New route to monoorganotin oxides and alkoxides from trialkynylorganotins

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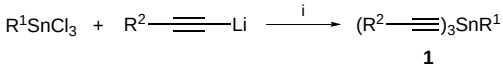
Functional monoorganotin oxides and alkoxides are synthesised in high yield by hydrolysis or alcoholysis of the corresponding trialkynylorganotins; the hydrolytic behaviour of trialkynylorganotins is the same as for trialkoxyorganotins.

Most metallic oxides can be prepared by the sol–gel process, the starting materials being usually metallo-organic compounds such as alkoxides.[1] Hydrolysis and condensation reactions of these precursors lead to the formation of a metal–oxo based macromolecular network. Generally, these sol–gel derived materials are subject to shrinkage and cracking upon solvent removal. Incorporation of organic phases, linked to the metal either by metal–oxygen–carbon or metal–carbon bonds, allows a strong improvement of the mechanical properties of the resulting hybrid materials.[2,3] These types of materials have been extensively studied with silicon,[3,4] which forms hydrolytically stable metal–carbon bonds. As tin affords such stable bonds, and changes its coordination number and oxidation state more readily than Si, organotin oxide derived hybrid materials should show interesting properties. So far, few tin based hybrids have been developed using functional organotin trialkoxides as precursors.[5] However, these precursors offer only a limited number of polymerizable or reactive organic functionalities.[5,6] Indeed, alkene-type double bonds could be introduced in the precursors but ester groups were found to be incompatible with both available methods of preparation of organotrialkoxytins. Reaction of ω-(alkoxycarbonylalkyl)trichlorotins with *tert*-amyl alcohol in the presence of diethylamine[7] did not lead to completion because the coordination of the metal by the functional group decreases its electrophilic properties. On the other hand, with sodium *tert*-amylate, intractable compounds were only obtained.[8]

Thus, other precursors, filling several requirements were sought for: they should be cleaved by water, prepared from conveniently obtained trichlorides and, finally, they should be as tolerant as possible towards functional groups. As alkynyltins are moisture sensitive compounds, alkynyl groups were thought to be good replacements for alkoxy groups. Actually, the hydrolysis of the tin–alkynyl bond is the reverse reaction of the useful access to alkynyltins by reaction of stannoxanes or alkoxyorganotins with terminal alkynes.[9]

Treatment[10] of functional trichloroorganotins[6] with 3 equiv. of hex-1-ynyllithium (Scheme 1) led to the corresponding alkyltrialkynyltins in good yields. They were stable enough to be manipulated in the air for short periods of time and to be purified by column chromatography on Florisil. Main results are presented in Table 1.



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Scheme 1 *Reagents and conditions*: i, toluene, −78 °C to room temp., 5 h; purification by chromatography on Florisil

Table 1 Preparation of trialkynylorganotins

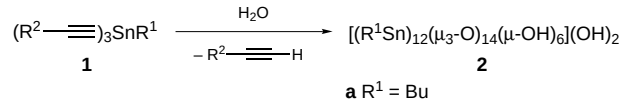
R^1	R^2	Yield (%)[a]
Me	Ph	71[b]
Bu	Me	83[b]
Bu	Bu	79[b]
Ph	Bu	75[b]
4-$(CH_2{=}CH)C_6H_4(CH_2)_4$	Bu	60[c]
$MeO_2C(CH_2)_2$	Bu	36
$AcO(CH_2)_3$	Bu	45
$AcO(CH_2)_5$	Bu	42
$MeCH{=}CHCO_2(CH_2)_5$	Bu	46

[a] Compounds **1** were isolated and fully characterised by ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy and mass spectrometry. [b] Chromatography was not necessary. [c] This compound was obtained by direct alkylation of a tetraalkynyltin.[11]

Upon hydrolysis (Scheme 2), either in chloroform with aqueous THF or in aqueous alcohols, tin–alkynyl bonds were cleaved and Sn–O–Sn bonds were formed. For alkyltrialkynyltins, $R^1Sn(C{\equiv}CR^2)_3$, solution ^{119}Sn NMR spectroscopy of the hydrolysed product showed two equally intense sharp signals at δ *ca.* −280 and −450, accompanied by two sets of satellites corresponding to ^2J(Sn–Sn) coupling constants of *ca.* 200 and 380 Hz.† These peaks are characteristic of the *closo* cluster $[(R^1Sn)_{12}(\mu_3O)_{14}(\mu_2OH)_6](OH)_2$,[12,13] where six tins are five-coordinate and six are six-coordinate. This compound was previously obtained from the hydrolysis of tris(isopropoxy)-butyltin.[13] Thus, as these trialkynylorganotins behave similarly to the corresponding trialkoxides, alkynyl groups appear to be the viable substitutes for alkoxy groups. Moreover, substitution of the alkynyl moiety by alkyl or aryl groups has no influence on the reaction as tris(phenylethynyl)-, tri(hex-1-ynyl)- and tri(prop-1-ynyl)-butyltins were hydrolyzed at about the same rate.

With 3-acetoxypropyl as substituent at the metal, a soluble oxo-polymer‡ in which all tin atoms are six-coordinate, a precursor of the corresponding organostannoic acid, was formed. The strong coordinating effect[14] of the functional group disfavors five-coordinate tin and formation of the corresponding *closo* cluster.

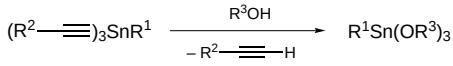
Reaction of trialkynylorganotins with alcohols was also studied (Scheme 3). To our knowledge, cleavage of [4-(ethenyloxy)but-1-ynyl]triethyltin with butanol giving butoxytriethyltin



1 **2**

a R^1 = Bu
b R^1 = 4-$(CH_2{=}CH)C_6H_4(CH_2)_4$
c R^1 = $AcO(CH_2)_5$
d R^1 = $MeCH{=}CHCO_2(CH_2)_5$

Scheme 2 *Reagents and conditions*: aqueous THF, 20 °C, 12 h



Scheme 3 *Reagents and conditions*: cyclohexane, 60 °C, 16 h; the compounds were purified by distillation

Table 2 Preparation of trialkoxyorganotins

	R^1	R^2	R^3	Yield (%)[a]
	Bu	Me	Bu^s	55
	Bu	Me	Bu^i	76
	Bu	Me	CH_2Ph	80
	Me	Ph	Bu^s	50
	Bu	Ph	Pr^i	59

was the only previous example of this reaction.[15] When primary or secondary alcohols were used, cleavage of alkynyl groups occurred readily upon moderate heating. Tertiary alcohols were not acidic enough to be useful. In this way, trialkoxymethyl- and trialkoxybutyl-tins[16] were prepared in good yields and results are presented in Table 2. The results show the higher reactivity of trialkynylorganotins compared to organosilanes. Indeed, Si–alkynyl bonds can be cleaved by alcohol molecules, but only at 80 °C and in the presence of F^- as catalyst.[17]

These results show that alkynyl derivatives of tin can be used instead of the corresponding alkoxides in sol–gel process and that these alkynyl derivatives are also good precursors of alkoxides. Moreover, these new precursors offer wide scope of opportunities for the introduction of a variety of organic functionalities inside tin oxide based hybrid materials.

Notes and References

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† ^{119}Sn NMR [74.6 MHz, $CDCl_3$, ^2J (^{119,117}Sn–^{119}Sn)/Hz] **2a** δ −282.2 (J 380, 177), −449.0 (J 380, 205); **2b** δ −280.0, −470.4 (unresolved satellites); **2c** δ −280.7 (J 373, 178), −443.7 (J 373, 207); **2d** δ −282.2, −449.0 (unresolved satellites).

‡ ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.0 (2 H, br). 1.9 (2 H, br), 2.0 (3 H, br), 4.1 (2 H, br); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 20.3, 21.6, 25.1, 67.8, 171.1; ^{119}Sn NMR (74.6 MHz, $CDCl_3$) δ −465 (0.5 Sn), −490 (0.5 Sn).

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