# Structural evidence for $\sigma_{C\text{-}Sn}$ - $\sigma^{*^{?}}_{C\text{-}O}$ hyperconjugation: low temperature crystal structure of *r*-5-methyl-*c*-2-trimethylstannylcyclohexan-1-*t*-ol

## Jonathan M. White[*] and Josie Giordano

*School of Chemistry, The University of Melbourn*
*E-mail: j.white@oxygen.chemistry.unimelb.edu.au*

## Abstract

The crystal structure of t he title ß-stannyl alcohol contains three molecules in the asymmetric unit.  Two are anti and one is gauche. Examination of C-OH bond distances in the antiperiplanar structures provides structural evidence for σC-Sn – σ*C-OH hyperconjugation.

**Keywords:** Carbon-tin hyperconjugation, stereoelectronic effects, low temp. X-ray crystallography, solid state NMR

## Introduction

The stabilisation of positive charge at the β position by group 4 metal substituents, the so-called group 4 β effect, is central to the che mistry of group 4 metal substituted organic compounds.[1-4] The most well known of these effects is the silicon β effect[2] which is best exemplified by the relative rates of unimolecular solvolysis of the antiperiplanar β-trimethylsilyl ester **1** which reacts $10^{12}$ times faster than the corresponding silicon free derivative **2**.[3] The remarkable rate enhancement of **1** suggests stabilisation of the intermediate β-silyl carbenium ion **3** of ca. 18 kcal/mol. The diminished reactivity of the gauche β-silylester **4** ($10^4$ rel. to **2**) is consistent with the mechanism of stabilisation being hyperconjugation between the C-Si σ bonding orbital

and the carbenium p orbital.[3] It has been demonstrated that stannyl and germyl substituents have an even greater stabilising effect on positive charge at the β position.[5] For example the trimethylgermyl ester **5** and the trimethylstannyl ester **6** react at rates $10^{14}$ and $>>10^{14}$ times faster than the corresponding metal free analogs. The C-M (M = Si, Ge, Sn) are particularly effective at stabilising positive charge by hyperconjugation for two reasons: the C-M (M = Si, Ge, Sn) σ bonds are high energy orbitals, resulting in a good energy match with the vacant carbenium ion orbital, and secondly, the C-M bonds are polarised towards the carbon, which results in particularly effective overlap with the adjacent p orbital. The ability of group IV substituents to stabilise positive charge at the β position increases down the group: Si < Ge << Sn. This trend might be expected to be related to the ionisation potentials of the C-M bonds (M = Si, Ge, Sn), these have been determined from photoelectron spectroscopy for the $Et_4M$ compounds[6] to be 10.04, 9.7, 8.7 e.v. resp. suggesting that a C-Si bond has similar donor properties to an oxygen non bonded pair[7] whereas a C-Sn bond is similar to a nitrogen lone pair,[8] and the C-Ge bonds is a slightly stronger donor than silicon. It has been demonstrated using low temperature x-ray crystallography that the presence of a trimethylsilyl or trimethylgermyl substituent antiperiplanar to a substituent at the β position results in lengthening and hence weakening of the C(alkyl)-O(ester) bond distance in the ground state.[4,9-11] For example the C-O bond lengths in the 2,4-dinitrobenzenesulfenate esters **7** and **8** are 1.490(2) and 1.492(2) Å resp. which are significantly lengthened w.r.t the corresponding unsubstituted analog **9** which has a C-O distance of 1.476(2).[11] The origin of the C-O bond lengthening was proposed to be the result of a hyperconjugative like $\sigma$-$\sigma^*$ interaction between the C-Si(Ge) bonding orbital and the C-O antibonding orbital (Figure 1), this interaction is close to optimum in the structures **7** and **8**. The strength of the $\sigma_C^*{}_M$-$\sigma_{C-O}$ interaction will depend largely on the energy difference between the $\sigma_{C-M}$ orbital and the $\sigma^*_{C-O}$ antibonding orbital,[12] while silicon and germanium have similar ground state effects,[11,13] a trimethylstannyl substituent is expected to have a much larger effects. We have attempted to synthesize ester derivatives derived from the trimethylstannyl alcohols **10** and **11**[11] in order to investigate the structural effects of $\sigma_C^*{}_{Sn}$-$\sigma_{C-O}$ hyperconjugation, however these attempts have been thwarted by the facile elimination of the ester and trimethylstannyl substituents, even the *p*-nitrophenoxy derivatives of **10** and **11** has proved too reactive too isolate and crystallise. Thus structural evidence for $\sigma_{C-Sn}$-$\sigma^*_{C-O}$ interactions has thus far been elusive.

## Results and Discussion

The alcohol **10** was isolated as an oil, but was found to crystallise slowly over a period of 6 months at 5$^{\circ}$ C. The x-ray structure of a rod-like crystal of 10 was determined at 130 K and is shown in Figure 2, **10** was found to exist in the solid state as three independent molecules in the assymmetric unit. Strikingly, two of the molecules (molecule one and molecule two) have the antiperiplanar conformation 1**0a** while molecule three exists in the gauche conformation **10b** (Table 1). The presence of two molecules of with the antiperiplanar conformation **10a** and one molecule with the conformation **10b** is also evident in the solid state nmr of 10 (Figure 3). The relevant features of the solid state nmr spectrum include the signals at -7.6 and -8.10 p.p.m which integrate to 2:1 for the $Me_3Sn$ carbons. Both the relative integrals and the relative chemical shift values are consistent with the presence of two axial $Me_3Sn$ substituents ($\delta$ -7.6) and one equatorial $Me_3Sn$ substituent at higher field ($\delta$ -8.10).[14] Splitting is also clearly resolved for the C1 carbon where signals at $\delta$ 70.5 and 610.2 p.p.m appear in the ratio 2:1. Interestingly the relative proportions of the antiperiplanar **10a** and gauche conformations **10b** observed in the solid state is similar to that observed in solution, thus at -100$^{\circ}$ C the $^{13}$C spectrum resolves into two sets of signals corresponding to **10a** and **10b** in the ratio 3:1. Molecular mechanics[15] calculations which were performed on the two conformations **10a** and **10b** predict that the gauche conformation **10b** is of lower energy on steric grounds (relative energies: **10b** 0.0 kcal/mol **10a** 0.510 kcal/mol). The observation that the anti conformation **10a** predominates in solution is consistent with the presence of stabilising $\sigma_{C-Sn}$-$\sigma^{*}_{C-O}$ hyperconjugation which is maximised in the anti conformation **10a** but is expected to be negligible in the gauche conformation **10b**, this interaction is not accounted for by the molecular mechanics calculations. tructural evidence for this interaction is provided by comparing the $C_1$-$O_1$ bond distances for the three molecules (Table 1). Molecules one and two which exist in the antiperiplanar conformation **10a** have C-O bond distances 1.451 and 1.452 Å resp. which while being essentially identical with each other appear to be lengthened w.r.t molecule three which exists in the gauche conformation **10b** for which the corresponding C-O distance is 1.436(10). The C-O distance observed for **10b** is typical for a secondary alcohol which is not influenced by any special electronic effects. [16] Although the $\sigma_{C-Sn}$-$\sigma_{C-O}^{*}$ interaction might be expected to result in lengthening of the C2-Sn distances of molecules in the antiperiplanar conformation **10a** relative to the gauche conformation **10b**, examination of Table 1 shows no significant differences between the three molecules. This is consistent with our observations on

silicon containing analogues in which structural effects on the C-Si bond are much smaller than those on the C-O bond distance. [4,9-11] It is interesting to note however that the Sn-Me bonds are shorter in molecules 1 and 2 than in molecule three which suggests participation of the group SnMe3 orbitals in the interaction.

Tentative structural evidence is therefore provided for the first time for the presence of $\sigma_{C-Sn}$-$\sigma^*_{C-O}$ hyperconjugation, which has been previously observed for silicon and germanium. The strength of the $\sigma_{C-M}$-$\sigma^*_{C-O}$ interaction depends on the energy difference between the donor orbital ($\sigma_{C-M}$) and the acceptor orbital ($\sigma^*_{C-O}$). Given that a C-Si bond has a similar energy to an oxygen lone pair orbital and that the $\sigma_{C-Si}$-$\sigma^*_{C-O}$ interaction results in similar structural effects as the $n_O$-$\sigma^*_{C-O}$ interaction,[4,10] it is interesting to compare the structural effects of the $\sigma_{C-Sn}$-$\sigma^*_{C-O}$ interaction present in **10b** with the corresponding $n_N$-$\sigma^*_{C-O}$ interaction, e.g as might occur in **12**. An examination of the Cambridge Crystallographic Database showed only one structure which is suitable for comparison; the heterocyclic derivative **13**. The molecule exists in a conformation which allows significant overlap between the nitrogen lone pair orbital and the $\sigma^*_{C-O}$ orbital, the C-O bond distance is 1.460 Å. suggesting that the $n_N$-$\sigma^*_{C-O}$ interaction results in structural effects of a similar order of magnitude to the $\sigma_{C-Sn}$-$\sigma^*_{CO}$ interaction.



**Figure 1**

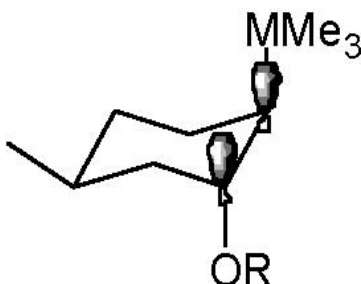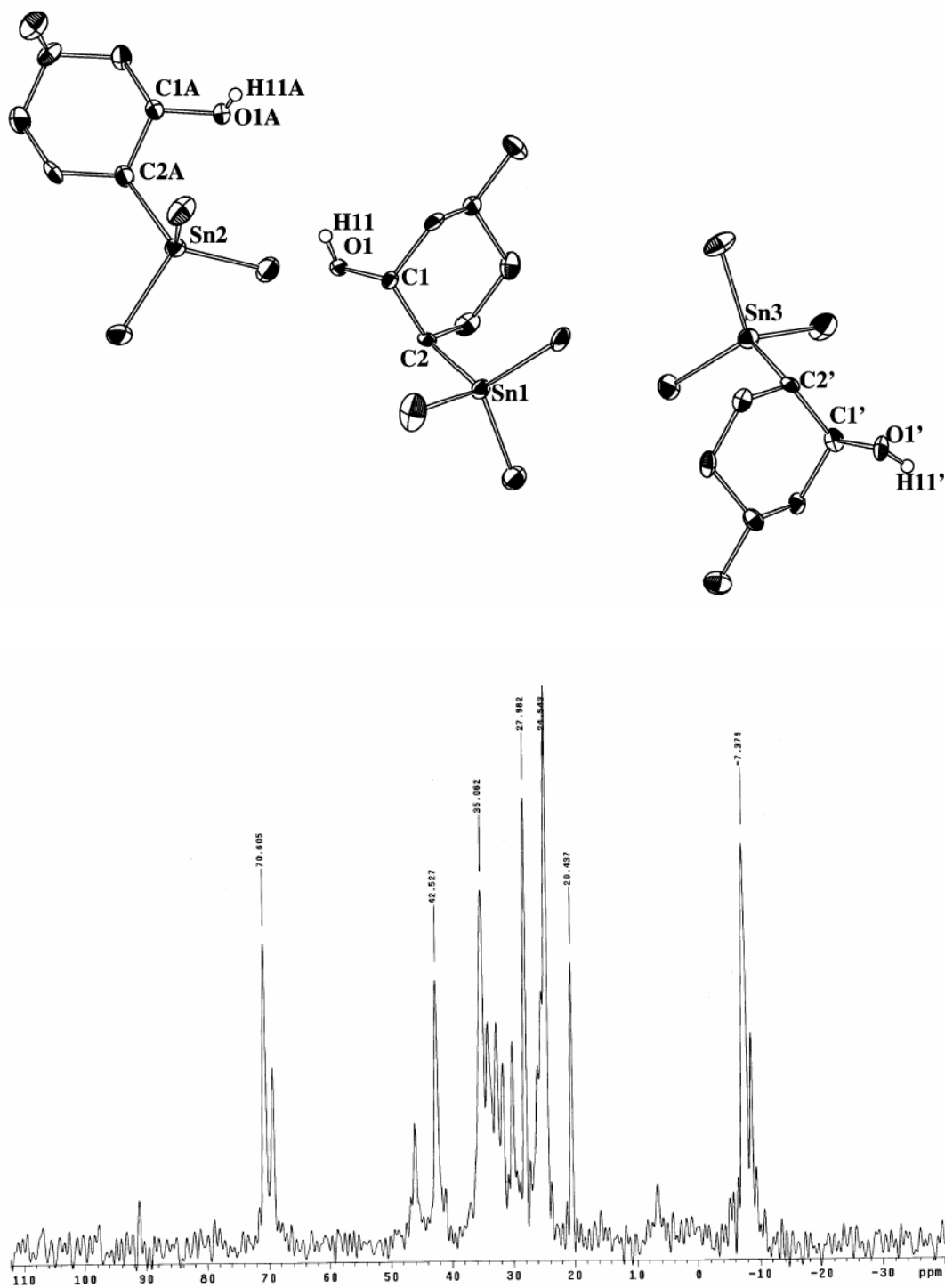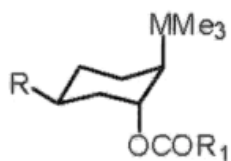**Figure 3**

**1**: M = Si, R$_1$ = CF$_3$, R = Bu$^t$
**5**: M = Ge, R$_1$ = CF$_3$, R = H
**6**: M = Sn, R$_1$ = CH$_3$, R = Bu$^t$

**2**
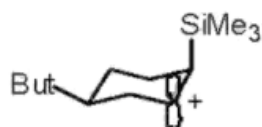
**3**
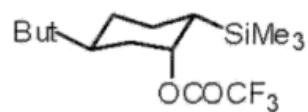
**4**
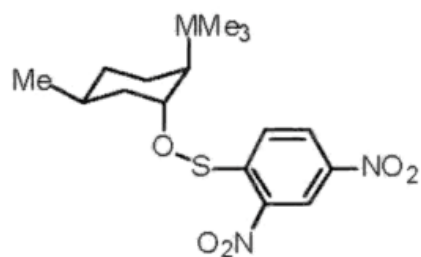
**7**: M = S i
**8**: M = Ge
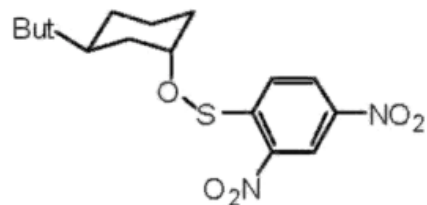
**9**
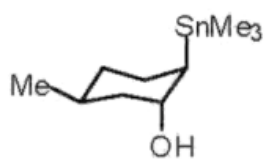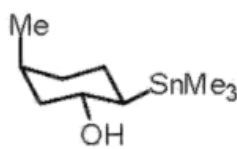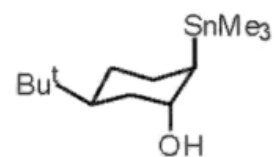
**10a**　　　　　**10b**　　　　　**11**
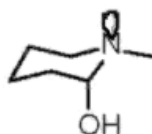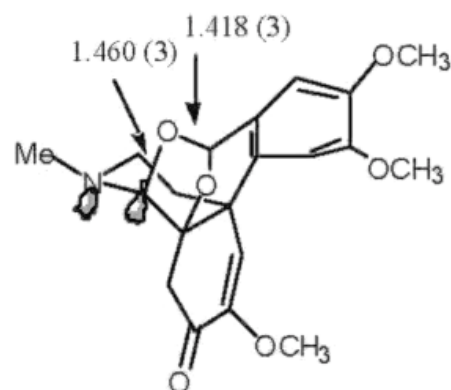


**12**　　　　　**13**

**Table 1.** Selected Structural parameters for **10**

|  | Molecule 1 | Molecule 2 | Molecule 3 |
|---|---|---|---|
| Sn-C2 | 2.168(7) | 2.159(8) | 2.164(9) |
| Sn-Me | 2.136 | 2.133 | 2.118 |
| C1-O1 | 1.452(8) | 1.451(8) | 1.436(10) |
| C1-C2 | 1.541(11) | 1.503(11) | 1.512(11) |
| O-C(1)-C(2)-Sn | -157.4(5) | 153.8(5) | 56.1(8) |

## Experimental Section

**General Procedures.** The solid state [13]C n.m.r spectrum of **10** was determined on a Varian Inova 300 MHz spectrometer operating at 75 MHz, the sample was spinning at 8000 Hz. Contact time was 2 millisecond, C-H cross polarisation pulsed with 2 second repitition, 50 KHz width, 90[o] pulse for 1H was 4.5 microseconds.

Diffraction data were recorded on an Enraf Nonius CAD4f diffractometer in the range $2^o < \theta < 25^o$ (7512 reflections collected, 6580 independent ($R_{int}$ 0.04)) operating in the $\theta/2\theta$ scan mode at low temperature (130.0(1) K). Data were corrected for Lorentz and polarization effects and for absorption (SHELX 76)[18]. Structures were solved by direct methods (SHELXS-86)[19] and were refined on $F^2$ (SHELXL-97).[20] Hydrogen atoms were located from difference fourier maps and allowed to refine without restraint with isotropic thermal parameters. The crystal was maintained at 130 K using an Oxford Cryostream cooling device. The thermal ellipsoid plot of **10** was drawn using the program ZORTEP.[21] Crystal data for **10:** $C_{10}H_{19}OSn$, M = 273.9, colourless rod (0.32 x 0.07 x 0.05 mm), m.p. 44-45[o] C, orthorhombic, space group $P2_12_12_1$, a = 6.765(1), b = 22.606(3), c = 24.518(4), V = 3479.5(10), F(000) = 1644, $\mu(MoK\alpha)$ = 2.00 mm$^{-1}$, Z = 4, $\rho_{calc}$ = 1.456 Mg/m$^{-3}$ . Final residuals were R1 0.043 for 5169 unique reflections with I > 2σ(I) and wR2 = 0.0754 (all data). Crystallographic data (excluding structure factors for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC -000000. Copies of this data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambrid ge CB2 1EZ, UK (fax: int code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk

## Acknowledgements

## References and Notes

1.  Egorochkin, A. N. *Russ. Chem. Rev*. **1985**, *53*, 445.
2.  Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
3.  Lambert, J. B.; Wang, G.; Finzel, R. B. Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.
4.  White, J. M. *Aust. J. Chem*. **1995**, *48*, 1227.
5.  Lambert, J. B.; Wang, G.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422.
6.  Schweig, A.; Weidner,U.; Manuel, G. *J. Organomet. Chem.* **1973**, *54*, 145.
7.  Bock, H.; Mollere, P.; Becker, G.; Fritz. G. *J. Organomet. Chem.* **1973**, *61*, 113.
8.  Worley, S. D. *Chem. Rev*. **1971**, *71*, 295.
9.  White, J. M.; Robertson, G. B. *J. Org. Chem.* **1992**, *57*, 4638.
10. Green, A. J.; Kuan. Y. L.; White, J. M. *J. Org. Chem.* **1995**, *60*, 2734.
11. Chan, V. Y.; Clark, C. I.; Giordano, J. Green, A.J.; Karalis, A.; and White, J. M. *J. Org. Chem.* **1996**, *61,* 5227.
12. Albright, T. A.; Burdett, J. K.; Whangho, W. Orbital Interactions in Chemistry, Wiley: New York, 1985.
13. Adcock, W.; Cox, D. P.; Kitching, W. *J. Organomet. Chem.* **1977**, *133*, 393.
14. Wickham, G.; Olszowy, H. A.; Kitching, W. *J. Org. Chem*. **1982**, *47*, 3788.
15. Molecular mechanics calculations using the MMX forcefield within PCMODEL version 4.0. Serena Software, Bloomington.
16. Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc*. **1984**, *106*, 6197.
17. Ayral-Kalous tan, S.; Agosta, W. C. *J. Org. Chem*. 1981, 4880.
18. SHELX76: Sheldrick, G. M. *Program for Crystal Structure Determination*, Cambridge: England, 1976.
19. SHELXS-86: Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C.; Goddard, R.; Eds; Oxford University Press, Oxford: England, 1985; pp 175-189.
20. SHELXL-97: Sheldrick, G. M. *Program for Crystal Structure Refinement*. Univ. of Gottingen, Germany, 1993.

21. ZORTEP: Zsolnai, L. *An interactive ORTEP Program*, University of Heidelberg, Germany, 1994.