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

PRELIMINARY COMMUNICATION

1,2-INTERMETALLIC SHIFTS OF ORGANIC GROUPS IN REACTIONS OF ORGANOTIN CHLORIDES WITH METALLIC ZINC

F.J.A. DES TOMBE,
Laboratory for Organic Chemistry, State University, Utrecht (The Netherlands)
G.J.M. VAN DER KERK and J.G. NOLTES
Institute of Organic Chemistry TNO, Utrecht (The Netherlands)

(Received May 24th, 1968)

Alkyltinzinc halides have recently been proposed as intermediates in the reaction of alkyltin chlorides with metallic zinc in triethylamine solution[1]. This communication reports some results of our study of the chemistry of organotinzinc derivatives.

In the presence of the strongly chelating agents TMED[*] and Bipy[**] Ph_3SnCl reacts with zinc–copper couple (prepared according to Le Goff[2]) in refluxing THF with formation of Ph_6Sn_2 (isolated in 60–80% yield):

$$2\ Ph_3SnCl + Zn/Cu \xrightarrow[TMED]{THF} Ph_3Sn{-}SnPh_3 + ZnCl_2 \cdot TMED \qquad (1)$$

However, in the absence of TMED or Bipy the products of this reaction are Ph_4Sn (isolated in 75–98% yield) and metallic tin:

$$4\ Ph_3SnCl + 2\ Zn/Cu \xrightarrow{THF} 3\ Ph_4Sn + Sn + 2\ ZnCl_2 \qquad (2)$$

The latter reaction if carried out in the presence of proton donors (*e.g.* MeOH, H_2O) affords benzene (90% yield as shown by GLC) and metallic tin:

$$Ph_3SnCl + Zn/Cu \xrightarrow[MeOH]{THF} 3\ C_6H_6 + Sn + ClZnOMe \qquad (3)$$

These different results may be explained by taking into account the influence of appropriate coordinating ligands on the chemical reactivity of $Ph_3SnZnCl$, the primary intermediate in reactions 1–3.

In an earlier communication we have reported the synthesis of the complex

---

[*] *N,N,N′,N′*-Tetramethylethylenediamine
[**] 2,2′-Bipyridyl

$Ph_3SnZnCl \cdot TMED$[3]. This complex forms $Ph_3Sn{-}SnPh_3$ upon reaction with Ph_3SnCl in THF, Ph_4Sn being formed in trace amounts only:

$$Ph_3SnZnCl \cdot TMED + Ph_3SnCl \xrightarrow{\text{THF}} Ph_3Sn{-}SnPh_3 + ZnCl_2 \cdot TMED$$

Uncomplexed $Ph_3SnZnCl$ has been obtained by the reaction of EtZnCl with Ph_3SnH in Et_2O followed by removal of Et_2O at 80° for 6 h at 10^{-4} mm as a yellow-coloured solid (Found: H, 3,43; Cl, 7,96; Sn, 26,7; Zn, 14,8%. Calcd. for $C_{18}H_{15}ClSnZn$, m.w. 450.9: H, 3,58; Cl, 7,86; Sn, 26,33; Zn, 14,50%) which decomposes at ~ 100°. In boiling benzene dimeric association is observed (Found: m.w. 873. Calcd. for dimer: m.w. 901.8).

Contrary to the TMED complex this compound affords exclusively Ph_4Sn (isolated in 88% yield) upon reaction with Ph_3SnCl. Benzene is formed upon reaction with methanol or water (THF solution):

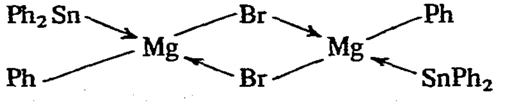
$$Ph_3SnZnCl + Ph_3SnCl \xrightarrow{\text{THF}} Ph_4Sn + [Ph_2Sn] \tag{4}$$

$$Ph_3SnZnCl \xrightarrow[\text{MeOH or } H_2O]{\text{THF}} C_6H_6 + [Ph_2Sn] \tag{5}$$

$Ph_3SnZnCl$ prepared *in situ* by hydrostannolysis of EtZnCl with Ph_3SnH in THF solution affords the same products with Ph_3SnCl, MeOH or H_2O.

The formation of $[Ph_2Sn]$ in these reactions has been confirmed by the formation of Ph_2SnMe_2 upon reaction with I_2 [after removal of Ph_4Sn by filtration (4) and removal of volatiles (5)], followed by reaction with MeMgI in Et_2O. The resulting mixture of phenylmethyltins was analyzed using NMR spectroscopy. *E.g.* treatment in this way of $[Ph_2Sn]$ formed in reaction (4) afforded $PhSnMe_3$ [$\delta(CH_3)$ 0.27 ppm], Ph_2SnMe_2 [$\delta(CH_3)$ 0.47 ppm] and $PhSnMe_3$ [$\delta(CH_3)$, 0.67 ppm, *cf.* ref. 4] in 13.0, 70.5 and 16.5% yield, respectively.

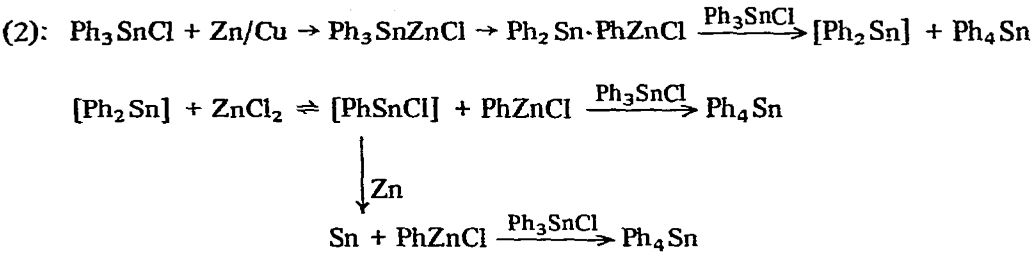
The nature of the products formed in the reactions of preformed $Ph_3SnZnCl \cdot TMED$ and *in situ* formed $Ph_3SnZnCl$ in THF suggests that in the latter compound a phenyl group has migrated from tin to zinc fully analogous to the recently reported 1,2-phenyl shift from tin to magnesium occurring upon removal of the complexing ligand from the Et_3N- or Et_2O-complex of $Ph_3SnMgBr$[5]. The latter unsolvated complex has been formulated as [5]:



However, the similarity of the phenyl NMR patterns of dimeric[6] Ph_3Al (which contains bridging phenyl groups[7]) in C_6D_6 and of $Ph_3SnZnCl$ in THF on one hand, and of monomeric[6] $Ph_3Al \cdot Et_2O$ in C_6D_6 and of $Ph_3SnZnCl \cdot TMED$ in THF on the other hand might be taken to indicate that a bridging rather than a fully transferred phenyl group is present in $Ph_3SnZnCl$ dissolved in THF. Recent NMR spectroscopic studies show that phenyl groups may act as highly effective bridges between aluminium atoms[8]. As evidenced by the formation of Ph_4Sn (4) and benzene (5) complete migration of the phenyl group from tin to zinc must have occurred in these reactions.

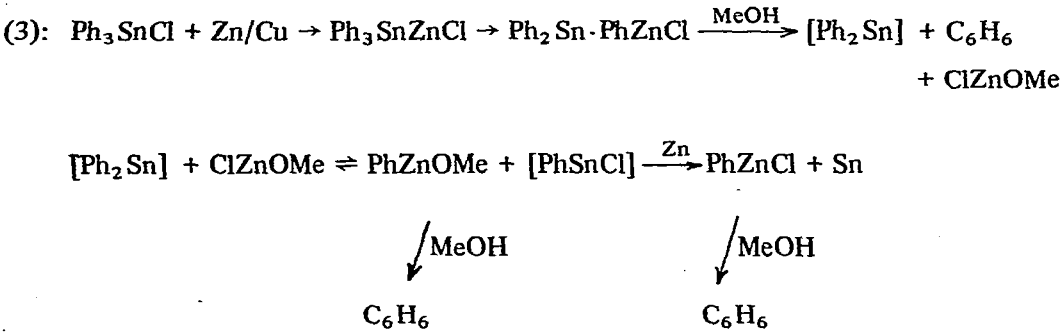
Upon addition of TMED to a solution of yellow-coloured $\mathrm{Ph_3SnZnCl}$ in THF very slow conversion (6–8 days) into white $\mathrm{Ph_3SnZnCl \cdot TMED}$ occurs. Subsequent reaction with $\mathrm{Ph_3SnCl}$ again affords exclusively $\mathrm{Ph_3Sn{-}SnPh_3}$. Apparently, phenyl groups are again bound to tin exclusively, the TMED ligand occupying the vacant coordination positions of the zinc atom.

The products isolated in reactions (2) and (3) can now be accounted for as follows:



$$(2):\ \mathrm{Ph_3SnCl + Zn/Cu \rightarrow Ph_3SnZnCl \rightarrow Ph_2Sn{\cdot}PhZnCl \xrightarrow{Ph_3SnCl} [Ph_2Sn] + Ph_4Sn}$$

$$\begin{tikzcd} \mathrm{\lbrack Ph_2Sn\rbrack + ZnCl_2 \rightleftharpoons} & \mathrm{\lbrack PhSnCl\rbrack} \arrow[d, "\mathrm{Zn}"] & \mathrm{+\ PhZnCl \xrightarrow{Ph_3SnCl} Ph_4Sn} \\ & \mathrm{Sn + PhZnCl \xrightarrow{Ph_3SnCl} Ph_4Sn} & \end{tikzcd}$$



$$(3):\ \mathrm{Ph_3SnCl + Zn/Cu \rightarrow Ph_3SnZnCl \rightarrow Ph_2Sn{\cdot}PhZnCl \xrightarrow{MeOH} [Ph_2Sn] + C_6H_6 + ClZnOMe}$$

$$\begin{tikzcd} \mathrm{\lbrack Ph_2Sn\rbrack + ClZnOMe \rightleftharpoons} & \mathrm{PhZnOMe} \arrow[d, "\mathrm{MeOH}"] & \mathrm{+\ \lbrack PhSnCl\rbrack \xrightarrow{Zn}} & \mathrm{PhZnCl} \arrow[d, "\mathrm{MeOH}"] & \mathrm{+\ Sn} \\ & \mathrm{C_6H_6} & & \mathrm{C_6H_6} & \end{tikzcd}$$

The reaction of $\mathrm{PhSnCl_3}$ or $\mathrm{Ph_2SnCl_2}$ with Zn/Cu in THF at 20° for several days, likewise, affords $\mathrm{Ph_4Sn}$. $\mathrm{Ph_3SnCl}$ is an intermediate as shown by thin layer chromatography. If Zn in stead of Zn/Cu is used $\mathrm{Ph_3SnCl}$ is the final product. Apparently in all these reactions 1,2-phenyl shifts take place from tin to zinc in intermediately-formed organotin–zinc derivatives.

The reaction of $\mathrm{Me_3SnCl}$ with Zn/Cu in refluxing THF affords $\mathrm{Me_4Sn}$ (isolated in 90% yield) and Sn. In the presence of methanol methane is formed quantitatively:

$$\mathrm{4\ Me_3SnCl + Zn/Cu \xrightarrow{THF} 3\ Me_4Sn + Sn + 2\ ZnCl_2} \tag{6}$$

$$\mathrm{Me_3SnCl + Zn/Cu \xrightarrow[MeOH]{THF} 3\ CH_4 + Sn + ZnCl_2} \tag{7}$$

The occurrence of 1,2-methyl shifts may account for the formation of these products. Strongly chelating agents do influence the product composition, although not as markedly as for the reaction of $\mathrm{Ph_3SnCl}$ with Zn/Cu. The presence of TMED and Bipy resulted in a $\mathrm{Me_4Sn/Me_6Sn_2}$ ratio of 15 and 0.7 respectively.

REFERENCES

1 K. Sisido and S. Kozima, *J. Organometal. Chem.*, 11 (1968) 503.
2 E. Le Goff, *J. Org. Chem.*, 29 (1964) 2048.
3 F.J.A. Des Tombe, G.J.M. van der Kerk, H.M.J.C. Creemers and J.G. Noltes, *Chem. Commun.*, (1966) 914.
4 M.R. Kula, E. Amberger and K.K. Mayer, *Chem. Ber.*, 98 (1965) 634.
5 H.M.J.C. Creemers, J.G. Noltes and G.J.M. van der Kerk, *J. Organometal. Chem.*, in the press.
6 T. Mole, *Austral. J. Chem.*, 16 (1963) 794.
7 J.F. Malone and W.S. McDonald, *Chem. Commun.*, (1967) 444.
8 E. Jeffery, T. Mole and J.K. Saunders, *Chem. Commun.*, (1967) 696; *Austr. J. Chem.*, 21 (1968) 137.