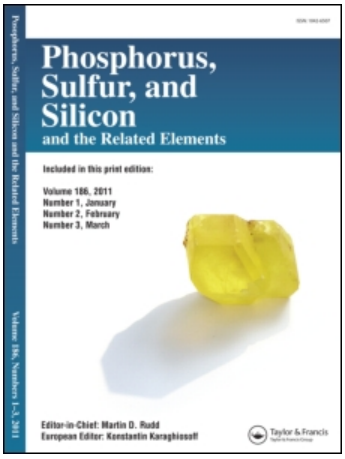

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article KÜHn, Silke , Hummeltenberg, Reinhard , SchÜrmann, Markus and Jurkschat, Klaus(1999) 'Synthesis of New Multidentate Silicon and Tin Containing Lewis Acids and their Potential for Anion Complexation', Phosphorus, Sulfur, and Silicon and the Related Elements, 150: 1, 333 — 338
To link to this Article: DOI: 10.1080/10426509908546402
URL: http://dx.doi.org/10.1080/10426509908546402

Phosphorus, Sulfur and Silicon, 1999, Vol. 150-151, pp. 333-338
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Synthesis of New Multidentate Silicon and Tin Containing Lewis Acids and their Potential for Anion Complexation

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Here we present the synthesis of both silicon and tin containing rings, their functionalisation and preliminary results towards their ability to form complexes with anions.

Keywords: Lewis acids; silicon; tin; anion complexation

INTRODUCTION

In recent years there has been a growing interest in designing host molecules for selective complexation of anions and neutral donor molecules[1]. One class of anion hosts are covalently bonded Lewis polyacids containing boron[2a], mercury[2b] or group 14 elements as Lewis acid centers[2c]. It has been reported that silicon[3a,3b] as well as tin[3c,3d] containing rings show transport abilities towards anions or form stable complexes with halide anions.

Here we report the synthesis of ring systems containing both silicon and tin and preliminary results on their behaviour towards anions.

RESULTS AND DISCUSSION

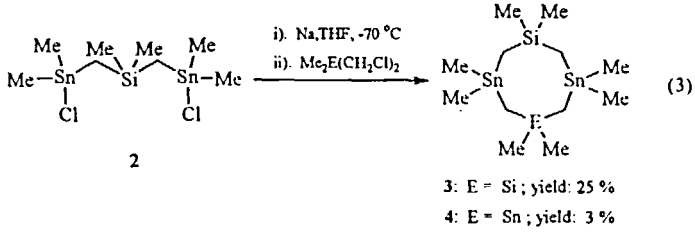
The reaction of bis(chloromethyl)dimethylsilane with trimethylsodium stannide afforded bis(trimethylstannylmethyl)dimethylsilane **1** as a colorless liquid (EQUATION 1).

$$Me_2Si(CH_2Cl)_2 + 2\,Me_3SnNa \xrightarrow[-2\,NaCl]{NH_3,\,-70\,^\circ C} \underset{\mathbf{1}}{Me_2Si(CH_2SnMe_3)_2} \qquad (1)$$

Treatment of **1** with dimethyldichlorostannane gave bis(chlorodimethylstannylmethyl)dimethylsilane **2** as a low melting solid in almost quantitative yield (EQUATION 2).

$$\underset{\mathbf{1}}{Me_2Si(CH_2SnMe_3)_2} + 2\,Me_2SnCl_2 \xrightarrow[-2\,Me_3SnCl]{} \underset{\mathbf{2}}{Me_2Si(CH_2SnClMe_2)_2} \qquad (2)$$

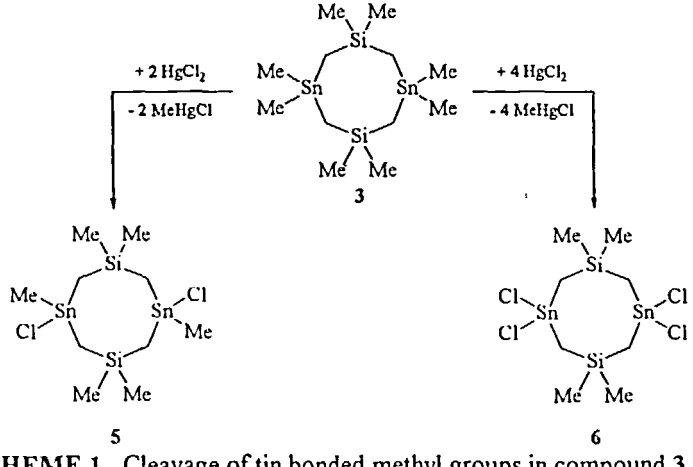
The reaction of bis(dimethylsodiumstannylmethyl)dimethylsilane with bis(chloromethyl)dimethylsilane and bis(chloromethyl)dimethylstannane provided 1,1,3,3,5,5,7,7-octamethyl-3,7-disila-1,5-distannacyclooctane **3** and 1,1,3,3,5,5,7,7-octamethyl-7-sila-1,3,5-tristannacyclooctane **4** respectively (EQUATION 3).



(3)

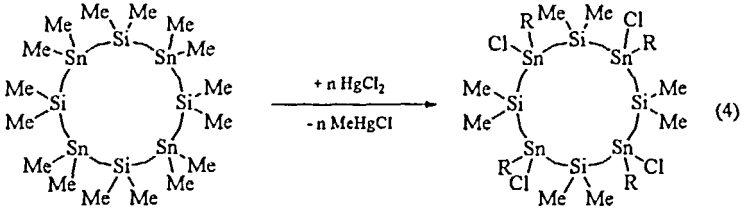
The reason for the lower yield of **4** is the increase of ring strain by substitution of silicon by tin.

The Lewis acids **5** and **6** have been obtained by reaction of **3** with mercuric chloride (SCHEME 1). Compound **5** occurs as a mixture of both isomers. The ratio of the isomers is approximately 7:4, but the data do not uniquely identify each isomer. No attempts were made to separate the isomers. The tin halides are colorless solids which show a reasonable solubility in chloroform and dichloromethane. They were characterized by NMR spectroscopy, mass spectrometry, and X-ray analysis. Both compounds **5** and **6** appear in a boat-boat conformation.



SCHEME 1 Cleavage of tin bonded methyl groups in compound **3**.

1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-3,7,11,15-tetrasila-1,5,9,13-tetrastannacyclohexadecane **7** was also formed (45% yield) during the reaction shown in EQUATION 3 (E = Si). The isolation of **7** was accomplished by Size-Exclusion-Chromatography. Treatment of **7** with $HgCl_2$ afforded the functionalized products **8** and **9** (EQUATION 4). Compounds **8** and **9** are only slightly soluble in common organic solvents.

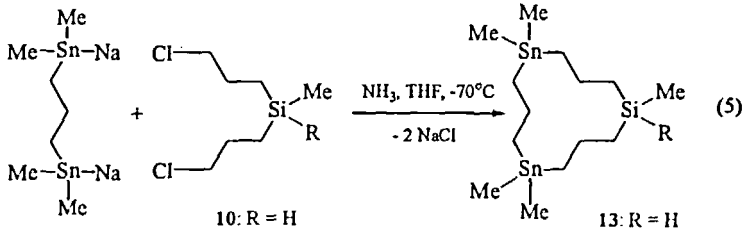


(4)

7

8: R = Me ; n = 4
9: R = Cl ; n = 8

Reaction of the bis(3-chloropropyl)silanes **10**, **11** and **12** with 1,3-bis(dimethylsodiumstannyl)propane gave the 1,5-distanna-9-silacyclododecanes **13**, **14** and **15** respectively, as colorless oils in yields of 25 to 30% (EQUATION 5).

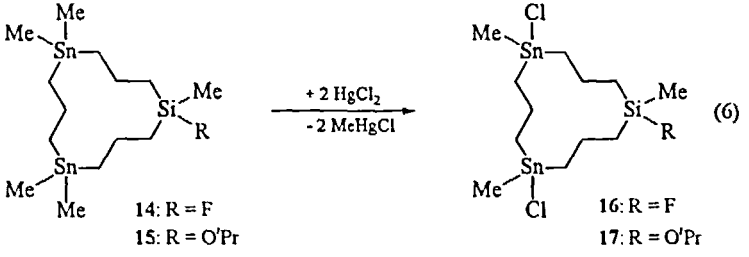


(5)

10: R = H
11: R = F
12: R = O^{i}Pr

13: R = H
14: R = F
15: R = O^{i}Pr

The synthesis of the organotin halides **16** and **17** was achieved by cleavage of the tin bonded methyl groups by reaction with $HgCl_2$ (EQUATION 6). Both organotin halides occur as mixtures of *cis*- and *trans*-isomers.

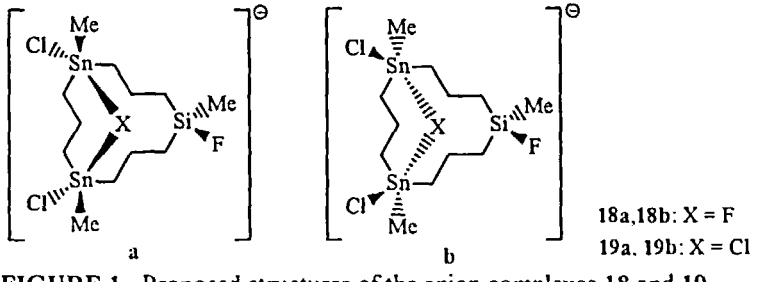


14: R = F
15: R = O'Pr

16: R = F
17: R = O'Pr

(6)

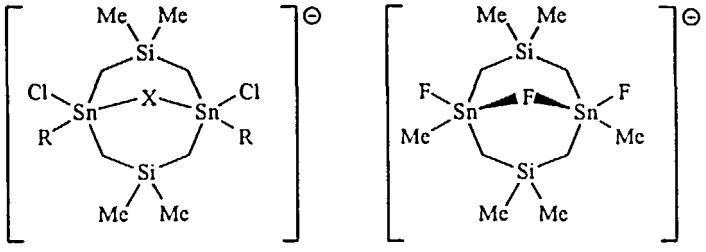
The formation of **18a**, **18b**, **19a**, and **19b** was examined by NMR titration. It was found that the addition of fluoride and chloride ions leads to formation of the corresponding 1:1 complexes, in which the anions bridge the tin atoms (FIGURE 1).



18a,**18b**: X = F
19a, **19b**: X = Cl

FIGURE 1 Proposed structures of the anion complexes **18** and **19**.

The complexation behavior towards fluoride and chloride ions of compounds **20** and **21** was also analyzed by NMR spectroscopy and electrospray mass spectrometry. The formation of stable 1:1 complexes was observed (FIGURE 2).



20: R = Me X = F, Cl
21: R = Cl

23

FIGURE 2 Anion complexes of eight-membered ring systems.

Complex **22** was formed by the addition of one mole equivalent of Bu_4NF to 1,5-difluoro-1,3,3,5,7,7-hexamethyl-3,7-disila-1,5-distannacyclooctane and is a stable, even at room temperature (FIGURE 2).

ACKNOWLEDGEMENTS

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

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