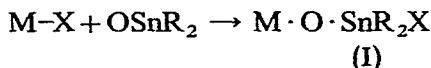


PRELIMINARY NOTE

Functionally substituted metallostanoxanes

It has recently been shown that organotin halides or carboxylates will react with dialkyltin oxides to give functionally substituted distannoxanes (I, $M = \text{Sn}$, $X = \text{halide or carboxylate}$)¹.



Similar reactions have now been established for derivatives of a number of other metals, leading to the formation of functionally substituted heterostannoxanes (I, $M = \text{Hg, Tl, Si, Ge, and Pb}$). All of these apparently represent new classes of compound.

Typical examples are shown in Table 1; some new distannoxanes are included for comparison. Satisfactory analyses have been obtained for all these compounds.

TABLE I

FUNCTIONALLY SUBSTITUTED METALLOSTANNOXANES

	Formula	M.p. (°C)	$\nu_{\max}(\text{MOSn}) (\text{cm}^{-1})$
II	$\text{PhHg} \cdot \text{O} \cdot \text{SnBu}_2\text{Cl}$	206–208	
III	$(\text{C}_6\text{F}_5)_2\text{Tl} \cdot \text{O} \cdot \text{SnBu}_2\text{Br}$	160 (dec.)	
IV	$\text{ClMe}_2\text{Si} \cdot \text{O} \cdot \text{SnBu}_2\text{Cl}$	38.5–40.5	1030
V	$(\text{AcO})\text{Me}_2\text{Si} \cdot \text{O} \cdot \text{SnBu}_2(\text{OAc})$	oil	1020
VI	$\text{ClPhMeSi} \cdot \text{O} \cdot \text{SnOct}_2\text{Cl}$	81–84	1020
VII	$\text{ClPhMeSi} \cdot \text{O} \cdot \text{SnPh}_2\text{Cl}$	oil	1030
VIII	$\text{Cl}_2\text{MeSi} \cdot \text{O} \cdot \text{SnMe}_2\text{Cl}$	180 (dec.)	1030
IX	$\text{ClMe}_2\text{Ge} \cdot \text{O} \cdot \text{SnBu}_2\text{Cl}$	ca. 25	875
X	$\text{Bu}_3\text{Sn} \cdot \text{O} \cdot \text{SnBu}_2\text{Br}$	140 (dec.)	670
XI	$\text{Bu}_3\text{Sn} \cdot \text{O} \cdot \text{SnBu}_2(\text{OAc})$	68–70	675
XII	$\text{Cl}_2\text{BuSn} \cdot \text{O} \cdot \text{SnMe}_2\text{Cl}$	92–94	
XIII	$\text{ClBu}_2\text{Pb} \cdot \text{O} \cdot \text{SnBu}_2\text{Cl}^a$	120–130 (dec.)	

^a Because dibutyllead dichloride is insoluble in benzene and toluene, this plumbostannoxane was prepared by heating the components in boiling tetrahydrofuran for 2 h.

The halide or carboxylate and dialkyltin oxide often reacted exothermically when they were mixed in benzene. The mixture was heated under reflux for 3–30 min until all the oxide dissolved; the solvent was then removed under reduced pressure and the metallostanoxane was recrystallised, often at low temperature.

The scope of the preparation is sometimes limited by the instability of the metallostanoxane (I) with respect to the metalloxane (MOM) and the halogenostannane (R_2SnX_2). For example, dibutyltin dichloride was isolated from the reaction between dibutyltin oxide and aluminium trichloride or silicon tetrachloride. 1,3-Dichloro-3,3-dibutyl-1,1-dimethyl-1-sila-3-stannoxane (IV) in boiling toluene decom-

posed in a few hours giving dimethylsiloxane and dibutyltin dichloride, and could not be synthesized from these components. It reacted rapidly with 9,10-phenanthroline in ethanol giving the siloxane and $\text{Bu}_2\text{SnCl}_2 \cdot \text{phen}$.

The metallostanoxanes were usually crystalline solids which were soluble in most common solvents, and often could be recrystallised from pentane, but the mercuristannoxane (II) dissolved only in hot toluene. In the infrared spectra they showed a very strong band associated with the asymmetric stretch of the $\text{M}-\text{O}-\text{Sn}$ group at a frequency some 50 cm^{-1} higher than that of the corresponding fully alkylated compounds². With the exception of the acetoxysilastannoxane (V) and the trichlorometallostanoxanes (*e.g.* VIII and XII), these spectra were unchanged when the compounds were exposed to the air for a few minutes.

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