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PRELIMINARY NOTE

Functionally substituted metallostannoxanes

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

$$\mathrm{M{-}X + OSnR_2 \rightarrow M\cdot O\cdot SnR_2X}$$
$$\text{(I)}$$

Similar reactions have now been established for derivatives of a number of other metals, leading to the formation of functionally substituted heterostannoxanes (I, M=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 1

FUNCTIONALLY SUBSTITUTED METALLOSTANNOXANES

	Formula	*M.p.* (°*C*)	ν_{max}(*MOSn*) (*cm*$^{-1}$)
II	$\mathrm{PhHg\cdot O\cdot SnBu_2Cl}$	206–208	
III	$\mathrm{(C_6F_5)_2Tl\cdot O\cdot SnBu_2Br}$	160 (dec.)	
IV	$\mathrm{ClMe_2Si\cdot O\cdot SnBu_2Cl}$	38.5–40.5	1030
V	$\mathrm{(AcO)Me_2Si\cdot O\cdot SnBu_2(OAc)}$	oil	1020
VI	$\mathrm{ClPhMeSi\cdot O\cdot SnOct_2Cl}$	81–84	1020
VII	$\mathrm{ClPhMeSi\cdot O\cdot SnPh_2Cl}$	oil	1030
VIII	$\mathrm{Cl_2MeSi\cdot O\cdot SnMe_2Cl}$	180 (dec.)	1030
IX	$\mathrm{ClMe_2Ge\cdot O\cdot SnBu_2Cl}$	*ca.* 25	875
X	$\mathrm{Bu_3Sn\cdot O\cdot SnBu_2Br}$	140 (dec.)	670
XI	$\mathrm{Bu_3Sn\cdot O\cdot SnBu_2(OAc)}$	68–70	675
XII	$\mathrm{Cl_2BuSn\cdot O\cdot SnMe_2Cl}$	92–94	
XIII	$\mathrm{ClBu_2Pb\cdot O\cdot SnBu_2Cl}$[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 metallostannoxane was recrystallised, often at low temperature.

The scope of the preparation is sometimes limited by the instability of the metallostannoxane (I) with respect to the metalloxane (MOM) and the halogenostannane ($\mathrm{R_2SnX_2}$). 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 decomposed 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 $Bu_2SnCl_2 \cdot$phen.

The metallostannoxanes 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 M–O–Sn group at a frequency some 50 cm^{-1} higher than that of the corresponding fully alkylated compounds[2]. With the exception of the acetoxysilastannoxane (V) and the trichlorometallostannoxanes (*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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