# Metathetical Reactions of Organotin Compounds; their Use in Amination

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WE have previously shown that organotin–nitrogen compounds, such as $Me_3Sn \cdot NMe_2$, are compounds of exceptional reactivity (comparable to Grignard reagents[1]), as exemplified by their reactions with (i) unsaturated substrates,[2] and (ii) protic species.[3]

We now report an extensive range of metathetical reactions (iii), which substantially increases their synthetic potential.

$$R_3Sn \cdot NMe_2 + X–A \rightarrow R_3Sn \cdot X + Me_2NA$$
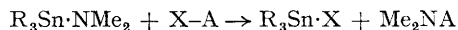
A *selection* of some reactions of $Me_3Sn \cdot NMe_2$, which follow this pattern, is shown in the Table; all the products have been characterised. A typical procedure was as follows. Boron trifluoride–diethyl ether complex (1·46 g.) in diethyl ether (10 ml.) was added slowly to dimethylamino-trimethylstannane (6·24 g.) in the same solvent

(10 ml.) at 20°. The reaction was violent and Me_3SnF (4·70 g.) was precipitated; the filtrate yielded $B(NMe_2)_3$ (1·32 g.).

The amination reactions owe their facility to the high donor strength of $R_3Sn \cdot NMe_2$, the weak and polar Sn–N bond, and the large values for the heats of formation of organotin products such as Me_3SnF. On the same basis, we have used $Me_3Sn \cdot PPh_2$ to prepare $As(PPh_2)_3$ (75%) and $Ph_2B \cdot PPh_2$ (75%), from AsF_3 and $Ph_2B \cdot SBu^n$, respectively. It is probable, therefore, that organotin compounds of general formula R_3SnY may frequently serve as intermediates for transfer of a moiety Y *via* Sn to another electrophilic site.

Related reactions, using Me_3SiY, have been widely investigated.[4] However, the tin compounds are several orders of magnitude more reactive.

For example, $Me_3Si \cdot NMe_2$ does not react with $CFCl{=}CF_2$, Me_3SnCl, or $BF_3 \cdot OEt_2$ (except to form the complex $BF_3 \cdot Me_3SiNMe_2$), whilst it may itself be readily obtained from Me_3SiCl and $Me_3Sn \cdot NMe_2$.

TABLE

Reagent	Product	(Yield %)	Reagent	Product	(Yield %)
$\frac{1}{3}BF_3 \cdot OEt_2$	$\frac{1}{3}B(NMe_2)_3$	(92)	$(OC)_5MnBr$	$(OC)_5Mn \cdot NMe_2$*	(78)
$CFCl{=}CF_2$	$CFCl{=}C(F)NMe_2$*	(69)	$(Et_3Al)_2$	$(Et_2Al \cdot NMe_2)_2$	(50)
C_6F_6	$C_6F_5NMe_2$†	(45)	Bu^n_3B	$Bu^n_2B \cdot NMe_2$	(86)
$HN(CF_3)_2$	$CF_3 \cdot NH \cdot CF_2NMe_2$*	(92)‡	Ph_3B	$Ph_2B \cdot NMe_2$	(59)
$\frac{1}{3}PF_3$	$\frac{1}{3}P(NMe_2)_3$	(~69)	$MeCO_2Et$	$MeCO \cdot NMe_2$	(65)
$\frac{1}{3}AsF_3$	$\frac{1}{3}As(NMe_2)_3$	(42)	$\frac{1}{2}CH_2(CO_2Et)_2$	$\frac{1}{2}CH_2(CO \cdot NMe_2)_2$	(79)
$\frac{1}{3}SbF_3$	$\frac{1}{3}Sb(NMe_2)_3$	(60)	$MeCOCH_2CO_2Et$	$MeCO \cdot CH_2 \cdot CO \cdot NMe_2$*	(82)
$\frac{1}{4}TiF_4$	$\frac{1}{4}Ti(NMe_2)_4$	(75)	$(EtO_2C)_2C{=}C(CO_2Et)_2$	$(EtO_2C)_2C{=}C\begin{smallmatrix}{}_{CO_2Et*}\\{}_{CO \cdot NMe_2}\end{smallmatrix}$	(95)
BCl_3	$Me_2N \cdot BCl_2$	(81)			
Me_3SiCl	$Me_3Si \cdot NMe_2$	(95)	$\frac{1}{4}(EtO_2C)_2C{=}C(CO_2Et)_2$	$\frac{1}{4}(Me_2N \cdot OC)_2C{=}C(CO \cdot NMe_2)_2$*	(96)
Cl_2	$ClNMe_2$	(88)	$Ph_2B \cdot OMe$	$Ph_2B \cdot NMe_2$	(97)
			$\frac{1}{3}B(OMe)_3$	$\frac{1}{3}B(NMe_2)_3$	(99)
			$\frac{1}{2}(MeCO)_2O$	$MeCO \cdot NMe_2$	(84)

* New compound
† Only in this instance was gentle reflux required
‡ Calculated from yield of Me_3SnF

[1] K. Jones and M. F. Lappert, *Organometallic Chem. Rev.*, 1966, **1**, 67.
[2] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1962, 358; T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 1965, 2157.
[3] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1964, 22; *J. Organometallic Chem.*, 1965, **3**, 295.
[4] E. W. Abel and D. A. Armitage, *J. Organometallic Chem.*, 1966, **5**, 326, and earlier references cited therein.