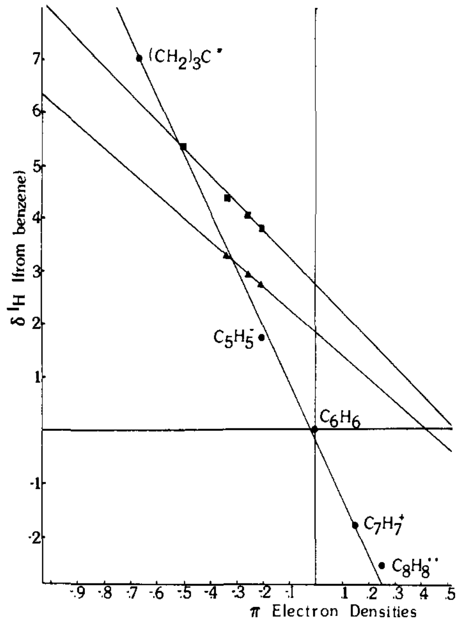

Figure 1. Correlation of π-electron density and ^1H NMR chemical shift for aromatic ions (●),[9,11] the terminal protons of linear delocalized anions, C_3H_5–C_3H_{11} (■),[12] and the δ protons of linear delocalized ions, C_5H_7-C_9H_{44} (▲).[12] The linear correlations of π-electron density and ^1H NMR chemical shift for the terminal protons and for the δ protons of linear anions also hold when those electron densities are calculated by the Pople method for odd linear ions,[13] and are significantly different from that shown by dianion **1** and the aromatic ions.

diadducts. It might be argued that in the Schlosser-prepared system the cross-conjugated dianion is in equilibrium with the linearly conjugated dianion, and the exclusive formation of product from the cross-conjugated dianion reflects only its greater reactivity. The observation that the linear dianion can be trapped when the counterions are TMEDA-chelated lithium suggests that if that dianion was present when the counterions were THF-chelated lithium it would also be trapped under the same reaction conditions.

One of the characteristics of an aromatic system is the presence of a diamagnetic ring current, present in both charged and neutral species. A plot of charge density at each carbon vs. chemical shift from benzene shows a straight-line relationship from benzene and the cyclic aromatic ions with six π electrons.[9] The trimethylenemethane dianion (δ 0.23)[10] shows the same linear relationship, which is significantly different from the relationship shown by the nonaromatic linear ions (Figure 1). By this method of evaluation, the trimethylenemethane dianion shows the same relationship between charge density and chemical shift as do benzene and the cyclic aromatic ions, and insofar as chemical shift is used as an indication of aromaticitiy, it is as aromatic as the above species. This is the first time that such a linear relationship has been reported for an acylic system.

We are presently looking at the preference for other cross-conjugated dianions to determine if the phenomenon is a general one.

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A New Geometrical Form for Tin. Synthesis and Structure of the Tetramethylammonium Chloride Adduct of the Spirobis(dithiastannole) $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$

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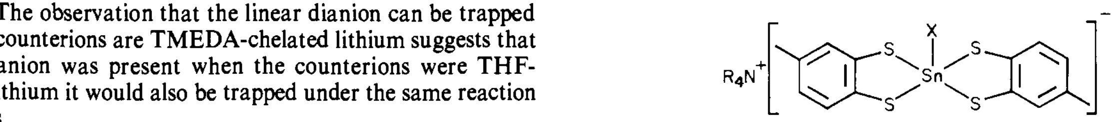
Although pentacoordinated tin compounds are not prevalent, X-ray structural work shows that the methylstannanes $(CH_3)_3SnCl$,[1] $(CH_3)_3SnF$,[2] and $(CH_3)_2SnF_2$[3] possess intermolecular tin–halogen bonding. For (ethyl L-cysteinato-*S*,*N*)(chlorodimethyl)stannate(IV), $(CH_3)_2Sn(Cl)SCH_2CH(NH_2)CO_2C_2H_5$, an X-ray study[4] showed that the tin atom is pentacoordinated owing to the formation of an intramolecular donor–acceptor nitrogen–tin bond. For all of these examples, the geometry around tin is trigonal bipyramidal.

We report here the preparation and X-ray study of the first tin compound having a rectangular-pyramidal geometry. The compound, tetramethylammonium 2-chloro-5,5′-dimethyl-2,2′-spirobis(1,3,2-benzodithiastannole) (**1**), was formed by the reaction of bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$, with 1 equiv of $(CH_3)_4N^+Cl^-$ in methyl cyanide at room temperature. Additional members (**2**–**4**) were also prepared.



1, X = Cl; R = Me
2, X = F; R = Et
3, X = Br; R = Et
4, X = I; R = Et

The structure of the monocyclic dithiastannole derivative **5**, $[(C_2H_5)_4N][C_7H_6S_2)Ph_2SnCl]$, which offers an interesting comparison with **1**, was also determined by X-ray crystallography. It was prepared by treating diphenyl (toluene-3,4-dithiolato)tin, $(C_7H_6S_2)SnPh_2$, with 1 equiv of $Et_4N^+Cl^-$ in methyl cyanide at 25 °C.

Crystal Data. $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$ (**1**) (bright yellow, mp 206–210 °C): monoclinic, space group *Cc* (C_s^4-No. 9),[5a] with a = 14.126 (4), b = 11.485 (6), c = 14.609 (5) Å; β = 100.37(3)°; Z = 4. $[(C_2H_5)_4N]^+[(C_7H_6S_2)Ph_2SnCl]^-$, (**5**) (colorless, mp 156–157 °C): monoclinic, space group $P2_1/c$ (C_{2h}^5-No. 14),[5b] with a = 12.344 (4), b = 11.975 (5), c = 19.120 (5) Å; β = 96.41 (2)°; Z = 4.

Data for both compounds were collected on an Enraf–Nonius CAD4 automated diffractometer by using graphite monochromated Mo K$\bar{\alpha}$ radiation and the θ–2θ scan mode, out to a maximum $2\theta_{\mathrm{MoK}\bar{\alpha}}$ of 50. Both structures were solved by using standard Patterson and difference Fourier techniques and were refined by using full-matrix least squares[6] (anisotropic for non-

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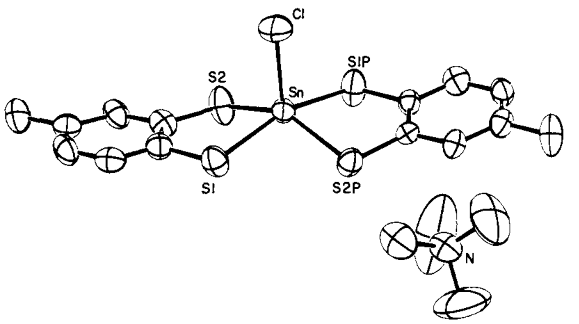

Figure 1. ORTEP plot of the complex $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$ (**1**), with thermal ellipsoids at the 50% probability level. Some Sn–ligand bond parameters: S2–Sn–S2P = 147.6 (1)°, S1P–Sn–S1 = 161.3 (1)°; Sn–Cl = 2.413 (4) Å, Sn–S2 = 2.437 (4) Å, Sn–S2P = 2.447 (3) Å, Sn–S1P = 2.458 (4) Å, Sn–S1 = 2.463 (3) Å; Cl–Sn–S1 = 98.9 (1)°; Cl–Sn–S2 = 106.0 (1)°; Cl–Sn–S1P = 99.8 (2)°; Cl–Sn–S2P = 106.4 (1)°.

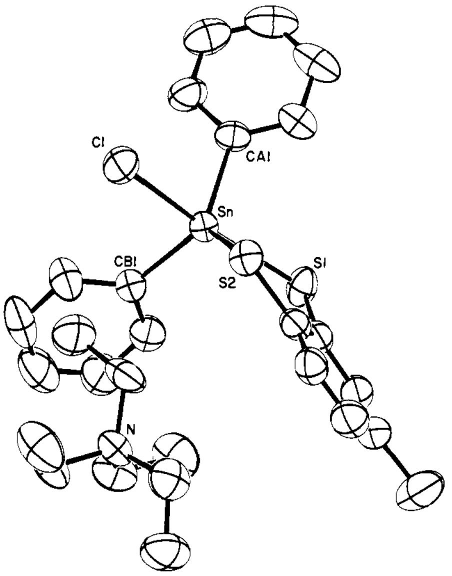

Figure 2. ORTEP plot of $[(C_2H_5)_4N]^+[(C_7H_6S_2)Ph_2SnCl]^-$ (**5**), with thermal ellipsoids at the 50% probability level. Some Sn–ligand bond parameters: Cl–Sn–S1 = 165.9 (1)°, CA1–Sn–CB1 = 121.2 (3)°, CA1–Sn–S2 = 120.6(2)°, CB1–Sn–S2 = 118.0(2)°; Sn–Cl = 2.588 (2) Å, Sn–CA1 = 2.152 (6) Å, Sn–CB1 = 2.146 (7) Å, Sn–S2 = 2.436 (2) Å, Sn–S1 = 2.544 (2) Å.

hydrogen atoms, fixed isotropic for nonmethyl hydrogen atoms). For **1**, a final conventional unweighted residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.039 was obtained on the basis of 1775 independent reflections having $I \geq 2\sigma(I)$. For **5** the final R value was 0.048 for the 3438 reflections having $I \geq 2\sigma(I)$.

Figures 1 and 2 show ORTEP plots of the molecular geometries of **1** and **5**, respectively. It is evident from the bond parameter data given in the legends that the spirocyclic derivative **1** is near rectangular pyramidal and the monocyclic derivative **5** is trigonal bipyramidal. On the basis of the dihedral angle method, as applied to cyclic phosphoranes,[7,8] **1** is displaced 77.0% (unit bond lengths) from a trigonal bipyramid toward a rectangular pyramid, and **5** is 14.3% displaced. These structural distortions are similar to those found in monocyclic and spirocyclic benzodioxaphosphoranes.[7,8] This may mean that the extent of stereochemical nonrigidity of pentacoordinated phosphorus and tin are closely related. However, further examples of substituent effects for tin(IV) are needed to make the comparison more meaningful.

The precursor in the preparation of **1**, $Sn(TDT)_2$, has been used for a long time in the calorimetric estimation of tin.[9] Its solid-state structure, although not known, has been inferred from Mössbauer[10,11] and infrared[12] data to be polymeric. The data support intermolecular Sn–S bonding and the presence of hexacoordinated tin. Hence, the pentacoordinated structure of tin(IV) in **1** is all the more unique. The discovery of this new structural form for **1**, similar to the structure we recently established for the germanium derivative, $[Et_4N]^+[(C_6H_4O_2)_2GeCl]^-$,[13] suggests the existence of a rectangular-pyramidal geometry for silicon(IV).

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Supplementary Material Available: Atomic coordinates (Tables I and II) and anisotropic thermal parameters (Tables III and IV) for **1** and **5**, respectively (6 pages). Ordering information is given in any current masthead page.

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[6] The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 5, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for Sn, Cl, and S were taken from the same source, pp 149–150.

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New Syntheses and Molecular Structures of the Decamethylmetallocene Dicarbonyls $(\eta^5\text{-}C_5Me_5)_2M(CO)_2$ (M = Ti, Zr, Hf)

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In view of the high current interest in η^5-pentamethylcyclopentadienyl derivatives of the transition and actinide metals,[1-14]

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