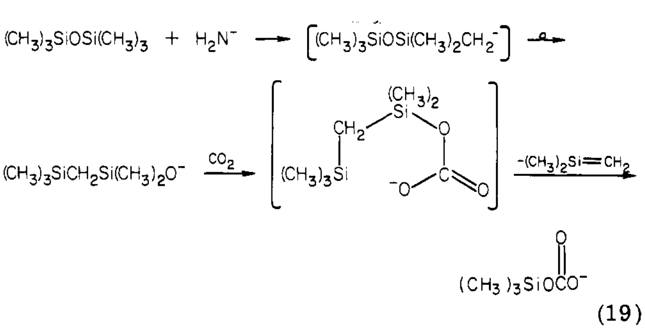
is formed but rearranges as the temperature is raised. When hexamethyldisiloxane and H_2N^- react in the FA, an M − 1 ion is obtained. It does not react with N_2O, suggesting that rearrangement is facile. To confirm this we reacted the M − 1 ion with the CO_2, a reagent which we have shown reacts with siloxides (CO_2 reacts with carbanions giving an adduct, but in this case we have demonstrated that no carbanion is present since no reaction with N_2O takes place.) to give carbonates. In this case, however, the simple carbonate is not obtained; rather $(CH_3)_2Si{=}CH_2$ is extruded as formulated in eq 19.



(19)

In summary, we have shown how N_2O can be used to distinguish among various anionic structures of silicon. In particular, silyl anions themselves react with N_2O for form siloxides by oxygen atom transfer, silicon-stabilized carbanions also react to form siloxides, but with loss of carbon, and pentacoordinate silicon anions do not react.

Acknowledgment. We wish to thank the Council on Research and Creative work of the University of Colorado graduate school and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the work. Also we acknowledge the experimental help given by J. J. Grabowski.

Registry No. $(CH_3)_4Si$, 75-76-3; $(CH_3)_3SiO^-$, 41866-81-3; $(CH_3)_3SiNH^-$, 88035-99-8; $(CH_3)_3SiCH_2^-$, 88036-00-4; N_2O, 10024-97-2; $(CH_3)_3Si{-}Si(CH_3)_3$, 1450-14-2; $(CH_3)_3Si$, 54711-92-1; $(CH_3)_3Si{-}H$, 993-07-7; $(CH_3)_2SiHO^-$, 43641-64-1; $(CH_3)_3SiCH{=}CH_2$, 754-05-2; $(CH_3)_2Si(CH_2^-)CH{=}CH_2$, 88036-01-5; $(CH_3)_2Si(O^-)CH{=}CH_2$, 88036-02-6; $(CH_3)_3SiCH_2CH_2CH_2CH_3$, 1000-49-3; $(CH_3)_2Si(O^-)CH_2CH_2CH_2CH_3$, 88036-03-7; $(CH_3)_3SiOSi(CH_3)_3$, 107-46-0; $(CH_3)_2Si{=}CH_2$, 4112-23-6; DMSCB, 2295-12-7; 1,1-dimethyl-1-fluoro-1-silacyclobutaneanion, 76346-24-2; trimethylfluorosilane anion, 76350-68-0; dimethylfluorosilanol anion, 88036-04-8; fluorotrimethylvinylsilane anion, 88036-05-9.

A Tin Four- to Five-Coordinate Reaction Path. Molecular Structures of the Cyclic Stannanes $(t\text{-Bu})_2Sn(OCH_2CH_2)_2NMe$ and $Me_2Sn(SCH_2CH_2)_2NMe$[1,2]

Robert G. Swisher and Robert R. Holmes*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

Received June 13, 1983

The molecular structures of *N*-methyl-5,5-di-*tert*-butyldiptychoxazstannolidine (**4**, $(t\text{-Bu})_2Sn(OCH_2CH_2)_2NMe$) and *N*-methyl-5,5-dimethyldiptychthiaazstannolidine (**5**, $Me_2Sn(SCH_2CH_2)_2NMe$) were determined by X-ray analysis. As a result, the two trigonal-bipyramidal forms **1** and **2** postulated to equilibrate in a fast intramolecular exchange by NMR were isolated for the first time. **4** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 12$) with $a = 22.655$ (5) Å, $b = 25.990$ (4) Å, $c = 9.036$ (2) Å, and $\beta = 106.97$ (2)°. The structure refined to $R = 0.074$ and $R_w = 0.098$. Three independent molecules are present per unit cell. **5** crystallizes in the orthorhombic space group $P2_12_12_1$ ($Z = 4$) with $a = 8.844$ (2) Å, $b = 9.253$ (3) Å, and $c = 14.309$ (12) Å. The structure refined to $R = 0.038$ and $R_w = 0.073$. Pentacoordination is achieved by N→Sn dative bonding in both compounds. For **4**, the most electronegative atoms, the ring oxygens, are located in apical positions. For **5**, the less electronegative ring sulfur atoms are situated equatorially leaving a methyl group and the N→Sn bond in apical positions. The N–Sn dative bond formed in an equatorial position for **4** is the first example of this type. The N→Sn dative bond in **4** (2.32 (2) Å average) is the shortest and the one in **5** (2.58 (1) Å) is the longest so far reported. The tin atom lies on the equatorial plane in **4**, whereas, for **5**, the tin atom is displaced 0.37 Å out of the equatorial plane toward the apical methyl group. In a series of related five-coordinated cyclic tin(IV) acid–base adducts that are shown to follow a tetrahedral to trigonal-bipyramidal coordinate and serve as a model for nucleophilic substitution of Sn(IV) tetracoordinate compounds, **5** has the most tetrahedral character. It is reasoned that intramolecular ligand exchange occurring by way of a Berry pseudorotation route at low temperatures and a dissociation–inversion route at higher temperatures is plausible. However, as the five-coordinated tin structures become more trigonal bipyramidal, a greater preference for intramolecular ligand exchange via the pseudorotation route is expected.

Introduction

Diptychstannolidines are examples of nonrigid pentacoordinated tin compounds that contain an intramolecular N→Sn dative bond. Most have been formed by the reaction of diorganotin(IV) derivatives with either diethanolamines or diethanthiolamines.[3] NMR data[4,5] support the two basic configurations, **1** and **2**, the particular one assumed depends on the nature of the groups

---

[1] (a) Pentacoordinated Molecules. 49. Presented at the 182nd American Chemical Society National Meeting, New York, Aug 1981; American Chemical Society: Washington, DC, 1981; Abstract No. INOR 144. Previous paper in the series: Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1983**, *22*, 3696.

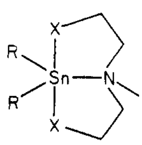
[2] This work represents a portion of the Ph.D. Thesis of R. G Swisher, University of Massachusetts, Amherst.

[3] Tzschach, A.; Pönicke, K. *Z. Anorg. Allg. Chem.* **1974**, *404*, 121.

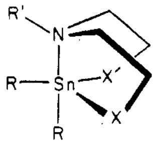
[4] Tzschach, A.; Weichmann, H.; Jurkschat, K. *J. Organomet. Chem. Libr.* **1981**, *12*, 293.

[5] (a) Zschunke, A.; Tzschach, A.; Jurkschat, K. *J. Organomet. Chem.* **1976**, *112*, 273. (b) Jurkschat, K.; Mügge, C.; Tzschach, A.; Zschunke, A.; Larin, M. F.; Pestunovich, V. A.; Voronkov, M. G. *Ibid.* **1977**, 139, 279. (c) Mügge, C.; Jurkschat, K.; Tzschach, A.; Zschunke, A. *Ibid.* **1979**, *164*, 135.

0276-7333/84/2303-0365$01.50/0



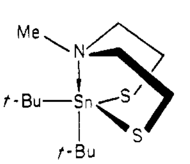
1



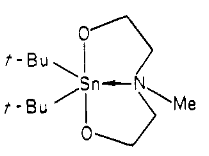
2

involved in their molecular makeup. In some cases, the NMR data indicate an equilibrium mixture of the two forms in solution.[4] A fast intramolecular exchange (Berry pseudorotation[6]) is postulated at reduced temperatures. At higher temperatures, a dissociation–inversion process is indicated by the NMR data[4,5] showing equivalence of the R groups.

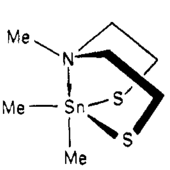
Specifically, the NMR data support structure 2 for $(t\text{-Bu})_2Sn(SCH_2CH_2)_2NMe$ (3),[5c] structure 1 for $(t\text{-Bu})_2Sn(OCH_2CH_2)_2NMe$ (4),[5a,b] and structure 2 for $Me_2Sn(SCH_2CH_2)_2NMe$ (5).[5c] In the solid state, interpretation of ^{119}Sn Mössbauer measurements[7] agrees with the solution structures for the latter two substances, 4 and 5, but for the first mentioned substance, 3, configuration 1 is indicated.



3[5c]



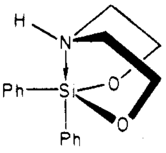
4[5a,b]



5[5c]

based on NMR data

Although crystal structures seem to be lacking for these stannolidines, an X-ray study of a related silicon derivative 6[8] shows equatorially positioned oxygen atoms. This contrasts with the structure indicated for 4 in solution[5a,b] which has oxygen atoms in axial locations of a trigonal bipyramid.



6[8]

There are two principal features of interest with regard to these pentacoordinated tin compounds, the relative preference of ligands for equatorial and axial sites of the trigonal bipyramid and the mechanism by which ligand exchange takes place. In general, if an intramolecular exchange is allowed without bond breakage, it should be possible to isolate structures in the solid state which contain equatorially positioned nitrogen atoms as well as those that contain axially positioned nitrogen atoms. One of these forms would be the activated state in any pseudorotational mechanism.[9] Thus far, all examples that have been analyzed by X-ray crystallography contain axial nitrogen atoms.[10–15] If a bond dissociation mechanism is followed in a ligand permutation, solid-state data on a series of related cyclic five-coordinated tin acid–base adducts should reflect a structural change from the tetrahedral to the trigonal-bipyramidal geometry as the Sn–N bond distance becomes shorter.

We have chosen the interesting pair of tin derivatives 4 and 5 for crystal structural determination. These substances allow for the possible isolation of the coordinated nitrogen atom in each of the two types of sites of a trigonal bipyramid and a comparison of ligand preferences in this geometrical framework as well as the determination of the extent of agreement with solution NMR results. In addition, mechanistic insight should be revealed in a comparison of the degree of tetrahedral distortion encountered with these derivatives.

Experimental Section

N-Methyl-5,5-di-*tert*-butyldiptychoxazstannolidine, 4, was prepared by the reaction of *N*-methyldiethanolamine with di-*tert*-butyltin oxide in the presence of potassium hydroxide in xylene solution according to a method by Zschunke et al.[5a] The crystals that were used for X-ray analysis were obtained from a benzene–*n*-hexane solution which had been refrigerated several days, mp 74–75 °C (lit.[5a] 68–70 °C).

N-Methyl-5,5-dimethyldiptychthiaazstannolidine, 5, was prepared by a four-step process according to Mugge et al.[5c] which starting with *N*-methyldiethanolamine, the first three steps involved the preparation of *N*-methyl-2,2′-dimercaptodiethylamine. Reaction of the latter ligand with dimethyltin oxide in xylene with a catalytic amount of potassium hydroxide yielded the desired product, 5, mp 68–70 °C (lit.[5c] 66 °C). Similar to 4, slow crystallization from a refrigerated benzene–hexane solution produced colorless crystals suitable for the X-ray study.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[16]

$(t\text{-Bu})_2Sn(OCH_2CH_2)_2NMe$, 4. A crystal of 4 having approximate dimensions 0.20 × 0.40 × 0.40 mm, which was mounted inside of a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray study. This crystal, as well as several others which were examined, diffracted poorly. poorly.

Crystal data of 4: space group $P2_1/c$ [C^5_{2h}—No. 14],[17] uniquely determiend from monoclinic $2/m$ diffraction symmetry and extinctions, $a = 22.655$ (5) Å, $b = 25.990$ (4) Å, $c = 9.036$ (2) Å, $\beta = 106.97$ (2)°, $Z = 12$, and $\mu_{\mathrm{MoK}\bar{\alpha}} = 1.509$ mm^{-1}. A total of 5811 independent reflections ($+h$, $+k$, $\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{\mathrm{MoK}\bar{\alpha}} \leq 43°$. No corrections were made for absorption.

The structure was solved by using a combination of Patterson and Fourier difference techniques and refined by using full-matrix least squares.[18] A total of 31 of the 51 non-hydrogen atoms were refined anisotropically. It was not possible to refine the thermal parameters for the remaining 20 non-hydrogen atoms, and these were included in the refinement with isotropic thermal parameters which were fixed at 12 Å^2. No attempt was made to include hydrogen atoms in the refinement. The final agreement factors[19] were $R = 0.074$ and $R_w = 0.098$ for 4121 reflections having $I \geq 2\sigma_I$. The only peaks of any consequence in a final difference

---

(6) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(7) Bancroft, G. M.; Das, V. G. K.; Sham, T. S.; Clark, M. G. *J. Chem. Soc., Dalton Trans.* **1976**, 643.

(8) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1974**, 2051.

(9) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*.

(10) Domazetis, G.; MacKay, M. F.; Magee, R. J.; James, B. D. *Inorg. Chim. Acta* **1979**, *34*, L247.

(11) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1976**, *118*, 183.

(12) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenegel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

(13) Sau, A. C.; Day, R. O.; Holmes, R. R., unpublished work.

(14) Day, R. O.; Holmes, R. R., unpublished work.

(15) Huber, F.; Haupt, H. J.; Preut, H.; Barbieri, R.; Lo Giudice, M. T. *Z. Anorg. Allg. Chem.* **1979**, *432*, 51.

(16) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 99.

(18) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 17, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Sn, O, and S were taken from the same source, pp 149–150.

(19) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. For 5, these values are for the configuration having the lowest R_w.

Table I. Atomic Coordinates in Crystalline (t-C$_4$H$_9$)$_2$Sn(OCH$_2$CH$_2$)$_2$NCH$_3$, 4[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Sn1	−639.0 (5)	3615.1 (4)	252.1 (12)
Sn2	2478.2 (5)	989.3 (4)	2352.9 (12)
Sn3	5763.1 (5)	3645.0 (5)	4050.0 (13)
O1	−217 (6)	2965 (5)	−212 (14)
O2	−638 (5)	4244 (4)	1599 (13)
O3	3229 (5)	818 (5)	4218 (15)
O4	1606 (5)	825 (5)	996 (13)
O5	5329 (7)	2998 (6)	4354 (18)
O6	5795 (7)	4309 (5)	2908 (16)
N1	242 (7)	3535 (6)	2361 (16)
N2	2232 (7)	207 (6)	3216 (19)
N3	4876 (8)	3645 (8)	1933 (21)
C1	296 (11)	2745 (10)	860 (24)
C2	340 (11)	2969 (10)	2569 (30)
C3	−213 (9)	4306 (7)	3024 (22)
C4	97 (13)	3761 (12)	3577 (28)
C5	−1480 (8)	3271 (8)	518 (24)
C6	−1455 (13)	2687 (11)	205 (33)
C7	−2034 (14)	3622 (11)	−245 (33)
C8	−1437 (10)	3266 (12)	2261 (28)
C9	−659 (10)	4040 (8)	−1857 (19)
C10	−1103 (12)	4511 (9)	−2033 (29)
C11	−962 (13)	3710 (11)	−3305 (30)
C12	6 (12)	4186 (11)	−1788 (27)
C13	785 (11)	3806 (15)	2071 (34)
C14	3218 (13)	330 (9)	4964 (28)
C15	2771 (14)	−120 (11)	3575 (34)
C16	1274 (10)	374 (9)	1257 (32)
C17	1831 (14)	−79 (11)	2075 (35)
C18	2244 (11)	1715 (8)	3348 (35)
C19	1775 (14)	2008 (10)	1947 (35)
C20	1903 (14)	1585 (11)	4442 (34)
C21	2846 (14)	2024 (11)	4001 (33)
C22	2842 (11)	833 (17)	187 (36)
C23	3365 (13)	637 (11)	585 (32)
C24	3506 (14)	1393 (11)	1298 (34)
C25	2652 (14)	1300 (11)	−677 (35)
C26	1890 (14)	285 (11)	4270 (35)
C27	4807 (14)	2804 (11)	3391 (35)
C28	4766 (13)	3110 (11)	1562 (33)
C29	5294 (15)	4464 (10)	1506 (26)
C30	4907 (14)	4047 (12)	952 (34)
C31	5777 (9)	4015 (10)	6235 (22)
C32	5160 (13)	4177 (11)	6247 (33)
C33	6106 (14)	3676 (11)	7615 (34)
C34	6239 (14)	4419 (11)	6644 (32)
C35	6565 (9)	3274 (9)	3664 (25)
C36	6562 (13)	3293 (11)	2052 (34)
C37	7138 (14)	3667 (11)	4467 (34)
C38	6729 (13)	2787 (11)	4541 (34)
C39	4332 (14)	3702 (11)	2479 (33)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

Fourier synthesis were in the immediate vicinity of carbon atoms. The rather high R factor and the fact that many of the ligand atoms seem poorly defined suggest static disorder. This is perhaps not surprising since *tert*-butyl groups comprise half of the ligand atoms. Several of the C–C bond lengths for atoms that are apparently involved in this disorder have values that are too large, within the limits of the error, when compared to acceptable values. We feel, however, that the structure is qualitatively correct and is of interest in this regard.

Me$_2$Sn(SCH$_2$CH$_2$)$_2$NMe, 5. A crystal of 5 having approximate dimensions 0.15 × 0.25 × 0.38 mm, which was mounted inside of a sealed thin-walled glass capillary as a precaution against moisture sensitivity, was used for the X-ray study.

Crystal data of 5: space group $P2_12_12_1$ [D_2^4—No. 19],[20] Z = 4, uniquely determined from orthorhombic mmm diffraction symmetry and extinctions, a = 8.844 (2) Å, b = 9.253 (3) Å, c = 14.309 (12) Å, and $\mu_{\mathrm{MoK}\bar{\alpha}}$ = 2.482 mm^{-1}. A total of 1551 independent reflections (+h, +k, +l) were measured by using the θ–2θ scan mode for 2° ≤ $2\theta_{\mathrm{MoK}\bar{\alpha}}$ ≤ 55°. No corrections were made for absorption.

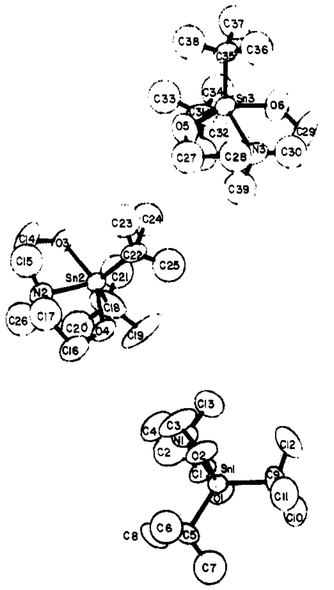


Figure 1. ORTEP plot of the three independent molecules of crystalline (t-C$_4$H$_9$)$_2$Sn(OCH$_2$CH$_2$)$_2$NCH$_3$, 4, with thermal ellipsoids at the 50% probability level.

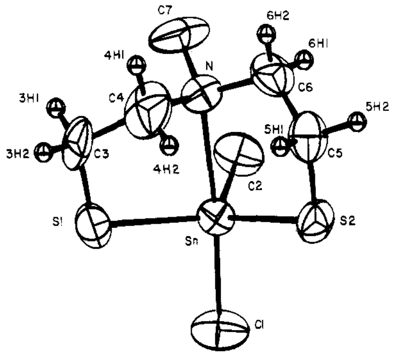


Figure 2. ORTEP plot of the (CH$_3$)$_2$Sn(SCH$_2$CH$_2$)$_2$NCH$_3$, 5, molecule with thermal ellipsoids at the 50% probability level for the non-hydrogen atoms. The hydrogen atoms are represented by spheres of arbitrary radius.

The structure was solved by using a combination of Patterson and Fourier difference techniques and refined by using full-matrix least squares.[18] The non-hydrogen atoms were refined anisotropically. Methyl hydrogen atoms could not be located and were omitted from the refinement. The methylene hydrogen atoms, fixed, were treated as isotropic scatterers. These hydrogen atom coordinates were calculated and updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement factors[19] were R = 0.038 and R_w = 0.073 for 1415 reflections having $I \geq 2\sigma_I$.

Results and Discussion

Molecular Structure of 4 and 5. The atom labeling schemes of 4 and 5, respectively, are given in the ORTEP plots of Figures 1 and 2. Atomic coordinates are listed in Table I for 4 and Table II for 5. Bond lengths and angles for 4 and 5 are presented in Tables III and IV, respectively. Anisotropic thermal parameters (Tables A and B) and least-squares planes (Table C) for both 4 and 5 are provided as supplementary material.

The structures of 4 and 5 agree with conclusions[5a-c] from NMR data on the general placement of atoms in a trigo-

---

[20] (20) Reference 17, p 105.

Table II. Atomic Coordinates in Crystalline $(CH_3)_2Sn(SCH_2CH_2)_2NCH_3$, 5[a]

atom type[b]	coordinates 10^4x	10^4y	10^4z
Sn	7881 (1)	6165 (1)	3474 (1)
S1	5407 (4)	6119 (5)	4216 (2)
S2	8021 (4)	5857 (4)	1790 (2)
N	7131 (12)	3488 (10)	3290 (6)
C1	8020 (18)	8494 (15)	3485 (12)
C2	9849 (17)	5389 (18)	4204 (11)
C3	4784 (18)	4317 (20)	4131 (13)
C4	5444 (20)	3540 (23)	3261 (15)
C5	7473 (18)	4000 (18)	1598 (8)
C6	7768 (19)	2983 (15)	2407 (10)
C7	7739 (28)	2579 (15)	4047 (11)

[a] See footnote *a* of Table I. [b] Atoms are labeled to agree with Figure 2.

nal-bipyramidal framework. However, considerable distortions from an idealized trigonal bipyramid are evident in the solid state.

The principal distortion for the diptychoxazstannolidine 4 is a small apical O–Sn–O angle which averages 150.5 (5)° for the three independent molecules found for 4 (Figure 1). This is due to the small endocyclic angles, O–Sn–N, averaging 74.9 (5)°, which are formed as a result of N→Sn dative bonding. The Sn-N bond length ranges from 2.30 to 2.34 Å over the three molecules. These values, although somewhat longer than the sum of the covalent radii for nitrogen and tin, 2.10 Å,[21] are much shorter than the sum of the van der Waals radii, 3.75 Å.[22] Thus, a rather strong N-Sn dative bond is indicated and represents the first example of an equatorially positioned one for a five-coordinate tin compound. The tin atom lies in the equatorial plane in each of the molecules of 4. The sum of the equatorial angles are 360° for each molecule and show no significant differences between each other.

In contrast, the diptychthiaazstannolidine 5 (Figure 2) has a much weaker N-Sn dative bond implied by the N-Sn bond length, 2.58 (1) Å, which is almost 0.3 Å longer than the N-Sn bond length for 4. In this case, the nitrogen atom is located in an apical position of a distorted trigonal bipyramid while the ring sulfur atoms are situated equatorially. The reduced N-Sn interactions for 5 relative to 4 is presumably associated with the presence of ring sulfur atoms of lower electronetgativity compared to the ring oxygen atoms in 4. As a result, the tin atom is not in the equatorial plane but displaced 0.37 Å out of this plane toward C1 of the opposite axial methyl group. The structure may be viewed as existing on a distortion coordinate between tetrahedral and trigonal bipyramidal. The axial N-Sn-C1 angle is 167.0 (4)°, with the axial atoms tilted away from the equatorial methyl group.

The manner in which the geometry of the three independent molecules of 4 differ is mainly in the orientation of the N-CH_3 group.

Comparisons with Related Molecules. Although the diptychoxazstannolidine 4 contains the only equatorial N→Sn dative bond in a pentacoordinated structure, several pentacoordinated tin compounds (7–12), with axial N-Sn coordination bonds are known.[10-15] Because of their axial disposition in a trigonal-bipyramidal framework, the lengths of the N→Sn bonds are in general longer than the N→Sn bond in 4, although, as Figure 3 demonstrates, the range of values 2.27–2.58 Å overlaps the N-Sn bond lengths found for 4, i.e., 2.30–2.34 Å.

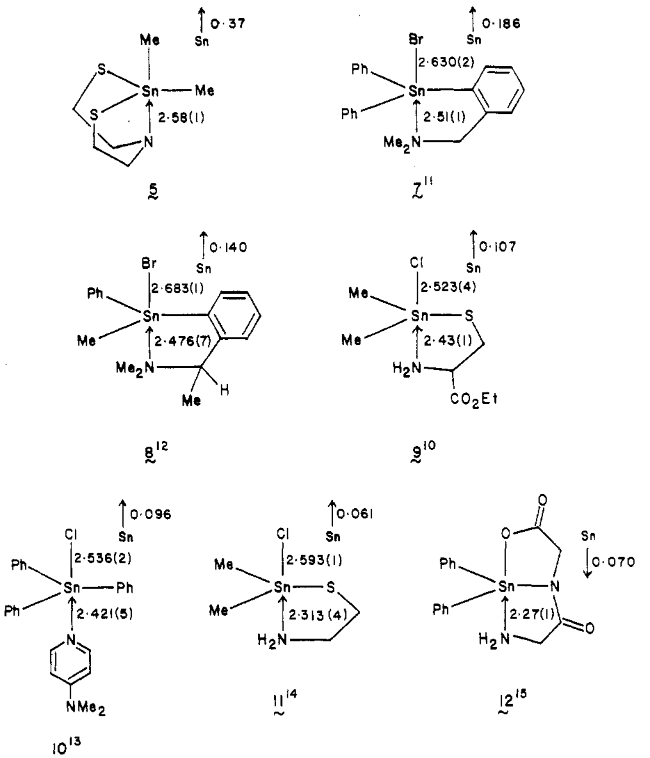


Figure 3. Discrete pentacoordinated tin(IV) compounds exhibiting N→Sn coordination bonds. The decrease in bond length correlates with the approach of the tin atom to the equatorial plane. References are indicated as superscripts to the compound identification number.

The decrease of the N-Sn bond length over this series correlates with the approach of the structure to trigonal bipyramidal from one having more tetrahedral character. The out-of-plane distance of the tin atom from the plane of the three equatorial ligands goes from 0.37 Å for 5 to −0.07 Å for 12. There is a general parallel with the increase in the electronegativity of the ligands attached to tin and the shortening of the N-Sn bond length. It is seen that for the halogen derivatives 7–11 that as the Sn-N bond shortens, the Sn-X (X = Br, Cl) bond lengthens. There also appears to be a secondary effect associated with the amine basicity tending to decrease the N-Sn bond length. The basicity order for the axial nitrogen atoms, 12 > 11 > 7, seems contributory.

The diptych structure 4 is consistent with the common observance of the most electronegative ligands occupying the apical positions of a trigonal bipyramid. The structure observed for 5 also is reasonable in view of the presence of ring sulfur atoms having reduced electronegativity. Noting that the related silane derivative 6[8] does not follow the electronegativity "rule" suggests that the lessened steric effect associated with the diequatorial orientation may be of significance. However, an overall rationale for the structures of these compounds must be postponed until further examples are studied.

In view of the long axial Sn–N bond length for 5, the longest in the series of Figure 3, it is reasonable to expect intramolecular ligand exchange for this somewhat tetrahedral derivative to occur by way of a dissociation–inversion mechanism as postulated to occur as the temperature is increased in solution NMR measurements.[4,5] Equally plausible in this case is the postulation of the fast Berry pseudorotational exchange at the lowest temperatures of the NMR studies,[4,5] particularly since our results on the structure of 4 and 5 establish the existence of both

---

[21] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1973; p 224.

[22] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table III. Bond Lengths (Å) and Angles (deg) in Crystalline $(t\text{-}C_4H_9)_2Sn(OCH_2CH_2)_2NCH_3$, 4[a,b]

molecule A		molecule B		molecule C	
		Bond Lengths			
Sn1-N1	2.33 (1)	Sn2-N2	2.30 (2)	Sn3-N3	2.34 (2)
Sn1-O2	2.04 (1)	Sn2-O3	2.06 (1)	Sn3-O5	2.01 (1)
Sn1-O1	2.05 (1)	Sn2-O4	2.04 (1)	Sn3-O6	2.02 (1)
Sn1-C9	2.19 (2)	Sn2-C18	2.22 (2)	Sn3-C31	2.19 (2)
Sn1-C5	2.18 (2)	Sn2-C22	2.37 (3)	Sn3-C35	2.17 (2)
O2-C3	1.37 (2)	O3-C14	1.44 (2)	O5-C27	1.35 (3)
C3-C4	1.60 (3)	C14-C15	1.80 (3)	C27-C28	1.81 (4)
C4-N1	1.37 (3)	C15-N2	1.44 (3)	C28-N3	1.44 (3)
O1-C1	1.40 (2)	O4-C16	1.45 (2)	O6-C29	1.49 (3)
C1-C2	1.63 (3)	C16-C17	1.73 (3)	C29-C30	1.39 (4)
C2-N1	1.49 (3)	C17-N2	1.38 (3)	C30-N3	1.39 (3)
		Bond Angles			
O1-Sn1-O2	150.1 (5)	O4-Sn2-O3	150.2 (5)	O6-Sn3-O5	151.3 (6)
O1-Sn1-N1	75.7 (5)	O4-Sn2-N2	74.5 (5)	O6-Sn3-N3	74.5 (6)
O1-Sn1-C5	99.2 (7)	O4-Sn2-C18	96.7 (8)	O6-Sn3-C31	95.3 (8)
O1-Sn1-C9	97.5 (7)	O4-Sn2-C22	88.7 (9)	O6-Sn3-C35	98.1 (7)
O2-Sn1-N1	74.5 (5)	O3-Sn2-N2	75.9 (5)	O5-Sn3-N3	74.5 (6)
O2-Sn1-C9	96.4 (6)	O3-Sn2-C18	95.1 (9)	O5-Sn3-C31	97.1 (8)
O2-Sn1-C5	96.4 (6)	O3-Sn2-C22	103.6 (7)	O5-Sn3-C35	96.6 (8)
N1-Sn1-C5	116.1 (7)	N2-Sn2-C22	107.8 (11)	N3-Sn3-C35	115.4 (7)
N1-Sn1-C9	123.5 (7)	N2-Sn2-C18	120.2 (8)	N3-Sn3-C31	121.4 (7)
C9-Sn1-C5	120.3 (8)	C18-Sn-C22	131.4 (12)	C31-Sn3-C35	123.2 (8)
Sn1-O1-C1	122.6 (11)	Sn2-O4-C16	121.8 (11)	Sn3-O6-C29	122.2 (15)
O1-C1-C2	108.7 (16)	O4-C16-C17	105.8 (18)	O6-C29-C30	109.8 (22)
C1-C2-N1	105.5 (19)	C16-C17-N2	101.2 (21)	C29-C30-N3	120.1 (26)
C2-N1-C13	112.6 (21)	C17-N2-C26	102.2 (20)	C30-N3-C39	110.2 (21)
C2-N1-Sn1	104.6 (12)	C17-N2-Sn2	113.3 (16)	C30-N3-Sn3	109.4 (17)
C2-N1-C4	112.6 (21)	C17-N2-C15	100.4 (21)	C30-N3-C28	128.2 (23)
C13-N1-Sn1	111.3 (13)	C26-N2-Sn2	109.7 (15)	C39-N3-Sn3	109.4 (16)
C13-N1-C4	109.7 (22)	C26-N2-C15	121.9 (21)	C39-N3-C28	94.1 (20)
Sn1-N1-C4	105.6 (14)	Sn2-N2-C15	108.9 (15)	Sn3-N3-C28	103.9 (15)
N1-C4-C3	108.5 (20)	N2-C15-C14	92.4 (19)	N3-C28-C27	104.6 (21)
C4-C3-O2	108.3 (16)	C15-C14-O3	109.3 (18)	C28-C27-O5	103.1 (22)
C3-O2-Sn1	122.1 (11)	C14-O3-Sn2	116.6 (13)	C27-O5-Sn3	126.8 (17)

[a,b] Refer to footnotes *a* and *b* of Table I.

Table IV. Bond Lengths (Å) and Angles (deg) in Crystalline $(CH_3)_2Sn(SCH_2CH_2)_2NCH_3$, 5[a,b]

	Bond Lengths		
Sn-N	2.58 (1)	C3-C4	1.55 (3)
Sn-S1	2.433 (3)	C4-N	1.49 (2)
Sn-S2	2.429 (4)	N-C7	1.47 (2)
Sn-C1	2.16 (1)	S2-C5	1.81 (2)
Sn-C2	2.15 (1)	C5-C6	1.51 (2)
S1-C3	1.76 (2)	C6-N	1.46 (2)
	Bond Angles		
N-Sn-S1	78.2 (3)	Sn-S2-C5	104.4 (4)
N-Sn-S2	78.4 (2)	S1-C3-C4	112 (1)
N-Sn-C1	167.0 (4)	S2-C5-C6	115 (1)
N-Sn-C2	86.4 (5)	C3-C4-N	112 (2)
C1-Sn-S1	93.7 (5)	C5-C6-N	113 (1)
C1-Sn-S2	97.0 (5)	C4-N-C6	112 (1)
C1-Sn-C2	106.5 (6)	C4-N-Sn	103 (1)
S1-Sn-S2	118.5 (1)	C4-N-C7	114 (1)
C2-Sn-S1	120.7 (5)	C6-N-C7	108 (1)
C2-Sn-S2	113.6 (5)	C6-N-Sn	107.2 (8)
Sn-S1-C3	105.5 (5)	C7-N-Sn	112.3 (8)

[a,b] Refer to footnotes *a* and *b* of Table II.

forms 1 and 2, i.e., nitrogen equatorial and nitrogen axial, respectively, that would be present in this exchange mechanism. However, as the Sn–N interaction increases in the series of cyclic compounds in Figure 3 and the structure approaches the trigonal bipyramid, a greater preference arises for ligand exchange to occur by way of the pseudorotational mechanism that is so prevalent for pentacoordinated phoshorus compounds.[9,23] The fact that the axial tin–halogen bond lengthens as the axial Sn–N bond shortens for the series in Figure 3 suggests this coordinate, tetrahedral distortion toward trigonal bipyramid, as a probable mechanistic pathway for reaction of four-coordinated tin(IV) derivatives undergoing substitution by way of nucleophilic attack at the tin center. This coordinate is analogous to the one described by Britton and Dunitz on acyclic Sn(IV) derivatives.[24]

Acknowledgment. The support of this research by the National Science Foundation is greatly appreciated, as is the generous allocation of computing time by the University of Massachusetts Computing Center. We also acknowledge Dr. Roberta O. Day for her many helpful discussions aiding this work.

Registry No. 4, 60511-12-8; 5, 69255-15-8.

Supplementary Material Available: Thermal parameters (Tables A and B), least-squares mean planes (Table C). and a listing of observed and calculated structure factor amplitudes for 4 and 5 (27 pages). Ordering information is given on any current masthead page.

---

(23) Holmes, R. R. *ACS Monogr.* **1980**, *No. 176*; *Acc. Chem. Res.* **1979**, *12*, 257.

(24) Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.