FACILE FORMATION OF HYPERCOORDINATED ORGANOTIN ANIONS CONTAINING SULFUR AND CHLORINE

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Abstract

Cyclic diorganotin sulfides, $(R_2SnS)_n$ ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}; n = 2, 3$) react with diorganotin chlorides, R_2SnCl_2 ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}$) to give tetracoordinated tetraorganodistannathianes, $R_2(Cl)SnSSn(Cl)R_2$ ($R = \text{Me}$ (1), $n\text{-Bu}$ (2), $t\text{-Bu}$ (3)). ^{119}Sn -, ^{13}C -, and ^1H -NMR studies reveal these compounds to be in equilibrium with their starting materials. Addition of $[(\text{Ph}_3\text{P})_2\text{N}]^+\text{Cl}^-$ to the reaction mixtures afforded pentacoordinated dinuclear complexes $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{S}(R_2SnCl)_2\text{Cl}]^-$ ($R = \text{Me}$ (4), $n\text{-Bu}$ (5), $t\text{-Bu}$ (6)) as stable crystalline solids. Molecular structures of 4 and 6 were established by single crystal X-ray diffraction.

Introduction

Dimeric tetraorganodistannoxanes containing chlorine atoms, $[R_2(Cl)SnOSn(Cl)R_2]_2$, are easily accessible by the reaction of diorganotin oxides, R_2SnO ($R = \text{aryl}, \text{alkyl}$) with diorganotin dichlorides, R_2SnCl_2 ($R = \text{aryl}, \text{alkyl}$) [1, 2]. The analogous synthesis of tetraorganodistannathianes, $R_2(Cl)SnSSn(Cl)R_2$ using diorganotin sulfides, R_2SnS , and diorganotin dichlorides, R_2SnCl_2 ($R = \text{aryl}, \text{alkyl}$) was previously reported, however, the products were not completely characterized at that time [3]. In this contribution we describe preliminary results on the synthesis and characterization of tetraorganodistannathianes, $R_2(Cl)SnSSn(Cl)R_2$ ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}$) and related dinuclear complexes, $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{S}(SnR_2Cl)_2\text{Cl}]^-$ ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}$) [4]. The former contain tetracoordinated tin atoms while the latter possess pentacoordinated tin atoms.

Results and discussion

The reaction between cyclic diorganotin sulfides, $(R_2SnS)_n$ ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}; n = 2, 3$), and diorganotin chlorides, R_2SnCl_2 ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}$) provided, after evaporation of the solvent, colorless microcrystalline materials, hereafter denoted as **A**, **B** and **C**, which have no sharp melting points. ^{119}Sn -, ^{13}C and ^1H NMR spectra of these materials suggest that **A**, **B** and **C** consist of mixtures containing tetraorganodistannathianes, $R_2(Cl)SnSSn(Cl)R_2$ ($R = \text{Me}$ (1), $n\text{-Bu}$ (2), $t\text{-Bu}$ (3)) and the starting compounds $(R_2SnS)_n$ and R_2SnCl_2 ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}; n = 2, 3$). The observations made in the NMR studies are fully consistent with the assumption that the reactants exist in equilibrium (Eq. 1).

In contrast to the dimeric tetraorganodistannoxanes, $[R_2(Cl)SnOSn(Cl)R_2]_2$ ($R = \text{Me}$ [5], $n\text{-Bu}$ [6]) the ^{119}Sn NMR chemical shifts observed for the tetraorganodistannathianes, $R_2(Cl)SnSSn(Cl)R_2$ ($R = \text{Me}$ (1), $n\text{-Bu}$ (2), $t\text{-Bu}$ (3)) clearly show their tin atoms to be tetracoordinated.

Moreover, electrospray mass spectra (negative ion detection mode) of the materials **A**, **B** and **C** reveal mass clusters related to the organotin anions $[R_2SnCl_3]^-$ ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}$) and $[\text{S}(SnR_2Cl)_2\text{Cl}]^-$ ($R = \text{Me}, n\text{-Bu}, t\text{-Bu}$), respectively. The observation of anions containing both

chlorine and sulfur atoms supports the existence of the tetraorganodistannathianes, $R_2(Cl)SnSSn(Cl)R_2$ ($R = \text{Me}$ (1), $n\text{-Bu}$ (2), $t\text{-Bu}$ (3)) in the materials **A**, **B** and **C**.

Repeating the reaction between the cyclic diorganotin sulfides, $(R_2SnS)_n$ ($R = \text{Me}$, $n\text{-Bu}$, $t\text{-Bu}$; $n = 2, 3$), and diorganotin chlorides, R_2SnCl_2 ($R = \text{Me}$, $n\text{-Bu}$, $t\text{-Bu}$) in the presence of $[(Ph_3P)_2N]^+Cl^-$ gave ionic complexes $[(Ph_3P)_2N]^+[S(SnR_2Cl)_2Cl]^-$ ($R = \text{Me}$ (4), $n\text{-Bu}$ (5), $t\text{-Bu}$ (6)) as colourless crystalline solids (Eq. 2).

1, $R = \text{Me}$

2, $R = n\text{-Bu}$

3, $R = t\text{-Bu}$

4, $R = \text{Me}$

5, $R = n\text{-Bu}$

6, $R = t\text{-Bu}$

Notably, the anions in the complexes 4 – 6 resemble those observed in the electrospray spectra of the solid materials **A** – **C** mentioned before. According to ^{119}Sn NMR spectroscopy, the tin atoms of the complexes 4 – 6 are pentacoordinated. The compounds $[(Ph_3P)_2N]^+[S(SnR_2Cl)_2Cl]^-$ ($R = \text{Me}$ (4), $t\text{-Bu}$ (6)) were studied by X-ray diffraction. The molecular structures of the anions are illustrated in Figure 1 and selected geometric parameters are listed in Table 1. Thus, both anions contain four-membered rings incorporating two tin atoms, one sulfur and one chlorine atom, respectively. The geometry of the tin atoms features a distorted trigonal bipyramid in which two carbon atoms and a sulfur atom occupy the equatorial positions, while the more electronegative chlorine atoms are situated in the axial positions. The four-membered ring in the anion of 4 adopts a slightly puckered conformation, whereas that in 6 is almost planar. Apart from this difference the structural parameters in both anions are virtually identical.

Figure 1. DIAMOND [7] presentation for the anions of $[(Ph_3P)_2N]^+[S(SnR_2Cl)_2Cl]^-$ ($R = \text{Me}$ (4), $t\text{-Bu}$ (6)).

The anions in compounds 4 – 6 represent rare examples of hypercoordinated organotin species revealing neither strong donors nor intramolecularly coordinating ligands.

Acknowledgement

The Australian Research Council is gratefully acknowledged for support.

Table 1. Selected geometrical parameters for the anions of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{S}(\text{SnR}_2\text{Cl})_2\text{Cl}]^-$ (R = Me (**4**), *t*-Bu (**6**)).

	4	6
Sn(1)-Cl(1)	2.474(2)	2.513(3)
Sn(1)-Cl(2)	2.744(2)	2.743(3)
Sn(2)-Cl(2)	2.828(2)	2.755(2)
Sn(2)-Cl(3)	2.481(2)	2.482(2)
Sn(1)-S(1)	2.399(2)	2.380(2)
Sn(2)-S(1)	2.390(2)	2.388(3)
Cl(1)-Sn(1)-Cl(2)	175.06(6)	166.55(8)
Cl(2)-Sn(2)-Cl(3)	173.63(6)	165.64(9)
S(1)-Sn(1)-Cl(1)	89.41(6)	85.12(8)
S(1)-Sn(1)-Cl(2)	85.65(6)	81.44(8)
S(1)-Sn(2)-Cl(2)	83.98(6)	81.04(7)
S(1)-Sn(2)-Cl(3)	90.64(6)	84.60(9)
Sn(1)-S(1)-Sn(2)	100.22(7)	108.11(9)
Sn(1)-Cl(2)-Sn(2)	82.50(5)	89.18(7)

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