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NMR Study of the Exchange Reactions between Allyltrialkyltin Compounds and Lewis Acids

Part 1. Exchanges with Boron Tribromide and Trifluoride and Titanium Tetrachloride

PAUL HARSTON, JAMES L. WARDELL*
Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE (U.K.)
DANIELE MARTON, GIUSEPPE TAGLIAVINI
Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Padova, Via Marzolo 1, I-35131 Padua (Italy)
and PETER J. SMITH
International Tin Research Institute, Kingston Lane, Uxbridge, Middlesex UB8 3PJ (U.K.)

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Abstract

Reactions between BX_3 (X = F or Br) and $TiCl_4$ with $R^1CH{=}CHCH_2SnR_3$ [**I**, R = Me, Bu or cyclohexyl(Cy); R^1 = H or Me] have been studied by NMR spectroscopy. Allyl group–bromine exchanges occur between **I** and BBr_3 at –60 °C; at higher temperatures (*c.* –10 °C) **I** (R = Me or Bu but not Cy) reacts further to give R_2SnBr_2. No allyl group–fluorine exchange products were detected from the reaction between **I** and $BF_3 \cdot Et_2O$ below –20 °C. However, at 25 °C **I** (R = Me, R^1 = H) reacts readily with $BF_3 \cdot Et_2O$, the predominant soluble tin product being Me_4Sn. Compounds **I** and $TiCl_4$ at 30 °C rapidly produce R_3SnCl and $[RCHCHCH_2]TiCl_3$.

Introduction

Organotin–haloboron exchange reactions have been variously shown to give organoboron species [1–15]; indeed, this type of reaction is one of the more useful routes to such compounds [1]. Organic groups transferred from tin to boron have included allyl [2–4], aryl [4–9], vinyl [4–10], benzyl [11, 12] and simple alkyl groups [9, 13, 14]. The reactivities of the organo–tin bonds in unsymmetric tetraorganotins are those expected for electrophilic reactions, e.g. with $R^1CH{=}CHCH_2SnR_3$ (R, R^1 = alkyl or phenyl), the allyl group being transferred (with retention of configuration) in preference to either an alkyl or a phenyl group [3, 4]. With BX_3 (X = Cl or Br but not F) either in excess, with higher reaction temperatures, or with prolonged reaction times, more than one organic group can be transferred from a tetraorganotin; see for example refs. 2 and 4. Based on the reaction conditions used for the exchanges BBr_3 (and BCl_3) is apparently much more reactive than BF_3; see for example ref. 4. The temperatures frequently employed for the BBr_3 and BCl_3 exchanges are however ambient or higher. It was considered to be of value to investigate the extent of the exchanges, especially of allyl–tin compounds, at lower temperatures. One reason for this interest is that BX_3 (and other metal halides, MX_N) are used as additional reagents in reactions involving allyl–tins and carbonyl compounds [16–19], eqn. (1). The influence of the metal halide on the stereochemistry has been ascribed to specific complexation with the aldehyde;

$$R^2CHO + \underset{(E)/(Z)}{R^1CH{=}CHCH_2SnR_3} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } BX_3} \underset{threo/erythro}{R^2CH(OH)CHR^1CH{=}CH_2} \qquad (1)$$

the complex then undergoing reaction with the allyl–tin. However, if the allyl–halide exchange between $R^1CH{=}CHCH_2SnR_3$ and MX_N readily occurs at the reaction temperature, an alternative description may have to be found. Recently, Denmark *et al.* [19] reported a ^{13}C NMR study of the interaction between allyltrimethyltin and $BF_3 \cdot Et_2O$ in $CDCl_3/CD_2Cl_2$ media at temperatures between –80 and 20 °C. They concluded that no metathesis to allyl–BF_2 and $Me_3SnF \cdot BF_3$ resulted but that disproportionation of $Me_3SnCH_2CH{=}CH_2$ to $\Sigma Me_nSn(CH_2CH{=}CH_2)_{4-n}$ resulted. Their results have prompted us to report our findings.

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*Author to whom correspondence should be addressed.

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We have studied interactions between $R^1CH=CHCH_2SnR_3$ [I, R^1 = H or Me; R = Me, Bu or cyclohexyl(Cy)] and BX_3 (X = Br or F) at temperatures between –70 and +30 °C using NMR spectroscopy, in particular ^{119}Sn NMR spectroscopy. In addition, reactions with $TiCl_4$ at 30 °C have been investigated.

Experimental

Lewis Acids

Boron tribromide, boron trifluoride etherate and titanium tetrachloride were of the best available commercial grade and were used as received.

Compounds

$Me_3SnCH_2CH=CH_2$, $Me_3SnCH_2CH=CHMe$ [(*E*):(*Z*) 1:0.93 mixture], $Bu_3SnCH_2CH=CH_2$, $Bu_3SnCH_2CH=CHMe$ [(*E*):(*Z*) 1:0.67 mixture], $Cy_3SnCH_2CH=CH_2$ and $Cy_3SnCH_2CH=CHMe$ [(*E*):(*Z*) mixture admixed with $Cy_3SnCHMeCH=CH_2$] were obtained by standard means from the allyl-Grignard and the trialkyltin chloride [e.g. 20, 21]. All compounds had the expected analyses; values of the ^{119}Sn chemical shifts are given in Table 1.

TABLE 1. ^{119}Sn NMR chemical shift values for I in $CDCl_3$ solution at 30 °C

I	δ ^{119}Sn[a]	
$Me_3SnCH_2CH=CH_2$	–2.4	(–5.4)[b]
(*E*)-$Me_3SnCH_2CH=CHMe$	–5.8	
(*Z*)-$Me_3SnCH_2CH=CHMe$	–9.0	
$Bu_3SnCH_2CH=CH_2$	–17.3	
(*E*)-$Bu_3SnCH_2CH=CHMe$[c]	–12.3	(–15.3)[c]
(*Z*)-$Bu_3SnCH_2CH=CHMe$[c]	–16.5	(–19.4)[c]
$Cy_3SnCH_2CH=CH_2$	–77.8	
(*E*)-$Cy_3SnCH_2CH=CHMe$	–69.7	
(*Z*)-$Cy_3SnCH_2CH=CHMe$	–75.2	
$Cy_3SnCHMeCH=CH_2$	–93.2	

[a] Positive values denote high frequency shifts from the reference Me_4Sn. [b] Literature value [22]. [c] Literature values [16] for neat liquids.

Procedure

All manipulations were conducted under anhydrous conditions. Solutions for the NMR study at low temperature were made up by the addition of a solution of the Lewis acid to a solution of I in the chosen solvent at –64 or –78 °C. The NMR tube was then placed in the spectrometer probe maintained at this temperature and the temperature altered to the desired temperature.

^1H NMR spectra were recorded on a Perkin-Elmer RA34 (220 MHz) spectrometer. Jeol FX-90Q instruments were used for ^{119}Sn NMR (at 33.35 MHz), for ^{11}B NMR (at 28.69 MHz) and for ^{19}F NMR (at 84.25 MHz) spectra. Reference samples (sealed into capillaries) were neat Me_4Sn (for ^{119}Sn NMR) and neat $BF_3 \cdot Et_2O$ (for both ^{11}B and ^{19}F NMR).

Results and Discussion

Interactions with Boron Tribromide

Compounds I (R = Me, Bu or Cy; R^1 = H or Me) react readily with BBr_3 at low temperatures; for example, the reaction between equimolar $Me_3SnCH_2CH=CH_2$ and BBr_3 in $CDCl_3$ solution occurred quantitatively at –60 °C to give Me_3SnBr [δ ^{119}Sn 145.3 ppm (rel. to Me_4Sn)] and $CH_2=CHCH_2BBr_2$ [δ ^{11}B 39.7 ppm (rel. to $BF_3 \cdot Et_2O$)], eqn. (2). No other tin or boron species was detected in the NMR spectra.

$$Me_3SnCH_2CH=CH_2 + BBr_3 \longrightarrow Me_3SnBr + CH_2=CHCH_2BBr_2 \qquad (2)$$

On raising the temperature, further reaction resulted in the formation of Me_2SnBr_2. This was initially detected at –10 °C in the ^{119}Sn NMR spectrum. (δ ^{119}Sn 68.7 ppm at –10 °C]. Longer reaction times and higher temperatures led to higher yields of Me_2SnBr_2; complete formation of Me_2SnBr_2 was only realized after several hours at 25 °C [Me_2SnBr_2 δ ^{119}Sn 70.6 ppm at 25 °C: literature value [23] 70 ppm (in benzene at 25 °C)]. The δ ^{119}Sn values for Me_3SnBr (and other R_3SnBr) varied with temperature over the range –60 to +30 °C (see Table 2), probably due to changes in association. It has been quoted

TABLE 2. Variation of δ ^{119}Sn for R_3SnBr in $CDCl_3$ solution with temperature

Compound	Temperature (°C)						
	–60	–50	–40	–30	–10	0	30
Me_3SnBr[a]	148.0	145.3	141.4	140.1	138.8	138.2	137.8
Bu_3SnBr	154.5	148.3	147.0	149.6	146.8		141.9
Cy_3SnBr	83.3			81.1		79.5	76.4

[a] Literature values [23] 130.7 ppm (neat) and 128 ppm (in benzene) at 30 °C.

[24] that, in the narrower temperature range of −5 to +35 °C, little if any change in values of δ ^{119}Sn for Me_3SnCl in CCl_4 or benzene solutions was found.

Formally the Me–Br exchange, leading to Me_2SnBr_2, would provide [(CH_2=$CHCH_2$)MeBBr], eqn. (3). However it was clear from the ^{11}B NMR

$$Me_3SnBr + CH_2{=}CHCH_2BBr_2 \longrightarrow$$

$$Me_2SnBr_2 + [(CH_2{=}CHCH_2)MeBBr] \qquad (3)$$

spectrum that disproportionation of the organoboron products was occurring. For example, at the reaction stage when Me_3SnBr and Me_2SnBr_2 were present in an approximate 1:2 mole ratio, three significant (as well as several minor) boron-containing products were indicated: these were $MeBBr_2$ (δ ^{11}B 63.5 ppm, literature value [25] 62.5 ppm), $(CH_2{=}CHCH_2)_3B$ (δ ^{11}B 80.4 ppm, literature value [25] 80.3 ppm) and an unknown compound (δ ^{11}B 49.0 ppm). A similar situation arises in CD_2Cl_2 solution; however in this solvent reaction proceeds more rapidly to Me_2SnBr_2 [δ ^{119}Sn 70.4 ppm at 25 °C: δ ^{1}H 1.34 ppm, $J(^{119}Sn–^1H)$ 67 Hz: literature values [23] δ ^{1}H 1.36 ppm, $J(^{119}Sn–^1H)$ 68 Hz]. When Me_2SnBr_2 was the sole tin species present, there were various organoboron species in solution, including among the major products $CH_2{=}CHCH_2BBr_2$ (δ ^{11}B 39.0 ppm) and $MeBBr_2$ (δ ^{11}B 63.5 ppm and δ ^{1}H 1.37 ppm: literature value [26] δ ^{1}H 1.43 ppm). Also present was a species having δ ^{11}B 28 ppm and was probably of the type $RB(OH)_2$, arising from hydrolysis.

As shown by ^{119}Sn NMR spectroscopy, (*E*)- and (*Z*)-MeCH=$CHCH_2SnR_3$ (R = Me, Bu or Cy) and $CH_2{=}CHCH_2SnR_3$ (R = Bu or Cy) all react with BBr_3 at −60 °C in $CDCl_3$ solution to give R_3SnBr [and consequently an allyboron dibromide (**II**)]. The (*E*)-isomer reacted faster than did the (*Z*)-isomer, this was also reported by Keck *et al.* [17b]. While at higher temperatures R_3SnBr (R = Me or Bu) further reacts to give R_2SnBr_2, Cy_3SnBr remains unaffected by **II**, see Table 3. This reduced reactivity of Cy_3SnBr, compared to Me_3SnBr and Bu_3SnBr, parallels findings towards other electrophiles. When an excess of BBr_3 (*c.* 60%) was used with $Cy_3SnCH_2CH{=}CH_2$, an additional tin-containing species (to Cy_3SnBr) was present in solution. This had a δ ^{119}Sn value of 71.8 ppm at 0 °C and 70.7 ppm at 60 °C compared to δ ^{119}Sn values for Cy_3SnBr of 83.3 to 76.9 ppm, it was assumed to be $Cy_3Sn^{(+)}BBr_4^{(-)}$.

Of interest, the reaction between (*E*)-, and (*Z*)-MeCH=$CHCH_2SnBu_3$ and BBr_3 in $CDCl_3$ solution, when maintained throughout at 25 °C gave Bu_3SnBr,

TABLE 3. Reactions of allyltrialkyltin compounds with BBr_3 in $CDCl_3$ solution

I	Temperature (°C) (reaction time)	Tin products (δ ^{119}Sn)^a	Remarks
$Me_3SnCH_2CH{=}CH_2$	−60 to −20	Me_3SnBr (145.3 to 139.5)^b	sole tin product
	−10	Me_3SnBr (138.8)	major product
		Me_2SnBr_2 (68.7)	minor product
	25 (24 h)	Me_2SnBr_2 (70.6)	sole tin product
(*E*)/(*Z*)-$Me_3SnCH_2CH{=}CHMe$	−60 to 0	Me_3SnBr (148.0 to 140.0)^b	
	30 (5 h)	Me_3SnBr (138.1)	major product
		Me_2SnBr_2 (69.4)	minor product
$Bu_3SnCH_2CH{=}CH_2$	−55 to −10	Bu_3SnBr (153.4 to 146.9)^b	
	25	Bu_3SnBr (141.8)	major product
		Bu_2SnBr_2 (90.7)	minor product
(*E*)/(*Z*)-$Bu_3SnCH_2CH{=}CHMe$	−60	Bu_3SnBr (154.9)	major product
		Bu_2SnBr_2 (100.9)	v. minor product
	−40	Bu_3SnBr (149.6)	(about 1:1)
		Bu_2SnBr_2 (97.2)	
	25 (24 h)	Bu_2SnBr_2 (96.0)	
$Cy_3SnCH_2CH{=}CH_2$	−60 to 30	Cy_3SnBr (83.3 to 76.9)^b	
(*E*)/(*Z*)-$Cy_3SnCH_2CH{=}CHMe$	−60 to 30	Cy_3SnBr (82.4 to 75.6)^b	

[a] Positive values denote high frequency shifts from the reference Me_4Sn. [b] Variation with temperature.

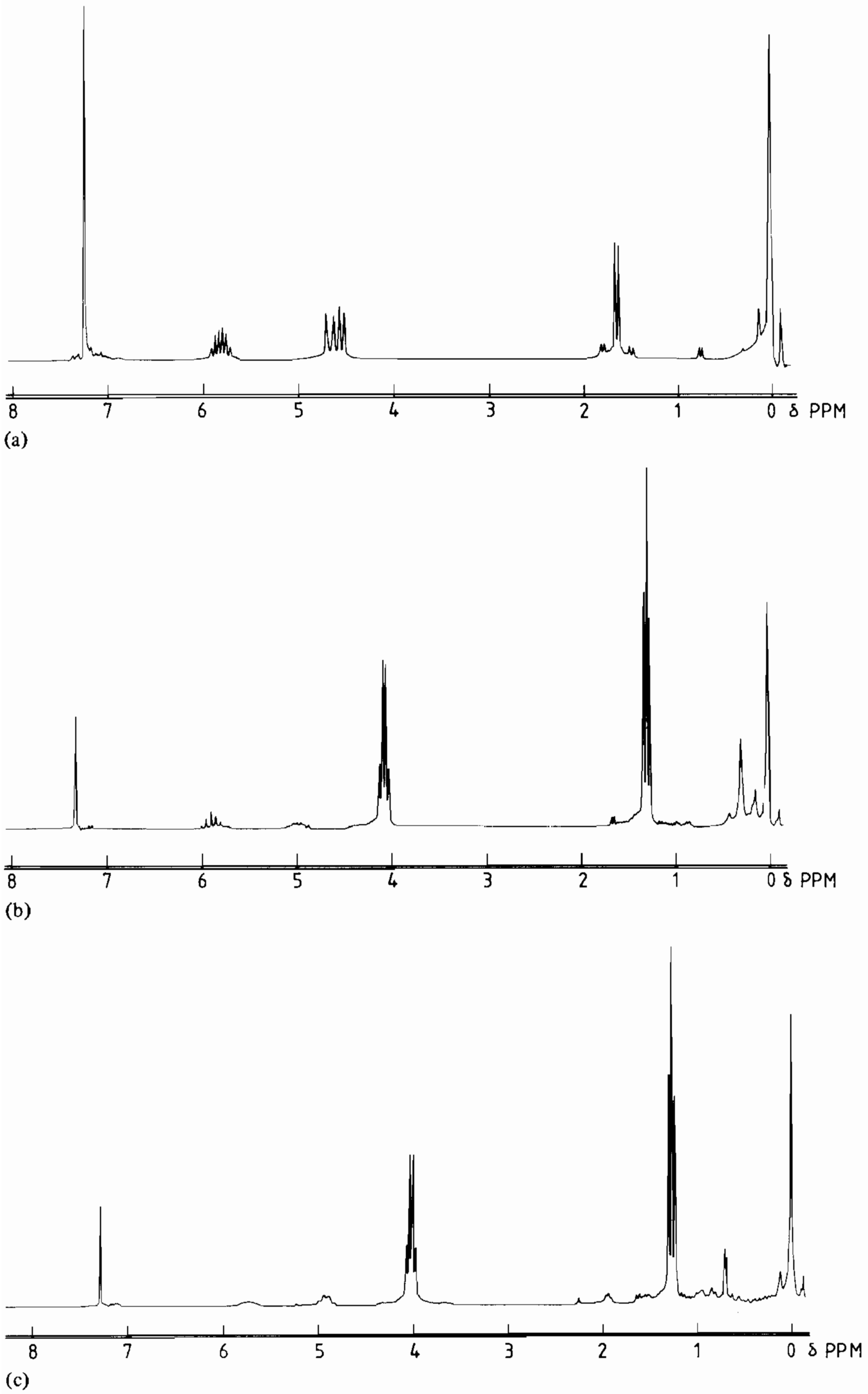

Fig. 1. ^1H NMR spectra of reaction between equimolar $Me_3SnCH_2CH{=}CH_2$ and $BF_3 \cdot Et_2O$ in CD_2Cl_2/C_6H_6 at 30 °C. (a) $Me_3SnCH_2CH{=}CH_2$, (b) $Me_3SnCH_2CH{=}CH_2 + BF_3 \cdot Et_2O$ after $\frac{1}{2}$ h, (c) $Me_3SnCH_2CH{=}CH_2 + BF_3 \cdot Et_2O$ after 64 h.

while the reaction allowed to warm-up gradually from –60 to 25 °C produced both Bu_3SnBr and Bu_2SnBr_2. Exchanges between $R^1CH{=}CHCH_2SnR_3$ [R^1 = Me or Ph] and haloboron compounds have been previously shown to proceed with retention of configuration [3,4].

Interactions with Boron Trifluoride Etherate

The results with $BF_3 \cdot Et_2O$ were less conclusive, although it is apparent that $BF_3 \cdot Et_2O$ is much less reactive than BBr_3. The ^{13}C NMR results of Denmark *et al.* [19] with $Me_3SnCH_2CH{=}CH_2$ and $BF_3 \cdot Et_2O$ indicated no exchange to $CH_2{=}CHCH_2BF_2$ and $Me_3SnF \cdot BF_3$ occurred. However redistribution of $Me_3SnCH_2CH{=}CH_2$ did result in the presence of $BF_3 \cdot Et_2O$ to give a mixture of $Me_nSn(CH_2CH{=}CH_2)_{4-n}$ ($n = 0–4$) compounds. This redistribution occurred during the temperature sequence $-80 \rightarrow 20 \rightarrow -80$ °C. Our results, using ^{19}F, ^{119}Sn and ^1H NMR confirm that no metathetic exchange happens between **I** and $BF_3 \cdot Et_2O$ and that Me_4Sn is a major product of the rearrangement of $Me_3SnCH_2CH{=}CH_2$.

In other work, Brinkman and Stone [4] reported the formation of $CH_2{=}CHCH_2BF_2$ from $(CH_2{=}CHCH_2)_4Sn$ and BF_3 on heating. The ^{19}F NMR spectra in our study clearly point to no fluorine/organo group (either allylic or alkyl) exchanges occurring between $BF_3 \cdot Et_2O$ and **I** ($R = Me$, $R^1 = H$; $R = Bu$, $R^1 = Me$) in $THF/CDCl_3$ at temperatures from -80 to *c.* -20 °C for short contact times.

On maintaining the reaction solution at temperatures between -25 and 0 °C for days, **I** was slowly removed (as shown by the ^{119}Sn NMR spectrum). However, no new soluble tin product was detected by ^{119}Sn NMR spectroscopy. Even when **I** had been totally consumed, there was still significant amounts of BF_3 left – as confirmed by both ^{11}B and ^{19}F NMR spectra. There were only minor amounts of other boron and fluorine containing species present in solution, e.g. the most significant fluorine product had a $\delta\ ^{19}F$ value of $+3.9$ ppm (rel. to $BF_3 \cdot Et_2O$). The reported ^{11}B chemical shift value for $CH_2{=}CHCH_2BF_2$ is -52 ppm (rel. to $BF_3 \cdot Et_2O$) [27]; this was not present in the reaction mixtures. Our interpretation of the results of the prolonged reactions, in particular the removal of the original allyl–tin species, the large amounts of BF_3 remaining (despite the 1:1 mole ratio of reagents), no soluble tin product and no new major soluble boron or fluorine containing products, is that allyl–fluorine exchange was not occurring. Instead, we believe that hydrolysis/protonolysis of **I** or its redistribution products, $Me_nSn(CH_2CH{=}CH_2)_{4-n}$ ($n = 1–4$), was resulting from strong proton acids, such as hydrofluoric acid or HBF_4, present in the reaction mixture. The formation of sparingly soluble R_3SnF or $R_3SnF \cdot BF_3$ would remove the tin from solution.

The $CH_2{=}CHCH_2SnMe_3–BF_3 \cdot Et_2O$ reaction was also carried out directly at 25 °C in CD_2Cl_2 solution. Allyltrimethyltin was readily consumed, as shown by the ^1H NMR spectrum (Fig. 1). This indicated two major tin compounds in a *c.* 1:1 integration ratio: a species **III**, having $\delta\ ^1H$ 0.31 ppm and $J(^{119}Sn–^1H)$ 58 Hz, and Me_4Sn [$\delta\ ^{119}Sn$ 1.75 ppm (rel. to neat Me_4Sn): $\delta\ ^1H$ 0.05 ppm, $J(^{119}Sn–^1H)$ 53 Hz; literature values [28]; $\delta\ ^1H$ 0.04 to -0.07 ppm, $J(^{119}Sn–^1H)$ 53 Hz]. Other tin containing products (all relatively minor) as shown by the ^{119}Sn NMR spectrum had $\delta\ ^{119}Sn$ values of -6.6, -9.2 and -26.1 ppm. With longer reaction times, compound **III** was replaced by another tin compound **IV** [$\delta\ ^1H$ 0.70 ppm and $J(^{119}Sn–^1H)$ 62 Hz] and more Me_4Sn [to give *c.* 55% of Me_4Sn based on **I**]. The chemical shift and coupling constant values for **III** and **IV** can be compared with values reported in MeOH solution for Me_3SnF $\delta\ ^1H$ 0.45 ppm, $J(^{119}Sn–^1H)$ 69 Hz for Me_3SnBF_4 $\delta\ ^1H$ 0.53 ppm, $J(^{119}Sn–^1H)$ 69 Hz, and for Me_2SnF_2 $\delta\ ^1H$ 0.75 ppm, $J(^{119}Sn–^1H)$ 84 Hz [29]). The proton signals of the allyl moiety were broad and ill-resolved unlike those of Et_2O and the methyltin compounds. No new boron compound was identified.

Interaction with Titanium Tetrachloride

The reaction of **I** with $TiCl_4$ (1 equiv.) in $CDCl_3$ was only studied at 30 °C. Complete and rapid formation of R_3SnCl resulted along with a brown precipitate of an allyl–titanium trichloride, $[RCHCHCH_2]$-$TiCl_3$ (**V**; $R = H$ or Me). Compounds **V** have been obtained by allylation of $TiCl_4$ with the allyl-Grignard reagent [30].

TABLE 4. Reaction of allyltrialkyltin compounds (**I**) with $TiCl_4$ in $CDCl_3$ solution at 30 °C

I	Tin product ($\delta\ ^{119}Sn$)^a
$Me_3SnCH_2CH{=}CHMe$	Me_3SnCl (+170.8)
$Me_3SnCH_2CH{=}CH_2$	Me_3SnCl (+165.9)
$Bu_3SnCH_2CH{=}CHMe$	Bu_3SnCl (+156.7)
$Bu_3SnCH_2CH{=}CH_2$	Bu_3SnCl (+150.3)
$Cy_3SnCH_2CH{=}CHMe$	Cy_3SnCl (+72.3)
$Cy_3SnCH_2CH{=}CH_2$	Cy_3SnCl (+72.3)

^{a}Positive values denote high frequency shifts from the reference Me_4Sn.

The precipitation of **V**, from the $CDCl_3$ solution effectively prevented further reaction occurring (Table 4). Keck *et al.* report that the reaction of $TiCl_4$, $CH_3CH{=}CHCH_2SnBu_3$ and an aldehyde proceeds to differing products depending upon the order of addition of starting material. It was reported that the addition of $CH_3CH{=}CHCH_2SnBu_3$ to $TiCl_4$, followed by addition of aldehyde (analogous to our own procedure), gave a product which would be expected to arise from the (E)-$CH_3CH{=}CHCH_2TiCl_3$ intermediate [17b].

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