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OXIDATIVE ADDITION REACTIONS OF DICYCLOPENTADIENYLTIN(II) AND OF TIN(II) BIS(ACETYLACETONATE) WITH ORGANIC HALIDES. THE PREPARATION OF COMPOUNDS OF THE TYPE $RSn(acac)_2X$

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Summary

Oxidative addition reactions of tin(II) bis(acetylacetonate) with organic halides provide a route to new monoorganotin(IV) bis(acetylacetonate) halides. Dicyclopentadienyltin(II) undergoes oxidative addition with methyl iodide, diiodomethane and ethyl bromoacetate, but with allyl bromide, benzyl bromide and triphenylmethyl bromide carbon—carbon coupling reactions and the formation of the corresponding cyclopentadienyltin(II) halide take place. Some of the reactions are accelerated by light. NMR spectroscopic data show that the $RSn(acac)_2X$ compounds have a *cis*-configuration. The compounds $YCH_2Sn(acac)_2X$ (e.g. Y = I, $CH{=}CH_2$, COOEt) provide the first examples of diastereotopic non-equivalence of methylene protons in organotin compounds containing a hexacoordinate chiral tin centre.

Introduction

Tin(II) halides are known to react with organic halides to form monoorganotin(IV) compounds. These reactions generally require elevated temperatures and the yields are low [1] (cf. refs. 2 and 3), e.g.:

$$SnI_2 + MeI \xrightarrow[4\,h]{160^\circ C} MeSnI_3\ (25\%)$$

However, reactions of this type can be accelerated and the yields improved considerably by using organoantimony catalysts [4,5].

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As part of our investigation of the direct-synthesis reaction for dialkyltin compounds ($Sn + 2RX \rightarrow R_2Sn^{IV}X_2$), we are interested in oxidative addition reactions of tin(II) compounds with organic halides, since tin(II) species are plausible intermediates in the direct synthesis ($Sn + RX \rightarrow RSn^{II}X$) [6]. In this paper we describe a study of the reactions of $(C_5H_5)_2Sn$ and of $Sn(acac)_2$ with reactive organic halides (for a preliminary account see ref. 7). Recently the reactions of some tin(II) bis(1,3-diketonates) with alkyl iodides have been reported [8].

Results and discussion

Reactions of dicyclopentadienyltin(II) with organic halides

The reaction of $(C_5H_5)_2Sn$ with methyl iodide in benzene solution proceeds smoothly in the presence of light even at room temperature. The oxidative addition product $Me(C_5H_5)_2SnI$ is formed in high yield. It has been previously reported that the reaction proceeds only at elevated temperature (50°C) [9]. Upon irradiation (λ_{max} = 254 and 366 nm) of the reaction mixture for 56 h at 15°C other products were formed [10]. In view of these conflicting results the following experiments were carried out. A sample of a concentrated solution of $(C_5H_5)_2Sn$ and MeI (molar ratio 1/2) in benzene was irradiated with an ordinary incandescent lamp, while the Pyrex reaction flask was cooled by ice-water. Within three hours $(C_5H_5)_2Sn$ had been converted into $Me(C_5H_5)_2SnI$ in a yield of more than 90%. In a second experiment another sample of the same solution was heated at 45°C for 7 h in the dark. NMR spectroscopy indicated that no reaction had occurred.

$$(C_5H_5)_2Sn \xrightarrow{MeI} \begin{array}{l} \xrightarrow{5^\circ C;\ 3\ h;\ light} Me(C_5H_5)_2SnI \\ \xrightarrow{45^\circ C;\ 7\ h;\ dark} \text{no reaction} \end{array}$$

These results point to a free radical mechanism for this reaction under the conditions used. However, the reaction may well be thermal in nature under the conditions employed by Albert and Schröer (viz. use of a large excess of methyl iodide [10]). Recently evidence has been presented that the oxidative addition of organic halides may proceed by a free radical chain mechanism [11] as well as by an S_N2 mechanism [12,13].

The reaction of $(C_5H_5)_2Sn$ with MeI is not straightforward, because the product $Me(C_5H_5)_2SnI$ initially formed undergoes a fast exchange reaction with $(C_5H_5)_2Sn$ to form $Me(C_5H_5)_3Sn$ and the slightly soluble C_5H_5SnI. C_5H_5SnI reacts slowly with MeI to give $Me(C_5H_5)SnI_2$, which slowly renders redistribution with $Me(C_5H_5)_3Sn$ to give $Me(C_5H_5)_2SnI$ in high yield:

$$\begin{tikzcd}
(C_5H_5)_2Sn + MeI \arrow[r] & Me(C_5H_5)_2SnI \arrow[r, shift left, "(C_2H_5)_2Sn"] & Me(C_5H_5)_3Sn + C_5H_5SnI\downarrow \arrow[l, shift left] \arrow[d, "MeI"] \\
 & & Me(C_5H_5)SnI_2 \arrow[ul, "Me(C_5H_5)_3Sn"]
\end{tikzcd}$$

^1H NMR data for the methyl cyclopentadienyltin compounds are given in Table 1.

TABLE 1

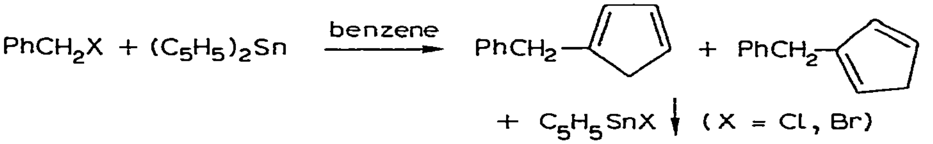
^{1}H NMR DATA [a] OF ALKYLCYCLOPENTADIENYLTIN(IV) COMPOUNDS

	δ(HC—Sn) [b]	J(Sn—CH) [c]	$\delta(C_5H_5)$ [b]	$J(Sn—C_5H_5)$ [c]	Ref.
$Me(C_5H_5)_3Sn$	—0.50	51.8/54.2	6.02	24.8/26.0	This work
	—0.51	50.7/53 2	5.94	24.7/25.7	[28] [d]
$Me(C_5H_5)_2SnI$	0.01	55.5/58.0	6.15	29.9/31.2	[7]
$Me(C_5H_5)SnI_2$	0.89	61.3/64.0	6.26	37.7/39.4	[7]
$ICH_2(C_5H_5)_3Sn$	1.38	16.3 [e]	6.04	26.0/27.1	This work
$ICH_2(C_5H_5)_2SnI$	1.92	15.2 [e]	6.20	30.8/32.2	This work
$H_2C[Sn(C_5H_5)_2I]_2$	—0.21	56.3/59.0	6.08	31.0/32.4	This work
$CH_2{=}CHCH_2(C_5H_5)_2SnBr$	1.60		6.07	28.8/30.2	This work

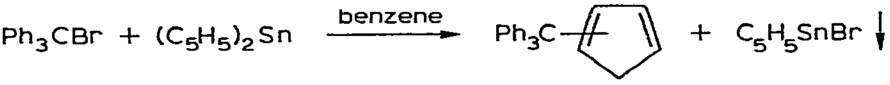
[a] $CDCl_3$ solution unless otherwise stated. [b] Downfield from TMS. [c] ^{117}Sn—CH/^{119}Sn—CH. [d] Solvent CS_2. [e] Coupling with the ^{117}Sn and ^{119}Sn nuclei not resolved

Analogously, $(C_5H_5)_2Sn$ reacts with CH_2I_2 in benzene at room temperature only in the presence of light. With an excess of CH_2I_2 the main product is $ICH_2(C_5H_5)_2SnI$. When an excess of $(C_5H_5)_2Sn$ is used, the product mixture contains among others $I(C_5H_5)_2SnCH_2Sn(C_5H_5)_2I$, $(C_5H_5)_3SnCH_2Sn(C_5H_5)_2I$ and C_5H_5SnI. NMR data for some of these compounds are listed in Table 1.

Reactions other than oxidative addition may occur upon interaction of $(C_5H_5)_2Sn$ with organic halides. Benzyl bromide and benzyl chloride afford C_5H_5SnBr and C_5H_5SnCl [14], respectively, and a mixture of benzylcyclopentadienes, which from their NMR spectra [15] have been identified as 1- and 2-benzylcyclopentadiene.



In the reaction of $(C_5H_5)_2Sn$ with triphenylmethyl bromide C_5H_5SnBr is formed in a fast reaction together with 1- and 2-triphenylmethylcyclopentadiene:



In the reaction of $(C_5H_5)_2Sn$ with allyl bromide the oxidative addition product $CH_2{=}CHCH_2(C_5H_5)_2SnBr$ is formed. Moreover, a C—C coupling reaction also takes place, with formation of a mixture of 1- and 2-allylcyclopentadiene and of C_5H_5SnBr. Other allyltin(IV) products, possibly resulting from redistribution of $CH_2{=}CHCH_2(C_5H_5)_2SnBr$ or oxidative addition of allyl bromide to C_5H_5SnBr are also present, but have not been identified. Analogously, in the reaction of $(C_5H_5)_2Sn$ with ethyl bromoacetate tin(IV) oxidative addition products are formed along with (ethoxycarbonylmethyl)cyclopentadienes and C_5H_5SnBr. While C—C bond formation via the reaction of organotin(IV) compounds with organic halides is well-known [16,17] the above reactions appear to be the first examples of C—C coupling by an organotin(II) compound.

Attempts to purify the oxidative addition products from the reactions of dicyclopentadienyltin with reactive organic halides by distillation resulted in decomposition.

Reactions of tin(II)bis(acetylacetonate)

Oxidative addition occurs upon the reaction of tin(II) bis(acetylacetonate)* with reactive organic halides at room temperature:

$$\mathrm{Sn(acac)_2 + RX \rightarrow RSn(acac)_2X}$$

$\mathrm{RX = MeI, PrI, CH_2I_2, CH_2{=}CHCH_2Br, PhCH_2Br, Ph_3CBr, BrCH_2COOEt}$

Although the reactions of $\mathrm{Sn(acac)_2}$ with MeI, PrI or $\mathrm{CH_2I_2}$ proceed even in the dark, the rates are strongly enhanced by light, suggesting a free radical mechanism. The reactions with allyl bromide and benzyl bromide are not notably influenced by light, but proceed much faster at elevated temperatures. The reaction of $\mathrm{Sn(acac)_2}$ with triphenylmethyl bromide proceeds to completion within a few minutes at room temperature. The other reactions require some hours or days for completion. The $\mathrm{RSn(acac)_2X}$ compounds have been isolated in better than 80% yield. The analytical and Mössbauer data for the prepared compounds are summarized in Table 2. For a discussion of the Mössbauer data of organotin(IV) acetylacetonates see ref. 24.

The reactions of $\mathrm{(C_5H_5)_2Sn}$ with organic halides are complicated by C—C coupling and exchange reactions. However, in the case of $\mathrm{Sn(acac)_2}$, neither reactions of the type A nor exchange reactions of the organotin(IV) product

$$\mathrm{Sn(acac)_2 + RX \nrightarrow Sn(acac)X + Racac} \qquad \text{(A)}$$

with $\mathrm{Sn(acac)_2}$ of the type B have been observed. Similarly, we have no evidence

$$\mathrm{RSn(acac)_2X + Sn(acac)_2 \nrightarrow RSn(acac)_3 + Sn(acac)X} \qquad \text{(B)}$$

for the occurrence of reaction C. Reactions B and C would produce $\mathrm{RSn(acac)_3}$,

$$\mathrm{2RSn(acac)_2X \nrightarrow RSn(acac)_3 + RSn(acac)X_2} \qquad \text{(C)}$$

which is unlikely to occur, since it would involve either seven-coordination of the tin atom or the presence of a monodentate acac-ligand.

In the reaction of $\mathrm{Sn(acac)_2}$ with an excess of $\mathrm{CH_2I_2}$ the product containing one tin atom is formed exclusively. The same holds for the reaction of $\mathrm{(C_5H_5)_2Sn}$ with an excess of $\mathrm{CH_2I_2}$. However, the organoantimony-catalyzed reaction of $\mathrm{SnBr_2}$ with $\mathrm{CH_2I_2}$ yields the bis-tin derivative as the main product even when an excess of $\mathrm{CH_2I_2}$ is used [5]:

$$\mathrm{Sn(acac)_2 + 2\ CH_2I_2 \xrightarrow[20^\circ C]{benzene} ICH_2Sn(acac)_2I}$$

$$\mathrm{SnBr_2 + 3\ CH_2I_2 \xrightarrow[100^\circ C]{R_3Sb} \underset{(10\%)}{ICH_2SnBr_2I} + \underset{(90\%)}{CH_2(SnBr_2I)_2}}$$

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* Several independent reports of the synthesis of tin(II) bis(acetylacetonate) and related compounds have appeared [18-21].

TABLE 2

ANALYTICAL AND PHYSICAL DATA

Compound	Analytical data; found (calcd.) (%)				M.p. (°C)	Mössbauer data	
	C	H	Br/I	Sn		*IS* [a] (mm/sec)	*QS* (mm/sec)
$MeSn(acac)_2I$	29.02 (28.79)	3.75 (3.74)	27.89 (27.66)	26.64 (25.87)	118-120 [b]	0.83	1.93
$PrSn(acac)_2I$	32.60 (32.07)	4.42 (4.35)	26.26 (26.06)	24.50 (24.38)	76-79	0.90	2.09
$CH_2{=}CHCH_2Sn(acac)_2Br$	35.29 (35.66)	4.44 (4.37)	18.15 (18.25)	27.22 (27.10)	79-82	0.91	1.70
$EtOOCCH_2Sn(acac)_2Br$	34.59 (34.75)	4.26 (4.37)	16.55 (16.51)	24.64 (24.53)	97-100	0.87	1.77
$ICH_2Sn(acac)_2I$	23.00 (22.59)	2.89 (2.76)	43.42 (43.40)	20.46 (20.30)	109-112	0.77	1.60
$PhCH_2Sn(acac)_2Br$	42.62 (41.85)	4.43 (4.34)	15.87 (16.38)	24.17 (24.32)			
$Ph_3CSn(acac)_2Br$	53.89 (54.41)	4.69 (4 57)	11.91 (12.48)	18.61 (18.54)	95-98 (dec.)	0.86	1.37

[a] Recorded at 77° K. The *IS* values are relative to $BaSnO_3$. [b] Lit. [8] m.p. 118° C.

The different course of these reactions is probably due to different reaction mechanisms. However, the reaction catalyzed by organoantimony compounds is heterogeneous.

The presence of four acac-Me and of two acac-CH proton signals in the ^{1}H NMR spectra of the RSn(acac)$_2$X compounds in CDCl$_3$ at temperatures below —10°C reveal a *cis*-configuration for these compounds. At higher temperatures (0-40°C) broadening and collapse of the acac ring proton signals and of the methyl signals takes place, which is attributed to an intramolecular averaging process which is common for organotin 1,3-diketonates [22,23].

As a result of the *cis*-configuration the tin atom in the RSn(acac)$_2$X compounds is a chiral centre. Therefore, the methylene protons in compounds YCH$_2$Sn(acac)$_2$X (Y = e.g., I, CH=CH$_2$, COOEt) are diastereotopic. This is reflected in the observation that both the chemical shift and the tin—proton coupling constant for the methylene protons in these compounds are different (e.g. for ICH$_A$H$_B$Sn(acac)$_2$I at —60°C in CDCl$_3$: $\delta(H_A) = 2.66$, $\delta(H_B) = 2.90$ ppm; $J(Sn—CH_A) = 29$ cps, $J(Sn—CH_B) = 41$ cps). Diastereotopic non-equivalence of methylene protons in organotin compounds containing a hexacoordinate chiral tin centre has not been previously observed (for the NMR behaviour of organotin compounds containing a four-coordinate chiral tin centre, see ref. 25-27). The ^{1}H NMR spectra of the RSn(acac)$_2$X compounds will be discussed in greater detail in a separate paper.

Experimental

All reactions and subsequent manipulations were conducted under dry oxygen—free nitrogen unless otherwise stated. Solvents were dried and distilled under nitrogen prior to use. NMR spectra, which were run by Miss T. Volp, were recorded on a Varian Associates HA-100 NMR spectrometer. Elemental analyses were carried out under the supervision of W.J. Buis by the Section Elemental Analysis of our Institute. $(C_5H_5)_2Sn$ has been prepared by the reaction of SnCl$_2$ [29] with two equivalents of C$_5$H$_5$Na [31] and purified by sublimation using the apparatus described in ref. 30.

Tin(II) bis(acetylacetonate)

15 g (0.65 mol) of sodium was dissolved in 200 ml of methanol. To the resulting solution 67 ml (0.65 mol) of acetylacetone was added with stirring. The stirring was continued for a half hour and the solvent removed in vacuum. To the white powder obtained, 200 ml of THF was added, followed by a solution of 61 g (0.32 mol) of anhydrous tin dichloride [29] in 150 ml of THF. The mixture was stirred for 2 h, 150 ml of benzene was added, and the mixture stored overnight. The supernatant organic layer was decanted from the precipitate and fractionated. The yield of tin(II) bis(acetylacetonate) was about 60 g (60%); b.p. 105°C/0.1 mmHg (lit. [18] b.p. 101°C/0.15 mm); n_D^{20} 1.5775; d 1.49; m.p. 18°C; yellow viscous liquid. Mol. wt. 302 (calcd. 317) (Found: C, 28.2; H, 4.45; Sn, 37.25. C$_{10}$H$_{14}$O$_4$Sn calcd.: C, 37.90; H, 4.45; Sn, 37.45%).

Methyldicyclopentadienyltin(IV) iodide

1.3 ml (21 mmol) of methyl iodide was added to a solution of 2.38 g (9.6

mmol) of $(C_5H_5)_2Sn$ in 3.5 ml of benzene. The mixture was stirred at room temperature for 8 h with exposure to sunlight. (Alternatively the reaction mixture was irradiated with an incandescent lamp of about 300 W). Within half an hour a dark-red precipitate was formed, which dissolved within 8 h. After standing overnight, the reaction mixture was evaporated in vacuum (15 mmHg) leaving a pale yellow oil. The ^1H NMR spectrum ($CDCl_3$) revealed the presence of $Me(C_5H_5)_2SnI$ (about 90%) together with a little $Me(C_5H_5)SnI_2$ and $Me(C_5H_5)_3Sn$.

Reaction of dicyclopentadienyltin(II) with methyl iodide in the dark and in the light.

2.39 (9.6 mmol) of $(C_5H_5)_2Sn$ was dissolved in 3.5 ml of benzene to give a clear colourless solution, to which 1.3 ml (21 mmol) of MeI (freshly distilled under N_2) was added in the dark from a syringe.

(*a*) 0.6 ml of the above described reaction mixture was transferred by a syringe to an NMR tube (nitrogen atmosphere) and the tube kept in a water-bath of 45°C for 7 h in the dark. The ^1H NMR spectrum was taken, and showed only the peaks of the starting materials.

(*b*) 2.0 ml of the above reaction mixture was transferred by a syringe to a Pyrex tube (diameter 1.5 cm) under nitrogen. The Pyrex tube was placed in a glass beaker containing ice-water (temp. 0-5°C). The reaction mixture was irradiated for 3 h with an incandescent bulb (250 W/Philips 13352 E/44) with a distance of 14 cm between the reaction tube and the lamp, the mixture being stirred magnetically. Within 15 min a dark-red precipitate (of C_5H_5SnI) had been formed, but after 3 h this had disappeared. The ^1H NMR spectrum of the mixture confirmed the absence of $(C_5H_5)_2Sn$ and the presence of $Me(C_5H_5)_2SnI$, together with minor amounts of $Me(C_5H_5)SnI_2$ and $Me(C_5H_5)_3Sn$.

Reaction of dicyclopentadienyltin(II) with allyl bromide

1.0 ml (11.5 mmol) of allyl bromide was added to a solution of 0.90 g (3.6 mmol) of dicyclopentadienyltin(II) in 1.0 ml of benzene, and the mixture was heated at 70°C for 2 h. The mother liquor was taken off from the colourless crystals which had separated, and the crystals were washed with 1.0 ml of benzene and dried in vacuum, leaving 0.70 g (72%) of C_5H_5SnBr [14]. The mother liquor was evaporated to give a waxy product (0.50 g) which was shown by ^1H NMR spectroscopy to consist of a mixture of allylcyclopentadienyltin(IV) compounds.

Reaction of dicyclopentadienyltin(II) with benzyl chloride

0.52 ml (4.5 mmol) of benzyl chloride was added to a solution of 1.13 g (4.5 mmol) of $(C_5H_5)_2Sn$ in 1.5 ml of benzene. After three weeks at room temperature colourless crystals had separated. After filtration the crystals were washed with 1 ml of benzene and dried in vacuum leaving 0.3 g (1.4 mmol) of cyclopentadienyltin(II) chloride [14]. The ^1H NMR spectrum of the mother liquor showed the signals of unreacted dicyclopentadienyltin(II), benzyl chloride and 1- and 2-benzylcyclopentadiene, whereas signals which can be assigned to cyclopentadienyltin(IV) compounds or to 5-benzylcyclopentadiene were absent.

Reaction of dicyclopentadienyltin(II) with triphenylmethyl bromide

To a solution of 1.81 g (7.3 mmol) of $(C_5H_5)_2Sn$ in 10 ml of benzene cooled in ice-water a solution of 2.35 g (7.3 mmol) of triphenylmethyl bromide in 10 ml of benzene was added with stirring during one minute. A voluminous white precipitate was formed. Stirring was continued for one hour. After the precipitate had settled, the mother liquor was taken off. The precipitate was washed twice with 8 ml of pentane and dried in vacuum, leaving 1.90 g (98%) of a white powder identified as C_5H_5SnBr [14]. The mother liquor was evaporated, leaving 1.80 g of pale yellow solid, which was identified as a mixture of 1- and 2-(triphenylmethyl)cyclopentadiene by ^1H NMR spectroscopy.

Methyltin(IV) bis(acetylacetonate) iodide

Methyl iodide (1.0 ml, 16 mmol) was added to $Sn(acac)_2$ (1.0 ml, 4.7 mmol) in 1.0 ml of benzene. When exposed to sunlight the reaction is completed within some hours. Volatile material was removed in vacuum, leaving a crystalline solid, which was washed twice with 8 ml of pentane and dried in vacuum. Yield 1.9 g (88%) of $MeSn(acac)_2I$, (Lit. [8] 86%).

Propyltin(IV) bis(acetylacetonate) iodide was prepared by the same procedure in 85% yield.

Allyltin(IV) bis(acetylacetonate) bromide

1.0 ml (11.5 mmol) of allyl bromide was added to a solution of 1.0 ml (4.7 mmol) of $Sn(acac)_2$ in 1.0 ml of benzene. This mixture was heated at 70°C for 6 h. The mixture was evaporated in vacuum leaving a yellow oil. The crystals obtained upon addition of 5 ml of pentane were washed with another 4 ml of pentane. The product was dried in vacuum and stored under nitrogen. The yield of allyltin(IV) bis(acetylacetonate) bromide was 1.85 g (90%).

(Carbethoxy)methyltin(IV) bis(acetylacetonate) bromide

0.55 ml (4.9 mmol) of ethyl bromoacetate was added to a solution of 1.0 ml (4.7 mmol) of $Sn(acac)_2$ in 1.5 ml of benzene. The mixture was exposed to sunlight for 3 days, after which the NMR spectrum showed the absence of the starting compounds. The solvents were removed in vacuum, leaving a yellow oil which crystallized upon the addition of 8 ml of pentane. The white crystalline compound was washed twice with 9 ml of pentane and dried in vacuum. Yield 1.95 g (85%).

Iodomethyltin(IV) bis(acetylacetonate) iodide

Diiodomethane (2.0 ml, 25 mmol) was added to $Sn(acac)_2$ (2.0 ml, 9.4 mmol) in 4 ml of benzene. The reaction is complete within one day upon exposure to sunlight. The benzene was removed in vacuum. Addition of 10 ml of pentane to the oil thus obtained gave a pale yellow solid. The solid was washed five times with 10 ml of pentane to remove unreacted diiodomethane, and then dried in vacuum, to give 5.5 g (90%) of a white powder.

Benzyltin(IV) bis(acetylacetonate) bromide

Benzyl bromide (1.2 ml, 10 mmol) was added to $Sn(acac)_2$ (1.0 ml, 4.7 mmol) in 1.0 ml of benzene. The mixture was kept for three weeks with intermittent exposure to sunlight. The ^1H NMR spectrum showed the formation of the product in a yield of about 70%. The benzene was removed in vacuum and the viscous oil obtained was washed with four portions of 8 ml of pentane to remove the unreacted benzyl bromide and $Sn(acac)_2$. The viscous oil could not be crystallized even after storage under vacuum, its ^1H NMR spectrum showed it to consist of $PhCH_2Sn(acac)_2Br$ in more than 90% purity. Attempts to further purify the product by distillation in vacuum resulted in decomposition.

Triphenylmethyltin(IV) bis(acetylacetonate) bromide

$Sn(acac)_2$ (1.0 ml, 4.7 mmol) was added to a solution of 1.52 g (4.7 mmol) of triphenylmethyl bromide in 4 ml of benzene. The mixture became orange, and within one hour a crystalline product separated. The crystals were filtered off, washed twice with 1 ml of pentane, and dried in vacuum, leaving triphenylmethyltin(IV) bis(acetylacetonate) bromide (1.5 g, 50%). From the mother liquor a second crop of crystals was obtained.

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