

Preliminary communication

$^{119\text{m}}\text{Sn}$ Mössbauer investigation of the reaction of dicyclopentadienyltin(II) with phenylmagnesium bromide

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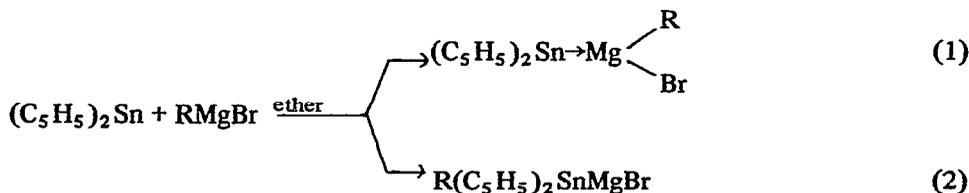
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Following studies on dicyclopentadienyltin(II)¹, which shows Lewis base activity in the formation of $(\text{C}_5\text{H}_5)_2\text{Sn} \rightarrow \text{BF}_3$ ², we sought to test the action of this stannylene compound on solutions of Grignard reagents. The two likely reaction pathways are the formation of a donor-acceptor adduct containing a coordinate tin(II) \rightarrow Mg bond, and carbenoid insertion into the magnesium-carbon bond which would result in the formation of a covalent tin(IV)-magnesium bond³:



Migration of R from magnesium to tin could convert the first product into the second.

These two structures can be easily distinguished by $^{119\text{m}}\text{Sn}$ Mössbauer spectroscopy, where the tin(II) adduct would be expected to exhibit an isomer shift (IS) greater than that of β -tin, while its tin(IV) isomer would be expected to have an IS smaller than that of β -tin^{3,4}.

The product of this reaction is in addition of interest in connection with the recent report of the reaction of triphenyltin hydride with Grignard reagents, where the product has been formulated as resulting from the 1,2-intermetallic shift of a phenyl group after hydrostannolysis of the magnesium-carbon bond⁵:

*An additional, although less likely, possibility is the formation of $\text{C}_5\text{H}_5\text{SnMgBr}$, containing a tin(II)-magnesium covalent bond with the release of RC_5H_5 .

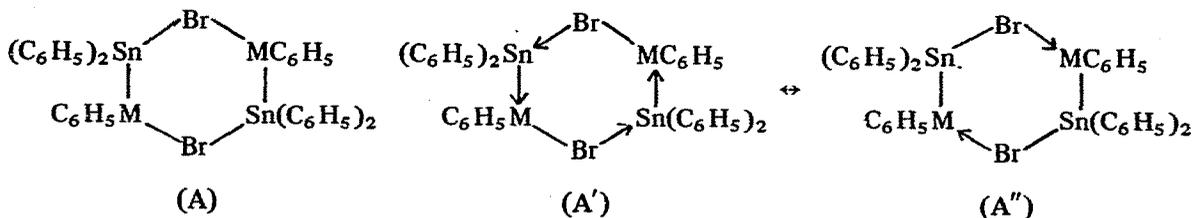
TABLE 1
 MÖSSBAUER DATA ^a

	IS ± 0.06 (mm/sec)	QS ± 0.12 (mm/sec)	I ^r
(C ₆ H ₅) ₃ SnMgBr (I)	1.52	—	1.53
C ₆ H ₅ (C ₅ H ₅) ₂ SnMgBr (II)	1.54	—	1.60
C ₆ H ₅ (CH ₃ C ₅ H ₄) ₂ SnMgBr (III)	1.56	—	1.65
(C ₆ H ₅) ₃ SnZnCl (IV)	1.56	—	1.49
(C ₆ H ₅) ₃ SnZnCl · TMED (V)	1.56	1.31	1.146 0.920

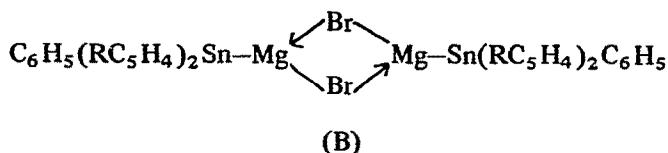
^a Recorded at 77°K vs. Ba^{119m}SnO₃ [New England Nuclear Corp.].

spectra in which prominent R₃Sn⁺ fragments appear, but the organotin magnesium and zinc compounds studied here are thermally cracked at 100° [thin-layer chromatography shows the formation of tetraphenyltin from both (I) and (IV)]. Thermal cracking at the temperatures required to volatilize these materials seems unavoidable, and evidence is at hand suggesting that thermal scrambling of groups occur readily. The mass spectrum of a mixture of tetraphenyltin, hexaphenylditin and ZnCl₂ · TMED at an inlet temperature of 160° shows fragments due to [(C₆H₅)₂SnCl]⁺ in the 310 region. It would, therefore, be unwise to draw conclusions concerning the presence of (C₆H₅)₃Sn-M moieties in the structures of (I) and (IV) from the observation of [(C₆H₅)₃Sn]⁺ fragments in the gas phase.

We conclude from the available data that a cyclic structure A (resonance structures A' and A'') with formally four-valent tin must be considered for (I) and (IV):



Compounds (II) and (III) which show chemical and Mössbauer behavior of the Sn^{IV} insertion products possibly occur as the bridged dimeric species (B).



EXPERIMENTAL SECTION

C₆H₅(RC₅H₄)₂SnMgBr. Phenylmagnesium bromide [freshly prepared from magnesium metal (0.3 g, 0.0125 g-atom) and bromobenzene (1.57 g, 0.01 mole) in ether (50 ml) and then filtered] was added slowly with stirring to bis(methylcyclopentadienyl)-

tin(II) (2.77 g, 0.01 mole) in ether (10 ml) at room temperature to precipitate a yellow solid (III) immediately which was filtered and dried *in vacuo* [m.p. 175° (decomp.)]. (Found: C, 47.6; H, 3.8%. $C_{18}H_{19}MgSnBr$ calcd.: C, 47.2; H, 4.2%) (II) was prepared similarly. (Found: C, 43.73; H, 3.88%. $C_{17}H_{17}MgSnBr$ calcd.: C, 44.67, H, 3.52%)

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