiAlH_4$ and heating an additional 1 h. After aqueous workup (saturated NH_4Cl solution) and removal of the solvent from the organic layer, Kugelrohr distillation gives slightly impure silole [3.6 g; bp 98–105 °C (0.05 mm) (91% crude)] which solidified on cooling. Recrystallization of the solid from absolute ethanol gave white crystals, mp 42–43 °C. (Anal. Calcd for $C_{13}H_{12}Si$: C, 79.53; H, 6.16. Found: C, 79.58; H, 6.22.)

General Conditions for Methylation of Hydrosilanes. Methylation of hydrosilanes is accomplished by the reaction of the silanes with NBS in CCl_4 at room temperature under irradiation with a sun lamp until no NBS remains (approximately 2 h). Succinimide is filtered from the solution and CCl_4 removed by water aspiration with protection by an anhydrous $CaCl_2$ drying tube. An oil is obtained that is dissolved in ether, transferred to a pressure addition funnel, and added to a 1.5 M excess of MeLi in ether. After the exothermic reaction is complete, the solution is refluxed for 1 h and hydrolyzed with NH_4Cl (saturated, aqueous). The ether layer is separated, the aqueous layer is extracted with ether, and the combined organic layers are dried over $MgSO_4$ before the solvent is removed.

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Bis(*o*-chlorophenyl)dimethylsilane, VIa. The oil from the preparation of bis(*o*-chlorophenyl)methylsilane (100 mmol, crude) is dissolved in CCl_4 (500 mL), and NBS (18 g, 100 mmol) added in three portions. The mixture is stirred until the reaction is complete as indicated by consumption of the NBS. After removal of CCl_4, the bromosilane is dissolved in ether (100 mL) and the solution added to MeLi (100 mL of 1.5 M, 150 mmol). After aqueous workup 16 g (57%) of VIa is obtained as a colorless solid. The product is recrystallized from ethanol to obtain the analytical sample.

Bis(*o*-bromophenyl)dimethylsilane, VIb. The oil from a preparation of bis(*o*-bromophenyl)methylsilane (19 g, crude, ca. 53 mmol) is dissolved in CCl_4 (500 mL) and NBS (9.5 g, 53 mmol) added. After the reaction is complete, the oil, which remains after removal of the CCl_4, is dissolved in ether (100 mL) and added to an excess of MeLi (100 mL of 1.6 M, 160 mmol). After aqueous workup, the crude oil is distilled (Kugelrohr), bp 114–148 °C (0.03 mm), to give a solid in 70% yield (14 g, crude, 37 mmol). An analytical sample is obtained by recrystallization from ethanol.

5,5-Dimethyldibenzosilole. To 5-methyl-5*H*-dibenzosilole (0.42 g, 2 mmol) dissolved in CCl_4 (25 mL) is added NBS (0.38 g, 2 mmol). The intermediate bromosilane oil is dissolved in ether (25 mL) and the mixture added to MeLi (2 mL of 1.6 M, 3 mmol). After aqueous workup the oil obtained crystallizes from ethanol and provides the silole as a white solid in 63% yield (0.28 g, 1.3 mmol); mp 58–59 °C (lit.[34] mp 60–61 °C).

Diphenyldimethylsilane. To diphenylmethylsilane (2.7 g, 14 mmol) in CCl_4 is added NBS (2.4 g, 14 mmol). The intermediate bromosilane dissolved in ether is then added to an excess of MeLi (20 mL of 1.5 M, 20 mmol). After aqueous workup the crude oil is distilled (Kugelrohr) and gives Ph_2SiMe_2 as a colorless oil in 33% yield (0.98 g, 4.6 mmol); bp 76–92 °C (0.1 mm) [lit.[35] bp 115–118 °C (4 mm)].

Attempt To Prepare Bis(*o*-chlorophenyl)dimethylsilane, Vb, from (*o*-Chlorophenyl)magnesium Bromide and Dimethyldichlorosilane. *o*-Chlorobromobenzene (38.3 g, 200 mmol) is dissolved in ether (250 mL) and the mixture added dropwise to magnesium turnings (9.6 g, 400 mmol) and refluxed 2 h. A positive Grignard test is observed. The filtered solution is transferred to an addition funnel and reacted with dimethyldichlorosilane (12.9 g, 100 mmol) in ether (200 mL) by the method of simultaneous addition. The solution is stirred at reflux overnight and hydrolyzed. An examination of the proton NMR spectrum of the crude oil showed no resonance in the methyl region which corresponded to an authentic sample of bis(*o*-chlorophenyl)dimethylsilane.

Generation of Dilithium Intermediates. Dilithium intermediates are prepared by the addition of bis(*o*-bromophenyl)dimethylsilane (2 g, 5.3 mmol) in Et_2O/THF (25 mL, 1:1) to a solution of a slight excess of *n*-BuLi (7 mL, 1.6 M, 11 mmol) at 0 °C, and the mixture is stirred 20 min before use. The appropriate diorganometal dichloride in Et_2O/THF (25 mL, 1:1) is added to the cold dilithium reagent and the resultant mixture stirred for 1 h at 0 °C and 1 h at room temperature and then refluxed for 1 h. After the usual aqueous workup the organic phase is dried with $MgSO_4$ and distillation of the solvents provides a crude oil. The crude oil is dissolved in hexanes and filtered to remove insoluble impurities before the indicated purification method is attempted. Physical constants and analytical data are given in Table VII.

9,9,10,10-Tetramethyl-9,10-dihydro-10-germa-9-silaanthracene, IIIa. In a 250-mL flask, bis(*o*-bromophenyl)dimethylsilane (3.7 g, 10 mmol) in Et_2O (100 mL) is added to *n*-BuLi (16 mL, 1.55 M, 25 mmol) at 0 °C over a 20-min period and the mixture then stirred 40 min. Dimethylgermanium dichloride (1.7 g, 10 mmol) in ether (5 mL) is added and the resultant mixture stirred overnight while being warmed to room temperature. After aqueous workup the crude oil obtained is partially purified by chromatography (silica gel, hexanes/CH_2Cl_2 as eluant). The eluted sample is purified further by Kugelrohr distillation to give an oil (1.2 g, crude 74%), bp 95–130 °C (0.04 mm). Dissolution in ethanol and cooling result in formation of crystalline IIIa which is recrystallized from ethanol to obtain the analytical sample.

9,9-Dimethyl-10,10-diphenyl-9,10-dihydro-10-plumba-9-silaanthracene, IIIc. Bis(*o*-bromophenyl)dimethylsilane (2.0 g, 5.4 mmol) in Et_2O/THF (50 mL, 1:1) is added to *n*-BuLi (7 mL, 1.6 M, 11 mmol) in Et_2O/THF (100 mL, 1:1) at 0 °C and the mixture stirred for 20 min after addition is complete. A slurry of diphenyllead dichloride (2.3 g, 5.4 mmol) in THF (25 mL) is added at 0 °C and the mixture refluxed 5 h and then stirred overnight. After workup, the oil is purified by chromatography (silica gel, hexanes/CH_2Cl_2 as eluant) to give an oil that solidifies. Recrystallization from Et_2O/EtOH (1:1) mixture gave 0.32 g (10%) of IIIa as a white solid.

General Procedure for Generation of Di-Grignard Reagents from Activated Magnesium. Excess activated "Reike" magnesium is generated in each run. A typical preparation employs $MgCl_2$ (7.5 g, 79 mmol), KI (6.0 g, 36 mmol), and potassium metal (6.0 g, 150 mmol) which are heated at reflux in THF (100 mL) for 3 h with stirring under argon atmosphere. The flask should be sufficiently large to contain any frothing that may occur during the exothermic reaction (Mg powder/THF slurries have spontaneously ignited during the course of this work). After dropwise addition of bis(*o*-chlorophenyl)dimethylsilane (5 g, 18 mmol) in THF (25 mL) to the magnesium slurry, the mixture is heated at reflux for 3 h after which the group 4 dichloride in THF (25 mL) is added at room temperature. The resultant mixture is either heated at reflux for 3 h or is stirred overnight and then heated at reflux for 1 h. Hydrolysis with NH_4Cl (saturated, aqueous) is followed by ether extraction, drying of the combined organic layers over $MgSO_4$, and evaporation of the solvents to give crude product mixtures. Before purification the oil is dissolved in hexanes and filtered to remove insoluble (white) material. Physical constants and analytical data are given in Table VII.

9,9,10,10-Tetramethyl-9,10-dihydro-9,10-disilaanthracene, IIc. To a slurry of activated magnesium generated from $MgCl_2$ (7.5 g, 76 mmol) is added bis(*o*-chlorophenyl)dimethylsilane (5.8 g, 21 mmol) in THF (25 mL) and refluxed 3 h. Dimethyldichlorosilane (2.7 g, 21 mmol) in THF (50 mL) is added, and the reaction is stirred overnight. After aqueous workup, pure crystalline IIc (2.4 g) can be obtained by recrystallization from ethanol.

9,10-Dimethyl-9,10-dihydro-9,10-disilaanthracene, IIa. To a slurry of activated magnesium generated from $MgCl_2$ (7.5 g, 76 mmol) is added bis(*o*-chlorophenyl)methylsilane (3.0 g, 11 mmol) in THF (50 mL), and the reaction mixture is refluxed for 3 h. Methyldichlorosilane (1.3 g, 11 mmol) in THF (50 mL) is added, and the solution is stirred for 4 h. After workup, Kugelrohr distillation [bp 90–138 °C (0.05 mm)] produced a crude oil (1.9 g, 70%) that contains IIa as a mixture of *E* and *Z* isomers. Crystallization from ethanol with cooling produced an analytical sample. After several (ca. six) recrystallizations from ethanol a single isomer is obtained: mp 59–61 °C.

9,9,10-Trimethyl-9,10-dihydro-9,10-disilaanthracene, IIb. To a slurry of activated magnesium generated from $MgCl_2$ (7.4 g, 76 mmol) is added bis (*o*-chlorophenyl)methylsilane (5.1 g, 18 mmol) in THF (50 mL), and the reaction mixture is refluxed for 3 h. Dimethyldichlorosilane (2.4 g, 19 mmol) in THF (25 mL) is added and the slurry stirred overnight. After workup, Kugelrohr distillation of the resultant oil provided 61% (2.9 g) of crude IIb, bp 90–130 °C (0.04 mm). An analytical sample is obtained by chromatography (silia gel, hexanes/CH_2Cl_2 as eluant) followed by Kugelrohr distillation to give a colorless oil, bp 92–98 °C (0.01 mm).

9,9,10-Trimethyl-10-phenyl-9,10-dihydro-9,10-disilaanthracene, IId. To a slurry of activated magnesium generated from $MgCl_2$ (7.5 g, 76 mmol) is added bis(*o*-chlorophenyl)dimethylsilane (5 g, 18 mmol) in THF (50 mL), and the reaction mixture is refluxed for 3 h. Methylphenyldichlorosilane (3.4 g, 18 mmol) is added and the slurry stirred overnight. Dissolution of the oil, obtained after aqueous workup, in ether/ethanol gives pure IId (1.6 g) as a white solid. Kugelrohr distillation of the mother liquor (140–230 °C, 0.01 mm) provides an additional 1.0 g of IId (total yield, 45%).

9,9-Dimethyl-10,10-diphenyl-9,10-dihydro-9,10-disilaanthracene, IIe. To a slurry of activated magnesium generated from $MgCl_2$ (7.5 g, 76 mmol) is added bis(*o*-chlorophenyl)dimethylsilane (5.4 g, 19 mmol) in THF (25 mL), and the reaction mixture is refluxed for 3 h. Diphenyldichlorosilane (4.8 g, 19 mmol) is added

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[34] Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 1883.

[35] Topchiev, A. V.; Nametkin, N. S.; Gu, C.; Leonova, N. A. *Dokl. Akad. Nauk SSSR* **1958**, *118*, 731.

Table VIII. Crystal Data and Summary of Intensity Data and Structure Refinement

	$C_{16}H_{20}GeSi$	$C_{16}H_{20}SiSn$
mol wt	313.0	359.1
space group	*Pbca*	$P2_1/n$
cell constants		
a, Å	9.585 (5)	18.897 (8)
b, Å	16.200 (12)	9.093 (6)
c, Å	21.236 (12)	19.439 (13)
β, deg		95.60 (4)
vol, Å^3	3324 (4)	3298 (4)
d(calcd), g cm^{-3}	1.25	1.45
d(obsd), g cm^{-3}	1.25 (1)	1.42 (1)
μ(calcd), cm^{-1}	20.0	16.1
cryst dimens, mm	0.14 × 0.28 × 0.16	0.66 × 0.42 × 0.42
radiatn	Mo Kα, 0.71069 Å	
2θ scan range	$2\theta(\text{Mo K}\alpha_1) - 1.0$ to $2\theta(\text{Mo K}\alpha_2) + 1.0$	
no. of reflctns scanned	3335	4711
no. of data > 3σ	1512	3475
no. of parameters varied	163	325
$R = \Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma\lvert F_o\rvert$	0.043	0.051
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$	0.054	0.074

Table IX. 9,9,10,10-Tetramethyl-9,10-dihydro-10-germa-9-silaanthracene Final Fractional Coordinates for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
C(1)	0.5577 (8)	0.4848 (5)	0.1537 (4)
C(2)	0.5265 (11)	0.5349 (5)	0.2048 (5)
C(3)	0.4245 (12)	0.5116 (6)	0.2455 (5)
C(4)	0.3497 (8)	0.4399 (5)	0.2363 (4)
C(5)	0.3348 (9)	0.1282 (5)	0.1350 (4)
C(6)	0.4049 (11)	0.0666 (5)	0.1036 (4)
C(7)	0.5162 (11)	0.0866 (6)	0.0656 (4)
C(8)	0.5528 (8)	0.1676 (6)	0.0590 (3)
Si,Ge(9)	0.5361 (1)	0.34360 (7)	0.07256 (5)
Si,Ge(10)	0.2687 (1)	0.29113 (6)	0.17616 (5)
C(11)	0.4857 (7)	0.4106 (4)	0.1434 (3)
C(12)	0.3789 (6)	0.3880 (4)	0.1855 (3)
C(13)	0.3709 (6)	0.2113 (4)	0.1287 (3)
C(14)	0.3826 (6)	0.2322 (4)	0.0895 (3)
C(15)	0.4371 (9)	0.2814 (5)	−0.0001 (4)
C(16)	0.7322 (8)	0.3515 (6)	0.0576 (4)
C(17)	0.0997 (7)	0.3164 (5)	0.0141 (10)
C(18)	0.2239 (9)	0.2571 (3)	0.0272 (15)

Table X. 9,9,10,10-Tetramethyl-9,10-dihydro-10-stanna-9-silaanthracene Final Fractional Coordinates for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
	Molecule A		
C(1)	0.3022 (5)	0.5796 (11)	0.2812 (5)
C(2)	0.3183 (6)	0.5799 (15)	0.2147 (6)
C(3)	0.3534 (7)	0.4669 (18)	0.1926 (5)
C(4)	0.3718 (5)	0.3461 (14)	0.2335 (5)
C(5)	0.2783 (6)	0.0437 (12)	0.4695 (6)
C(6)	0.2258 (7)	0.0520 (7)	0.5158 (7)
C(7)	0.1968 (7)	0.1853 (18)	0.5319 (7)
C(8)	0.2203 (5)	0.3902 (12)	0.5039 (5)
Si(9)	0.3017 (1)	0.4914 (2)	0.4204 (1)
Sn(10)	0.38129 (4)	0.16105 (7)	0.36928 (4)
C(11)	0.3194 (4)	0.4677 (9)	0.3260 (4)
C(12)	0.3549 (4)	0.3483 (10)	0.3034 (5)
C(13)	0.3021 (4)	0.1734 (9)	0.4416 (4)
C(14)	0.2727 (4)	0.3099 (9)	0.4574 (4)
C(15)	0.3838 (6)	0.5583 (13)	0.4687 (5)
C(16)	0.2268 (7)	0.6260 (11)	0.4251 (6)
C(17)	0.3718 (7)	−0.0365 (13)	0.3108 (8)
C(18)	0.4832 (7)	0.1773 (17)	0.4246 (9)
	Molecule B		
C(1)	0.0191 (5)	0.7894 (10)	0.7619 (5)
C(2)	0.0299 (7)	0.8491 (12)	0.8269 (7)
C(3)	0.0744 (8)	0.7837 (15)	0.8738 (7)
C(4)	0.1097 (6)	0.6545 (13)	0.8583 (5)
C(5)	0.0741 (5)	0.1481 (10)	0.6769 (6)
C(6)	0.0316 (6)	0.0892 (11)	0.6225 (6)
C(7)	−0.0097 (6)	0.1787 (12)	0.5799 (6)
C(8)	−0.0074 (5)	0.3267 (11)	0.5887 (5)
Si(9)	0.0377 (1)	0.6023 (2)	0.6492 (1)
Sn(10)	0.14896 (3)	0.38928 (7)	0.77038 (3)
C(11)	0.0508 (4)	0.6636 (9)	0.7421 (4)
C(12)	0.0974 (5)	0.5904 (10)	0.7932 (4)
C(13)	0.0780 (4)	0.2990 (9)	0.6880 (4)
C(14)	0.0356 (4)	0.3928 (9)	0.6432 (4)
C(15)	0.1135 (5)	0.6661 (10)	0.6044 (5)
C(16)	−0.0477 (5)	0.6744 (11)	0.6069 (5)
C(17)	0.1609 (7)	0.2470 (14)	0.8592 (6)
C(18)	0.2512 (6)	0.4211 (16)	0.7371 (7)

in THF (50 mL), and the slurry is stirred overnight. After the usual workup a solid is obtained after removal of the solvents. Recrystallization of the solid from ethanol provides 4.6 g (61%) of pure IIe as a white solid.

9,9,10,10-Tetramethyl-9,10-dihydro-10-germa-9-silaanthracene, IIIa. To a slurry of activated magnesium generated from $MgCl_2$ (5.0 g, 53 mmol) is added bis(*o*-chlorophenyl)dimethylsilane (2.7 g, 9.5 mmol in THF (25 mL), and the reaction mixture is refluxed for 3 h. Dimethylgermanium dichloride (1.7 g, 9.5 mmol) in THF (25 mL) is added, and the mixture is refluxed for an additional 3 h. After workup, the oil residue is purified by chromatography (silica gel, hexanes/CH_2Cl_2 as eluant). Kugelrohr distillation of the appropriate fraction (90–130 °C, 0.01 mm) provides 0.99 g (33%) crude IIIa. Trituration with ethanol provides crystalline IIIa.

9,9,10,10-Tetramethyl-9,10-dihydro-10-stanna-9-silaanthracene, IIIb. To a slurry of activated magnesium generated from $MgCl_2$ (7.5 g, 76 mmol) is added bis(*o*-chlorophenyl)dimethylsilane (5.0 g, 18 mmol) in THF (25 mL), and the reaction mixture is refluxed for 3 h. A slurry of dimethyltin dichloride (3.9 g, 18 mmol) in THF (25 mL) is added, and the slurry is stirred overnight. After workup the oil residue is purified by chromatography (silica gel, hexanes/CH_2Cl_2 as eluant). Kugelrohr distillation provides 3.6 g (56%) of crude product, bp 102–120 °C (0.01 mm). The distilled oil is dissolved in ethanol and on cooling provides crystalline IIIb. An analytical sample is obtained by recrystallization from ethanol.

X-ray Structure Analyses of IIIa and IIIb. Single crystals of each compound were obtained by recrystallization from ethanol and mounted on a glass fiber for data collection on a Nicolet P3 diffractometer. Pertinent crystal and intensity data are given in Table VIII. Details of data collection procedures and programs for calculations have been described previously.[36]

Both structures were solved by an iterative application of the Σ_2 relationship with 250 and 293 normalized structure factors of

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[36] See program references in: Corey, E. R.; Paton, W. F.; Corey, J. Y. *J. Organomet. Chem.* **1979**, *179*, 241. Bellavance, P. L.; Corey, E. R.; Corey, J. Y.; Hey, G. W. *Inorg. Chem.* **1977**, *16*, 462.

magnitude 1.30 and 1.60 or greater for compounds IIIa and IIIb, respectively. An E map based on the set of phases for the solution with a consistency index of 0.950 (second highest) and 0.999 (highest) for IIIa and IIIb, respectively, gave a partial solution for each structure. Successive Fourier syntheses revealed the remaining non-H atom locations. Anisotropic least-squares refinement of all non-hydrogen atoms resulted in final atom locations for which the largest parameter shift was less than 10% of its standard deviation. Final positional parameters with estimated standard deviations are given in Tables IX and X. Hydrogen atoms were included at calculated positions with C–H bond distances of 0.95 Å. Hydrogen atom positions were recalculated after each cycle of least-squares refinement and assigned isotropic thermal parameters equal to the equivalent B (Å^2) of the carbon to which it is bonded. Scattering factors for the neutral atoms were taken from ref 37: those for silicon, germanium, and tin were corrected for anomalous dispersion. Maximum residual electron densities in the final electron difference map for IIIa and IIIb were 0.30 and 0.99 e/Å^3, respectively.

During the refinement of IIIa a disorder of the silicon and germanium atoms was identified. Refinement of the occupancy factors for Ge and Si revealed a 50/50 disorder for these atoms; the refinement was completed by using an average Si–Ge scattering factor curve.

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Registry No. (E)-IIa, 87938-51-0; (Z)-IIa, 87938-61-2; IIb, 87938-52-1; IIc, 33022-24-1; IId, 87938-53-2; IIe, 87938-54-3; IIIa, 87938-55-4; IIIb, 87938-56-5; IIIc, 87938-57-6; Va, 87938-58-7; Vb, 75302-84-0; VIa, 87938-59-8; VIb, 87938-60-1; $MeHSiCl_2$, 75-54-7; Ph_2SiMe_2, 778-24-5; $MePh_2SiH$, 776-76-1; MeLi, 917-54-4; Me_2GeCl_2, 1529-48-2; Ph_2PbCl_2, 2117-69-3; Me_2SiCl_2, 75-78-5; $MePhSiCl_2$, 149-74-6; Me_2SnCl_2, 753-73-1; NBS, 128-08-5; *o*-dibromobenzene, 583-53-9; *o*-chlorobromobenzene, 694-80-4; 5-methyl-5*H*-dibenzosilole, 53268-89-6; *o,o'*-dibromobiphenyl, 13029-09-9; 5,5-dimethyldibenzosilole, 13688-68-1; methylchlorosilane, 993-00-0.

Supplementary Material Available: Tables of hydrogen atom coordinates and thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms, least-squares planes, molecular drawings with anisotropic thermal ellipsoids, and structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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(37) "International Tables for X-ray Crystallography"; Henry, N. F. M., Lonsdale, L., Eds.; Kynoch Press: Birmingham, England, 1952; Vol. 1.

Structure of (Biphenylene)- and (Triphenylene)Cr(CO)$_3$. An Analysis of the Bonding of Cr(CO)$_3$ to Bicyclic Polyenes

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The preparation and description of the molecular structure of (biphenylene)Cr(CO)$_3$, **1**, and (triphenylene)Cr(CO)$_3$, **2**, are given. The crystal data are as follows: (1) a = 7.065 (4) Å, b = 11.066 (5) Å, c = 8.030 (4) Å, β = 98.43 (3)°, Z = 2, space group $P2_1/m$; (2) a = 12.994 (5) Å, b = 14.766 (5) Å, c = 9.393 (4) Å, β = 121.63 (3)°, Z = 4, space group $C2/m$. The structures were refined to R_w values of 0.033 and 0.027 for **1** and **2**, respectively. The bond localization in biphenylene is somewhat reduced in the Cr(CO)$_3$ complex. While the conformations of the Cr(CO)$_3$ group in **2** and all other polynuclear (benzenoid)Cr(CO)$_3$ complexes have the symmetry unique carbonyl ligand pointed away from the uncoordinated portion of the polyene, the conformation for **1** is reversed. Molecular orbital calculations at the extended Hückel level were carried out to establish the bonding in **1** and the related (naphthalene)Cr(CO)$_3$. A rationale is given for this conformational preference, and a general theoretical strategy is developed to predict the favored conformation in any bicyclic (polyene)ML$_3$ complex.

Introduction

Polycyclic hydrocarbons have fascinated organic chemists for many years with their preparation and physical properties.[2] Naturally, this has been extended to the transition-metal complexes of these compounds.[3] Of particular interest has been the ability of transition metals to stabilize antiaromatic polyenes, with cyclobutadiene[4] being the prime example. Structurally, while singlet cyclobutadiene is probably rectangular,[5] the Fe(CO)$_3$ complexes among others are square.[6] Biphenylene[7] is another well-known example which in the ligand itself shows bond localization as deduced from X-ray[8a,b] and electron dif-

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[1] (a) Northern Illinois University. (b) University of Alabama. (c) University of Houston. (d) University of Massachusetts. (e) Camille and Henry Dreyfus Teach-Scholar, 1980–1984; Alfred P. Sloan Research Fellow, 1982–1984.

[2] (a) "Nonbenzenoid Aromatics", Snyder, J. P., Ed.; Academic Press: New York, 1969. (b) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: New York, 1964. (c) "Cyclobutadiene and Related Compounds"; Cava, M. P., Mitchell, M. J., Eds.; Academic Press: New York, 1967.

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