Stabilizing 1,3-Diaxial Interaction between a Metal (Group 14) and a Heteroatom. Fixation of Six-Membered Carbacycles to the 1,3-Diaxial Conformer

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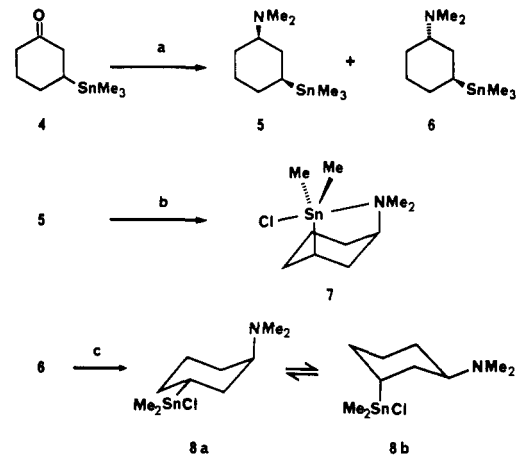
Fixation of the molecular geometry of six-membered carbacycles to the 1,3-diaxial conformer by a stabilizing 1,3-diaxial interaction between tin and nitrogen atoms is described. In analogy with (*cis*-3-(benzyloxy)cyclohexyl)chlorodimethylstannane (**2a**), intramolecular Sn–N hypervalent interaction biases the structure of chlorodimethyl(*cis*-3-(dimethylamino)cyclohexyl)stannane (**7**) toward the 1,3-diaxial conformation, whereas (*cis*-3-(benzyloxy)cyclohexyl)chlorodimethylgermane (**15**) and (*cis*-3-(benzyloxy)-cyclohexyl)dimethylfluorosilane (**16**) prefer the diequatorial conformation. The difference between the preferred conformations of **2** and **15** or **16** is discussed in terms of the *A* values of $(CH_3)_3M$ (M = Sn, Ge, and Si) groups and the polarizability of C–M (M = Sn, Ge, and Si) bonds.

Introduction

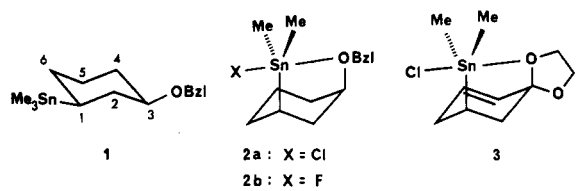
When reacting substrates can adopt more than two stable conformations in solution, the product complexity obtained often arises from the coformational flexibility of the substrates. For example, it has been reported that lithium aluminum hydride reduction of 4-methylcyclohexanone afforded an 80% predominance of *trans*-4-methylcyclohexanol, while in the reaction of conformationally more homogeneous 4-*tert*-butylcyclohexanone a 92% predominance of *trans*-4-*tert*-butylcyclohexanol was obtained.[1] Factors that control the conformational flexibility mostly consist of steric interactions and electronic effects (stereoelectronic effects, orbital interactions, dipole moment, negative and positive hyperconjugations, etc.).[2] Conformational fixation of substrates by internal chelation evoked with adding external metals provides a useful method for attaining high stereo- and regioselectivity.[3] Another way for imposing a rigid conformation on substrates is an introduction of new covalent bonds: Stork's synthesis of *trans*-8-methyl-1,5-hydrindandione involves a stereoselective conjugate addition of an organocuprate to a cyclohexenone made conformationally rigid by the attachment of a 1,3-lactone.[4,5]

The diaxial conformation of cis-1,3-disubstituted cyclohexanes is particularly unfavorable in terms of 1,3-diaxial interactions caused by van der Waals repulsion.[6] Thus, (*cis*-3-(benzyloxy)cyclohexyl)trimethylstannane (**1**) shows no evidence of any intramolecular donor–acceptor interaction, and both substituents are equatorial. We have reported, however, that, on replacement of one of the methyl groups of **1** with a electronegative ligand such as chlorine, intramolecular hypervalent Sn–O interaction becomes important due to the increased acidity[7,8] of the tin atom of **2**, and, as a result, **2** adopts a 1,3-diaxial conformation. This is termed the stabilizing 1,3-diaxial interaction.[9] This interaction makes the stereoselective osmylation of the double bond of **3** possible.[9]

Scheme I[a]



[a] Reagents: (a) Me_2NH·HCl, Et_3N, $NaBH_3CN$, MeOH, 25 °C; (b) Me_2SnCl_2 (1 equiv), CH_2Cl_2, reflux; (c) Me_2SnCl_2 (6 equiv), dioxane, reflux.



In order to disclose the applicability of this conformational fixation by the stabilizing 1,3-diaxial interaction, an electron-donating oxygen atom was replaced by a more basic nitrogen atom, which shows a good donor ability toward a Lewis acidic tin atom.[10] Furthermore, silicon

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Table I. ^{13}C and ^{1}H NMR Parameters of Group 14 Substituted Cyclohexanes[a,b]

	carbon					proton		
compd	C_1	C_3	C_5	MMe	NMe	MMe	NMe	C_3–H
5	23.8 (402)	65.5 (70.3)	28.4 (73.3)	−11.9 (308)	41.4	0.01 (51.8)[c]	2.29	
6	23.8 (399)	62.7 (26.4)	24.8 (27.8)	−10.1 (303)	42.2	0.07 (50.8)[c]	2.32	
7	34.1 (588)	62.3 (24.9)	22.2 (27.8)	2.1	43.2, 48.1	0.62 (55.7),[c] 0.77 (58.6)[c]	2.28	
8	32.1 (463)	63.1 (32.2)	24.5 (35.2)	0.1 (363)	41.7	0.59 (51.3)[c]	2.29	
9	24.3 (356)	70.2 (13.2)	25.2 (11.7)	−9.2 (315)	47.2, 47.3	0.17 (51.8)[c]	3.33, 3.35	
12	25.7	79.0	26.8	−4.3	69.9[d]	0.07		3.28 (17.4)[e]
14	24.1	78.8	26.5	−5.2	69.6[d]	0.25		3.27 (17.2)[e]
15	30.2	77.6	25.3	1.2	69.8[d]			3.38 (17.7)[e]
16	24.8 (13.2)[f]	78.4	25.3	−3.3 (14.7)[f]	69.8[d]	0.19 (7.3)[g]		3.34 (17.3)[e]

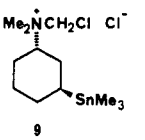
[a] Chemical shifts in ppm. [b] Unless otherwise noted, numbers in parentheses refer to coupling constants $^{n}J(^{119}Sn-^{13}C)$ in hertz. [c] Coupling constants $^{2}J(^{119}Sn-^{1}H)$ in hertz. [d] Chemical shifts of benzylic carbons. [e] Half-band width in hertz. [f] Coupling constants $^{2}J(^{19}F-^{13}C)$ in hertz. [g] Coupling constants $^{3}J(^{19}F-^{1}H)$ in hertz.

and germanium (group 14 metals) analogues of **2** were synthesized. We report herein the results in detail.

Results and Discussion

Synthesis of Nitrogen Analogues. Reductive amination of the carbonyl group of 3-(trimethylstannyl)-cyclohexanone (**4**)[11] with dimethylamine and sodium cyanoborohydride in methanol[12] afforded a mixture of the cis dimethylamine **5** and the trans isomer **6** (Scheme I). Separation by alumina column chromatography gave **6** as a major product (32% yield) and **5** as a minor product (24% yield). Extensive studies by Kitching and his coworkers show that the $^{3}J(^{119}Sn-^{13}C)$ value serves as a valuable tool for determining the axial or equatorial nature of stannyl groups of cyclohexylstannanes.[11,13] Large $^{3}J(^{119}Sn-^{13}C)$ values (to C_3 and C_5) of **5**, shown in Table I, indicate the equatorial trimethylstannyl group and, therefore, the 1,3-cis structure was assigned. On the other hand, the conformationally flexible trans isomer **6** shows reasonable $^{3}J(^{119}Sn-^{13}C)$ values of 26.4 and 27.8 Hz: the reported *A* values of dimethylamino and trimethylstannyl groups are 2.1[14] and 1.06 kcal/mol,[15] respectively, and suggest an 85% predominance of the conformer bearing an axial stannyl group. The 40:60 ratio (GC) of **5** to **6**, presumably produced through sodium cyanoborohydride reduction of the imminium intermediate, is in a marked contrast with the results of lithium aluminum hydride reduction of **4**, **11**, and **13**, which gives the corresponding cis alcohols in 84–89% selectivity.[11,16]

The attempted chlorodemethylation of these aminostannanes **5** and **6** with iodosylbenzene activated by boron trifluoride–diethyl ether[9] gave poor results due to the considerable difficulty of purification of the products from the acidic reaction mixture. The comproportionation reaction with dimethyltin dichloride has been well documented, and the byproduct trimethyltin chloride could be easily removed from products.[17] Exposure of **5** to 1 equiv of dimethyltin dichloride in refluxing dichloromethane for 17 h, followed by the removal of volatile trimethyltin chloride at 60 °C in vacuo, afforded the cis chlorostannane **7** in 63% yield. In the reaction of **6**, however, a trace amount of the desired **8** was obtained with a 45% recovery of the starting material, even after refluxing for 42 h. The major product obtained was the unexpected (chloromethyl)dimethylammonium chloride **9**, in which the trimethylstannyl group remains intact. The chloromethylation can be interpreted in terms of the activation of dichloromethane toward the nucleophilic attack of the tertiary amino group by the formation of the pentacoordinated tin compound **10**. Application of this interesting reaction is under progress.



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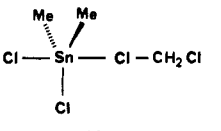

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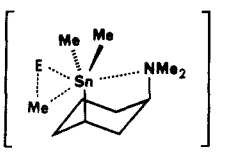
These reactivity differences are probably attributable to the intramolecular nucleophilic assistance at tin by the dimethylamino group in the case of **5**, as has been observed before.[18] The possible transition state for the chlorination of **5** is shown below in which *E* represents dimethyltin dichloride. Replacing the solvent from dichloromethane



to 1,4-dioxane and using excess amounts of dimethyltin dichloride, **6** afforded the desired trans chlorostannane **8** in 54% yield.

Synthesis of Silicon and Germanium Analogues. Conjugate addition of (trimethylgermyl)lithium[19] to cyclohexanone gave **11** in 49% yield. In the reaction, the generation of (pentamethyldigermyl)lithium in situ lowered the yield of **11**.[20] Lithium aluminum hydride re-

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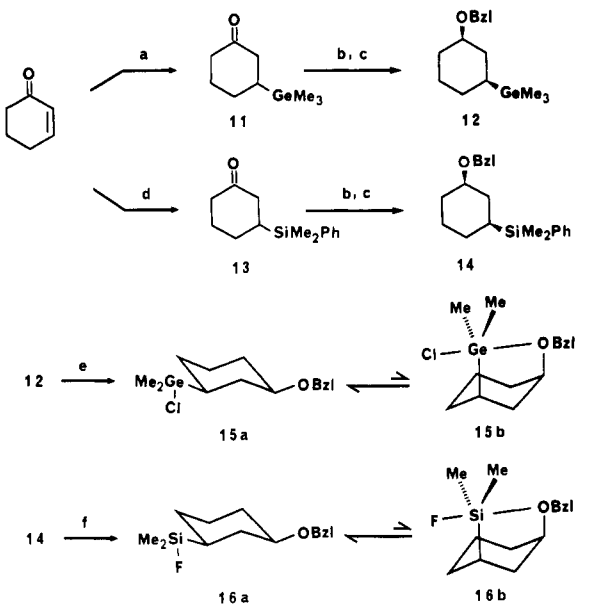
Scheme II[a]



[a] Reagents: (a) Me_3GeLi, THF–HMPA, −78 °C; (b) $LiAlH_4$, THF, 0 °C; (c) $PhCH_2Br$, NaH, DMF, 25 °C; (d) $PhMe_2SiLi$, THF–HMPA, −78 °C; (e) $(PhIO)_n$, BF_3–Et_2O, CH_2Cl_2, 25 °C, and then aqueous NH_4Cl; (f) HBF_4–Et_2O, CH_2Cl_2, 0 °C.

duction afforded a mixture of the corresponding cis and trans alcohols in an 87:13 ratio, which was determined by ^1H NMR signals of C_3–H, and then benzylation gave rise to **12** in overall 51% yield (Scheme II). Similarly, reduction of 3-(dimethylphenylsilyl)cyclohexanone (**13**),[21] prepared by the addition of (dimethylphenylsilyl)lithium to cyclohexenone, gave an 89:11 mixture of the corresponding cis and trans alcohols.[11] Benzylation gave the silane **14** in 72% yield from **13**.

Trimethylstannane **1** undergoes iodosylbenzene-mediated chlorodemethylation at 0 °C within 30 min;[9] however, trimethylgermane **12** required room temperature. Thus, treatment of **12** with iodosylbenzene and boron trifluoride–diethyl ether in dichloromethane at room temperature for 2 h afforded **15** in 84% yield. Fluorodephenylation of **14** was carried out according to the method developed by Fleming,[22] and the fluorosilane **16** was obtained by the reaction with tetrafluoroboric acid–diethyl ether in dichloromethane at 0 °C (68% yield). Iodine(III)-mediated fluorodephenylation of **14** (C_6H_5IO, BF_3·Et_2O, CH_2Cl_2, 25 °C, 24 h, and then NH_4F) gave similar results.

Conformational Analysis. Selected ^{13}C and ^1H NMR data are presented in Table I. It was demonstrated by the following NMR analysis that, similarly to the cis chlorostannane **2a**, the nitrogen analogue **7** adopts a 1,3-diaxial conformation in a solution of noncoordinating solvent ($CDCl_3$). In contrast to the large $^3J(^{119}Sn–^{13}C)$ values (to C_3 and C_5) of **5**, showing an exclusive predominance of the diequatorial conformation, the small values of 24.9 and 27.8 Hz were observed for **7**, which indicate the axial nature of the chlorostannyl group. On the other hand, a small increase of the vicinal $^{119}Sn–^{13}C$ couplings on going from the 1,3-trans isomer **6** to **8** was observed, indicating no appreciable change in the conformations. This is in a good agreement with a reported increase in the case of the transformation of tetrabutyltin to tetrahedral chlorotributyltin.[23]

Coupling constants $^1J(^{119}Sn–^{13}C)$ are shown to be very sensitive to the structure of organotin compounds.[17a,24] A larger increase (186 Hz) of the value (to C_1) on going from **5** to **7** compared to that (64 Hz) of trans isomers (**6** → **8**) can be explained in terms of an increase in the coordination number of the tin atom of **7** from four to five. Pentacoordination at the tin of **7** was further supported by the $^2J(^{119}Sn–^1H)$ coupling constants (to CH_3):[25] for **7** the value amounts to about 57 Hz (vs about 51 Hz in **5**, **6**, and **8**) which is a value normally observed for triorganotin halides with pentacoordination at tin. High field shift of the ^{119}Sn NMR signal of **7**, which appeared at δ 7.4 ppm, relative to that of **8** (δ 147.8 ppm) shows pentacoordination at the tin.

The ^{13}C chemical shifts of the NMe_2 of **7** are 43.2 and 48.1 ppm, reflecting coordination of the nitrogen to the tin which would cause a downfield shift with respect to the chemical shift for the NMe_2 of the tetraorganotin **5**.[25b] The γ-effect is generally observed for any carbon in a gauche orientation with respect to another carbon or heteroatom.[26] A large upfield shift (−6.3 ppm) of C_5 of **7** compared to that of **5** is probably ascribed to the steric compression caused by the tin and nitrogen atoms in gauche γ-positions, which is possible in the 1,3-diaxial structure.

The two methyl groups attached to the tin of **7** are diastereotopic. They show two signals in the ^1H NMR spectrum, with nearly the same value for $^2J(^{119}Sn–^1H)$. The result clearly shows that both methyl groups occupy an equatorial position in the trigonal-bipyramidal arrangement, and, therefore, the chlorine and nitrogen atoms are in apical positions, as was observed in **2**. Pyramidal inversion at nitrogen in trialkylamines is usually a low-energy process.[27] Thus, the NMe_2 groups of **5**, **6**, and **8** in the ^{13}C NMR spectra appears as one singlet. In **7** the intramolecular Sn–N interaction makes the NMe_2 group diastereotopic, which appears as two singlets at 43.23 and 48.09 ppm.

All the spectral data described above indicate that the stabilizing 1,3-diaxial interaction between the tin and nitrogen atoms in **7** plays an important role in determining the conformation in solution. On the other hand, the chlorodimethylgermane **15** and fluorodimethylsilane **16** predominantly adopt a diequatorial conformation in solution, which was determined by the ^1H NMR spectra: the ^1H chemical shift and the half-band width of C_3–H in **15** and **16** are nearly the same as those of **12** and **14**. This is in a marked contrast with the reported diaxial conformation of the corresponding tin analogues **2a** and **2b**.[9]

Why the Ge–O and Si–O hypervalent interaction is not strong enough to prefer the 1,3-diaxial conformation for **15** and **16**, in contrast to the effective Sn–O interaction in **2**? There may be two possible reasons to answer the

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question. First is the difference in the *A* values reported by Kitching and co-workers: $SnMe_3$ (1.06 kcal/mol), $GeMe_3$ (2.1–2.2 kcal/mol),[13b] and $SiMe_3$ (2.4–2.6 kcal/mol).[11,28] The sequence reflects decreasing C–M bond lengths. Therefore, the destabilizing 1,3-diaxial interaction between the halogenodimethylmetal (group 14) group and the axial C_5–H in the diaxial conformer is probably increased in the order of **2**, **15**, and **16**. The second factor concerned with the conformational stability may be the polarizability of C–M bonds. The higher polarizability of the Sn–C bond than that of the Ge–C and Si–C bonds, together with the availability of d orbitals, makes organotins reasonably better Lewis acids.[8,29]

Experimental Section

Melting points were determined with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-202 spectrophotometer. NMR spectra were recorded on either a JEOL JNM-FX 100 or a JEOL JNM-GX 400 spectrometer. Chemical shifts (^1H, ^{13}C) were reported in parts per million (ppm) downfield from internal tetramethylsilane. ^{119}Sn NMR shifts (ppm) were reported relative to external tetramethyltin. Mass spectra (MS) were taken on a JEOL JMS-DX 300 spectrometer. Column chromatography was performed on aluminum oxide 90 (Merck, neutral, 70–230 mesh, activity four) or Kieselgel 60 (Merck, 230–400 mesh). Thin-layer chromatography (TLC) was carried out on Kieselgel 60 F-254 (Merck). Dioxane and THF were distilled from sodium and benzophenone. Dichloromethane and methanol were distilled from calcium hydride.

Synthesis of (3-(Dimethylamino)cyclohexyl)trimethylstannanes (5 and 6). To a solution of 3-(trimethylstannyl)-cyclohexanone (**4**)[11] (2.1 g, 8.0 mmol) in absolute methanol (24 mL) was added dimethylamine hydrochloride (3.9 g, 48 mmol) in nitrogen, followed by molecular sieves (3 Å, 4 g), triethylamine (3.2 g, 32 mmol), and sodium cyanoborohydride (0.34 g, 5.3 mmol). The reaction mixture was stirred at room temperature for 3.5 h. The methanol was removed in vacuo, and the residue was taken up in 50 mL of water. The aqueous solution was brought to pH >10 with 1 N NaOH and extracted with three 30-mL portions of dichloromethane. The combined extracts were dried (Na_2SO_4) and evaporated in vacuo to give 1.96 g of a crude oil. The ratio of cis isomer **5** to trans isomer **6** was determined to be 40:60 by analytical gas chromatography (GC) (20% Silicone GE SF-96 on Chromosorb W, 2 m, 130 °C). Alumina column chromatography (1–2% ethyl acetate/hexane) afforded 0.81 g (32%) of **6** and 0.57 g (24%) of **5**. **5**: GC retention time 36.0 min; IR ($CHCl_3$) 2920, 2850, 2780, 1455, 1370, 1185, 1090, 1015, 960, 655, 525 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 6 H), 2.19 (m, 1 H), 2.01–1.67 (m, 4 H), 1.36–1.09 (m, 5 H), 0.01 (s, 9 H, $^2J(^{119}Sn-^1H)$ = 51.8 Hz); ^{13}C NMR (25 MHz, $CDCl_3$) δ 65.5 ($^3J(^{119}Sn-^{13}C)$ = 70.3 Hz), 41.4, 33.3 ($^2J(^{119}Sn-^{13}C)$ = 14.6 Hz), 30.7 ($^2J(^{119}Sn-^{13}C)$ = 14.7 Hz), 28.8, 28.4 ($^3J(^{119}Sn-^{13}C)$ = 73.3 Hz), 23.8 ($^1J(^{119}Sn-^{13}C)$ = 402 Hz), −11.9 ($^1J(^{119}Sn-^{13}C)$ = 308 Hz); MS *m/z* (relative intesity) 276 (4, M^+ − Me), 165 (2), 126 (100); HRMS calcd for $C_{10}H_{22}NSn$ (M^+ − Me) 276.0775, found 276.0782. **6**: GC retention time 32.8 min; IR ($CHCl_3$) 2920, 2850, 2780, 1450, 1370, 1260, 1160, 1015, 655, 525 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6 H), 2.18 (m, 1 H), 1.97 (m, 1 H), 1.88–1.63 (m, 6 H), 1.38 (m, 1 H), 1.28 (m, 1 H), 0.07 (s, 9 H, $^2J(^{119}Sn-^1H)$ = 50.8 Hz); ^{13}C NMR (25 MHz, $CDCl_3$) δ 62.7 ($^3J(^{119}Sn-^{13}C)$ = 26.4 Hz), 42.2, 33.1 ($^2J(^{119}Sn-^{13}C)$ = 11.7 Hz), 30.4 ($^2J(^{119}Sn-^{13}C)$ = 11.7 Hz), 29.6, 24.8 ($^3J(^{119}Sn-^{13}C)$ = 27.8 Hz), 23.8 ($^1J(^{119}Sn-^{13}C)$ = 399 Hz), −10.1 ($^1J(^{119}Sn-^{13}C)$ = 303 Hz); MS *m/z* (relative intensity) 276 (3, M^+ − Me), 165 (2), 126 (100); HRMS calcd for $C_{10}H_{22}NSn$ (M^+ − Me) 276.0775, found 276.0788.

Synthesis of Chlorodimethyl(*cis*-3-(dimethylamino)-cyclohexyl)stannane (7). A solution of **5** (80 mg, 0.28 mmol) and dichlorodimethylstannane (61 mg, 0.28 mmol) in dichloromethane (1 mL) was refluxed for 17 h under nitrogen. The solvent was removed in vacuo. Alumina column chromatography (5% methanol/dichloromethane) afforded 54 mg (63%) of the chlorostannane **7**: mp 123–130 °C (recrystallized from diethyl ether); IR (KBr) 2920, 2850, 1455, 1205, 1055, 960, 915, 770, 540 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.40 (2 H), 2.28 (s, 6 H), 2.10 (m, 2 H), 1.88 (m, 3 H), 1.69 (m, 1 H), 1.47 (m, 2 H), 0.77 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 58.6 Hz), 0.62 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 55.7 Hz); ^{13}C NMR (25 MHz, $CDCl_3$) δ 62.3 ($^3J(^{119}Sn-^{13}C)$ = 24.9 Hz), 48.1 (br), 43.2 (br), 34.1 ($^1J(^{119}Sn-^{13}C)$ = 588 Hz), 33.6 ($^2J(^{119}Sn-^{13}C)$ = 17.6 Hz), 28.7, 28.6 ($^2J(^{119}Sn-^{13}C)$ = 26.4 Hz), 22.2 ($^3J(^{119}Sn-^{13}C)$ = 27.8 Hz), 2.1 (br); MS *m/z* (relative intensity) 311 (0.2, M^+), 296 (4, M^+ − Me), 276 (3, M^+ − Cl), 126 (100); HRMS calcd for $C_{10}H_{22}ClNSn$ (M^+) 311.0463, found 311.0471. Anal. Calcd for $C_{10}H_{22}ClNSn$: C, 38.69; H, 7.14; Cl, 11.42; N, 4.51. Found: C, 38.35; H, 7.07; Cl, 11.49; N, 4.55.

Synthesis of Chlorodimethyl(*trans*-3-(dimethylamino)-cyclohexyl)stannane (8). A solution of **6** (464 mg, 1.6 mmol) and dichlorodimethylstannane (1.4 g, 6.4 mmol) in dioxane (10 mL) was refluxed for 67 h under nitrogen. The solvent was removed in vacuo. Alumina column chromatography (2% methanol/dichloromethane) afforded 268 mg (54%) of the chlorostannane **8** as a colorless oil: IR ($CHCl_3$) 2940, 2780, 1450, 1260, 1015, 660, 540 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 6 H), 2.27 (m, 1 H), 2.13 (m, 2 H), 1.86 (m, 5 H), 1.40 (m, 1 H), 1.29 (m, 1 H), 0.59 (s, 6 H, $^2J(^{119}Sn-^1H)$ = 51.3 Hz); ^{13}C NMR (25 MHz, $CDCl_3$) δ 63.1 ($^3J(^{119}Sn-^{13}C)$ = 32.2 Hz), 41.7, 32.1 ($^1J(^{119}Sn-^{13}C)$ = 463 Hz), 31.5, 29.1, 28.8, 24.5 ($^3J(^{119}Sn-^{13}C)$ = 35.2 Hz), 0.12 ($^1J(^{119}Sn-^{13}C)$ = 363 Hz); MS *m/z* (relative intensity) 311 (0.2, M^+), 296 (0.4, M^+ − Me), 276 (0.9, M^+ − Cl), 126 (100); HRMS calcd for $C_{10}H_{22}ClNSn$ (M^+) 311.0463, found 311.0453.

Reaction of 6 with Dichlorodimethylstannane in Dichloromethane. A solution of **6** (297 mg, 1.02 mmol) and dichlorodimethylstannane (270 mg, 1.23 mmol) in dichloromethane (2 mL) was refluxed for 42 h under nitrogen. The solvent was removed in vacuo. Alumina column chromatography (1–5% methanol/dichloromethane) gave 137 mg (36%) of the chloromethylammonium chloride **9** and 134 mg (45%) of **6**. **9**: mp 155–156 °C (recrystallized from ethyl acetate–chloroform); ^1H NMR (400 MHz, $CDCl_3$) δ 5.64, 5.60 (AB type, J = 10.3 Hz, each 1 H), 3.44 (tt, J = 11.9, 3.4 Hz, 1 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 2.4–1.8 (m, 6 H), 1.75–1.50 (m, 2 H), 1.35 (m, 1 H), 0.17 (s, 9 H, $^2J(^{119}Sn-^1H)$ = 51.8 Hz); ^{13}C NMR (25 MHz, $CDCl_3$–CD_3OD 1:1) δ 70.2 ($^3J(^{119}Sn-^{13}C)$ = 13.2 Hz), 68.1, 47.3, 47.2, 29.7 ($^2J(^{119}Sn-^{13}C)$ = 11.7 Hz), 28.6 ($^2J(^{119}Sn-^{13}C)$ = 8.8 Hz), 26.2, 25.2 ($^3J(^{119}Sn-^{13}C)$ = 11.7 Hz), 24.3 ($^1J(^{119}Sn-^{13}C)$ = 356 Hz), −9.2 ($^1J(^{119}Sn-^{13}C)$ = 315 Hz); MS (FAB) *m/z* 340 (M^+ − Cl). Anal. Calcd for $C_{12}H_{27}Cl_2NSn$: C, 38.44; H, 7.26; N, 3.74. Found: C, 38.20; H, 7.15; N, 3.82.

Synthesis of 3-(Trimethylgermyl)cyclohexanone (11). To a solution of (trimethylgermyl)lithium in hexamethylphosphoric triamide (HMPA)–THF (1:2, 45 mL), prepared from trimethylgermanium chloride (1.98 g, 12.9 mmol) and lithium pieces (0.53 g),[19,20] was added 2-cyclohexenone (0.96 g, 10 mmol) at −78 °C over 10 min under nitrogen. The reaction mixture was stirred for 1 h at the temperature, quenched with a saturated aqueous NH_4Cl solution, and extracted with diethyl ether. After the usual workup, flash column chromatography using silica gel (5–10% ethyl acetate/hexane) gave 1.06 g (49%) of **11** as a colorless oil: IR ($CHCl_3$) 2950, 1700, 1445, 1315, 1210, 825, 600 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 2.52–1.96 (m, 5 H), 1.96–1.10 (m, 4 H), 0.12 (s, 9 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 212.3, 43.6, 42.0, 29.8, 28.7, 27.1, −4.5; MS *m/z* (relative intensity) 216 (21, M^+), 201 (16), 119 (100), 105 (15); HRMS calcd for $C_9H_{18}GeO$ (M^+) 216.0567, found 216.0567.

(*cis*-3-(Benzyloxy)cyclohexyl)trimethylgermane (12). To a solution of **11** (602 mg, 2.8 mmol) in THF (10 mL) was added lithium aluminum hydride (53 mg, 1.4 mmol) at °C under nitrogen, and the mixture was stirred for 0.5 h at the temperature. Ethyl acetate (2 mL) was added dropwise. The mixture was acidified with 1 N HCl and extracted with ethyl acetate. Usual workup gave a crude mixture of (*cis*-3-hydroxycyclohexyl)- and (*trans*-3-hydroxycyclohexyl)trimethylgermanes (600 mg, 99%). The ratio of cis to trans isomer was determined to be 87:13 by the ^1H NMR analysis. The cis alcohol: IR ($CHCl_3$) 3600, 3440, 2930, 2860, 1445,

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1105, 1030, 955, 820, 595 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 3.54 (m, 1 H, $W_{1/2}$ = 17 Hz), 2.10–0.80 (m, 9 H), 0.07 (s, 9 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 71.9, 37.7, 36.0, 27.3, 26.6, 25.5, –4.5; MS m/z (relative intensity) 218 (0.1, M^+), 203 (0.3), 185 (6), 137 (23), 119 (100); HRMS calcd for $C_9H_{20}GeO$ (M^+) 218.0725, found 218.0725.

The crude mixture of alcohols (530 mg, 2.44 mmol) was dissolved in 3 mL of dimethylformamide (DMF), and then sodium hydride (60% in mineral oil, 108 mg, 2.69 mmol) was added at 0 °C under nitrogen. The mixture was stirred for 0.5 h at room temperature. Benzyl bromide (460 mg, 2.69 mmol) was added, and the mixture was stirred for 14 h. Usual workup gave an oil, which was purified by flash column chromatography using silica gel (2% ethyl acetate/hexane) to give 382 mg (51% yield from **11**) of the cis germane **12** as a colorless oil: IR ($CHCl_3$) 2940, 2860, 1600, 1500, 1450, 1360, 1105, 1065, 820, 700, 600 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.32 (m, 5 H), 4.56 (s, 2 H), 3.28 (m, 1 H, $W_{1/2}$ = 17.4 Hz), 2.25–0.70 (m, 9 H), 0.07 (s, 9 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 139.4, 128.4, 127.7, 127.4, 79.0, 69.9, 34.8, 32.9, 27.8, 26.8, 25.7, –4.3; MS m/z (relative intensity) 308 (0.7, M^+), 293 (27), 225 (50), 211 (44), 119 (100); HRMS calcd for $C_{16}H_{26}GeO$ (M^+) 308.1193, found 308.1164. Anal. Calcd for $C_{16}H_{26}GeO$: C, 62.60; H, 8.54. Found: C, 62.41; H, 8.27.

(*cis*-3-(Benzyloxy)cyclohexyl)dimethylphenylsilane (14). Reduction of 3-(dimethylphenylsilyl)cyclohexanone (**13**)[21] (1.37 g, 5.9 mmol) with lithium aluminum hydride (114 mg, 3.0 mmol) in THF (12 mL) at 0 °C for 0.5 h under nitrogen gave a crude mixture of (*cis*-3-hydroxycyclohexyl)- and (*trans*-3-hydroxycyclohexyl)silanes. The ratio of cis to trans isomers was determined to be 89:11 by the ^1H NMR analysis. The cis alcohol: IR ($CHCl_3$) 3610, 3440, 3020, 2940, 2860, 1425, 1250, 1115, 1035, 960, 900, 820 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.60–7.25 (5 H), 3.48 (m, 1 H, $W_{1/2}$ = 17.2 Hz), 2.02 (s, 1 H), 2.0–0.60 (m, 9 H), 0.25 (s, 6 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 137.8, 133.9, 128.8, 127.6, 71.7, 36.4, 35.8, 26.6, 26.1, 24.1 ($^1J(^{29}Si-^{13}C)$ = 54.2 Hz), –5.2 ($^1J(^{29}Si-^{13}C)$ = 52.8 Hz); MS m/z (relative intensity) 234 (29, M^+), 217 (25), 190 (38), 156 (50), 137 (100); HRMS calcd for $C_{14}H_{22}OSi$ (M^+) 234.1441, found 234.1446.

Benzylation of the crude mixture of the alcohols using sodium hydride (60% in mineral oil, 285 mg, 7.1 mmol) and benzyl bromide (1.2 g, 7.1 mmol) in DMF (7 mL), after separation by flash column chromatography using silica gel (3% ethyl acetate/hexane), afforded 1.38 g (72% yield from **13**) of the cis silane **14** as a colorless oil: IR ($CHCl_3$) 3010, 2930, 2860, 1495, 1450, 1360, 1245, 1110, 1065, 815, 695 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.56–7.16 (m, 10 H), 4.52 (s, 2 H), 3.27 (m, 1 H, $W_{1/2}$ = 17.2 Hz), 2.25–0.70 (m, 9 H), 0.25 (s, 6 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 139.2, 137.7, 133.8, 128.8, 128.2, 127.6, 127.4, 127.2, 78.8, 69.6, 33.3, 32.7, 26.6, 26.5, 24.1 ($^1J(^{29}Si-^{13}C)$ = 55.7 Hz), –5.2 ($^1J(^{29}Si-^{13}C)$ = 51.3 Hz); MS m/z (relative intensity) 324 (0.1, M^+), 309 (5), 247 (25), 227 (49), 197 (10) 164 (85), 135 (100), 91 (100); HRMS calcd for $C_{21}H_{28}OSi$ (M^+) 324.1909, found 324.1931.

Chlorodemethylation of Trimethylgermane 12 with Iodosylbenzene. Boron trifluoride–diethyl ether (138 mg, 0.94 mmol) was added dropwise to a stirred suspension of **12** (207 mg, 0.67 mmol) and iodosylbenzene (208 mg, 0.94 mmol) in dichloromethane (6 mL) at 0 °C under nitrogen. The mixture was allowed to stir at 0 °C for 0.5 h and at room temperature for 2 h. A large excess of a saturated aqueous NH_4Cl solution was added, and the mixture was stirred vigorously for 0.5 h. The reaction mixture was poured into water and extracted with dichloromethane. Usual workup left an oil, which was dried at 2 Torr for 24 h to give 185 mg (84%) of the chlorogermane **15** as a colorless oil: IR ($CHCl_3$) 3000, 2940, 2860, 1500, 1450, 1355, 1110, 1070, 835, 615, 585 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.32 (m, 5 H), 4.59 (s, 2 H), 3.38 (m, 1 H, $W_{1/2}$ = 17.7 Hz), 2.40–1.0 (m, 9 H), 0.64 (s, 6 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 138.8, 128.2, 127.5, 127.4, 77.6, 69.8, 33.2, 32.1, 30.2, 26.4, 25.3, 1.2; MS m/z (relative intensity) 313 (0.3, M^+ – Me), 246 (1), 139 (59), 91 (100); HRMS calcd for $C_{14}H_{20}ClGeO$ (M^+ – Me) 313.0413, found 313.0422. Anal. Calcd for $C_{15}H_{23}ClGeO$: C, 55.03; H, 7.08. Found: C, 55.03; H, 6.88.

Fluorodephenylation of Dimethylphenylsilane 14 with Tetrafluoroboric Acid–Diethyl Ether. To a solution of **14** (91 mg, 0.28 mmol) in dichloromethane (3 mL) at 0 °C under nitrogen was added dropwise tetrafluoroboric acid–diethyl ether (85% purity, 0.25 mL, 1.3 mmol), and the mixture was stirred for 2 h. The reaction mixture was poured into cold water and extracted with dichloromethane. Usual workup left an oil, which was purified by chromatography on LiChroprep RP-8 (Merck, acetonitrile–water 84:16), to give 51 mg (68%) of the fluorosilane **16** as a colorless oil: IR ($CHCl_3$) 3010, 2930, 2850, 1600, 1495, 1450, 1255, 1110, 1065, 855 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.45–7.10 (m, 5 H), 4.57 (s, 2 H), 3.34 (m, 1 H, $W_{1/2}$ = 17.3 Hz), 2.30–0.60 (m, 9 H), 0.19 (d, $^3J(^{19}F-^1H)$ = 7.3 Hz, 6 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 139.1, 128.4, 127.5, 127.4, 78.4, 69.8, 32.8, 32.0, 26.4, 25.3, 24.8 ($^2J(^{19}F-^{13}C)$ = 13.2 Hz), –3.3 ($^2J(^{19}F-^{13}C)$ = 14.7 Hz); MS m/z (relative intensity) 266 (0.4, M^+), 251 (4), 233 (2), 184 (21), 133 (41), 91 (100); HRMS calcd for $C_{15}H_{23}FOSi$ (M^+) 266.1502, found 266.1502.

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