Synthesis of Organometallic Compounds containing Zn–Sn and Cd–Sn Bonds

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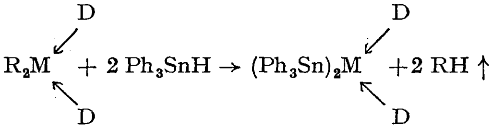
A CONSIDERABLE number of compounds containing tin bonded to a transition metal[1] or to a main-group metal of Group V (Sb, Bi)[2] or IV (Ge, Sn, Pb)[3] have been reported. However, only one analogue containing a Group IIB metal has been described. Reaction of $ZnCl_2$ with Ph_3SnK in liquid NH_3 followed by extraction with tetrahydrofuran (THF) has been reported to yield unsolvated $(Ph_3Sn)_2Zn$.[4]

It is well known that both organo-zinc and -cadmium derivatives are very susceptible to attack by protic species. Recently it has been established that reactions of organotin hydrides (in particular triaryltin hydrides) with appropriate substrates involve electrophilic attack of the organotin hydride hydrogen.[5] This suggested to us the synthesis of Zn–Sn and of Cd–Sn derivatives by a hydrostannolysis reaction.

The reaction of Et_2Zn or Me_2Cd with Ph_3SnH in pentane or benzene results in the deposition of metallic Zn or Cd (*cf.* the reaction[6] of Et_2Zn with Et_3SnH).

We have found that the metal–metal bonded compounds are obtained in excellent yields under mild conditions (—20°; conc. ~ 1 mmol./ml.) by carrying out the hydrostannolysis of R_2M in a solvating solvent (Et_2O, THF, DME) or by using a pre-formed co-ordination complex of R_2M (*e.g.*, with TMED or Bipy). In each case the relevant co-ordination complex is isolated:



$$R_2\overset{D}{\underset{D}{M}} + 2\,Ph_3SnH \rightarrow (Ph_3Sn)_2\overset{D}{\underset{D}{M}} + 2\,RH\uparrow \qquad (1)$$

(M = Zn, Cd)

Upon reaction of EtZnCl or MeCdCl (from equimolar amounts of Me_2Cd and $CdCl_2$ in Me_2SO) either in solvated form or as a pre-formed complex[7] with Ph_3SnH (—40°; conc. ~ 2 mmol./ml.) selective hydrostannolysis of the M–C bond occurs*

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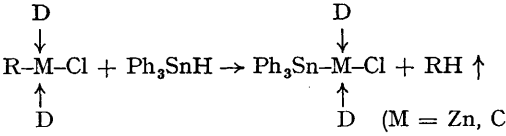
* The first reaction of this type was observed by Mr. J. Boersma.

yielding the corresponding stannylmetal chloride complex:



$$R\text{-}\underset{\underset{D}{\uparrow}}{\overset{\overset{D}{\downarrow}}{M}}\text{-}Cl + Ph_3SnH \rightarrow Ph_3Sn\text{-}\underset{\underset{D}{\uparrow}}{\overset{\overset{D}{\downarrow}}{M}}\text{-}Cl + RH\uparrow \quad (2)$$

(M = Zn, Cd)

Co-ordination saturation of M not only promotes reactions (1) and (2) as a result of the enhanced nucleophilicity of R (*cf.* ref. 8), but also contributes to the stability of the reaction products. Our attempts to remove THF from the THF complex of $(Ph_3Sn)_2Zn$ at 50°/10^{-3} mm. Hg resulted in gradual decomposition.

A number of representative complexes are listed in the Table.

TABLE

Some complexes containing Zn–Sn *and* Cd–Sn *bonds*[a]

	Yield (%)	M.p. (°c)
$(Ph_3Sn)_2Zn$,TMED[b]	84	172—174[5]
$(Ph_3Sn)_2Zn$,Bipy[c]	85	141—144[5]
$(Ph_3Sn)_2Zn$,DME[d]	48	103—104
$Ph_3SnZnCl$,TMED	87	158—159
$Ph_3SnZnCl$,DME	61	73—76
$(Ph_3Sn)_2Cd$,TMED	85	175 (dec.)
$(Ph_3Sn)_2Cd$,Bipy	87	154 (dec.)
$(Ph_3Sn)_2Cd$,DME	30	110 (dec.)
$Ph_3SnCdCl$,TMED	82	175 (dec.)

[a] All compounds gave satisfactory analytical data.
[b] TMED = *NNN'N'*-Tetramethylethylenediamine.
[c] Bipy = 2,2'-Bipyridyl.
[d] DME = Dimethoxyethane.

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