Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

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

P.G. HARRISON and J.J. ZUCKERMAN
Department of Chemistry, State University of New York at Albany, Albany, New York 12203 (U.S.A.)

J.G. NOLTES
Institute for Organic Chemistry, TNO, Utrecht (The Netherlands)

(Received February 22nd, 1971; in revised form June 15th, 1971)

Following studies on dicyclopentadienyltin(II)[1], which shows Lewis base activity in the formation of $(C_5H_5)_2Sn \rightarrow BF_3$[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)→Mg bond, and carbenoid insertion into the magnesium–carbon bond which would result in the formation of a covalent tin(IV)–magnesium bond★:

$$(C_5H_5)_2Sn + RMgBr \xrightarrow{\text{ether}} (C_5H_5)_2Sn{\rightarrow}Mg(R)(Br) \quad (1)$$

$$(C_5H_5)_2Sn + RMgBr \xrightarrow{\text{ether}} R(C_5H_5)_2SnMgBr \quad (2)$$

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

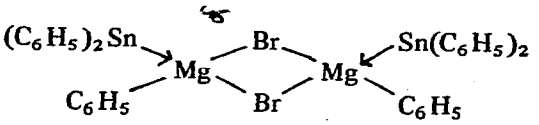
These two structures can be easily distinguished by ^{119m}Sn Mössbauer spectroscopy, where the tin(II) adduct would be expected to exhibit an isomer shift (IS) greater than that of β-tin, while its tin(IV) isomer would be expected to have an IS smaller than that of β-tin[3,4].

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 bond[5]:

★An additional, although less likely, possibility is the formation of $C_5H_5SnMgBr$, containing a tin(II)–magnesium covalent bond with the release of RC_5H_5.

$$(C_6H_5)_3SnH + RMgBr \cdot N(C_2H_5)_3 \xrightarrow{-RH} (C_6H_5)_3SnMgBr \cdot N(C_2H_5)_3 \longrightarrow$$

$$\xrightarrow{-N(C_2H_5)_3} \quad \text{(I)} \qquad (3)$$



Diphenylstannylene would seem to be stabilized in this species by complexation with the magnesium. Indeed, the product behaves as a phenylmagnesium species (formation of benzene upon hydrolysis; formation of tetraphenyltin upon reaction with triphenyltin chloride; and formation of trimethylphenyltin upon reaction with trimethyltin chloride) and acts as a source of diphenyltin groups in reactions with methyl iodide to yield diphenylmethyltin iodide, and with dicobalt octacarbonyl to yield the diphenyltin insertion product[5] The analogous triphenyltinzinc chloride similarly behaves as a phenylzinc species and also serves as a source of diphenylstannylene[6]. The action of dicyclopentadienyltin(II) could result in species such as these directly, without going through the intermetallic migration of the organic group.

The addition of dicyclopentadienyltin(II) or bis(methylcyclopentadienyl)tin(II) to phenylmagnesium bromide in ether results in the immediate precipitation of a yellow solid whose microanalytical data agree with the formulation:

$$(RC_5H_4)_2Sn + C_6H_5MgBr \rightarrow C_6H_5(RC_5H_4)_2SnMgBr \qquad (4)$$

(II, R = H; III, R = CH_3)

The products proved too insoluble for molecular weight determination. (II) fails to give either benzene (GLC) or Sn–H species (IR) after 24 h. in pentane/water at room temperature, conditions under which (I) gives benzene, but benzene is produced in 30% yield in *m*-xylene/water at 100° for 12 h. (II) also fails to give trimethylphenyltin after treatment with trimethyltin chloride in pentane at 35° for 6 h, conditions under which (I) gives trimethylphenyltin or tetraphenyltin with triphenyltin chloride. Reaction of (II) with trimethyltin chloride in *m*-xylene at 100° for 22 h gives trimethylphenyltin in 1–3% yield. These results show that (II) is not a phenylating agent, suggesting that the product of the reaction between dicyclopentadienyltin(II) and the Grignard reagent is not the adduct. The ^{119m}Sn Mössbauer spectra of (II) and (III) contain sharp singlet resonances well below that for β-tin, thereby ruling out a structure containing tin as tin(II). The mass spectrum of (III) lacks a parent ion, but displays a prominent $C_6H_5(CH_3C_5H_4)_2Sn^+$ peak and three tin-containing fragments of higher mass than the monomer.

In order to investigate the nature of (I) and the analogous zinc species[6,7] (IV) and (V) whose formulae are found in Table 1, further, we have recorded their mass and Mössbauer spectra. The Mössbauer data appear in Table 1. All the IS values listed are in the region associated with organotin(IV) compounds[3,4], and are within experimental error of one another. The spectrum of a rapidly frozen solution of (I) in benzene at 77°K is qualitatively the same as for the neat solid. All the compounds studied give rise to mass

TABLE 1

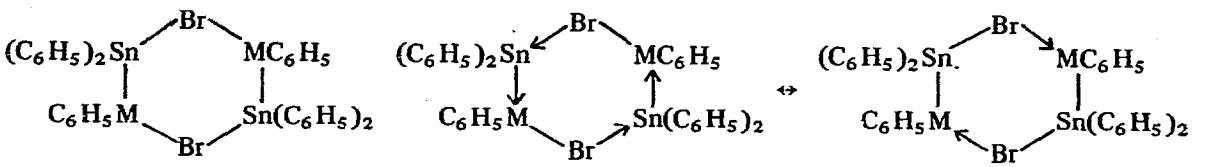
MÖSSBAUER DATA[a]

	IS ± 0.06 (mm/sec)	QS ± 0.12 (mm/sec)	Γ
$(C_6H_5)_3SnMgBr$ (I)	1.52	–	1.53
$C_6H_5(C_5H_5)_2SnMgBr$ (II)	1.54	–	1.60
$C_6H_5(CH_3C_5H_4)_2SnMgBr$ (III)	1.56	–	1.65
$(C_6H_5)_3SnZnCl$ (IV)	1.56	–	1.49
$(C_6H_5)_3SnZnCl \cdot TMED$ (V)	1.56	1.31	1.146
			0.920

[a] Recorded at 77°K *vs.* $Ba^{119m}SnO_3$ [New England Nuclear Corp.].

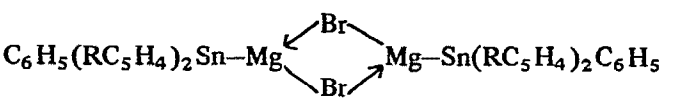
spectra in which prominent R_3Sn^+ fragments appear, but the organotin magnesium and zinc compounds studied here are thermally cracked at 100° [thin-layer chromatography shows the formation of tetraphenyltin from both (I) and (IV)]. Thermal cracking at the temperatures required to volatilize these materials 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 $ZnCl_2 \cdot TMED$ at an inlet temperature of 160° shows fragments due to $[(C_6H_5)_2SnCl]^+$ in the 310 region. It would, therefore, be unwise to draw conclusions concerning the presence of $(C_6H_5)_3Sn$–M moieties in the structures of (I) and (IV) from the observation of $[(C_6H_5)_3Sn]^+$ 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):



(A) (A′) (A″)

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



(B)

EXPERIMENTAL SECTION

$C_6H_5(RC_5H_4)_2SnMgBr$. 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%)

ACKNOWLEDGEMENT

This work is supported by the National Science Foundation (U.S.) under Grant GP-16544. (P.G.H. and J.J.Z.) and by the International Tin Research Council, London (J.G.N.).

REFERENCES

1 P.G. Harrison and J.J. Zuckerman, *J. Amer. Chem. Soc.*, 91 (1969) 6885.
2 P.G. Harrison and J.J. Zuckerman, *J. Amer. Chem. Soc.*, 92 (1970) 2577.
3 J.J. Zuckerman in I.J. Gruverman (Ed.), *Mössbauer Effect Methodology, Vol. 3*, Plenum Press, New York, 1967, p. 15.
4 J.J. Zuckerman, *Advan. Organometal. Chem.*, 9 (1971) 21.
5 H.M.J.C. Creemers, J.G. Noltes and G.J.M. van der Kerk, *J. Organometal. Chem.*, 14 (1968) 217.
6 F.J.A. Des Tombe, G.J.M. van der Kerk and J.G. Noltes, *J. Organometal. Chem.*, 13 (1968) P9.
7 F.J.A. Des Tombe, G.J.M. van der Kerk, H.M.J.C. Creemers and J.G. Noltes, *Chem. Commun.*, (1966) 914.