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Preliminary communication

BIS[(TRIMETHYLSTANNYL)CYCLOPENTADIENYL] TIN(II), $(Me_3Sn^{IV}C_5H_4)_2Sn^{II}$: THE FIRST EXAMPLE OF A COMPOUND CONTAINING ORGANOTIN(II) AND ORGANOTIN(IV) IN ONE MOLECULE

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Summary

The reaction of $(C_5H_5)_2N$ with 2 mol equivalents of Me_3SnNEt_2 gives $(Me_3SnC_5H_4)_2Sn$, the first compound containing organotin(II) and organotin(IV) in one molecule.

Inorganic molecules containing tin atoms in two different valence states, viz. tin(II) and tin(IV), have been described [1]. We report below the synthesis and characterization of the first example of a compound containing organotin(II) and organotin(IV) moieties in one molecule, bis[(trimethylstannyl)cyclopentadienyl] tin(II).

$$(C_5H_5)_2Sn + 2\,Me_3SnEt_2 \rightarrow \underset{\text{(I)}}{(Me_3SnC_5H_4)_2Sn} + 2\,Et_2NH \qquad (1)$$

A solution of 2.98 g (0.012 mol) of dicyclopentadienyltin(II) and 5.69 g (0.024 mol) of trimethyl (diethylamino)tin in 5 ml of dry benzene was heated for 6 h at 70°C under dry, oxygen-free nitrogen. According to ^1H NMR spectrometry about 60% of the starting materials had been converted. Distillation gave 1.1 g (16%) of compound I, a slightly yellowish-green oily liquid, extremely sensitive to oxygen and moisture; b.p. 156—160°C/0.06 mmHg, n_D^{20} 1.631 (Found: C, 33.0; H, 4.7; Sn, 61.7. $Sn_3C_{16}H_{26}$ calcd.: C, 33.45; H, 4.56; Sn, 61.98%). Attempts to determine the molecular weight by vapour pressure osmometry in benzene failed because of the extreme air-sensitivity of the compound.

The ^1H NMR spectrum shows the methyltin resonance at δ (Me—Sn) 0.23 ppm; $J(^{117/119}Sn—Me)$ 53/55 Hz, whereas the cyclopentadienyl proton resonances consist of two unresolved multiplets at 5.6—5.9 Hz and 5.9—6.2 Hz (ratio 1/1). No spectral changes were observed over the temperature range —20 to +100°C.

The ^{119m}Sn Mössbauer data confirm the presence of tetravalent tin and divalent tin in the ratio 2/1 (cf. Table 1).

TABLE 1

^{119m}Sn MÖSSBAUER DATA RECORDED AT 77 K; *I.S.* VALUES RELATIVE TO SnO_2 AT ROOM TEMPERATURE

Compound	*I.S.* (mm/s)	*Q.S.* (mm/s)
I	1.30	0
	3.58	0.89
Me_4Sn	1.30	0
$(C_5H_5)_2Sn$	3.72	0.81

In the absence of crystallographic data (attempts to grow single crystals failed) no definite conclusions can be drawn about the structure and bonding of this unusual compound. Unsubstituted dicyclopentadienyltin(II) has an angular "sandwich" structure in the vapour phase, in which the rings are centrally σ- (pseudo π-)bonded [2]. The cyclopentadienyl ring in solid cyclopentadienyltin(II) chloride is bonded in the same way [3]. In contrast cyclopentadienyltin(IV) compounds possess a fluxional, σ-bonded diene-type ring, around which the metal atom migrates via 1,2- or 1,3-metallotropic shifts [4]. Whether both types of bonding are present in compound I remains to be established.

Preliminary attempts to introduce more than one trimethyltin group per cyclopentadiene ring in dicyclopentadienyltin(II) have been unsuccessful.

$$(C_5H_5)_2Sn + n\,Me_3SnNEt_2 \rightarrow [C_5H_{5-n}(SnMe_3)_n]_2Sn + n\ Et_2NH \qquad (2)$$
$$(n = 2, 3)$$

In addition to compound I substantial amounts of bis(trimethylstannyl)cyclopentadiene and tris(trimethylstannyl)cyclopentadiene are formed.

References

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