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Preliminary communication

Cyclopentadienyltin(II) halides. A novel type of divalent organotin compounds

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So far only a few true divalent organotin compounds are known, *viz.* dicyclopentadienyltin[1], its boron trifluoride complex[2], bis(methylcyclopentadienyl)tin[3] and bis(phenylbarenyl)tin[4]. The divalent character of these compounds has been confirmed by Mössbauer spectroscopy. Very recently the preparation of a dialkylstannylene–pentacarbonylchromium complex has been reported[5]. However, no conclusive Mössbauer data were presented.

We report here the synthesis of divalent organotin compounds of the type C_5H_5SnX ($X = Cl$, Br). Although such species have been occasionally suggested as intermediates[2,6,7] they have not been isolated as such.

Cyclopentadienyltin halides precipitate as white, crystalline solids upon mixing concentrated THF solutions of dicyclopentadienyltin and the tin dihalide.

$$\underset{(I)}{(C_5H_5)_2Sn} + SnX_2 \xrightarrow{THF} 2C_5H_5SnX_2 \downarrow$$

(IIa) $X = Cl$
(IIb) $X = Br$

Analytical and molecular weight data are given in Table 1.

TABLE I

ANALYTICAL AND MOLECULAR WEIGHT DATA FOR C_5H_5SnX

Compound *C_5H_5SnX*	*Analysis*[a] *Found (calcd.)*				*Mol. wt.*[b] *Found (calcd.)*	*M.p. (°C)*
	C	H	X	Sn		
X = Cl	27.10	2.24	16.27	53.7	217	130–133
	(27.39)	(2.30)	(16.17)	(54.1)	(219)	
X = Br	22.81	1.98	30.19	45.39	256	160–162
	(22.77)	(1.91)	(30.30)	(45.01)	(264)	

[a] The elemental analyses were carried out at the Micro-Analytical Department of our Institute.
[b] Ebulliometric in THF.

The ^{119m}Sn Mössbauer spectral parameters are given in Table 2.

TABLE 2

^{119m}Sn MOSSBAUER DATA[a]

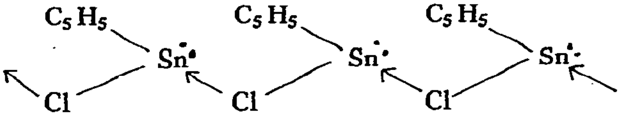
	IS ± 0.06 (mm/sec)	*QS ± 0.06 (mm/sec)*
C_5H_5SnCl	1.65	1.05
C_5H_5SnBr	1.64	0.99
$(C_5H_5)_2Sn$	1.66 (1.64)[b]	0.81 (0.86)[b]
$SnCl_2$	2.00 (2.07)[c]	0.56 (0)[c]
$SnBr_2$	1.88 (1.93)[c]	0 (0)[c]

[a] Recorded at 77°K. The *IS* values are relative to α-Sn at 77°K. [b] Ref. 2. [c] Ref. 8.

The Mössbauer data clearly show the compounds to be derivatives of divalent tin. Furthermore, it can be concluded from the spectra that the products contain only one kind of tin atom. Thus, in the solid state a complex such as $(C_5H_5)_2Sn{\cdot}SnX_2$ can be ruled out.

The mass spectrum of C_5H_5SnCl displays $C_5H_5Sn^+$ as the most abundant tin-containing fragment. The parent peak $[C_5H_5SnCl]^+$ has a relative intensity of 9.3 percent★.

The PMR spectra of IIa and IIb in THF show a singlet at $\delta \approx 6.05$ ppm. No ^{117,119}Sn–C–H coupling was observed. This can be explained by a rapid exchange of the cyclopentadienyl groups [*cf.*[2] $(C_5H_5)_2Sn$: $\delta = 5.89$ ppm, $J(^{117,119}Sn\text{–}C\text{–}^1H) = 15.5$ Hz].



(III)

For these cyclopentadienyltin(II) halides a structure such as III seems probable. This structure involves stabilization by intermolecular tin–halogen bridging, which precludes polymerization with formation of tin(IV) species containing metal–metal bonds (*cf.* ref. 9). The synthesis of other compounds of the type C_5H_5SnX in which X is a monoanionic ligand with pronounced donor properties would thus be of interest.

Our observation that C_5H_5SnCl can also be prepared by the reaction of I with anhydrous hydrochloric acid in THF suggests that the reaction of I with acidic compounds is generally applicable for the synthesis of C_5H_5SnX compounds★★. *E.g.*, the reaction of I

★For the mass spectrum of $(C_5H_5)_2Sn$, see ref. 2.

★★Reactions of $(C_5H_5)_2Sn$ with proton active species leading to inorganic tin(II) derivatives have been studied recently[10].

with phenol in THF gives rise to the formation of cyclopentadienyltin phenoxide, $C_5H_5SnOC_6H_5$.

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REFERENCES

1 E.O. Fischer and H. Grubert, *Z. Naturforsch. B,* 11 (1956) 423.
2 P.G. Harrison and J.J. Zuckerman, *J. Amer. Chem. Soc.*, 92 (1970) 2577.
3 L.D. Dave, D.F. Evans and G. Wilkinson, *J. Chem. Soc.*, (1959) 3684.
4 Yu. A. Aleksandrov, V.I. Bregadse, V.I. Goldanskii, L.J. Zakhardin, O.Yu. Okhlobystin and V.V. Khrapov, *Dokl. Akad. Nauk SSSR,* 165 (1965) 593.
5 T.J. Marks, *J. Amer. Chem. Soc.*, 93 (1971) 7090.
6 P.G. Harrison and J.J. Zuckerman, *J. Amer. Chem. Soc.*, 91 (1969) 6885.
7 F.J.A. des Tombe, *Ph. D. Thesis, University of Utrecht*, 1969.
8 J.D. Donaldson and D.G. Nicholson, *J. Chem. Soc. A*, (1970) 145.
9 M. Massol, J. Satgé, P. Rivière and J. Barrau, *J. Organometal. Chem.*, 22 (1970) 599.
10 P.G. Harrison, *J. Chem. Soc., Chem. Commun.*, in press.