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SYNTHESIS OF BIS(TETRAMETHYLSTIBONIUM)TETRACYCLOPENTADIENYLSTANNATE

A NOVEL TYPE OF ORGANOTIN(II) COMPOUND

KLAAS D. BOS, ERIC J. BULTEN, HARRY A. MEINEMA and JAN G. NOLTES

Institute for Organic Chemistry TNO, P.O. Box 5009, Utrecht (The Netherlands)

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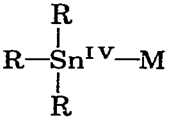
Summary

Reaction of dicyclopentadienyltin(II) with pentamethylantimony gives $[Me_4Sb]_2{}^+\ [(C_5H_5)_4Sn]^{2-}$, the first example of an anionic organotin(II) species.

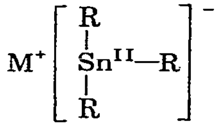
Introduction

Although inorganic anionic tin(II) species, such as the $SnCl_3^-$ ion, have been known for a long time (for a review see ref. 1), anionic organotin(II) compounds of the type $(R_3Sn)^-\ M^+$ or $(R_4Sn)^{2-}\ 2M^+$ so far have not been reported. Triphenyltin lithium shows a Mössbauer isomer shift of 1.36 mm/s [2] and must thus be regarded as a tin(IV) compound, probably containing a rather covalent tin—lithium bond (structure A). If the oxidation state of tin does depend on the degree of covalency of the triorganotin—cation bond relation, it would seem that the more electropositive alkali metal ions and, in particular, tetra-alkylammonium or tetra-alkylstibonium ions should be better counter ions than the lithium ion for species involving divalent tin (structures B and C). Furthermore, B and C will be favoured by electron-withdrawing R groups.



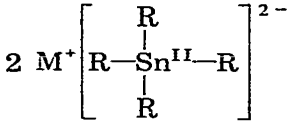
$R{-}\overset{R}{\underset{R}{Sn^{IV}}}{-}M$

(A)



$M^+\left[\overset{R}{\underset{R}{Sn^{II}}}{-}R\right]^-$

(B)



$2\ M^+\left[R{-}\overset{R}{\underset{R}{Sn^{II}}}{-}R\right]^{2-}$

(C)

In the present paper we report the first example of an organotin(II) compound of type C.

Results and discussion

Pentamethylantimony and dicyclopentadienyltin(II) react in benzene solution to give a pale-yellow precipitate. The IR spectrum indicates that the product contains the Me_4Sb^+ group (absorptions at 582 and 866 cm^{-1}; see ref. 3). The Mössbauer spectrum (IS 3.93 mm/s relative to SnO_2; QS 0.52 mm/s) showed the tin to be in the divalent state. An ^1H NMR spectrum (DMSO solution) proved the presence of cyclopentadienyl and methyl groups in the ratio 1/2 (see Experimental). The elemental analysis showed a Sb/Sn ratio of 2/1. On the basis of these results, it is concluded that the product has the composition $[Me_4Sb]_2{}^+[(C_5H_5)_4Sn]^{2-}$. The reaction is represented by the following equation:

$$2\,Me_5Sb + 2(C_5H_5)_2Sn \rightarrow \underset{(I)}{[Me_4Sb]_2{}^+[(C_5H_5)_4Sn]^{2-}} + \frac{1}{n}[Me_2Sn]_n$$

Compound I is spontaneously inflammable in air. The elemental analysis is consistent with the presence of 5% of a dimethyltin polymer.

Attempts to prepare further examples of compounds of type C so far have been unsuccessful. The reaction of tin(II) dichloride with pentamethylantimony has been carried out with the aim of obtaining the methylstannate(II) derivative II or III:

$$\underset{(II)}{[Me_4Sb]^+[MeSnCl_2]^-} \qquad \underset{(III)}{[Me_4Sb]_2{}^+[Me_2SnCl_2]^{2-}}$$

Instead, tetramethylstibonium trichlorostannate was obtained (IV). This result can be explained in terms of the occurrence of the following reactions:

$$SnCl_2 + Me_5Sb \rightarrow Me_4Sb^+Cl^- + [MeSnCl] \qquad (1)$$

$$Me_4Sb^+Cl^- + SnCl_2 \rightarrow \underset{(IV)}{[Me_4Sb]^+[SnCl_3]^-} \qquad (2)$$

The dark-red colour which forms in the reaction mixture may be taken as an indication for the formation of [MeSnCl] or of secondary products arising from this compound (step 1). Similarly, a dark red product which has not been fully identified had been obtained from the reaction of tetramethyltin with tin(II) dichloride in acetone solution [4]. Compound IV has been obtained in a separate experiment by the 1/1 reaction of tetramethylstibonium chloride with tin(II) dichloride (step 2).

The reaction of dicyclopentadienyltin(II) with cyclopentadienyllithium in THF solution was carried out in an attempt to synthesize lithium tricyclopentadienylstannate:

$$(C_5H_5)_2Sn + C_5H_5Li \xrightarrow{?} Li^+[(C_5H_5)_3Sn^{II}]^-$$

The ^1H NMR spectrum of the reaction mixture showed one cyclopentadienyl peak at δ 5.75 ppm. No cyclopentadienyl—tin couplings were observed. Dicyclopentadienyltin(II) in THF shows a peak at δ 5.88 ppm and cyclopentadienyllithium in THF shows a peak at δ 5.64 ppm. A Mössbauer spectrum of the white solid, obtained upon evaporation of the reaction mixture to dryness, was identical with that of pure dicyclopentadienyltin(II). The available data offer no support for the formation of lithium tricyclopentadienylstannate(II) in the solid. Apparently fast exchange of cyclopentadienyl groups between tin and lithium takes place in THF solution.

Experimental

All manipulations were carried out under dry, oxygen-free nitrogen. The solvents were distilled from $LiAlH_4$ under nitrogen before use.

Bis(tetramethylstibonium)tetracyclopentadienylstannate(II), $[Me_4Sb]_2{}^+$ $[C_5H_5)_4Sn]^{2-}$

Dicyclopentadienyltin(II) (2.81 g, 11.3 mmol) was dissolved in 25 ml of benzene in a centrifuge bottle (provided with a nitrogen inlet). A solution of 1.75 ml (2.22 g, 11.3 mmol) of pentamethylantimony [5] in 15 ml of benzene was added with stirring. A pale-yellow solid precipitated and the temperature rose to about 30° C. Stirring was continued for 2 h, the mixture was centrifuged and the supernatant liquid was removed by syringe. After addition of 15 ml of benzene to the precipitate the mixture was stirred for 10 min and centrifuged. The liquid was removed and the precipitate dried in vacuum, leaving 2.75 g of a pale-yellow solid. Anal.: Found: C, 43.4; H, 5.5; Sb, 29.8; Sn, 18.3. Calcd. for $[Me_4Sb]_2{}^+$ $[(C_5H_5)_4Sn]^{2-}$: C, 45.27; H, 5.97; Sb, 32.78; Sn, 15.98%. Calcd. for $[Me_4Sb]_2{}^+$ $[(C_5H_5)_4Sn]^{2-}$ contaminated with 5% $[Me_2Sn]$: C, 43.89; H, 5.88; Sb, 31.22; Sn, 19.02%.

The product obtained is extremely sensitive to air. The ^1H NMR spectrum of the product in DMSO-d_6 revealed a C_5H_5/Me ratio of 4/7.8 {δ(C_5H_5) 5.37 ppm; δ(Me) 1.47 ppm}.

Reaction of tin(II) dichloride with pentamethylantimony

A solution of pentamethylantimony (0.4 ml, 2.6 mmol) in 8 ml of THF was added dropwise with stirring to an ice-cooled solution of tin(II) dichloride (0.85 g, 4.5 mmol) in 10 ml of THF. The addition took 10 min. A yellow precipitate was formed and stirring was continued for 30 min. The liquid was separated from the precipitate and discarded. The precipitate was washed with 5 ml of THF, and dried in vacuum (1 mmHg at 40°C), leaving 0.40 g of a pale-yellow solid. Anal.: Found: C, 11.83; H, 3.04; Cl, 25.91; Sn, 28.7. calcd. for $[Me_4Sb]^+$ $[SnCl_3]^-$: C, 11.81; H, 2.97; Cl, 26.14; Sn, 29.17%. The infrared spectrum of this solid was identical with that of the product obtained from the reaction of tin(II) dichloride with tetramethylstibonium chloride.

Tetramethylstibonium trichlorostannate, $[Me_4Sb]^+$ $[SnCl_3]^-$

Tetramethylstibonium chloride (0.40 g, 1.84 mmol) was suspended in 30 ml of THF. A solution of tin(II) dichloride (0.35 g, 1.84 mmol) in 10 ml of THF was added dropwise with stirring and the mixture was refluxed for 2 h. The cooled mixture was filtered through a glass filter disc to remove some insoluble material. The clear filtrate was concentrated to a volume of 10 ml. The crystalline product was filtered from the cooled solution and dried in vacuum, leaving 0.22 g of a white solid. Anal.: Found: Cl, 26.12. Calcd. for $[Me_4Sb]^+ [SnCl_3]^-$: Cl, 26.14%.

Reaction of dicyclopentadienyltin(II) with cyclopentadienyllithium

A solution of cyclopentadienyllithium (0.93 g, 12.9 mmol) in 15 ml of THF was added to a solution of dicyclopentadienyltin(II) (3.2 g, 12.9 mmol) in 6 ml of THF. The mixture became yellow. The ^1H NMR spectrum showed one peak at δ 5.75 ppm. The spectrum remained unchanged upon cooling the sample to —100°C. No cyclopentadienyl—tin couplings were observed.

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