tightly ion paired cation (type C nucleophiles), is also controlled by electrostatics, although here it is the electrophilic metal that exerts the dominant influence. The preferred attack trajectory is, therefore, syn to electron-rich functionality on the substrate.

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Intramolecular Hypervalent Sn–O Interaction. The Origin for Fixation of Six-Membered Carbocycles to the 1,3-Diaxial Conformer and for Stereoselective Osmylations

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Abstract: Reported for the first time are the synthesis and characterization of 1,3-diaxial six-membered carbocycles, in which intramolecular Sn–O hypervalent interaction is essential for the conformational preference. When one of the methyl groups of (*cis*-3-(benzyloxy)cyclohexyl)trimethylstannane (**1a**), which exists predominantly as a 1,3-diequatorial conformer, is replaced by a highly electronegative substituent such as halogen by utilizing BF₃-activated iodosylbenzene, the resulting (*cis*-3-(benzyloxy)cyclohexyl)halogenodimethylstannane **2a** (X = Cl), both in solution and the solid state, adopts a 1,3-diaxial conformation as a result of an intramolecular hypervalent interaction between the tin and etheric oxygen atoms. This is termed the "stabilizing 1,3-diaxial interaction". The tin atom of **2a** (X = Cl) has a distorted trigonal-bipyramidal configuration with the oxygen and chlorine atoms in apical positions. The stabilizing 1,3-diaxial interaction makes possible a highly stereoselective osmylation of (5,5-(ethylenedioxy)cyclohex-3-enyl)chlorodimethylstannane (**2d**). Dimethylhalogenostannyl groups were converted into the corresponding hydroxyl groups with retention of configuration.

Diaxial conformation of cis-1,3-disubstituted cyclohexanes is particularly unfavorable in terms of 1,3-diaxial interactions.[2] The destabilizing interaction caused by van der Waals repulsion biases the zwitterion structure of *cis*-3-aminocyclohexanecarboxylic acid toward the diequatorial conformation, even though strong electrostatic attraction between both axial substituents would be expected to occur in the diaxial structure of the zwitterion.[3] We report herein the synthesis and characterization of the first examples of 1,3-diaxial six-membered carbocycles, in which a "stabilizing 1,3-diaxial interaction" between tin and oxygen atoms plays an essential role in determining the conformational preference.

Tetraalkyltins, because of their low Lewis acidity, produce hypervalent pentacoordinated complexes only in reactions with strong nucleophiles such as alkyllithiums.[4] Thus, *cis*-cyclohexylstannane **1a** shows no evidence of any intramolecular donor–acceptor interaction and both substituents are equatorial.[5]

Scheme 1
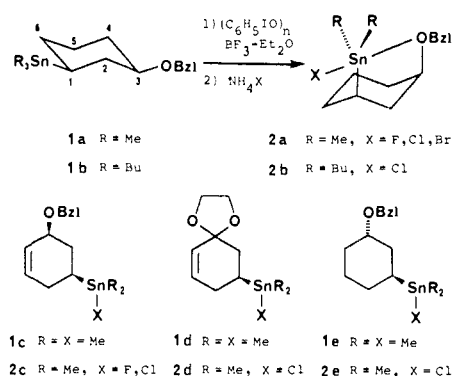
On replacement of one of the methyl groups of **1a** with a highly electronegative ligand such as halogen, the tin atom of **2a** becomes sufficiently acidic that the intramolecular hypervalent Sn–O interaction[6,7] can be expected to become important. We therefore

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Table I. ^{119}Sn–^{13}C Coupling Constants, Half-Band Width of Protons, and ^{119}Sn Chemical Shifts for Compounds **1** and **2**[a]

compd	$^3J(^{119}Sn$–$^{13}C)$[b] C_3, C_5	$W_{1/2}$[c] C_3–H	compd	$^3J(^{119}Sn$–$^{13}C)$[b] C_3, C_5	$W_{1/2}$[c] C_3–H	^{119}Sn[d]
1a	77.2, 71.8	21.4	**2a** (X = F)	19.4, 27.8	9.3	82.0[e]
			2a (X = Cl)	13.2, 23.5	9.6	75.0
			2a (X = Br)	13.2, 23.5	9.1	61.7
1b	70.5, —[f]	26.0	**2b**	13.2, 24.2	10.5	76.7
1c	64.3, 57.2	15.0	**2c** (X = F)	24.7, 10.3	11.0	76.2[g]
			2c (X = Cl)	22.0, 8.8	10.8	70.8
1d	54.9, 52.8		**2d**	20.5, 8.8		88.9
1e	45.3, 48.4	11.7	**2e**	59.2, 64.5	10.9	158.0

[a] In $CDCl_3$. [b] Coupling constants in hertz. [c] Half-band width in hertz. [d] ^{119}Sn chemical shifts (ppm) are related to external tetramethyltin. [e] Coupling constant $^1J(^{19}F$–$^{119}Sn)$ is 2095 Hz. [f] Not determined. [g] Coupling constant $^1J(^{19}F$–$^{119}Sn)$ is 2072 Hz.

tried selective cleavage of the methyl–tin bond of **1a** utilizing iodosylbenzene/boron trifluoride in dichloromethane at 0 °C.[8] Quenching of the reaction mixture with aqueous NH_4Cl afforded the desired chlorostannane **2a** (X = Cl) in 89% yield. Quenching with aqueous NH_4F and NH_4Br gave the corresponding fluoro- and bromostannanes **2a** (X = F and Br) in 84 and 80% yields, respectively. Similarly, halostannanes **2b–e** were prepared in good yields.

The ^{13}C NMR spectra display a large decrease of $^3J(^{119}Sn$–$^{13}C)$ values (to C_3 and C_5) in solution of noncoordinating solvent ($CDCl_3$) on going from *cis*-tetraalkyltins **1a–c** to *cis*-halogenotins **2a–c**, which clearly shows the change of stannyl groups from equatorial to axial arrangement (Table I).[9] On the other hand, a small increase of the vicinal ^{119}Sn–^{13}C couplings was observed in the case of the corresponding trans isomers (from **1e** to **2e**), showing no appreciable change on the conformations.[10] The small half-band width of C_3–H in the ^1H NMR spectra of **2a–c** also indicates the axial nature of the benzyloxy substituent. Thus, these results clearly show that in solution, the conformational change from 1,3-diequatorial to 1,3-diaxial structures occurs with the conversion of **1a–c** to **2a–c**. The fixation of the 1,3-diaxial conformation for **2a–c** can be attributable to the formation of intramolecular donor–acceptor complexes with a five-coordinate tin atom as a result of an intramolecular hypervalent interaction between tin and etheric oxygen atoms. This is termed the "stabilizing 1,3-diaxial interaction". Pentacoordination at the tin atoms of **2a–c** was further supported by ^{119}Sn chemical shifts.[11]

The ^{13}C NMR spectra of **2a** (X = Cl) show dynamic behavior: two singlets of δ 0.8 and -0.5 for the methyl groups at −28 °C *in CDCl₃ coalesce at 4 °C. The free activation energy has been calculated to be 13.8 kcal/mol.* Since the stereoisomerization at tin in the pentacoordinate 1,3-diaxial conformer of **2a** (X = Cl) by a Berry pseudorotation mechanism is energetically unfavorable[6e,f] and external ligands such as pyridine and tetrahydrofuran lower the coalescence temperature, the mechanism responsible for the coalescence can be interpreted in terms of a rapid dissociation–inversion process.
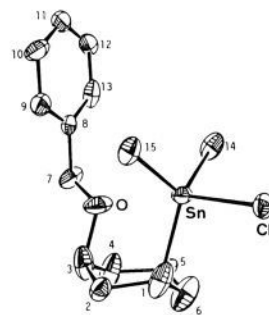
(7) (a) Oae, S. *Phosphorus and Sulfur* **1986**, *27*, 13. (b) Oae, S. *Croat. Chem. Acta* **1986**, *59*, 129.
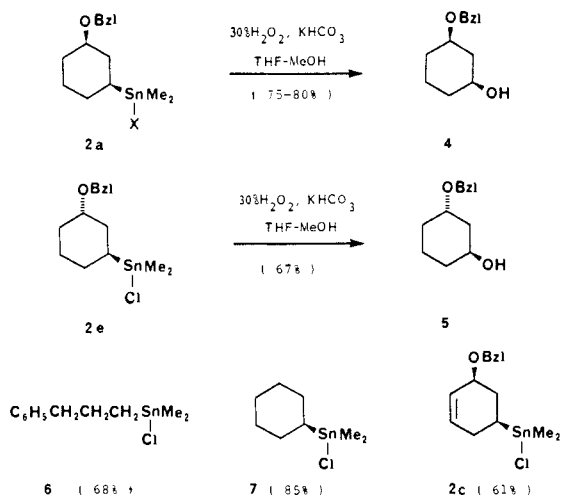
(8) Iodosylbenzene activated by boron trifluoride etherate has been shown to cleave C–Si bonds under mild conditions: (a) Ochiai, M.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *J. Chem. Soc., Chem. Commun.* **1982**, 1108. (b) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351. (c) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 4501.

(9) The $^3J(^{119}Sn$–$^{13}C)$ value, showing a sensitive dependence on dihedral angle, can serve as a valuable tool for determining the axial or equatorial nature of stannyl groups of cyclohexylstannanes: (a) Doddrell, D.; Burfitt, I.; Kitching, W.; Bullpitt, M.; Lee, C.; Mynott, R. J.; Considine, J. L.; Kuivila, H. G.; Sarma, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 1640. (b) Kitching, W.; Olszowy, H.; Waugh, J. *J. Org. Chem.* **1978**, *43*, 898. (c) Filippo, J. S.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834. (d) Wickham, G.; Olszowy, H. A.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 3788. (e) Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893.

(10) The amount that increased agreed well with the reported value of 13 Hz in the case of the transformation of Bu_4Sn to tetrahedral Bu_3SnCl: Al-Allaf, T. A. K. *J. Organomet. Chem.* **1986**, *306*, 337.

(11) For example, the high field shift of the ^{119}Sn NMR signal of **2a** (X = Cl) relative to those of **2e** and trialkyltin chloride with quasitetrahedral arrangement results from an increase in electron density at the tin atom and shows an increase in the coordination number of the tin atom from four to five.[6a]

Figure 1. X-ray structure of **2a** (X = Cl). Selected bond distances (Å): Sn–O = 2.72 (2), Sn–Cl = 2.438 (5), Sn–C_1 = 2.26 (3). Bond angles (deg): O–Sn–Cl = 167.5 (4), C_1–Sn–Cl = 97.8 (8), C_1–Sn–O = 70.0 (9), C_{14}–Sn–O = 90.4 (8), C_1–Sn–C_{14} = 128.0 (10), C_1–Sn–C_{15} = 112.1 (10).

Scheme II
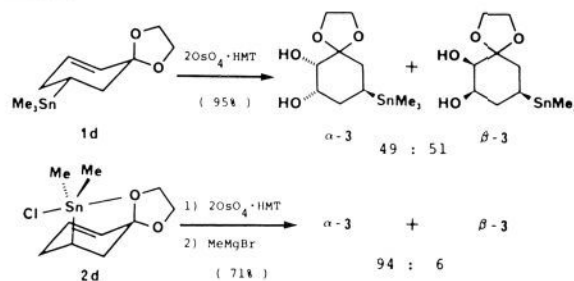
Single-crystal X-ray diffraction analysis of **2a** (X = Cl) at −110 °C features a 1,3-diaxial arrangement with a tin–oxygen bond distance of 2.72 (2) Å, which is considerably shorter than the sum of the van der Waals radii of tin and oxygen and corresponds to a formal bond order of about 0.3 (Figure 1).[12] The tin atom has a distorted trigonal-bipyramidal configuration with the oxygen and chlorine atoms in apical positions and with equatorial angles of 117.9° (mean value for C_1–Sn–C_{14}, C_1–Sn–C_{15}, and C_{14}–Sn–C_{15}) differing slightly from the ideal value of 120°. The tin atom lies 0.32 Å below the plane defined by the three carbon atoms C_1, C_{14}, and C_{15}.[13]

Molecular geometry appears to play an important role in determining the stereochemical course of the reaction. As one application of the new concept, that is, the fixation of molecular geometry by the stabilizing 1,3-diaxial interaction, we developed a highly stereoselective osmylation for olefins.

Osmium tetroxide oxidation of the unsaturated trimethylstannane **1d** utilizing hexamethylenetetramine (HMT)[14] as a

(12) (a) Drager, M. *Z. Anorg. Allg. Chem.* **1976**, *424*, 183. (b) Drager, M. *Z. Anorg. Allg. Chem.* **1976**, *423*, 53.

(13) On the other hand, the X-ray structure of fluorostannane **2a** (X = F), which is shown to be a monomer in chloroform solution by vapor pressure osmometry and adopts a 1,3-diaxial conformation, revealed a fluorine-bridged polymeric structure containing a cyclohexyl ring with 1,3-diequatorial stannyl and benzyloxy groups.

(14) Cleare, M. J.; Hydes, P. C.; Griffith, W. P.; Wright, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 941.

Scheme III

nitrogenous ligand shows no stereoselectivity and gives a mixture of stereoisomeric vicinal glycols α- and β-**3** in a ratio 49:51. However, when a stannyl group is fixed to an axial position by the stabilizing 1,3-diaxial interaction between tin and acetal oxygen atoms, such as in chlorostannane **2d**, a high degree of stereoselectivity can be achieved: osmylation of **2d**, after methylation with methylmagnesium bromide, afforded α-**3** stereoselectively in good yield (Scheme II). This probably results from steric hindrance exhibited by the axially oriented, bulky stannyl group with a trigonal-bipyramidal configuration in **2d**.

Finally, we note that dimethylhalogenostannyl groups can be converted into the corresponding hydroxyl groups with retention of configuration by employing the method developed by Tamao and co-workers in organosilicon chemistry.[15] Oxidation of halogenostannanes **2a** and **2e** with alkaline hydrogen peroxide in tetrahydrofuran/methanol produced the cis-alcohol **4** and the trans-alcohol **5**, respectively, in good yields. Similarly, chlorostannanes **2c** (X = Cl), **6**, and **7** afforded the corresponding secondary and primary alcohols, as shown in Scheme III.

Conclusions. We have developed a new concept for the fixation of the molecular geometry of six-membered carbocycles to the 1,3-diaxial conformer by stabilizing 1,3-diaxial interaction between tin and oxygen atoms. As an application of this new method for conformational fixation, a highly stereoselective osmylation of the olefin **2d** has been achieved. The new method for the conversion of dimethylhalogenostannyl groups into hydroxyl groups, combined with the iodine(III)-mediated selective cleavage of the methyl–tin bond of trimethyltins, offers an efficient procedure for the transformation of trimethylstannyl groups into hydroxyl groups with retention of configuration.

Experimental Section

^{119}Sn NMR shifts (ppm) were reported relative to external tetramethyltin (Me$_4$Sn). Analytical gas chromatography (GC) was performed on a Shimadzu GC-9A gas chromatograph with a column of 1.5% silicone DC QF-1 on Chromosorb W (2 m) or FS-WCOT OV-101 (25 m). Kieselgel 60 (Merck, 230-400 mesh) and alumina (Woelm, neutral) were used for flash chromatography. Thin-layer chromatography (TLC) was carried out on Kieselgel 60 F254 (Merck). Reactions requiring an inert atmosphere were run under a slight positive pressure of nitrogen.

General Procedure for the Cleavage of a Carbon–Tin Bond of Tetraalkylstannanes: The Preparation of (cis-3-(Benzyloxy)cyclohexyl)-chlorodimethylstannane (2a, X = Cl). (cis-3-(Benzyloxy)cyclohexyl)-trimethylstannane (**1a**) was prepared from cis-3-(trimethylstannyl)-cyclohexanol[9d] by treatment with benzyl bromide and sodium hydride in dimethylformamide at room temperature for 17 h in 84% yield. Boron trifluoride–diethyl ether (0.156 g, 1.1 mmol) was added dropwise to a stirred suspension of **1a** (0.353 g, 1.0 mmol) and iodosylbenzene (0.242 g, 1.1 mmol) in dichloromethane (4 mL) at 0 °C. A yellow color was developed. The mixture was allowed to stir at 0 °C for 30 min. A large

excess of a saturated aqueous ammonium chloride solution was added and the mixture was stirred vigorously at 0 °C for 1 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried over anhydrous MgSO$_4$ and concentrated under aspirator vacuum. Flash chromatography (9:1 chloroform/methanol) afforded 0.331 g (89%) of the chlorostannane **2a** (X = Cl) as a white crystalline solid. An analytical sample was prepared by recrystallization from diethyl ether/petroleum ether: mp 66-68 °C; IR (CHCl$_3$) 2940, 1500, 1450, 1360, 1040, 695, 540 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.25 (m, 5 H), 4.56, 4.44 (AB type, J = 11.7 Hz, each 1 H), 3.83 (br s, 1 H), 2.22-1.82 (m, 6 H), 1.61 (m, 2 H), 1.35 (m, 1 H), 0.58 (s, 3 H, $^2J(^{119}$Sn$-^1$H) = 59.1 Hz), 0.47 (s, 3 H, $^2J(^{119}$Sn$-^1$H) = 57.1 Hz); ^{13}C NMR (25 MHz, CDCl$_3$) δ 136.6, 128.5, 128.4, 74.0 ($^3J(^{119}$Sn$-^{13}$C) = 13.2 Hz), 70.5, 35.5 ($^2J(^{119}$Sn$-^{13}$C) = 11.7 Hz), 30.7 ($^1J(^{119}$Sn$-^{13}$C) = 516 Hz), 28.3 ($^2J(^{119}$Sn$-^{13}$C) = 17.6 Hz), 27.8, 20.4 ($^3J(^{119}$Sn$-^{13}$C) = 23.5 Hz), -0.4 ($^1J(^{119}$Sn$-^{13}$C) = 369 Hz); MS m/z (relative intensity) 359 (31, M$^+$ - Me), 339 (5, M$^+$ - Cl), 291 (5), 185 (12), 91 (100); HRMS calcd for C$_{14}$H$_{20}$OClSn (M$^+$ - Me) 359.0224, found 359.0190. Anal. Calcd for C$_{15}$H$_{23}$OClSn: C, 48.24; H, 6.21; Cl, 9.52. Found: 48.38; H, 6.09; Cl, 9.51.

(cis-3-(Benzyloxy)cyclohexyl)fluorodimethylstannane (2a, X = F). The fluorostannane **2a** (X = F) was prepared from 91 mg (0.26 mmol) of **1a**, 68 mg (0.31 mmol) of iodosylbenzene, and 44 mg (0.31 mmol) of boron trifluoride–diethyl ether in dichloromethane (1 mL) according to the general procedure. Quenching of the reaction mixture with a saturated aqueous ammonium fluoride solution followed by standard workup gave 77 mg (84%) of **2a** (X = F): mp 164-165 °C (diethyl ether/dichloromethane); IR (CHCl$_3$) 3010, 2940, 1500, 1445, 1360, 1200, 1040, 700, 530, 470 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39-7.26 (m, 5 H), 4.55, 4.43 (AB type, J = 11.7 Hz, each 1 H), 3.82 (m, 1 H), 2.20-2.08 (m, 2 H), 2.03-1.81 (m, 3 H), 1.66-1.53 (m, 3 H), 1.33 (m, 1 H), 0.43 (s, 3 H, $^2J(^{119}$Sn$-^1$H) = 59.1 Hz), 0.32 (s, 3 H, $^2J(^{119}$Sn$-^1$H) = 57.6 Hz); ^{13}C NMR (25 MHz, CDCl$_3$) δ 136.7, 128.5, 128.4, 74.1 ($^3J(^{119}$Sn$-^{13}$C) = 19.4 Hz), 70.3, 35.5 ($^2J(^{119}$Sn$-^{13}$C) = 11.7 Hz), 28.7 ($^2J(^{119}$Sn$-^{13}$C) = 20.5 Hz), 28.1 ($^1J(^{119}$Sn$-^{13}$C) = 539 Hz), 28.0, 20.4 ($^3J(^{119}$Sn$-^{13}$C) = 27.8 Hz), -2.1 ($^1J(^{119}$Sn$-^{13}$C) = 410 Hz); MS m/z (relative intensity) 343 (33, M$^+$ - Me), 275 (4), 241 (9), 169 (19), 91 (100); HRMS calcd for C$_{14}$H$_{20}$OFSn (M$^+$ - Me) 343.0519, found 343.0493. Anal. Calcd for C$_{15}$H$_{23}$OFSn: C, 50.46; H, 6.49; F, 5.32. Found: C, 50.63; H, 6.40; F, 5.21.

(cis-3-(Benzyloxy)cyclohexyl)bromodimethylstannane (2a, X = Br). The bromostannane **2a** (X = Br) was prepared from 0.11 g (0.31 mmol) of **1a** according to the general procedure. Quenching with a saturated aqueous ammonium bromide solution followed by standard workup gave 103 mg (80%) of **2a** (X = Br): mp 75-77 °C (diethyl ether/petroleum ether); IR (CHCl$_3$) 3000, 2940, 2840, 1500, 1450, 1260, 1040, 695, 540, 525 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.25 (m, 5 H), 4.57, 4.45 (AB type, J = 11.7 Hz, each 1 H), 3.84 (m, 1 H), 2.22-2.05 (m, 3 H), 2.01-1.79 (m, 3 H), 1.62 (m, 2 H), 1.35 (m, 1 H), 0.69 (s, 3 H, ^2J-(^{119}Sn$-^1$H) = 58.6 Hz), 0.57 (s, 3 H, $^2J(^{119}$Sn$-^1$H) = 56.2 Hz); ^{13}C NMR (25 MHz, CDCl$_3$) δ 136.4, 128.5, 128.4, 73.9 ($^3J(^{119}$Sn$-^{13}$C) = 13.2 Hz), 70.4, 35.5 ($^2J(^{119}$Sn$-^{13}$C) = 13.2 Hz), 31.4 ($^1J(^{119}$Sn$-^{13}$C) = 506 Hz), 28.1 ($^2J(^{119}$Sn$-^{13}$C) = 17.6 Hz), 27.7, 20.3 ($^3J(^{119}$Sn$-^{13}$C) = 23.5 Hz), 0.29 ($^1J(^{119}$Sn$-^{13}$C) = 344 Hz); MS m/z (relative intensity) 403 (49, M$^+$ - Me), 337 (13), 229 (48), 199 (13), 135 (14), 91 (100); HRMS calcd for C$_{14}$H$_{20}$OBrSn (M$^+$ - Me) 402.9719, found 402.9703. Anal. Calcd for C$_{15}$H$_{23}$OBrSn: C, 43.11; H, 5.55; Br, 19.12. Found: C, 42.87; H, 5.50; Br, 19.63.

(cis-3-(Benzyloxy)cyclohexyl)dibutylchlorostannane (2b). (cis-3-(Benzyloxy)cyclohexyl)tributylstannane (**1b**) was prepared from 3-(tri-butylstannyl)cyclohexanone[16] by stereoselective reduction (NaBH$_4$/methanol/0 °C/30 min, cis:trans = 89:11, 92% yield) followed by benzylation of the resulting alcohol (75% yield). The chlorostannane **2b** was prepared from 0.800 g (1.67 mmol) of **1b** according to the general procedure. Purification by flash chromatography (95:5 chloroform/methanol) gave 0.696 g (91%) of **2b** as a colorless oil: IR (CHCl$_3$) 3010, 2940, 1500, 1455, 1045, 870, 695, 605 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39-7.28 (m, 5 H), 4.58, 4.46 (AB type, J = 11.7 Hz, each 1 H), 3.78 (m, 1 H), 2.15-1.00 (m, 21 H), 0.89 (t, J = 7.3 Hz, 3 H), 0.88 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.4, 128.0, 127.9, 127.7, 74.0 ($^3J(^{119}$Sn$-^{13}$C) = 13.2 Hz), 70.3, 35.8 ($^2J(^{119}$Sn$-^{13}$C) = 9.5 Hz), 31.0 ($^1J(^{119}$Sn$-^{13}$C) = 435 Hz), 28.7 ($^2J(^{119}$Sn$-^{13}$C) = 16.9 Hz), 28.2, 27.8 ($^2J(^{119}$Sn$-^{13}$C) = 27.9 Hz), 27.8 ($^2J(^{119}$Sn$-^{13}$C) = 25.7 Hz), 26.9 ($^3J(^{119}$Sn$-^{13}$C) = 76.3 Hz), 26.9 ($^3J(^{119}$Sn$-^{13}$C) = 68.2 Hz), 21.2 ($^3J(^{119}$Sn$-^{13}$C) = 24.2 Hz), 19.1 ($^1J(^{119}$Sn$-^{13}$C) = 372 Hz), 17.6 ($^1J(^{119}$Sn$-^{13}$C) = 349 Hz), 13.5; MS m/z (relative intensity) 423 (2, M$^+$ - Cl), 401 (42, M$^+$ - Bu), 269 (7), 91 (100); HRMS calcd for C$_{17}$H$_{26}$OClSn (M$^+$ - Bu) 401.0694, found 401.0672.

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Intramolecular Hypervalent Sn-O Interaction

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(*cis*-5-(Benzyloxy)cyclohex-3-enyl)fluorodimethylstannane (2c, X = F). Synthesis of the cyclohexenylstannane 1c was carried out by the following reaction sequence. Tin-directed regioselective sulfenylation of 3-(trimethylstannyl)cyclohexanone (lithium diisopropylamide/methyl methanethiosulfonate/THF/-70 °C/2 h) afforded a 80:20 cis/trans mixture of 2-(methylthio)-5-(trimethylstannyl)cyclohexanones in 83% yield.[17] Oxidation of the sulfide with sodium metaperiodate and β-elimination of the resulting sulfoxide by thermolysis[18] gave 5-(trimethylstannyl)cyclohex-2-enone in 53% yield. Lithium aluminum hydride reduction of the above cyclohexenone followed by the benzylation of the resulting allyl alcohol produced the benzyl ether 1c in 62% yield. According to the general procedure, 0.35 g (1.0 mmol) of 1c was converted to the fluorostannane 2c (X = F). Quenching with a saturated aqueous ammonium fluoride solution gave 264 mg (74%) of 2c (X = F): mp 147-149 °C (ethyl acetate); IR (CHCl₃) 3010, 2920, 1640, 1500, 1390, 1310, 1030, 940, 700, 550, 470 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.26 (m, 5 H), 6.13 (m, 1 H), 5.92 (m, 1 H), 4.53, 4.51 (AB type, J = 12.2 Hz, each 1 H), 3.90 (m, 1 H), 2.68 (m, 1 H), 2.58 (m, 1 H), 2.14 (m, 1 H), 2.00 (dt, J = 13.2, 2.9 Hz, 1 H), 0.39 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 62.5 Hz), 0.29 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 61.5 Hz); ¹³C NMR (25 MHz, CDCl₃) δ 136.6, 134.9 ($^3J(^{119}Sn-^{13}C)$ = 10.3 Hz) 128.5, 128.4, 128.2, 125.0, 70.4, 70.0 ($^3J(^{119}Sn-^{13}C)$ = 24.7 Hz), 32.2 ($^2J(^{119}Sn-^{13}C)$ = 10.3 Hz), 29.4 ($^2J(^{119}Sn-^{13}C)$ = 20.5 Hz), 23.8 ($^1J(^{119}Sn-^{13}C)$ = 519 Hz), -2.5 ($^1J(^{119}Sn-^{13}C)$ = 425 Hz); MS *m/z* (relative intensity) 341 (15, M⁺ - Me), 275 (8), 257 (14), 169 (19), 151 (14), 91 (100); HRMS calcd for C₁₄H₁₈OFSn (M⁺ - Me) 341.0364, found 341.0409. Anal. Calcd for C₁₅H₂₁OFSn: C, 50.75; H, 5.96; F, 5.35. Found: C, 50.99; H, 6.13; F, 5.20.

(*cis*-5-(Benzyloxy)cyclohex-3-enyl)chlorodimethylstannane (2c, X = Cl). The chlorostannane 2c (X = Cl) was prepared from 0.35 g (1.0 mmol) of 1c according to the general procedure. Purification by flash chromatography (85:15 chloroform/methanol) gave 300 mg (81%) of 2c (X = Cl): mp 92-93 °C (diethyl ether/petroleum ether); IR (CHCl₃) 3010, 2920, 1640, 1500, 1390, 1310, 1035, 695, 545, 525 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.26 (m, 5 H), 6.13 (m, 1 H), 5.92 (m, 1 H), 4.53, 4.51 (AB type, J = 11.7 Hz, each 1 H), 3.92 (m, 1 H), 2.67 (m, 1 H), 2.61 (m, 1 H), 2.18 (m, 1 H), 2.11 (m, 1 H), 2.01 (dt, J = 13.7, 2.9 Hz, 1 H), 0.54 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 62.0 Hz), 0.44 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 60.1 Hz); ¹³C NMR (25 MHz, CDCl₃) δ 136.5, 134.7 ($^3J(^{119}Sn-^{13}C)$ = 8.8 Hz), 128.5, 128.4, 128.2, 124.9, 70.6, 70.1 ($^3J(^{119}Sn-^{13}C)$ = 22.0 Hz), 32.4 ($^2J(^{119}Sn-^{13}C)$ = 11.7 Hz), 29.1 ($^2J(^{119}Sn-^{13}C)$ = 17.6 Hz), 26.6 ($^1J(^{119}Sn-^{13}C)$ = 504 Hz), 0.47, -0.82; MS *m/z* (relative intensity) 357 (15, M⁺ - Me), 337 (4, M⁺ - Cl), 293 (7), 185 (14), 151 (7), 91 (100); HRMS calcd for C₁₄H₁₈OClSn (M⁺ - Me) 357.0068, found 357.0085. Anal. Calcd for C₁₅H₂₁OClSn: C, 48.50; H, 5.70; Cl, 9.54. Found: C, 48.57; H, 5.55; Cl, 9.56.

(5,5-(Ethylenedioxy)cyclohex-3-enyl)chlorodimethylstannane (2d). Acetal 1d was obtained from the reaction of 5-(trimethylstannyl)cyclohex-2-enone with ethylene glycol and triethyl orthoformate under the presence of d-10-camphorsulfonic acid at room temperature for 22 h in 50% yield. With use of the general procedure, 0.590 g (1.95 mmol) of 1d yielded the chlorostannane 2d (476 mg, 76%) as an oil: IR (CHCl₃) 2920, 1635, 1395, 1200, 1125, 1030, 950, 550 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.07 (m, 1 H), 5.57 (m, 1 H), 4.10 (m, 2 H), 3.92 (m, 1 H), 3.76 (dd, J = 14.2, 6.8 Hz, 1 H), 2.65 (m, 1 H), 2.54 (m, 1 H), 2.32 (m, 1 H), 2.16 (dd, J = 13.2, 3.4 Hz, 1 H), 2.02 (m, 1 H), 0.62 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 58.1 Hz), 0.56 (s, 3 H, $^2J(^{119}Sn-^1H)$ = 63.5 Hz); ¹³C NMR (25 MHz, CDCl₃) δ 133.7 ($^3J(^{119}Sn-^{13}C)$ = 8.8 Hz), 127.8, 106.7 ($^3J(^{119}Sn-^{13}C)$ = 20.5 Hz), 65.6, 63.9, 36.7 ($^2J(^{119}Sn-^{13}C)$ = 8.8 Hz), 30.3 ($^1J(^{119}Sn-^{13}C)$ = 492 Hz), 28.5 ($^2J(^{119}Sn-^{13}C)$ = 17.6 Hz), -0.99 ($^1J(^{119}Sn-^{13}C)$ = 390 Hz); MS *m/z* (relative intensity) 309 (11, M⁺ - Me), 289 (15, M⁺ - Cl), 280 (12), 245 (11), 185 (81), 139 (100); HRMS calcd for C₉H₁₄O₂ClSn (M⁺ - Me) 308.9704, found 308.9684.

(*trans*-3-(Benzyloxy)cyclohexyl)chlorodimethylstannane (2e). The stereoselective reduction of 3-(trimethylstannyl)cyclohexanone (potassium tri-*sec*-butylborohydride/THF/-78 °C/30 min, cis:trans = 2:98, 84% yield) followed by the benzylation of the resulting alcohol (80% yield) afforded the *trans*-benzyl ether 1e. With use of the general procedure, 0.353 g (1.0 mmol) of 1e yielded the chlorostannane 2e (321 mg, 86%) as an oil: IR (CHCl₃) 3010, 2940, 1500, 1445, 1350, 1090, 1060, 700, 540, 520 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.24 (m, 5 H), 4.55, 4.50 (AB type, J = 12.2 Hz, each 1 H), 3.58 (m, 1 H), 2.19 (tt, J = 10.3, 3.9 Hz, 1 H), 2.04 (dt, J = 13.7, 4.6 Hz, 1 H), 2.0-1.55 (m,

6 H), 1.46 (m, 1 H), 0.55 (s, 6 H, $^2J(^{119}Sn-^1H)$ = 51.8 Hz); ¹³C NMR (25 MHz, CDCl₃) δ 139.2, 128.2, 127.4, 127.3, 74.2 ($^3J(^{119}Sn-^{13}C)$ = 59.2 Hz), 69.9, 33.9 ($^2J(^{119}Sn-^{13}C)$ = 17.6 Hz), 30.5, 29.2 ($^2J(^{119}Sn-^{13}C)$ = 17.6 Hz), 28.6 ($^1J(^{119}Sn-^{13}C)$ = 443 Hz), 23.1($^3J(^{119}Sn-^{13}C)$ = 64.5 Hz), -3.0 ($^1J(^{119}Sn-^{13}C)$ = 319 Hz); MS *m/z* (relative intensity) 374 (10, M⁺), 359 (26, M⁺ - Me), 267 (10), 189 (39), 171 (82), 91 (100); HRMS calcd for C₁₅H₂₃OClSn (M⁺) 374.0459, found 374.0411.

Osmium Tetroxide Oxidation of Trimethylstannane 1d. To a solution of 1d (32 mg, 0.11 mmol) in THF (1 mL) was added osmium tetroxide-hexamethylenetetramine complex (C₆H₁₂N₄·2OsO₄, 65 mg, 0.10 mmol) at 0 °C. The reaction mixture was stirred for 4 h at 0 °C and then for 2 h at room temperature. Hydrogen sulfide was bubbled through at 0 °C and the resulting black precipitate was filtered off through Celite. Concentration of the filtrate and purification by preparative TLC (2:1 ethyl acetate/hexane) afforded a stereoisomeric mixture of diols α-3 and β-3 (34 mg, 95%). The ratio of α-3:β-3 was determined to be 49:51 by analytical GC (FS-WCOT OV-101, 140 °C). The diols were separated by preparative TLC (9:1 chloroform/methanol). α-3: GC retention time 30.70 min; R_f 0.48 (9:1 chloroform/methanol); mp 72-74 °C (diethyl ether/petroleum ether); IR (CHCl₃) 3530, 2920, 1295, 1155, 1080, 905, 530 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.12 (m, 2 H), 4.04 (m, 1 H), 3.98 (m, 2 H), 3.60 (d, J = 3.4 Hz, 1 H), 2.30 (br s, 2 H), 1.99 (m, 1 H), 1.81 (m, 1 H), 1.68-1.41 (m, 3 H); MS *m/z* (relative intensity) 323 (100, M⁺ - Me), 261 (14), 231 (7), 165 (68), 113 (34), 99 (32); HRMS calcd for C₁₀H₁₉O₄Sn (M⁺ - Me) 323.0305, found 323.0299. Anal. Calcd for C₁₁H₂₂O₄Sn: C, 39.21; H, 6.58. Found: C, 39.13; H, 6.51. β-3: GC retention time 34.39 min; R_f 0.43 (9:1 chloroform/methanol); IR (CHCl₃) 3580, 3460, 2920, 1120, 1055, 855, 530 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.02-3.94 (m, 4 H), 3.73 (ddd, J = 11.2, 4.9, 2.9 Hz, 1 H), 3.70 (br s, 1 H), 2.15 (br s, 2 H), 1.86 (t, J = 13.9 Hz, 1 H), 1.75 (m, 1 H), 1.60 (m, 1 H), 1.51 (m, 1 H), 1.24 (tt, J = 13.9, 3.4 Hz, 1H); MS *m/z* (relative intensity) 323 (100, M⁺ - Me), 279 (8), 205 (10), 165 (68), 115 (32); HRMS calcd for C₁₀H₁₉O₄Sn (M⁺ - Me) 323.0305, found 323.0278.

Osmium Tetroxide Oxidation of Chlorodimethylstannane 2d. The procedure was the same as that described for 1d except that stirring was continued for 13 h at room temperature. The crude product obtained from the reaction of 40 mg (0.12 mmol) of 2d was dissolved in THF (0.5 mL). Methylmagnesium bromide (1.86 mL of a 0.65 M solution in THF, 1.20 mmol) was added at 0 °C and the mixture was stirred for 30 min. The mixture was quenched with an aqueous ammonium chloride solution and extracted with ethyl acetate. Usual workup left an oil, which was purified by preparative TLC (2:1 ethyl acetate/hexane) yielding 29 mg (71%) of a mixture of α-3 and β-3 in a ratio 94:6.

General Procedure for the Stereospecific Conversion of Halogenostannanes to Alcohols: Formation of *cis*-3-(Benzyloxy)cyclohexanol (4). To a solution of 2a (X = Cl, 37 mg, 0.10 mmol) in methanol (0.5 mL) and THF (0.5 mL) was added potassium hydrogen carbonate (30 mg, 0.30 mmol) and 30% hydrogen peroxide (0.05 mL, 0.50 mmol) at room temperature and the mixture was stirred for 24 h. The mixture was quenched with a 5% aqueous sodium sulfite solution and extracted with ethyl acetate. The organic layer was washed with brine, dried, and then concentrated in vacuo to give an oil, which was purified by preparative TLC (1:1 ethyl acetate/hexane) yielding 17 mg (80%) of the cis-alcohol 4 as an oil: GC (QF-1, 150 °C) retention time 7.78 min; R_f 0.56 (1:1 ethyl acetate/hexane); IR (CHCl₃) 3610, 3480, 3020, 2950, 2880, 1710, 1610, 1490, 1450, 1355, 1210, 1050, 690 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.25 (m, 5 H), 4.58, 4.53 (AB type, J = 11.7 Hz, each 1 H), 3.75 (m, 1 H), 3.57 (m, 1 H), 2.18 (br s, 1 H), 2.07 (d, J = 12.7 Hz, 1 H), 1.88 (m, 1 H), 1.82-1.43 (m, 5 H), 1.29 (m, 1 H); MS *m/z* (relative intensity) 206 (1, M⁺), 188 (58), 144 (7), 107 (76), 91 (100); HRMS calcd for C₁₃H₁₈O₂ (M⁺) 206.1307, found 206.1314. The structure of 4 was determined by comparison with the authentic sample prepared from *cis*-1,3-cyclohexanediol. The presence of trans-isomer 5 was not detected by analytical GC.

The fluorostannane 2a (X = F) was converted to 4 selectively in 75% yield according to the procedure described for 2a (X = Cl), except that the reaction mixture was heated at 60 °C for 4 h. The reaction of the bromostannane 2a (X = Br) (60 °C, 10 h) also gave the alcohol 4 in 78% yield.

trans-3-(Benzyloxy)cyclohexanol (5). This alcohol was prepared from 37 mg (0.10 mmol) of 2e according to the general procedure. The reaction mixture was heated at 60 °C for 3 h. Preparative TLC (10:1 chloroform/methanol) afforded 14 mg (67%) of 5 as an oil: GC (QF-1, 150 °C) retention time 6.49 min; R_f 0.61 (1:1 ethyl acetate/hexane); IR (CHCl₃) 3610, 3430, 3010, 2940, 2870, 1720, 1490, 1450, 1205, 1055, 965, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.24 (m, 5 H), 4.53, 4.50 (AB type, J = 11.7 Hz, each 1 H), 4.09 (m, 1 H), 3.80 (m, 1 H), 1.95 (m, 1 H), 1.78 (m, 1 H), 1.72-1.58 (m, 5 H), 1.56 (br s, 1 H), 1.41 (m, 1 H); MS *m/z* (relative intensity) 206 (1, M⁺), 188 (2), 115 (34),

(17) Deprotonation of 3-dimethyl(phenyl)silylcyclohexanone with lithium diisopropylamide has been reported to proceed in favor of enolate formation away from the silyl group to the extent of >95:5: Engel, W.; Fleming, I.; Smithers, R. H. *J. Chem. Soc., Perkin Trans. 1* 1986, 1411.

(18) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* 1976, 98, 4887.

91 (100); HRMS calcd for $C_{13}H_{18}O_2$ (M$^+$) 206.1307, found 206.1305. The structure of **5** was determined by comparison with the authentic sample prepared from *trans*-1,3-cyclohexanediol.

cis-**5-(Benzyloxy)-3-cyclohexen-1-ol.** This alcohol was prepared from 33 mg (0.09 mmol) of **2c** (X = Cl) in 61% yield according to the general procedure (60 °C, 8 h): IR (CHCl$_3$) 3600, 3480, 3000, 2930, 1500, 1450, 1090, 1050, 695 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37–7.27 (m, 5 H), 5.91 (m, 1 H), 5.83 (m, 1 H), 4.61, 4.58 (AB type, J = 11.7 Hz, each 1 H), 4.10 (m, 1 H), 4.04 (m, 1 H), 2.55 (br s, 1 H), 2.28 (m, 2 H), 2.06 (m, 2 H); MS m/z (relative intensity) 204 (2, M$^+$), 186 (3), 113 (6), 107 (48), 91 (100); HRMS calcd for $C_{13}H_{16}O_2$ (M$^+$) 204.1150, found 204.1135.

3-Phenylpropanol. With use of the general procedure for the methyl–tin bond cleavage, 0.566 g (2.0 mmol) of trimethyl(3-phenylpropyl)-stannane afforded chlorodimethyl(3-phenylpropyl)stannane (**6**) (524 mg, 86%) as a colorless oil: IR (CHCl$_3$) 3020, 2930, 2860, 1600, 1500, 1450, 695, 545 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 7.22 (m, 5 H), 2.67 (t, J = 7.3 Hz, 2 H), 2.00 (m, 2 H), 1.32 (m, 2 H), 0.58 (s, 6 H, ^{2}J-(^{119}Sn–^{1}H) = 55.7 Hz); ^{13}C NMR (25 MHz, CDCl$_3$) δ 141.4, 128.4, 128.3, 125.9, 39.4 (^{3}J(^{119}Sn–^{13}C) = 68.9 Hz), 27.3 (^{2}J(^{119}Sn–^{13}C) = 23.5 Hz), 18.4 (^{1}J(^{119}Sn–^{13}C) = 403 Hz), –1.6 (^{1}J(^{119}Sn–^{13}C) = 353 Hz); MS m/z (relative intensity) 289 (36, M$^+$ – Me), 269 (7, M$^+$ – Cl), 185 (55), 119 (14), 91 (100); HRMS calcd for $C_{10}H_{14}ClSn$ (M$^+$ – Me) 288.9806, found 288.9826. 3-Phenylpropanol was prepared from 84 mg (0.28 mmol) of **6** in 68% yield according to the general procedure (room temperature, 30 h).

Cyclohexanol. With use of the general procedure for the methyl–tin bond cleavage, 0.525 g (2.0 mmol) of trimethylstannylcyclohexane yielded chlorocyclohexyldimethylstannane (**7**) (449 mg, 84%) as a colorless oil: IR (CHCl$_3$) 2930, 2850, 1445, 1170, 950, 540, 520 cm^{-1}; ^{1}H NMR (100 MHz, CDCl$_3$) δ 2.2–1.1 (11 H), 0.58 (s, 6 H, ^{2}J(^{119}Sn–^{1}H) = 51.8 Hz); ^{13}C NMR (25 MHz, CDCl$_3$) δ 34.0 (^{1}J(^{119}Sn–^{13}C) = 443 Hz), 30.0 (^{2}J(^{119}Sn–^{13}C) = 17.6 Hz), 28.3 (^{3}J(^{119}Sn–^{13}C) = 73.3 Hz), 26.6, –3.2 (^{1}J(^{119}Sn–^{13}C) = 314 Hz); MS m/z (relative intensity) 268 (5, M$^+$), 253 (5), 185 (8), 150 (5), 83 (100); HRMS calcd for C_8H_{17}ClSn (M$^+$) 268.0040, found 268.0006. Cyclohexanol was prepared from

0.10 g (0.37 mmol) of **7** in 85% yield according to the general procedure (room temperature, 19 h).

X-ray Structure Determination of 2a. A single crystal of **2a** was mounted on the tip of a glass fiber with epoxy and subjected for X-ray diffraction experiments. A Rigaku four-circle diffractometer AFC-5 with Ni-filtered Cu Kα radiation from a rotating anode operated at 40 kV and 200 mA was used. The crystal was cooled in the gas flow from a liquid nitrogen cooling device to decrease decomposition which had been observed at room temperature as 24% decrease of intensity during data collection. The crystal data determined at –110 °C were monoclinic $P2_1/n$, a = 12.886 (4) Å, b = 16.551 (2) Å, c = 8.123 (2) Å, and $β$ = 107.67 (2)°; V = 1650.8 (7) Å^3, Z = 4, d_x = 1.503 g cm^{-3}, and $μ$(Cu Kα) = 122.3 cm^{-1}. Intensity data were collected on the same diffractometer with 2θ–ω scan mode in the range of 2θ < 120°. The dimensions of the crystal were 0.25 × 0.08 × 0.15 mm. 2380 unique reflections were measured, of which 2182 were observed with $F > σ(F)$. The average intensity of the three monitor reflections decreased 11% during data collection at low temperature. No corrections were made for the intensity decrease and absorption effect. The structure was solved by the heavy atom method. The positions and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares including the predicted non-methyl hydrogens in the structure factor calculation. 1764 reflections with $F > 3$ $σ(F)$ were used for the refinement with $w = (σ^2(F) + 0.004F^2)^{-1}$. The final R and R_w were 0.096 and 0.115, respectively.

Supplementary Material Available: Tables of crystallographic details, atomic coordinates and isotropic temperature factors, bond lengths, and bond angles and the molecular structure of **2a** (X = Cl and F) (12 pages). Ordering information is given on any current masthead page.