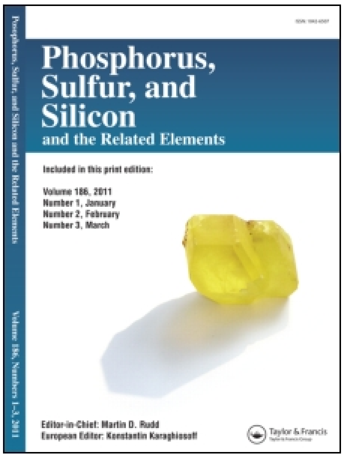


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Syntheses, Dynamic Stereochemistry, and Unusual Reactivity of Intramolecularly Coordinated Organotin Fluorides

Nicole Pieper; Ralf Ludwig; Markus SchÜrmann; Klaus Jurkschat; Monique Biesemans; Ingrid Verbruggen; Rudolph Willem

To cite this Article Pieper, Nicole , Ludwig, Ralf , SchÜrmann, Markus , Jurkschat, Klaus , Biesemans, Monique , Verbruggen, Ingrid and Willem, Rudolph(1999) 'Syntheses, Dynamic Stereochemistry, and Unusual Reactivity of Intramolecularly Coordinated Organotin Fluorides', Phosphorus, Sulfur, and Silicon and the Related Elements, 150: 1, 305 — 310

To link to this Article: DOI: 10.1080/10426509908546398

URL: http://dx.doi.org/10.1080/10426509908546398

Phosphorus, Sulfur and Silicon, 1999, Vol. 150-151, pp. 305-310
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Syntheses, Dynamic Stereochemistry, and Unusual Reactivity of Intramolecularly Coordinated Organotin Fluorides

NICOLE PIEPER[a], RALF LUDWIG[a], MARKUS SCHÜRMANN[a],
KLAUS JURKSCHAT[a], MONIQUE BIESEMANS[b],
INGRID VERBRUGGEN[b] and RUDOLPH WILLEM[b]

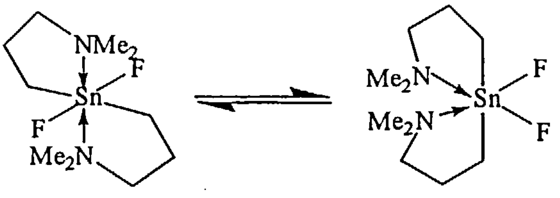
[a]*Lehrstuhl für Anorganische Chemie II der Universität Dortmund, D-44221 Dortmund, Germany and* [b]*Free University of Brussels, V.U.B., High Resolution NMR Centre, Pleinlaan 2, B-1050 Brussels, Belgium*

The addition of $Bu_4NF{\cdot}3H_2O$ to a solution of intramolecularly hexacoordinated $[Me_2N(CH_2)_3]_2SnF_2$ (1) in CH_2Cl_2 gives the zwitterionic species $[Me_2(ClCH_2)N^+(CH_2)_3][Me_2N(CH_2)_3]SnF_3^-$ (2) and $[Me_2(ClCH_2)N^+(CH_2)_3]_2SnF_4^{2-}$(3). On the other hand, $[CH_2(Me)N(CH_2)_3]_2SnF_2$ (4) does not react with fluoride ions. Density functional calculations on the model compound $[H_2N(CH_2)_3]_2SnF_2$ (1') show the LUMO of its *cis* isomer to be lower in energy than that of its *trans* isomer. Also reported are the synthesis and structure of the intramolecularly P(O)-coordinated organotin fluoride $[C_6H_4CH_2P(O)Ph_2]_2SnF_2$ (5).

Keywords: organotin fluoride; hypercoordination; density functional calculation

INTRODUCTION

Compounds of the type R_3SnF and R_2SnF_2 (R = Me, *n*-Bu, Ph) show strong intermolecular Sn-F-Sn bridges and consequently they are almost insoluble in common organic solvents[1]. However, addition of fluoride ions[2] or the use of intramolecularly coordinating built-in ligands[3] provides soluble organotin fluorides which can easily be studied in solution by NMR spectroscopy. Recently, we reported the synthesis, structure, and dynamic stereochemistry of $[Me_2N(CH_2)_3]_2SnF_2 \cdot 2H_2O$ (1)[4]. In solution, compound 1 exhibts a *cis-trans* equilibrium between the major species **1a** and the minor species **1b** (SCHEME 1). In the solid state the *all-trans* isomer **1a** was found.

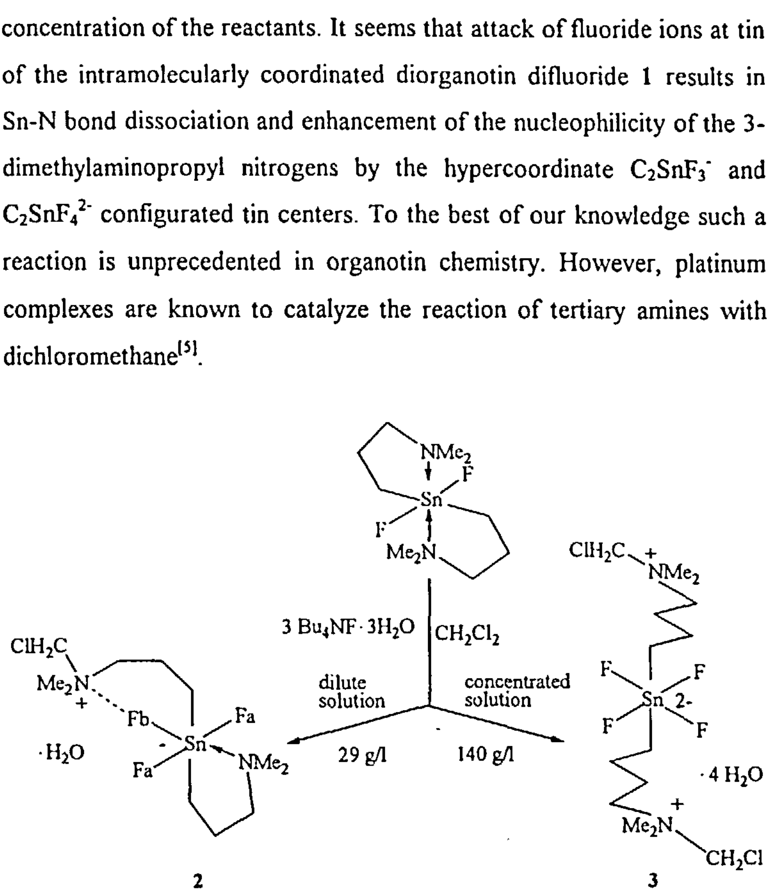


1a (80 %) **1b** (20 %)

SCHEME 1 *Cis-trans* equilibrium of 1 in solution.

RESULTS AND DISCUSSION

The diorganotin difluoride **1** reacts with an excess of $Bu_4NF \cdot 3H_2O$ in dichloromethane to give the zwitterionic compounds **2** and **3** (SCHEME 2) which were characterized by elemental analyses, multinuclear NMR spectroscopy, and in case of **3**, also by X-ray analysis (FIGURE 1). Which of the two compounds **2** and **3** is formed depends on the concentration of the reactants. It seems that attack of fluoride ions at tin of the intramolecularly coordinated diorganotin difluoride 1 results in Sn-N bond dissociation and enhancement of the nucleophilicity of the 3-dimethylaminopropyl nitrogens by the hypercoordinate $C_2SnF_3^-$ and $C_2SnF_4^{2-}$ configurated tin centers. To the best of our knowledge such a reaction is unprecedented in organotin chemistry. However, platinum complexes are known to catalyze the reaction of tertiary amines with dichloromethane[5].



SCHEME 2 Addition of fluoride ions to a solution of **1** in CH_2Cl_2 to provide compounds **2** and **3**.

Density functional calculations[6] using the B3LYP method and the LANL2DZ basis set in the Gaussian 94 program were performed on isomers of the model compound $[H_2N(CH_2)_3]_2SnF_2$ (**1'**) which is comparable to **1**. The calculations show that the *all-trans* isomer **1a'**, being related to 1a, is energetically preferred. However, the LUMO of the *cis* isomer **1b'**, being related to **1b**, is of lower energy than the

LUMO of **1a'** which suggests that the fluoride attack at tin in a solution of **1** and $Bu_4NF \cdot 3H_2O$ in CH_2Cl_2 takes place at the *cis* isomer **1b**.

TABLE 1 Density functional calculations of **1'**.

	1a'(all-trans)	*1b'(cis)*
ΔE	0 kJ/mol	8.879 kJ/mol
LUMO	1.3358 eV	1.1208 eV

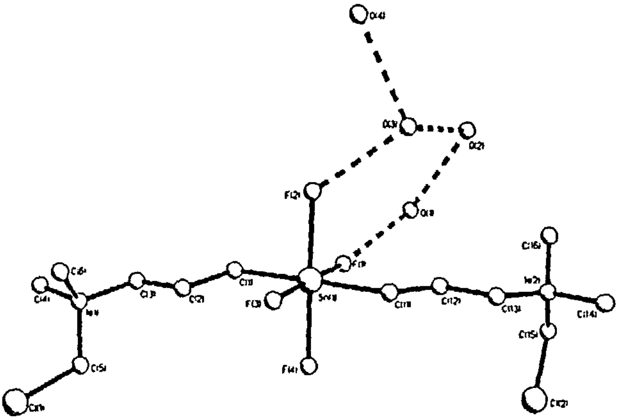
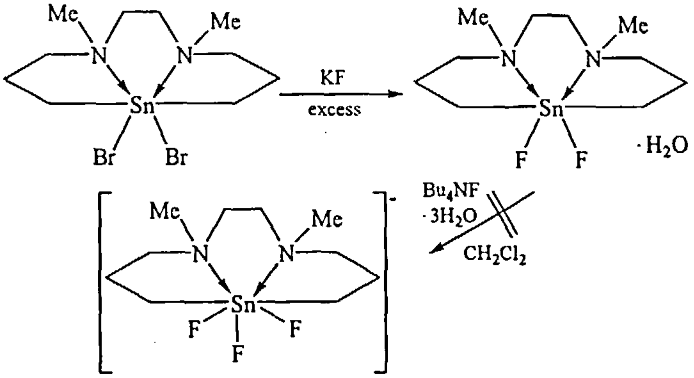


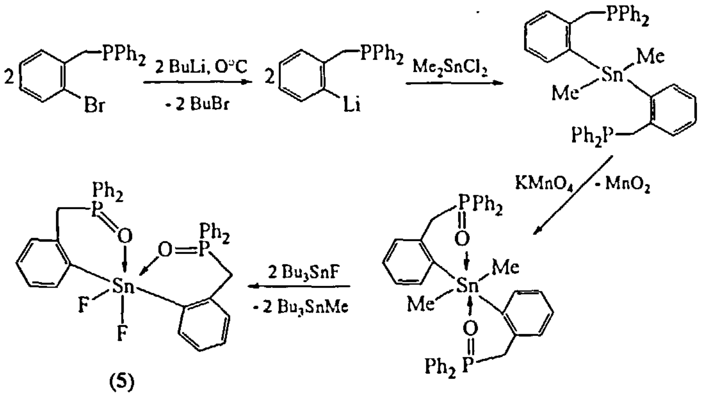
FIGURE 1 Molecular structure of **3**; selected bond lengths: Sn-F 2.059(4) - 2.108(4)Å; selected bond angles: F-Sn-F 180.0°, C-Sn-C 180.0°.

In contrast to compound **1**, no fluoride attack at tin occurs on the related *cis*-octahedral configurated diorganotin difluoride **4** and consequently no reaction of a mixture of **4** and $Bu_4NF \cdot 3H_2O$ with CH_2Cl_2 was observed (SCHEME 3). This different behavior of **1** and **4** towards fluoride ions originates in the higher energy of the Sn-N dissociation associated with the rigid ligand system in **4**.



SCHEME 3 Synthesis of 4 and addition of fluoride in CH_2Cl_2.

The synthesis of the intramolecularly P(O)-coordinated diorganotin difluoride $[C_6H_4CH_2P(O)Ph_2]_2SnF_2$ (5)[7] is shown in SCHEME 4. Similar to **1**, compound **5** undergoes a *cis-trans* equilibrium in solution which is slow on the ^{119}Sn NMR time scale at room temperature. However, in contrast to **1** the *cis* isomer dominates (90 %) and is found in the solid state (FIGURE 2).



SCHEME 4 Synthesis of $[C_6H_4CH_2P(O)Ph_2]_2SnF_2$ (5).

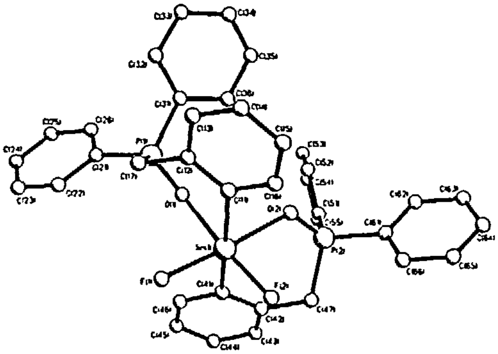


FIGURE 2 Molecular structure of compound 5; selected bond lengths: Sn-F 2.008(3)/2.012(3)Å, Sn-O 2.259(3)/ 2.255(3) Å; selected bond angle: C-Sn-C 170.61(15)°.

ACKNOWLEDGEMENTS

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

References

[1] H. Bai; R.K. Harris; H.Reuter, *J. Organomet. Chem.* 408 167 (1991).
[2] D. Dakternieks; H. Zhu, *Organometallics* 11 3820 (1992).
[3] U. Kolb; M. Dräger; M. Dargatz; K. Jurkschat, *Organometallics* 14 2827 (1995) and references cited therein.
[4] N. Pieper; C. Klaus-Mrestani; M. Schürmann; K. Jurkschat; M. Biesemans; I. Verbruggen; J.C. Martins; R. Willem, *Organometallics* 16 1043 (1997).
[5] M. Mas; J. Sola; X. Solans; M. Aguilo, *Inorganica Chimica Acta* 133 217 (1987).
[6] B.B. Laird; R.B. Ross; T. Ziegler, *Chemical Aplications of Density Functional Theory*, ACS Symposium Series 629 (1996).
[7] N. Pieper, *PhD Thesis*, University of Dortmund (1998).