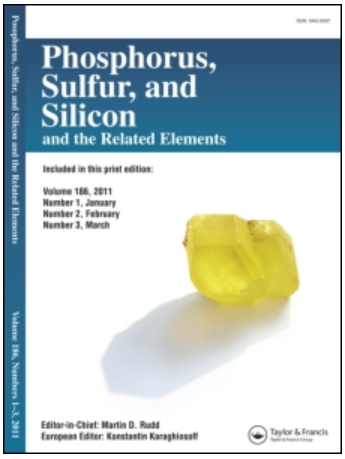

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Robert R. Holmes[a]; Roberta O. Day[a]; V. Chandrasekhar[a]; Soheila Shafeizad[a]; John J. Harland[a]; Denise N. Rau[a]; Joan M. Holmes[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, USA

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NEW RING SYSTEMS OF ELEMENTS OF MAIN GROUPS IV AND V

ROBERT R. HOLMES, ROBERTA O. DAY, V. CHANDRASEKHAR, SOHEILA SHAFEIZAD, JOHN J. HARLAND, DENISE N. RAU and JOAN M. HOLMES

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

The synthesis of $[PhSn(O)O_2CC_6H_{11}]_6$ represents the first example of tin(IV) in a drum-shaped molecule. The formation of the dimeric composition, $[(MeSn(O)O_2CC_6H_{11})_2(MeSn(O_2CC_6H_{11})_3]_2$, appears to be an intermediate hydrolysis product on the way to the drum composition. The X-ray structure reveals an "unfolded" drum array. The distannoxane unit which is represented as the sides of the drum is found in additional new dimeric compositions, $[(SCH_2CH_2O)_2SnCl]_2[H][Et_4N]$, $[((CN)_2C_2S_2)_2SnOH]_2$, and $[BuSnCl_2(OH) \cdot H_2O]_2$. These all have six-coordinated tin atoms which contrasts to the dimeric aryl distannoxanes recently isolated, $[Ph_2(Cl)SnOSnPh_2(X)]_2$, X = OH, Cl, containing five-coordinated tin. Also isolated are the new ring containing, five-coordinated tin derivatives, $[(SCH_2CH_2S)_2Sn]_2[SCH_2CH_2S][Et_3NH]_2$ and $[(SC(CN)C(CN)S)_2SnMe][Et_4N]$. The former has two trigonal bipyramidal tin atoms while the latter composition has a square pyramidal geometry. Related ring systems of new five-coordinated derivatives of silicon, germanium, arsenic, and antimony that span the range between the two ideal five-coordinated geometries also have been structurally characterized.

1. INTRODUCTION

We describe new tin(IV) cyclic systems having the four-membered $(—Sn—O—)_2$ distannoxane ring as a subunit. In these compounds, the coordination numbers at the tin centers range from five to seven. This study illustrates how a likely mode of formation of a novel hexameric composition $[PhSn(O)O_2CC_6H_{11}]_6$ is determined from the synthesis and structural study of possible lower member intermediates.

A second study focuses on new cyclic containing five-coordinated complexes of silicon, germanium, tin, arsenic, and antimony and a determination of the factors influencing their geometry. A comparison with analogous phosphorus systems and five-coordinated transition metal complexes illustrates differences in structural principles between the main-group and transition elements. These differences are partly based on changes in relative energy between the trigonal bipyramid and square or rectangular pyramid as d orbital composition varies and partly on ligand requirements, particularly those due to basicity and ring constraints. It is established that the structural principles for phosphoranes and isoelectronic anionic five-coordinated silicon derivatives are closely analogous. This comparison suggests similar models for applicable nucleophilic substitution reactions of these two elements.

2. DISTANNOXANE BASED TIN(IV) COMPOUNDS

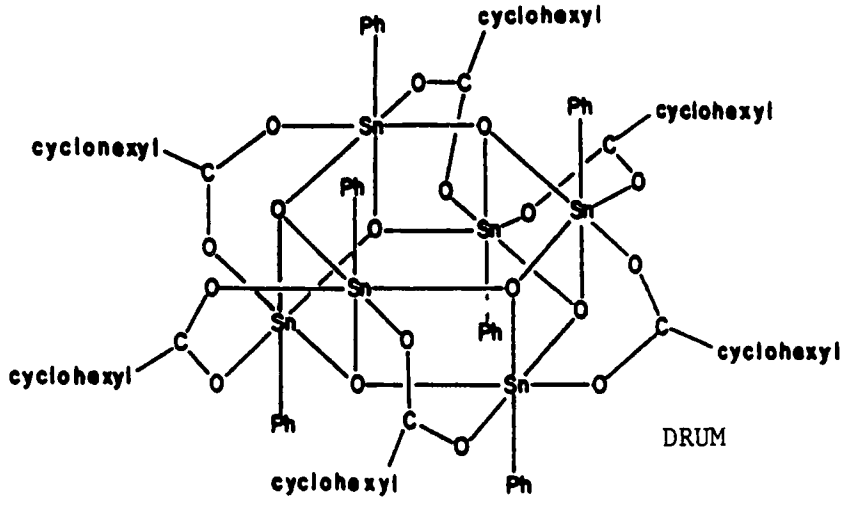
The synthesis and crystal structure of $[PhSn(O)O_2CC_6H_{11}]_6$ represents the first example of tin(IV) in a drum-shaped molecule.[1] The upper and lower faces, which

contain the tristannoxane unit, Sn_3O_3, are linked by tricoordinated oxygen atoms and bidentate carboxylate groups whereas the sides of the drum contain distannoxane units. It was first crystallized as a side product from the formation of triphenyltin cyclohexanoate, $Ph_3SnO_2C(C_6H_{11})$. A more direct route involves the reaction of $PhSnCl_3$ with the sodium salt of the acid in CCl_4 solution, followed by a hydrolysis step which gave the compound, a powdery substance present in a mixture of products.

$$PhSnCl_3 + Na^+C_6H_{11}CO_2^- \xrightarrow{CCl_4} PhSn(Cl_2)O_2CC_6H_{11} + NaCl$$

$$\downarrow + H_2O$$

$$PhSn(O)O_2CC_6H_{11} + 2HCl \quad \text{mp, } 340°C \text{ (d)}$$



DRUM

The dimeric composition, $[(MeSn(O)O_2CC_6H_{11})_2(MeSn(O_2CC_6H_{11})_3]_2$ obtained from the reaction of methylstannonic acid and cyclohexanecarboxylic acid appears to be an intermediate hydrolysis product on the way to the drum composition, especially since the organotin oxocarboxylate composition, $RSn(O)O_2CR'$, is known[2] to form

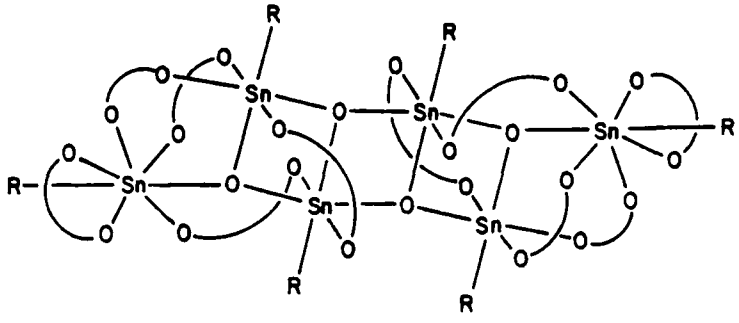
$$MeSn(O)OH + 3C_6H_{11}CO_2H \rightarrow [MeSn(C_6H_{11}CO_2)_3]$$

(not isolated)

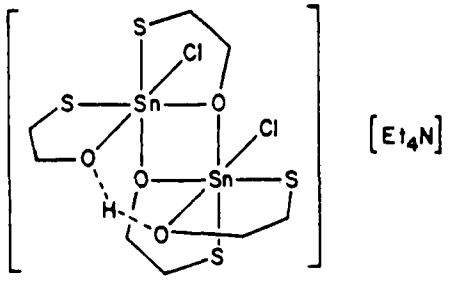
$$\{[MeSn(O)C_6H_{11}CO_2]_2[MeSn(C_6H_{11}CO_2)_3]\}_2 \quad \text{mp, } 250\text{–}260°C \text{ (d)}$$

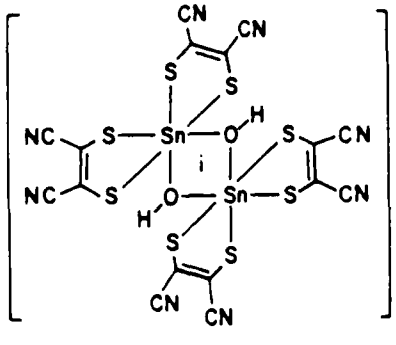
from the hydrolysis of organotin tricarboxylates, $RSn(O_2CR')_3$. The X-ray structure shows this to a remarkable degree. Hexacoordinated tin atoms are end-capped by

seven-coordinated tin atoms in an "unfolded" drum array. This provides the first example of an organotin tricarboxylate geometry.

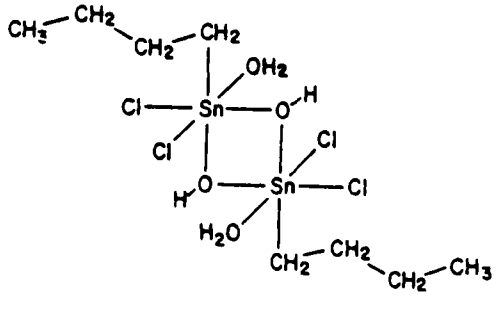


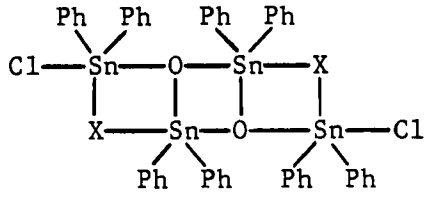
The distannoxane unit which is represented as the sides of the drum is found in additional new dimeric compositions, $[(SCH_2CH_2O)_2SnCl]_2[H][Et_4N]$, $[((CN)_2C_2S_2)_2SnOH]_2$, and $[BuSnCl_2(OH) \cdot H_2O]_2$. The latter shows extensive three dimensional hydrogen bonding and is analogous in structure to $[EtSnCl_2(OH) \cdot H_2O]_2$.[3] These all have six-coordinated tin atoms which contrasts to the dimeric aryl distannoxanes recently isolated,[4] $[Ph_2(Cl)SnOSnPh_2(X)]_2$, X = OH, Cl, containing five-coordinated tin.





$[Et_4N]_2$





X = OH (mp 192°C); X = Cl (mp 195°C)

3. NONRIGID CYCLIC FIVE-COORDINATED COMPOUNDS

The main Group IV elements, Si, Ge and Sn, and the main Group V elements, P, As, and Sb, can be incorporated into ring systems in five-coordinated form, providing series isoelectronic with each other.[5] In spirocyclic systems, molecular nonrigidity is experienced in that introduction of electron-attracting ring substituents shift the structure toward a square pyramid whereas ring saturation, use of electron-releasing ring substituents, or use of heteroring atoms of two different kinds attached to the central atom shift the structural form toward the trigonal bipyramid. The same factors are found to govern geometry in each series. These factors are illustrated in the following new derivatives.

Use of the ethanedithiol ligand, $HSCH_2CH_2SH$, and the maleonitrile dithiol ligand, HSC(CN)C(CN)SH, has led to the isolation of the new ring-containing, five-coordinated tin derivatives, respectively,

$$[(SCH_2CH_2S)_2Sn]_2[SCH_2CH_2S][Et_3NH]_2 \text{ and } [(SC(CN)C(CN)S)_2SnMe][Et_4N].$$

The former has two trigonal bipyramidal

$$3Sn(SCH_2CH_2S)_2 + 2Et_3N + H_2O \rightarrow$$

$$[(SCH_2CH_2S)_2Sn]_2[SCH_2CH_2S][Et_3NH]_2 + [(SCH_2CH_2S)SnO]$$

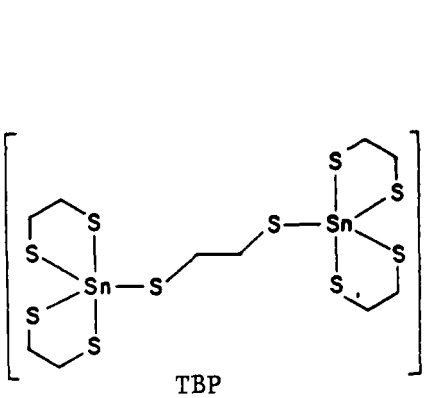
mp, 129–131°C

$$MeSnCl_3 + 2Na^{+-}SC(CN)C(CN)S^{-}Na^{+} + Et_4NCl \rightarrow$$

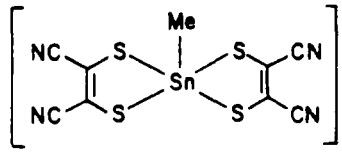
$$[(SC(CN)C(CN)S)_2SnMe][Et_4N] + 4NaCl$$

mp, 121–123°C

tin atoms linked by a dithiolate group and exhibits only Sn-S bonding whereas the latter composition has a square pyramidal geometry with an axial methyl group. Like donor atoms are present in each ring system but ring unsaturation is present in the derivative that forms the square pyramid.



TBP



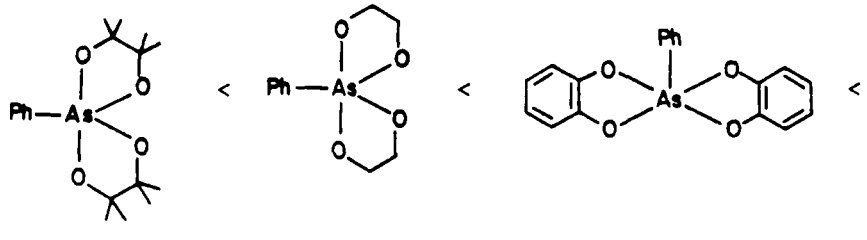
SP

$[Et_4N]$

$[Et_3NH]_2$

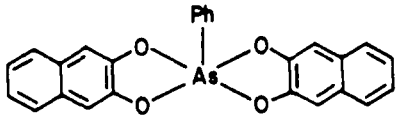
These five-coordinated stannoles are representative[6] in showing a strong tendency for the formation of tin-sulfur linkages. In contrast, five-coordinated germanium-containing sulfur linkages are rare. Most of the germanium derivatives contain germanium-oxygen bonds.[7] An example of this type is illustrated by the preparation of the methyl germanate, $[(C_6Cl_4O_2)_2GeMe][Et_4N]$, from $MeGeCl_3$ and the 1:1 adduct of triphenylphosphine oxide and tetrachlorocatechol, $Ph_3P = O \cdot C_6Cl_4(OH)_2$. It shows a structure 85.5% displaced toward the rectangular pyramid (RP) as measured by the dihedral angle method.[8] The presence of electron-attracting ring substituents is conducive to the formation of the RP as found with five-coordinated derivatives of phosphorus,[9] antimony, and silicon[10] containing this ligand.

A series of symmetrically substituted phenyl arsoranes has been prepared[11] with electron delocalization increasing in the order:



18 41.9 94.8, 99.2

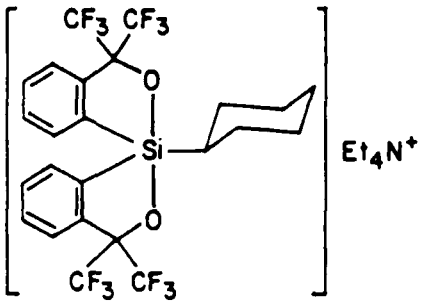
% TBP → RP



99.4

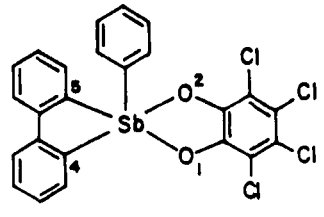
Structural displacement (% TBP → RP) follows this same order[11] in line with reduced bond electron pair repulsions.

The anionic silicate,



prepared from the dilithio derivative of hexafluorocumyl alcohol and cyclohexyltrichlorosilane, has a trigonal bipyramidal structure consistent with the presence of dissimilar ring donor atoms. Using the same spirocyclic catechol ring system and counterion, the series of anionic silicates, $[(C_6H_4O_2)_2SiR][Et_4N]$, shows an order of structural displacement from the TBP toward the RP: 91.4% (R = *t*-Bu), 63.8 (R = *n*-Bu), 30.8 (R = *l*-Np), that parallels the order of electron-donating ability of the fifth ligand.[12] This is in keeping with previously derived structural principles.[5]

In the case of antimony compounds, lattice effects take on more prominence in influencing observed geometrical distortions. The crystallographic structures of $SbPh_5$ and $(Ph_3SbO_2C_6H_4)_2 \cdot H_2O$ fall into this category. Our recent work[13] has shown that a rectangular pyramid, devoid of lattice effects, is stabilized in the same way as other main group elements, by forming a bicyclic system comprised of two unsaturated rings containing like donor atoms in any one ring. The latter is formed from phenylbiphenylenestibine and chloranil. Other new five-coordinated derivatives, $Ph_3Sb(O_2C_6Cl_4)$, $Ph_3Sb[S_2C_2(CN)_2]$, and $(p\text{-}MeC_6H_4)Sb(O_2C_2Me_4)_2$, have TBP structures.[13]



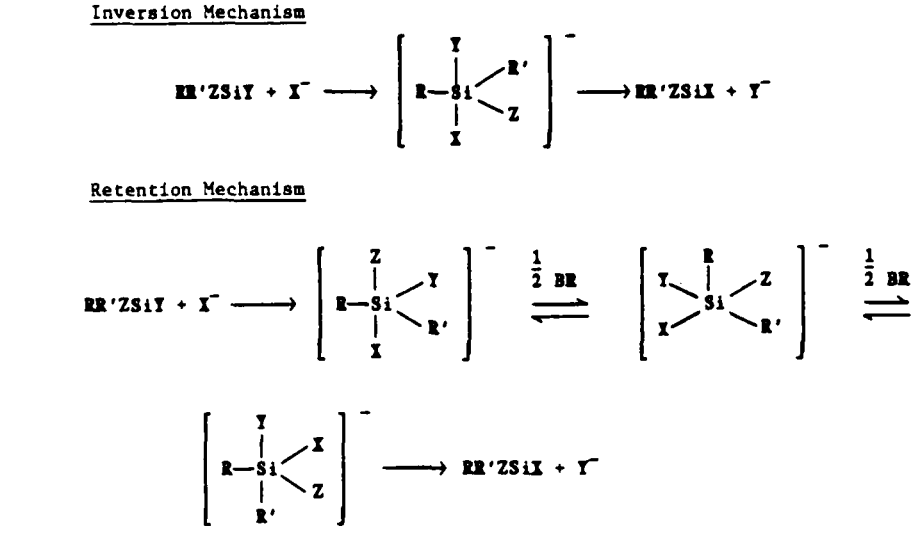
SP

The limiting trans basal angle θ, defining the square pyramidal geometry, is close to 150° for main-group elements. This contrasts with transition-metal elements that form square pyramidal geometries having a limiting trans θ angle which varies from 140° to 175° depending on d orbital configuration.[14] For example, d^2 Mo(IV) has a θ angle of 140°, d^6 Ru(II), about 160°, and d^9 Cu(II), near 174°. Even for a given d orbital occupancy, the θ value varies with magnetic properties, e.g., low spin Ni(II) has an ideal θ angle of 173°, whereas for high spin Ni(II), the θ angle is 161°.[14] A further difference between main-group and transition-element pentacoordination is found in the ease with which some transition elements assume a square or rectangular pyramidal structure, even with acyclic ligands, especially for elements in a d^6

state. However, the general trend prevails that structural displacement toward the square pyramid increases as the ring structure of the ligands increase.[15] This trend is apparent for both high and low spin transition-metal complexes, although ring unsaturation, as required for main-group elements, is not necessary to achieve a square pyramidal structure.[15]

For all of the main-group elements in Groups IV and V, series of five-coordinated derivatives have now been prepared that structurally span the range of geometries between the trigonal bipyramid and the square or rectangular pyramid.[15] Further, the structural principles governing displacement between these two geometries apply across these main-group elements and depend for the most part on ligand influences and central atom propensity toward nonrigid behavior in the five-coordinated state.[14,15] The analogy is particularly close for phosphoranes and isoelectronic anionic pentacoordinated silicon derivatives.

Use of this information is appropriate to provide a model for nucleophilic substitution reactions that proceed by way of a five-coordinated intermediate or transition state for the latter two elements. For phosphorus compounds, the inversion and retention pathways of importance for chiral derivatives have been postulated as follows:



The retention scheme, proceeding by way of a trigonal bipyramid-square pyramid interchange (i.e., a Berry pseudorotation process), is supported by our present work demonstrating that the structures of pentacoordinated anionic silicates readily traverse the TBP-SP coordinate and suggests, comparably to that of phosphoranes, that this coordinate is one of low energy. The retention mechanism depicted is supported by molecular orbital calculations on silicon systems[17] and is consistent with the nonrigid character associated with these hypervalent species.

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