J. Chem. Soc. (A), 1969

## Amido Derivatives of Metals and Metalloids. Part VIII.<sup>1</sup> Metathetical Reactions of Organostannanes; Their Use in Amination

By T. A. George and M. F. Lappert,\* The Chemical Laboratory, University of Sussex, Brighton BN1 9QJ

Aminostannanes are shown to be effective aminating agents for a wide variety of substrates, via a metathetical ligand-exchange reaction. Thus, fluorine can be substituted in hexafluorobenzene, chlorotrifluoroethylene, bistrifluoromethylamine, trifluoroborane-ether, trifluoro-phosphine, -arsine, and -stibine, and titanium tetrafluoride; and chlorine in trichloroborane, chlorotrimethylsilane, and molecular chlorine, by an amino-group with concomitant formation of the organotin halide. Similarly, hydrogen (attached to boron) is displaced from triethylamine-borane; and butyl, phenyl, and ethyl groups are displaced from tributylborane, triphenylborane, and triethylalane. Methoxyand ethoxy-groups are displaced from trimethoxyborane, diphenylmethoxyborane, and some carboxylic esters; and acetate can also be replaced. Phosphinostannanes undergo similar reactions, as demonstrated by the exchange of diphenylphosphino- and butylthio-ligands.

It is suggested that these amination reactions owe their facility to the high donor strength of R<sub>3</sub>SnNMe<sub>2</sub> and the weak and polar Sn-N bond. In the cases where pseudo-ionic products are formed, e.g., R<sub>3</sub>SnF, the large values for their heats of formation are considered to be important.

EARLIER in this series we have dealt with the preparation and characterization of aminostannanes, stannylamines, and stannazanes,<sup>2</sup> aminostannylation of unsaturated substrates,<sup>3</sup> and reactions of aminostannanes with protic species.<sup>4</sup> This paper describes a wide range of substitution reactions [equation (1); where LM-X is a derivative of the metal, metalloid, or non-metal M; X is a group such as F, Cl, Br, OR<sup>2</sup>, OAc, R<sup>2</sup>, or Ph; L represents the sum of the ligands other than X attached to M; and Y is NMe<sub>2</sub> or PPh<sub>2</sub>]. A preliminary report of some of

<sup>1</sup> Part VII, T. A. George and M. F. Lappert, J. Organometallic Chem., 1968, 14, 327.

<sup>a</sup> K. Jones and M. F. Lappert, J. Chem. Soc., 1965, 1944. <sup>a</sup> T. A. George, K. Jones, and M. F. Lappert, J. Chem. Soc., 1965, 2157.
 <sup>4</sup> K. Jones and M. F. Lappert, J. Organometallic Chem., 1965,

295.
 T. A. George and M. F. Lappert, Chem. Comm., 1966, 463.

these reactions has been published.<sup>5</sup> The new reactions are summarised in equations (2)—(23). The  $Me_2N/OR$ and Me<sub>2</sub>N/OCOMe exchange reactions [equations (19)— (23)] will not be discussed further (but see Part X, which is concerned with  $LM \cdot NR_2 / > C=O$  and  $LM \cdot NR_2 / > S=O$  systems).

$$R_3Sn-Y + LM-X \longrightarrow R_3Sn-X + LM-Y \qquad (1)$$

$$Me_3Sn \cdot NMe_2 + C_6F_6 \longrightarrow Me_3SnF + C_6F_5NMe_2$$
 (2)

 $Me_3Sn \cdot NMe_2 + CF_2 = CFCl \longrightarrow Me_SnF$ 

$$Me_3SnF + CFNMe_2 = CFCl$$
 (3)

$$\frac{\text{Me}_{3}\text{Sn}\cdot\text{NMe}_{2} + (\text{CF}_{3})_{2}\text{NH} \longrightarrow}{\text{Me}_{3}\text{SnF} + [(\text{Me}_{2}\text{N}\cdot\text{CF}_{2})\text{NH}(\text{CF}_{3})?]}$$
(4)

$$3Me_{3}Sn \cdot NMe_{2} + BF_{3},OEt_{2} \longrightarrow 3Me_{3}SnF + B(NMe_{2})_{3} + OEt_{2} \quad (5)$$

$3Me_3Sn \cdot NMe_2 + PF_3 \longrightarrow 3Me_3SnF + P(NMe_2)_3$	(6)
$3Me_{a}Sn \cdot NMe_{2} + AsF_{3} \longrightarrow$	
$3Me_3SnF + As(NMe_2)_3$	(7)

$$3Me_3Sn \cdot NMe_2 + SbF_3 \longrightarrow$$
  
 $3Me_3SnF + Sb(NMe_2)_3$  (8)

 $4Me_3Sn \cdot NMe_2 + TiF_4 4Me_3SnF + Ti(NMe_2)_4$ (9)

$$Me_3Sn \cdot NMe_2 + BCl_3 \longrightarrow Me_3SnCl + Cl_2B \cdot NMe_2$$
 (10)

$$\frac{Me_{3}Sn\cdot NMe_{2} + Me_{3}SiCl \longrightarrow}{Me_{3}SnCl + Me_{3}Si\cdot NMe_{2}}$$
(11)

$$Et_3Sn \cdot NMe_2 + Cl_2 \longrightarrow Et_3SnCl + ClNMe_2$$
 (12)

$$3Me_3Sn \cdot NMe_2 + BH_3, NEt_3 \longrightarrow$$
  
 $3Me_3SnH + B(NMe_2)_3 + NEt_3$  (13)

 $Me_3Sn \cdot NMe_2 + BBu_3 \longrightarrow$  $Me_{3}SnBu^{n} + Bu^{n}_{2}B \cdot NMe_{2}$ (14) Me<sub>3</sub>Sn·NMe<sub>9</sub> + BPh<sub>9</sub> --->

$$Me_{3}SnPh + Ph_{2}B\cdot NMe_{2} \quad (15)$$

$$2Me_{3}Sn\cdot NMe_{2} + (AlEt_{2})_{2} \longrightarrow$$

$$2\mathrm{Me}_{3}\mathrm{SnEt} + (\mathrm{Et}_{2}\mathrm{Al}\cdot\mathrm{NMe}_{2})_{2} \quad (16)$$

$$3Me_{3}Sn \cdot NMe_{2} + 3B(OMe)_{3} \longrightarrow 3Me_{3}SnOMe + B(NMe_{2})_{3} + 2B(OMe)_{3}$$
(17)

 $Me_3Sn \cdot NMe_2 + Ph_2B \cdot OMe \longrightarrow$  $Me_{3}Sn \cdot OMe + Ph_{2}B \cdot NMe_{2}$ (18)

$$\begin{array}{c} Me_{3}Sn \cdot PPh_{2} + Ph_{2}B \cdot SBu^{n} \longrightarrow \\ Me_{3}Sn \cdot SBu^{n} + Ph_{2}B \cdot PPh_{2} \end{array} (19)$$

$$Me_{3}Sn \cdot NMe_{2} + AcOX \longrightarrow Me_{3}Sn \cdot OAc + Me_{2}NX \quad (20)$$
$$(X = H, Ac, or CH_{2}:CH)$$

$$(X = H, Ac, or CH_2)$$

 $R_{3}^{1}Sn \cdot NMe_{2} + R^{2}OY -$ 

$$R^{1}_{3}Sn \cdot OR^{2} + Me_{2}NY \quad (21)$$

$$(R^{2} = Me \text{ or Et}; Y = Ac, AcCH_{2}CO,$$

$$CH_{2}:C(Me)CO, \text{ or } (EtO_{2}C)_{2}C:C(CO_{2}Et)CO]$$

 $D1 C_{m} OD2 + M_{o}$ 

$$2Me_{3}Sn \cdot NMe_{2} + CH_{2}(CO_{2}Et)_{2} \longrightarrow \\ 2Me_{3}SnOEt + CH_{2}(CO \cdot NMe_{2})_{2} \quad (22)$$

$$4\operatorname{Bu}_{3}^{n}\operatorname{Sn} \operatorname{NMe}_{2} + (\operatorname{EtO}_{2}C)_{2}C=C(\operatorname{CO}_{2}\operatorname{Et})_{2} \longrightarrow 4\operatorname{Bu}_{3}^{n}\operatorname{Sn} \operatorname{OEt} + (\operatorname{Me}_{2}\operatorname{N} \operatorname{OC})_{2}C=C(\operatorname{CO} \operatorname{NMe}_{2})_{2} \quad (23)$$

Characteristic of these reactions is that they mostly proceed smoothly in good yield, and at room temperature, especially where trimethyltin fluoride is produced [reactions (2)-(9)]; the products are easily separated. The ease with which aminostannanes aminate a variety of substituted boranes [reactions (5), (10), (13), (14), (15), (17), and (18)] is particularly unexpected.

<sup>6</sup> H. C. Clark, R. J. O'Brien, and J. Trotter, J. Chem. Soc., 1964, 2332.

R. D. Chambers and R. H. Mobbs, 'Advances in Fluorine <sup>ch</sup> R. D. Chambers and K. H. Mobbs, Advances in Fubline Chemistry,' ed. M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1965, vol. 4.
 <sup>a</sup> R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, J. Amer. Chem. Soc., 1950, 72, 3646.

Reactions (2)-(12).--A driving force for reactions (2)—(9) is the high heat of formation of the insoluble solid trimethyltin fluoride (which is formed from the reactants in solution). This may, in part, be due to a lattice-energy contribution. X-Ray diffraction shows 6 trimethyltin fluoride to be a polymer, with five-coordinate tin and bridging fluorines, rather than an ionic crystal.

Dimethylaminotrimethylstannane reacted rapidly with chlorotrifluoroethylene. Nucleophilic attack on chlorotrifluoroethylene is considered almost always to occur at the diffuoromethylene group as a result of the mesomeric effect of the fluorine.<sup>7</sup>

Diethylamine readily adds to chlorotrifluoroethylene.8 Likewise, Grignard reagents<sup>9</sup> and organolithium compounds<sup>10</sup> add to fluoro-olefins but the adducts readily undergo elimination reactions. It is probable, therefore, that the mechanism of reaction (3) involves initial addition, and subsequent elimination of trimethyltin fluoride. Tin-nitrogen addition to a carbon-carbon double bond (e.g., to CH2=CHCN) has previously been demonstrated.<sup>1</sup>

<sup>19</sup>F N.m.r. data on products of reaction (3)

	1		• /
δF <sub>a</sub> <sup>a</sup>	119-46	δF	124.94
δF <sub>b</sub>	124.52	δF <sub>d</sub>	135.53
$J(\mathbf{F}_{\mathbf{a}}\mathbf{H})^{b}$	$3 \cdot 4 \pm 0 \cdot 1$	$J(\mathbf{\bar{F}_{e}H})$	$1.8 \pm 0.1$
$J(\mathbf{F_bH})$	$1.8 \pm 0.1$	$J(\mathbf{F}_{\mathbf{d}}\mathbf{H})$	$3\cdot 2 \pm 0\cdot 1$
$J(\mathbf{F_aF_b})$		$J(\mathbf{F}_{\mathbf{e}}\mathbf{F}_{\mathbf{d}})$	
$[\sim (F_b F_a) \dots$	$20.0\pm0.5$	$[\sim(F_dF_e)]$	$119.5 \pm 1$
<sup>a</sup> CFCl <sub>3</sub> as	internal standar	d (p.p.m.). <sup>b</sup>	Coupling con-
stants in c./sec.			

The <sup>19</sup>F n.m.r. spectrum of the liquid (b.p. 95.5°) product of reaction (3) consists of four sets of doublets centred at 119.46, 124.52, 124.94, and 135.53 p.p.m. Each component of these doublets is further split into a poorly resolved septet due to the F-H interactions. On the basis of  $J_{\rm FF}$  values <sup>10,11</sup> the two pairs of septets centred at 119.46 and 124.52 p.p.m. have been assigned (see Table) to the cis-isomer and those at 124.94 and 135.53 p.p.m. have been assigned to the trans-isomer. An examination of H-F coupling constants in several fluoro-olefins and their organometallic derivatives, 10, 12 On the shows that  $J_{\mathrm{HF}(\mathrm{gem})} > J_{\mathrm{HF}(\mathrm{trans})} > J_{\mathrm{HF}(\mathrm{cis})}$ . basis of the above trend, resonances at 119.46 and 124.52 p.p.m. are assigned to the F atoms geminal and trans to the amido-proton, respectively in the *cis*-isomer. Similarly, resonances at 124.94 and 135.53 p.p.m. are assigned to the F atoms geminal and cis to the amidoproton, respectively in the *trans*-isomer. Integration indicates that each isomer is present in roughly equal abundance.

Under conditions similar to 'those used for reaction

<sup>&</sup>lt;sup>9</sup> P. Tarrant and D. A. Warner, J. Amer. Chem. Soc., 1954, 76, 1624. <sup>19</sup> H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem.* 

Phys., 1956, 24, 4179. <sup>11</sup> H. M. McConnell and C. A. Reilly, J. Chem. Phys., 1956, 25,

 <sup>184.
 &</sup>lt;sup>12</sup> E. Pitcher and F. G. A. Stone, Spectrochim. Acta, 1961, 17,

(3), dimethylaminotrimethylsilane did not react with chlorotrifluoroethylene. This demonstrates the greater nucleophilicity of aminostannanes and the greater lability of the Sn-N compared with the Si-N bond [see also ref. (1)].

Dimethylaminotrimethylstannane readily aminates chlorotrimethylsilane [equation (11)]. A related reverse reaction has been demonstrated by Abel, Brady, and Lerwill <sup>13</sup> (Me<sub>3</sub>SnBr-Me<sub>3</sub>SiNHEt); it was necessary to heat the 1.: 1 complex initially formed.



Whilst  $Me_3Si \cdot NMe_2$  reacts with  $BF_3$  to give a 1:1 complex which is stable up to  $100^{\circ}$ , equation (5) shows the higher reactivity of the analogous tin compounds. This must be due to a combination of factors, amongst which relative M-N bond strengths and nitrogen basicities are the most obvious.

Reactions similar to (6)—(9) have been shown to occur between aminosilanes and a number of fluorophosphoranes.<sup>14,15</sup> The tin amide did not react with severally  $PbF_4$ ,  $BiF_3$ ,  $FeF_3$ ,  $CoF_3$ , and  $ZrF_4$  (although with  $ZrF_4$ , 8% of the theoretical Me<sub>3</sub>SnF was obtained).

Dimethylaminotrimethylstannane reacted with bromopentacarbonylmanganese(I) exothermally, but the product was not thoroughly characterized. The fact that chloropentacarbonylmanganese(I) and dimethylamine hydrochloride were recovered after treatment of the product with dry hydrogen chloride is, however, indicative of an aminomanganese bond being formed in the initial reaction. Knox <sup>16</sup> has found that an orange solid product from  $BrMn(CO)_5 + Me_2NLi$  probably contains (mass spectral evidence) Me<sub>2</sub>N·Mn(CO)<sub>5</sub>.

Reactions (13)--(19).-The reduction of Me<sub>3</sub>Sn·NMe<sub>2</sub> by triethylamine-borane probably proceeds by displacement of the triethylamine and immediate decomposition of the resulting complex Me<sub>3</sub>Sn·NMe<sub>2</sub>, BH<sub>3</sub>, to give initially an aminoborane but eventually, trisdimethylaminoborane and trimethylstannane.

Reagents such as [Al(NMe2)3]2 which aminate alkylboranes,<sup>17</sup> are less effective than the Sn-N compounds. However, Me<sub>3</sub>Sn·NMe<sub>2</sub> did not react with tetraethylgermane, triphenylphosphine, tri-n-butylstibine, or diethyl sulphide.

Exchange occurred very readily between NMe<sub>2</sub> and OMe groups (equation 17 and 18), but it was not possible to prepare bismethoxydimethylaminoborane. The probable intermediates (MeO)<sub>2</sub>B·NMe<sub>2</sub> and MeO·B(NMe<sub>2</sub>)<sub>2</sub> were not isolated, and presumably 18 disproportionated to yield the symmetrical boranes.

Reaction (19) suggests that scheme (1) is valid beyond the realm of Y=NMe<sub>2</sub>. Related to (19), arsenic(III) fluoride and Me<sub>3</sub>Sn·PPh<sub>2</sub> gave Me<sub>3</sub>SnF and a product believed to be  $As(PPh_2)_3$ .

In conclusion, it is clear that organotin compounds of the type R<sub>3</sub>SnY may frequently serve as intermediates for transfer of a moiety Y via Sn to another electrophilic site.

## EXPERIMENTAL

General Procedures.—Diethyl ether and hydrocarbon solvents were dried over sodium wire and dichloromethane was distilled from phosphorus pentoxide. Liquid starting materials were distilled before use. Solid metal and nonmetal fluorides were obtained from Alfa Inorganics, Inc., and were used without further purification. Bromopentacarbonylmanganese(I) andtetraethyl ethylenetetracarboxylate were prepared according to published procedures.19,20 The aminostannanes were prepared as previously reported.<sup>2</sup> In experiments, not detailed here, where we report lack of reaction, the reagents were invariably recovered almost quantitatively and were fully characterized. Molecular weights were determined isopiestically with a Mecrolab vapour-pressure osmometer, refractive indices with an Abbé-type refractometer using sodium-D light, m.p.'s in sealed capillary tubes, i.r. spectra on Perkin-Elmer 237 and 337 instruments, and mass spectra on an AEI Model MS 9 spectrometer (details of spectra are in ref. 21). Products of reactions, when known compounds, were identified as described, and additionally by comparison of i.r. spectra with those of authentic samples.

Reaction of Dimethylaminotrimethylstannane with Hexafluorobenzene.-Dimethylaminotrimethylstannane (6.57 g., 0.03 mole) in light petroleum (b.p. 20-40°; 20 ml.) was added to hexafluorobenzene (5.88 g., 0.03 mole). A white solid was immediately precipitated. The suspension was heated under reflux (2 hr.), and trimethyltin fluoride (5.08 g., 88%) was filtered off. Removal of solvent yielded dimethylaminopentafluorobenzene (3.00 g., 45%), b.p. 35°/3 mm. (cf., 22 b.p. 88°) (Found: C, 45·1; H, 2·9; N, 6·6; F, 45.0. Calc. for  $C_8H_5F_5N$ : C, 45.5; H, 2.8; N, 6.6; F, 45.0%). The mass spectrum showed the parent-ion peak at 211 (Calc. for  ${}^{12}C_{6}^{19}F_{5}{}^{14}N_{1}$ , 211).

Reaction of Dimethylaminotrimethylstannane with Chlorotrifluoroethylene.---(Experiment of Mr. R. C. SRIVASTAVA.) Chlorotrifluoroethylene (10.35 g., 0.09 mole) was condensed into dimethylaminotrimethylstannane (18.48 g., 0.09 mole) in dec-1-ene (30 ml.) at  $-196^{\circ}$ . The solution was allowed to attain 0°, whereupon an orange precipitate appeared. Volatiles were trapped out at  $-78^{\circ}$  and the orange solid, on recrystallisation from absolute ethanol, was identified as trimethyltin fluoride (12.38 g., 76%) (Found: C, 19.9; H, 4.9; F, 10.2. Calc. for C<sub>3</sub>H<sub>9</sub>FSn: C, 19.7; H, 4.7; F, 10.4%). Distillation of the volatiles gave a mixture (see Discussion) of cis- and trans-1-chloro-2-dimethylamino-1,2-difluoroethylene (9.00 g., 72%), b.p. 96°/760 mm.,

<sup>19</sup> J. J. Eisch and R. B. King, 'Organometallic Syntheses,' Academic Press, New York and London, 1965, vol. 1, p. 174. <sup>20</sup> C. S. Palmer and P. W. McWherter, Org. Synth., Coll. Vol. I,

1941, p. 245; B. B. Corson and W. L. Benson, Org. Synth., Coll. Vol. II, 1943, p. 273.

<sup>21</sup> T. A. George, D.Phil. Thesis, Sussex, 1966.
 <sup>22</sup> L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, J. Res. Nat. Bur. Stand., 1963, 67, A, 481.

<sup>13</sup> E. W. Abel, D. B. Brady, and B. R. Lerwill, Chem. and Ind., 1962, 1333.

<sup>14</sup> R. Schmutzler, Angew. Chem. Internat. Edn., 1964, 3, 753.

<sup>&</sup>lt;sup>15</sup> M. Becke-Goehring and G. Wunsch, Annalen, 1958, 618, 43.

<sup>&</sup>lt;sup>16</sup> G. R. Knox, personal communication.

<sup>&</sup>lt;sup>17</sup> J. K. Ruff, *J. Org. Chem.*, 1962, **27**, 1020. <sup>18</sup> D. W. Aubrey, M. F. Lappert, and M. K. Majumdar, *J.* Chem. Soc., 1962, 4088.

v<sub>max.</sub> 1725 cm.<sup>-1</sup> (Found: C, 34·3; H, 4·4; Cl, 24·2; F, 25.9; N, 9.5. C<sub>4</sub>H<sub>6</sub>ClF<sub>2</sub>N requires C, 33.9; H, 4.2; Cl, 25.6; F, 26.7; N, 9.8%), which polymerised with time. The mass spectrum gave a parent-ion peak at 143 (Calc. for <sup>12</sup>C<sub>4</sub><sup>1</sup>H<sub>6</sub><sup>37</sup>Cl<sup>19</sup>F<sub>2</sub><sup>14</sup>N, 143).

In another experiment on the same scale, a second fraction (0.86 g., 7%), b.p.  $128^{\circ}/760$  mm.,  $\nu_{max}$  1665 cm.<sup>-1</sup>, was recovered, and is believed to be an isomer of the above products. The mass spectrum showed a parent-ion peak at 143, and no ions at higher m/e.

Reaction of Dimethylaminotrimethylstannane with Bis(trifluoromethyl)amine.—Bis(trifluoromethyl)amine (0.73 g., 0.005 mole) was condensed into dimethylaminotrimethylstannane (0.99 g., 0.005 mole) in light petroleum (b.p. 40- $60^{\circ}$ , 20 ml.) at  $-196^{\circ}$ . A vigorous reaction occurred as the mixture warmed up, and a white solid appeared. Volatiles were collected in a trap at  $-78^{\circ}$ , and the solid was identified as trimethyltin fluoride (0.80 g., 92%). N-Dimethylaminodifluoromethyl-N-trifluoromethylamine was probably the other product, since the mass spectrum gave a parention peak at 178 ( ${}^{12}C_4{}^{1}H_7{}^{19}F_5{}^{14}N_2$  requires 178) and no ions at higher m/e; the i.r. (gas phase) spectrum: 3440w  $[v(N-H); cf., (CF_3)_2NH$  has v(N-H) at 3460 cm.<sup>-1</sup>], 2960s, 2930s, sh, 2875s, 2730w, 1500s, 1460s, 1380m, 1341s, 1268s, 1205s, 1145m, 1080m, 1020m, 950m, and 800m.

Reaction of Dimethylaminotrimethylstannane with Trifluoroborane-Ether.-Trifluoroborane-ether (1.46 g., 0.01 mole) in diethyl ether (10 ml.) was slowly added to dimethylaminotrimethylstannane (6.24 g., 0.03 mole) in the same solvent (10 ml.). A violent reaction occurred. Trimethyltin fluoride (4.70 g., 86%) (Found: C, 19.9; H, 4.8; F, 10.3%), was filtered off and, after removal of solvent, tris-(dimethylamino)borane (1.32 g., 92%), b.p.  $42^{\circ}/10$  mm.,  $n_{\rm D}^{25}$  1·4450 (cf.,<sup>23</sup> b.p. 39°/10 mm.,  $n_{\rm D}^{25}$  1·4453), was obtained.

Reaction of Dimethylaminotrimethylstannane with Trifluorophosphine.—Trifluorophosphine (1.0 g., 0.01 mole) was condensed into dimethylaminotrimethylstannane (7.08 g., 0.03 mole) in light petroleum (b.p. 20-40°, 10 ml.) at -196°. The mixture was allowed to attain room temperature; the trifluorophosphine refluxed from a cold finger at  $-120^{\circ}$ . A white solid was filtered off and was identified as trimethyltin fluoride (2.01 g., 32%). Tris(dimethylamino)phosphine (0.41 g., 89%), b.p. 50°/10 mm. (cf.,<sup>24</sup> b.p. 20°/3 mm.) (Found: N, 24.9. Calc. for  $C_6H_{18}N_3P$ : N,  $25 \cdot 8\%$ ), was obtained from the filtrate.

Reaction of Dimethylaminotrimethylstannane with Trifluoroarsine.—Dimethylaminotrimethylstannane (7.88 g., 0.04 mole) was added dropwise to trifluoroarsine (1.67 g., 0.01 mole) in diethyl ether (15 ml.). A violent reaction ensued with the formation of a white precipitate. This was filtered off and identified as trimethyltin fluoride (5.95 g., 85%). The filtrate afforded tris(dimethylamino)arsine (1·1 g., 42%), b.p. 60°/10 mm. (cf.,<sup>25</sup> b.p. 55-57°/ 10 mm.) (Found: N, 19.7. Calc. for C<sub>6</sub>H<sub>18</sub>AsN<sub>3</sub>: N, 20.3%).

Reaction of Dimethylaminotrimethylstannane with Trifluorostibine.-Dimethylaminotrimethylstannane (7.28 g., 0.035 mole) was added to trifluorostibine (2.18 g., 0.01 mole) in benzene (50 ml.) and the mixture was stirred (12 hr.). The solid was filtered off, washed with benzene, and the solvent removed. The solid was identified as trimethyltin fluoride (4.82 g., 75%) and the liquid as tris(dimethylamino)stibine (1.86 g., 60%), b.p. 30°/0.5 mm. (cf.,<sup>26</sup> b.p. 32-34°/ 0.45 mm.) (Found: N, 15.8. Calc. for C<sub>6</sub>H<sub>18</sub>N<sub>3</sub>Sb: N, 16.5%).

Reaction of Dimethylaminotrimethylstannane with Titanium Tetrafluoride .--- Dimethylaminotrimethylstannane (8.4 g., 0.04 mole) was added to titanium tetrafluoride (1.285 g., 0.01 mole) suspended in benzene (30 ml.). An immediate reaction occurred with the formation of an orange solid. Trimethyltin fluoride (6.59 g., 90%) was filtered off and washed with benzene  $(2 \times 20 \text{ ml.})$ . Benzene was removed and the orange residue was identified as tetrakis(dimethylamido)titanium (1.73 g., 75%), b.p. 50°/0.05 mm. (cf.,27 b.p. 50°/0.05 mm.) (Found: N, 24.6. Calc. for C<sub>8</sub>H<sub>24</sub>N<sub>4</sub>Ti: N, 25.0%).

Reaction of Dimethylaminotrimethylstannane with Trichloroborane.-Trichloroborane (2.0 g., 0.017 mole) was added to dimethylaminotrimethylstannane (1.76 g., 0.0085 mole) in light petroleum at  $-78^{\circ}$ . Solvent was removed at  $20^{\circ}/0.01$  mm., and the condensate was trapped at  $-78^{\circ}$ . The solid product was identified as trimethyltin chloride (1.36 g., 80%), m.p. 45° (cf., 28 m.p. 37-38°), and the trapped liquid as dichlorodimethylaminoborane (0.87 g., 81%), b.p. 51-53°/90 mm. (cf.,23 b.p. 52-54°/92 mm.) (Found: Cl, 58.0. Calc. for  $C_2H_6BCl_2N$ : Cl, 57.0%).

Reaction of Dimethylaminotrimethylstannane with Chlorotrimethylsilane.—Chlorotrimethylsilane (2.86 g., 0.026 mole) in diethyl ether (10 ml.) was added to dimethylaminotrimethylstannane (5.47 g., 0.026 mole) in the same solvent (10 ml.). An exothermic reaction ensued. After removal of solvent (20°/100 mm.), dimethylaminotrimethylsilane (2.94 g., 95%), b.p. 86° (cf., 29 b.p. 85-86°), was distilled off. The residue, trimethyltin chloride (4.43 g., 84%), m.p. 43°, solidified on cooling.

Reaction of Dimethylaminotriethylstannane with Chlorine. -Chlorine was passed through dimethylaminotriethylstannane (8.93 g., 0.04 mole) in light petroleum (b.p. 100-120°; 20 ml.) for 1 hr. Distillation gave (i) the yellow, oily N-chlorodimethylamine (2.5 g., 88%), b.p. 42° (cf., 30 b.p. 43°) (Found: Cl, 45.0; N, 17.4. Calc. for C<sub>2</sub>H<sub>6</sub>ClN: Cl, 44.7; N, 17.6%); (ii) light petroleum, b.p. 20°/9 mm.; and (iii) triethyltin chloride (7.2 g., 83%), b.p.  $50^{\circ}/2$  mm. (cf.,<sup>28</sup> b.p. 94°/13 mm.)

Reaction of Dimethylaminotrimethylstannane with Bromo-Dimethylaminotrimethylpentacarbonylmanganese(1).--stannane (2.8 g., 0.01 mole) in dichloromethane (10 ml.) was added dropwise to bromopentacarbonylmanganese(I) (3.70 g., 0.01 mole) in the same solvent (70 ml.). Solvent was removed and the orange sludge solidified on cooling  $(-20^{\circ})$ . The solid was washed with light petroleum (b.p.  $20-40^{\circ}$ ; 25 ml.) and then filtered off. The filtrates were combined and solvent was removed to leave an orange solid. Its i.r. characteristics (Nujol) were: 2095s,sh, 2075s, 2055vs, 2025vs, 1998vs, 1960s, sh, 1942vs, 1900vs, 1740m, 1260m, 1210w, 1188w, 1152w, 1123w, 1072m, 1042m, 1020m, 900m, 800w, 722m, 695m, 668m, 650s,sh, 638vs, 620s,sh, 545m,sh, 528m, and 505m. Hydrogen chloride was bubbled through the orange solid (1.1 g.) in carbon

 <sup>&</sup>lt;sup>23</sup> H. Steinberg and R. J. Brotherton, 'Organoboron Chemistry,' Interscience, New York, 1966, vol. 2.
 <sup>24</sup> A. B. Burg and P. J. Slota, J. Amer. Chem. Soc., 1958, 80,

<sup>1107.</sup> 

<sup>25</sup> K. Mödritzer, Chem. Ber., 1959, 92, 2637.

<sup>&</sup>lt;sup>26</sup> K. Moedritzer, Inorg. Chem., 1964, 3, 609.

D. C. Bradley and I. M. Thomas, J. Chem. Soc., 1960, 3857.
 R. K. Ingham, S. D. Rosenberg, and H. Gilman, Chem. Rev., 1960, 60, 459.

<sup>&</sup>lt;sup>29</sup> R. Fessenden and J. S. Fessenden, Chem. Rev., 1961, 61,

<sup>&</sup>lt;sup>30</sup> E. Allenstein, Z. anorg. Chem., 1961, 308, 1.

## J. Chem. Soc. (A), 1969

tetrachloride (20 ml.). The resulting white solid was filtered off and identified as dimethylamine hydrochloride (0.3 g., 88%), m.p.  $170^{\circ}$  (cf.,<sup>31</sup> m.p.  $171^{\circ}$ ).

Reaction of Dimethylaminotrimethylstannane with Triethylamine-Borane.—Triethylamine-borane (1.94 g., 0.017 mole) in light petroleum (b.p. 20—40°; 10 ml.) was added slowly to dimethylaminotrimethylstannane (10.6 g., 0.051 mole). An exothermic reaction occurred. Distillation gave: (i) light petroleum (b.p. 20—40°); (ii) trimethyltin hydride (6.11 g., 78%), b.p. 54° (cf.,<sup>28</sup> b.p. 59°); (iii) triethylamine (1.6 g., 88%), b.p. 89° (cf.,<sup>31</sup> b.p. 89°); and (iv) tris(dimethylamino)borane (1.96 g., 80%), b.p. 60°/30 mm.

Reaction of Dimethylaminotrimethylstannane with Tributylborane.—Dimethylaminotrimethylstannane (1.82 g., 0.09 mole) was added to tri-n-butylborane (1.59 g., 0.09 mole) in diethyl ether (10 ml.). An exothermic reaction ensued. Solvent was removed and distillation gave: (i) unchanged dimethylaminotrimethylstannane (0.48 g., 0.02 mole), b.p.  $60^{\circ}/18$  mm. (cf.,<sup>2</sup> b.p. 128°/760 mm.); (ii) butyltrimethylstannane (1.20 g., 62%), b.p. 70°/18 mm. (cf.,<sup>28</sup> b.p. 149—150°/726 mm.); and (iii) dibutyldimethylaminoborane (1.20 g., 86%), b.p. 110°/18 mm. (cf.,<sup>17</sup> b.p. 77°/9 mm.).

Reaction of Dimethylaminotrimethylstannane with Triphenylborane.—Dimethylaminotrimethylstannane (6·49 g., 0·026 mole) was added to triphenylborane (6·39 g., 0·026 mole) in benzene (40 ml.). An immediate exothermic reaction took place. After removal of solvent, distillation gave: (i) phenyltrimethylstannane (3·16 g., 50%), b.p. 70—80°/3 mm. (cf.,<sup>28</sup> b.p. 203—208°/760 mm.); and (ii) dimethylaminodiphenylborane (2·24 g., 59%), b.p. 80—82°/ 0·002 mm. (cf.,<sup>17</sup> b.p. 96—98°/0·01 mm.) (Found: N, 6·5. Calc. for C<sub>14</sub>H<sub>16</sub>BN: N, 6·7%).

Reaction of Dimethylaminotrimethylstannane with Triethylalane.—Dimethylaminotrimethylstannane (5.5 g., 0.03 mole) in light petroleum (b.p. 20—40°; 10 ml.) was added to triethylalane (3.04 g., 0.03 mole) in the same solvent (10 ml.). An exothermic reaction occurred, the mixture was cooled, and the solvent was removed. The residue gave ethyltrimethylstannane (3.53 g., 59%), b.p. 105° (cf.,<sup>28</sup> b.p. 106°/746 mm.), and dimethylaminodiethylalane (1.74 g., 50%), b.p. 83°/0.4 mm. [Found:  $C_2H_5$  (as  $C_2H_6$ ), 46·0; Me<sub>2</sub>N (as Me<sub>2</sub>NH), 33·2; Al, 20·4. Calc. for  $C_6H_{16}AlN$ :  $C_2H_5$ , 44·9; Me<sub>2</sub>N, 34·1; Al, 20·9%]. The mass spectrum showed a parent-ion peak at 258 (Calc. for  ${}^{12}C_{12}{}^{14}H_{32}{}^{27}Al_{2}{}^{14}N_{2}$ , 258).

Reaction of Dimethylaminotrimethylstannane with Trimethoxyborane.—Dimethylaminotrimethylstannane (3.86 g., 0.018 mole) in light petroleum (b.p.  $20-40^{\circ}$ , 10 ml.) was added to trimethoxyborane (1.93 g., 0.018 mole) in the same solvent (10 ml.). The white precipitate was methoxytrimethylstannane (2.05 g., 57%), m.p. 71°. Solvent was removed, and distillation of the resulting liquid gave trimethoxyborane (1.28 g.), b.p. 66° (cf.,<sup>32</sup> b.p. 68°), and trisdimethylaminoborane (0.88 g., 98%), b.p. 40°/10 mm.

<sup>31</sup> 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, 4th edn. Reaction of Dimethylaminotrimethylstannane with Diphenylmethoxyborane.— Dimethylaminotrimethylstannane (2.58 g., 0.01 mole) in light petroleum (b.p. 20—40°, 10 ml.) was slowly added to diphenylmethoxyborane (2.43 g., 0.01 mole) in the same solvent (10 ml.). The white precipitate was filtered off, washed with solvent (10 ml.), and identified as methoxytrimethylstannane (2.39 g., 98%), m.p. 70°, sublimed at 25°/0.01 mm. Solvent was removed, and distillation afforded dimethylaminodiphenylborane (2.51 g., 97%), b.p. 75—77°/0.01 mm. (Found: N, 6.3. Calc. for C<sub>14</sub>H<sub>16</sub>BN: N, 6.4%).

Reaction of Diphenylphosphinotrimethylstannane and Trifluoroarsine.-Trifluoroarsine (1.69 g., 0.01 mole) in diethyl ether (30 ml.) was added dropwise to diphenylphosphinotrimethylstannane (13.31 g., 0.038 mole) in the same solvent (10 ml.). An orange precipitate was immediately formed. The solid was filtered off, heated under reflux (0.5 hr.) in benzene (100 ml.), and filtered hot. The residual solid was trimethyltin fluoride (6.1 g., 87%) (Found: C, 19.3; H, 5.2%). The benzene-soluble solid was probably tris(diphenylphosphino)arsine (6.0 g., 75%), sublimed 150°/0.01 mm. (Found: C, 67.7; H, 4.8. Calc. for  $C_{36}H_{30}AsP_3$ : C, 68.5; H, 4.7%). Its i.r. characteristics (Nujol) were: 1300m, 1260m, 1180s, 1160m, 1130m, 1110m, 1090m, 1070m, 1045m, 1028m, 1000m, 968m, 920w, 905w, 895w, 850w, 748s, 740s, 725m, 695vs, 670w,sh, 620w, 560s, 520w, 518s, 500vs, 490s, sh, 460m, and 438w.

Reaction of Diphenylphosphinotrimethylstannane with Butylthiodiphenylborane.— Diphenylphosphinotrimethylstannane (2.21 g., 0.006 mole) in diethyl ether (10 ml.) was added dropwise to butylthiodiphenylborane (1.61 g., 0.006 mole) in the same solvent (10 ml.). Solvent was removed, benzene (20 ml.) was added, and the mixture was heated under reflux (12 hr.). Benzene was removed and the white solid diphenylphosphinodiphenylborane (1.91 g., 75%) was precipitated, filtered off, and washed. [A sample (0.5 g.) was warmed with aqueous-alcoholic hydrogen peroxide; phenol was removed by steam distillation, and diphenylphosphinic acid, m.p. 194-196°, was isolated.] The liquid product from the residue was butylthiotrimethylstannane (1.61 g., 88%), b.p. 54-55°/0.06 mm. (cf., 33 b.p. 44°/0.05 mm.).

Gifts of chemicals from M. and T. Chemicals, Ltd., (Dr. W. J. Considine) (Me<sub>3</sub>SnCl), Dr. R. E. Banks [(CF<sub>3</sub>)<sub>2</sub>NH], Dr. M. Green (ClFC:CF<sub>2</sub>), Dr. R. Jefferson (Et<sub>3</sub>N·BH<sub>3</sub> and Ph<sub>2</sub>BSBu<sup>n</sup>), and Mr. B. S. Lemmon (PF<sub>3</sub>) are gratefully acknowledged. We thank Mr. R. C. Srivastava for data on the ClFC:CF<sub>2</sub> experiment. We thank Pure Chemicals, Ltd. and the U.S. Army (through its European Office) for their generous support of this work, and Dr. G. R. Knox for some unpublished information.

## [8/826 Received, June 14th, 1968]

<sup>32</sup> H. Steinberg, 'Organoboron Chemistry,' Interscience, New York, 1964, vol. 1.

<sup>33</sup> E. W. Abel and D. B. Brady, J. Chem. Soc., 1965, 1192.