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On the use of mixtures of organotin species for catalytic enantioselective ketone allylation—a detective story †

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In the presence of enantiopure $MTBH_2$ (monothiobinaphthol, 2-hydroxy-2′mercapto-1,1′-binaphthyl; 0.2 eq.) quantitative allylation of ArC(=O)Me takes place with impure $Sn(CH_2CH{=}CH_2)_4$ (prepared from allyl chloride, air-oxidised magnesium and $SnCl_4$) to yield *tert*-homoallylic alcohols in 85–92% ee. In the same process highly purified, or commercial, $Sn(CH_2CH{=}CH_2)_4$ yields material of only 35–50% ee. The origin of these effects is the presence of small amounts of the compounds, $EtSn(CH_2CH{=}CH_2)_3$, $ClSn(CH_2CH{=}CH_2)_3$ $ClSnEt(CH_2CH{=}CH_2)_2$ in the tetraallyltin sample and the presence of traces of water (which inhibits achiral background reactions). All the triallyl and diallyl species enhance the stereoselectivity in the catalytic allylation reaction, the chlorides more so than the ethyl compound. Hydrolysis of $ClSnEt(CH_2CH{=}CH_2)_2$ affords crystallographically characterised $Sn_4(\mu_3\text{-}O)(\mu_2\text{-}Cl)_2Cl_2Et_4(CH_2CH{=}CH_2)_4$. Reaction of this latter compound with $MTBH_2$ leads to the most potent catalyst.

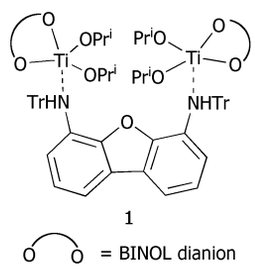
Introduction

To date only five catalytic procedures for highly enantioselective nucleophilic allylation of prochiral ketones have appeared in the literature despite the fact these yield intrinsically useful *tert*-homoallylic alcohol fragments.

Tagliavini and co-workers have used a titanium(IV) catalyst to allylate aryl/methyl ketones in up to 80% ee.[1] The catalyst (20 mol%) is prepared from BINOL, $TiCl_2(OPr^i)_2$ and either $Sn(CH_2CH{=}CH_2)_4$ or $BuSn(CH_2CH{=}CH_2)_3$, and this is used in the presence of $Sn(CH_2CH{=}CH_2)_4$ as the terminal allyl source. Allylation of acetophenone in dichloromethane at room temperature resulted in the derived *tert*-alcohol in quantitative yield in 65% ee. Only 2-acetonaphthone gives over 80% ee, and this requires a 40 mol% catalyst loading. The dialkyl ketone, cyclohexyl methyl ketone is allylated with only a 29% ee. Although this represents the first procedure for catalytic enantioselective ketone allylations, the enantioselectivities remained unsatisfactory and high catalytic loadings are required.

The second catalytic procedure is that reported by Maruoka, using the aldehyde allylation catalyst **1**.[2] This bis-titanium(IV)-BINOL complex was used at catalyst loadings of 30 mol% for enantioselective allylation of acetophenone and 2-acetonaphthone using $Sn(CH_2CH{=}CH_2)_4$. The former ketone is allylated in 92% ee and 96% yield and the latter in 93% ee and 98% yield. Whilst the enantiomeric excesses of the product alcohols are high, 60 mol% of BINOL is used as the catalyst contains two molecules of BINOL. The scope of the catalyst is currently limited to aryl/methyl ketones.

Recently two useful systems have been disclosed. Walsh reported a titanium(IV)-BINOL catalysed system for ketone allylation using $Sn(CH_2CH{=}CH_2)_4$.[3] This catalyst is characterised by its wide utility, simple preparation and critical dependence on isopropanol as a key additive. Excellent yields and stereoselectivities are realised in these reactions. For example, benzylideneacetone is allylated in 90% ee and 99% chemical yield. However, this system also requires a fairly high catalyst loading (20–30 mol%). Finally, Shibasaki has presented a notable silicon-based allylation which yields 60% ee in the allylation of acetophenone under Cu/BINAP catalysis (15 mol%).[4]



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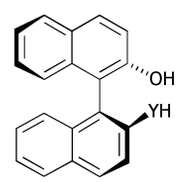
= BINOL dianion



(S_a)-BINOL (Y = O)
(S_a)-$MTBH_2$ (Y = S)

We have made a contribution to this area and disclosed the first highly selective catalyst that does not use titanium. Unusually, we have discovered that this catalytic system required mixtures of organotinallyl species to be used to attain high enantioselectivities. Some details of this chemistry have been communicated[5] but we give here the full details of our investigation into this unique and complicated system.

Aside from the catalytic systems above a few stoichiometric reagents are able to provide *tert*-homoallylic alcohols in high ee. Some examples include: Brown's allyldiisopinocampheylborane reagent that attains 75% ee upon reaction 3-butyn-2-one but other ketones give only low ee.[6] An improved borane reagent (allyl-10-phenyl-9-borabicyclo[3.3.2]decane), introduced by Soderquist fairs better, aryl/methyl ketones are allylated in up to 99% ee whilst dialkyl ketones give up to 84% ee.[7] Tietze has described highly selective allylation of aliphatic methyl ketones using a norpseudoephedrine auxiliary. However, the auxiliary is destroyed in this chemistry.[8] Loh and co-workers have reported the allylation of aryl/trifluoromethyl ketones using an indium-mediated enantioselective addition of allylic bromides (up to 70% ee) in the presence of stoichiometric amounts of cinchonidine.[9]

Results and discussion

We began our investigation into ketone allylation based on the seminal work of Baba[10] who demonstrated that heating BINOL in the presence of $Sn(CH_2CH{=}CH_2)_4$ and a methanol co-promoter led to a reagent (200 mol%) that showed some efficacy in the asymmetric allylation of acetophenone (up to 60% ee). Substituting BINOL by (S_a)-$MTBH_2$ but using an otherwise identical protocol lead to the desired *tert*-alcohol in

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/ob/b3/b313384b/

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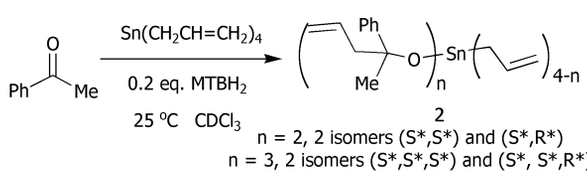
quantitative yield and 43% ee after 16 h. Encouragingly, reducing the ligand loading to 20 mol% fashioned a catalytic system that still lead to complete conversion and low levels of enantioselectivity (16–37% ee) in overnight runs. These initial trials using Ph(C=O)Me revealed a number of key observations that can be summarised thus: i) the best catalysts are attained by pre-heating the $MTBH_2$ ligand with excess tetraallyltin (1 : 5.5, 2 h) in toluene or dichloromethane followed by reaction with the ketone at room temperature (no conversion takes place below ~15 °C); ii) the catalytic reaction is strongly dependent on the presence of additives [*e.g.* while methanol (1–2 eq.) dramatically lowers the product ee the presence of trace amounts of water raises it]; iii) the $MTBH_2$-catalysed reactions are strongly dependent on the source of tetraallyltin reagent used (different commercial batches as well as those prepared in-house gave consistently high conversions but different ee values); iv) the reactions often develop a beautiful yellow colouration as the allylation proceeds. The disentanglement of these factors is discussed below.

Inhibition of autocatalysis by added water

When the course of several allylation reactions of acetophenone using $MTBH_2$ and tetraallyltin are monitored by chiral GC it is found that the initial product ee can be very high (up to 92% ee) at low conversions (typically ~30% at 1 h). However, as the reaction proceeds the product ee falls as a function of time leading to low overall selectivity (typically 34–50% ee) after 16 h. Such behaviour is indicative of a background reaction. Young has proposed that the tin alkoxides formed in such reactions act as autocatalytic Lewis acids to promote further carbonyl additions of $Sn(CH_2CH{=}CH_2)_4$ and that this Lewis acidity can be further promoted by addition of methanol to engender the formation of $Sn(OMe)_n(CH_2CH{=}CH_2)_{4-n}$ species (n = 1–4).[11] Monitoring the $MTBH_2$-catalysed reaction in $CDCl_3$ by ^{119}Sn NMR spectroscopy revealed the formation of four signals at δ_{Sn} −81, −82, −230 and −231 assigned to tin alkoxide species **2** existing as mixtures of diastereomers (Scheme 1). The observed tin chemical shifts are consistent with the formation dialkoxides (n = 2) and trialkoxides (n = 3) respectively. ‡ [12] No mono alkoxide (n = 1) is present. Attempted preparation of **2** (n = 1) from $ClSn(CH_2CH{=}CH_2)_3$ and $PhMeC(CH_2CH{=}CH_2)ONa$ led only to disproportionation products (tetraallyl tin and **2** with n > 1) under condition mimicking the reaction mixture. Consistent with multiple allyl transfer from tetraallyltin an excess of this reagent (δ_{Sn} −47) remains at the end of the reaction (using 1.0 equivalents to acetophenone). Alternatively, transformations using only 0.25 equivalents are still successful (but with reduced yield and ee: 72% and 26% respectively).



Scheme 1 Production of Lewis acidic initial products.

It was noted that this undesired background reactivity is suppressed in reactions involving *undried* solvents. Fortuitously, this allowed us to eliminate one of the major causes of non-reproducibility in the reactions (trace water contamination in one of the reaction components) and so focus on only primary catalytic events. We tentatively suggest two mechanisms by which water may help prevent background autocatalysis. Firstly, it is known that coordination of σ-Lewis donors to isoelectronic literature tin enolate species strongly inhibits their addition to aldehydes by reducing their Lewis acidity.[13] A similar effect is likely to operate in our allyl transfer reactions. Secondly, *in situ* hydrolysis of **2** would generate the product alcohol and this may lead to removal of potential tin Lewis acids as non-reactive oligomers. In either case, from a practical perspective, it proved best to use either rigorously dried solvents alone and short reaction times (referred to from here on as "dry conditions") or to deliberately dope such dry systems with added trace water (referred to from here on as "wet conditions") for overnight runs.

Effect of the organotinallyl source

Initial experiments using commercial tetraallyltin led to the formation of *tert*-alcohols in ~35% ee under "dry" conditions and up to 50% under "wet" conditions. These results are also attained using $Sn(CH_2CH{=}CH_2)_4$ prepared by the standard *Inorganic Synthesis* approach of O'Brien ($SnCl_4$ + allylmagnesium chloride)[14] provided fresh (silver) magnesium turnings are used to prepare the Grignard reagent. Serendipitously, we prepared one batch of tetraallyltin using an old (>2 years, black-coloured) sample of magnesium turnings. Although this led to $Sn(CH_2CH{=}CH_2)_4$ as the major product (>80%) a number of other contaminants were also present. However, we were astonished to find essentially quantitative conversions and high stereoselectivities (85–92% ee) on testing this mixture in the $MTBH_2$-catalysed allylation of acetophenone under standard conditions. This observation raises two questions: "Is this a feature of just this one particular magnesium source?" and "What is the active agent responsible for the 6 to 9 fold increase in stereoselectivity?"

The first question was addressed by preparing other samples of impure tetraallyltin from alternative black magnesium sources from other laboratories—these gave reproducibly the same catalytic results although the mixture composition (as assessed by ^1H and ^{119}Sn NMR spectroscopy) varied slightly from batch to batch. Electron microscopy/EDS studies of typical black magnesium turnings revealed that the surface is rich in domains containing oxygen and some carbon. We assign the domains as areas containing surface oxide with some additional carbonate.

The composition of the impure tetraallyltin mixtures were accessed by multinuclear NMR and GCMS studies. These revealed that the major impurity in the mixture is $EtSn(CH_2CH{=}CH_2)_3$ (δ_{Sn} −33) but also variable amounts of $ClSn(CH_2CH{=}CH_2)_3$ (δ_{Sn} +60), and very small amounts of two initially unknown species (δ_{Sn} −19 and +92, see later) were present. Partial NMR spectra (^1H and ^{119}Sn) of typical mixtures are shown in Fig. 1 together with the ee values they attain in Ph(C=O)Me allylation under "wet" conditions. The ethyl compound results from EtBr (used as a promoter in the literature synthesis of allylmagnesium chloride). Apparently, EtMgBr formation is favoured in the surface modified (black) magnesium. Reactions using d_5-EtBr confirmed this as the ethyl source. The triallyltinchloride results from incomplete reaction of the $SnCl_4$. As $EtSn(CH_2CH{=}CH_2)_3$ initially appeared to show the most promise as the key additive its synthesis was targeted but this proved problematic. This compound is reported only once in the literature, with no experimental details.[15] In our hands, reactions of $ClSn(CH_2CH{=}CH_2)_3$ with $ZnEt_2$ (under practically all conditions) or alternative preparations using Kocheshkov-type reactions,[16] or reactions of $EtSnCl_3$ with allylmagnesium chloride commonly led only to complex mixtures of $Et_nSn(CH_2CH{=}CH_2)_{4-n}$ (n = 0–3) due to allyl replacement and redistribution.

Due to these problems we turned our attention to the reaction of $BuSnCl_3$ (which is commercially available) and

‡ Compounds **2** have not been reported in the literature before but ^{119}Sn chemical shift data for $Bu_2Sn(OBu^t)_2$ −34 and $BuSn(OCH_2Bu^t)_3$ −194 (ref. 12) is consistent with the assignment; it is normal for allyl analogues of alkyltin species to resonate at lower frequencies.

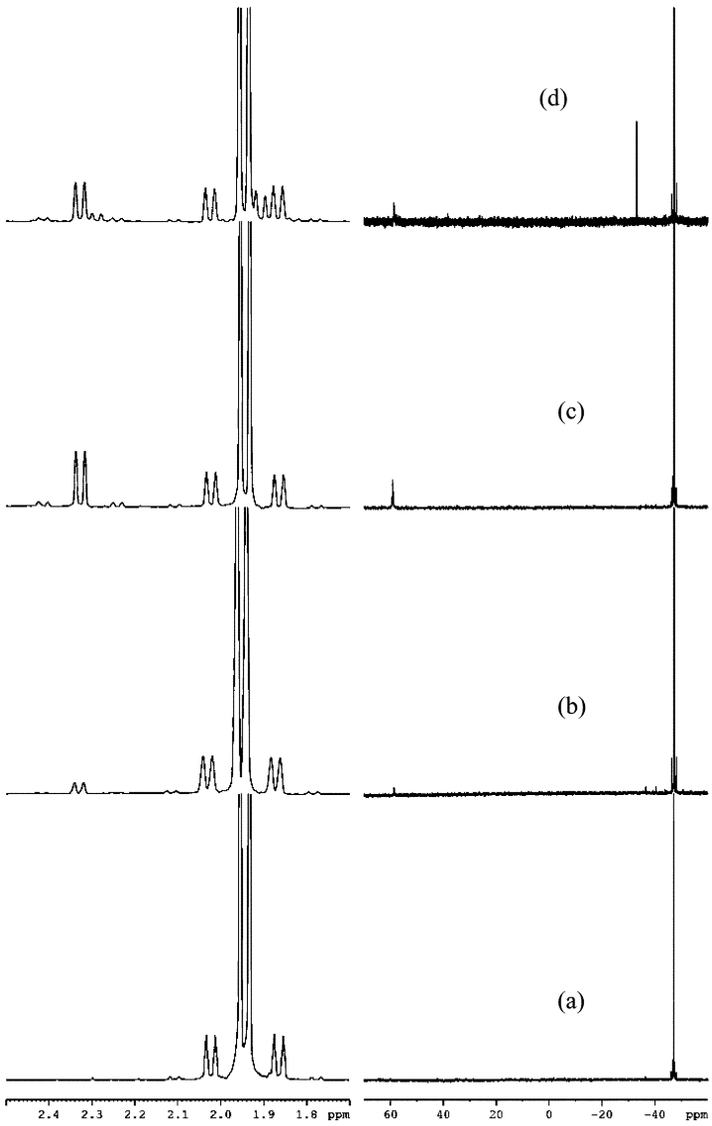


Fig. 1 Partial ^{1}H (1.7–2.5 ppm, left) and ^{119}Sn (−50 – +65 ppm, right) NMR spectra of pure and slightly contaminated tetrallyltin. Sample (a), pure commercial tetraallyltin (gave 38% ee); (b), Trace contamination with triallyltinchloride (gave 62% ee); (c), significant contamination with triallyltin chloride (gave 71% ee); (d), contamination with ethyltriallytin (major) and triallyltinchloride (minor) (gave 83% ee).

CH_2=$CHCH_2MgCl$ which afforded $BuSn(CH_2CH{=}CH_2)_3$ (δ_{Sn} −35) in good yield (90%). Only two minor contaminants (~5%) are found in these preparations with δ_{Sn} +92 and −22. They are assigned to $ClBuSn(CH_2CH{=}CH_2)_2$ and $Bu_2Sn(CH_2CH{=}CH_2)_2$ respectively based on comparison with authentic material and with literature[17] ^{119}Sn NMR shifts respectively.

With a good source of $BuSn(CH_2CH{=}CH_2)_3$ in hand this was used to allylate acetophenone. Unexpectedly, it proved a poor allyl source on its own providing $PhC(OH)(CH_2CH{=}CH_2)Me$ in 31% yield and 11% ee under standard "dry" conditions after 20 h. However, when mixed with tetraallyltin the ee value from the catalytic reaction rose dramatically. The optimal ratio was determined to be 0.7 : 0.3 tetraallyltin : butyltriallyltin empirically. Under "dry" conditions this system delivered the product alcohol in 89% yield and 68% ee after an overnight run. By dosing this "dry" system with water the selectivity was improved further by eliminating background reactions. The optimum amount of water was found to be 40 mol% (based on acetophenone). Under these conditions acetophenone was allylated in 97% yield and 87% ee. These conditions were screened against a range of ketone structures yielding the *tert*-$R^1C(OH)(CH_2CH{=}CH_2)R^2$ **3** (Table 1).

Varying the substrate structure revealed that the catalyst is very intolerant of increased steric demands close to the carbonyl group (compare runs leading to alcohols **3b**, **3c** and **3h**). The presence of electron withdrawing substituents on the aryl ring is favourable for both yield and ee (see runs leading to **3d**–**3g** and **3i**). Conversely, the presence of electron releasing substituents is detrimental (see **3j**–**3k**). The presence of a methoxy substituent in the 4-position leads to a surprisingly low ee value of 29%. Doucet reported that the allylation of 4-methoxybenzaldehyde using a BINOL-Ti catalyst and allyltributyltin leads only to traces of the homoallylic alcohol product, and this was also suggested to be due to the electron-releasing ability of the methoxy substituent.[18] These observations suggest competing background reactions in such substrates. Finally, non aryl/methyl ketones are not allylated in synthetically useful selectivities by our catalyst (runs leading to **3l**–**3q**).

By running the reactions under strictly anhydrous conditions enantioselectivities in the 85–87% range could be increased to 90–92% ee in favourable cases. However, the yield in such reactions suffered due to the need to keep reaction times short to avoid ee erosion by background autocatalysis. Encouragingly, we could demonstrate the viability of a sub 10 mol% catalyst

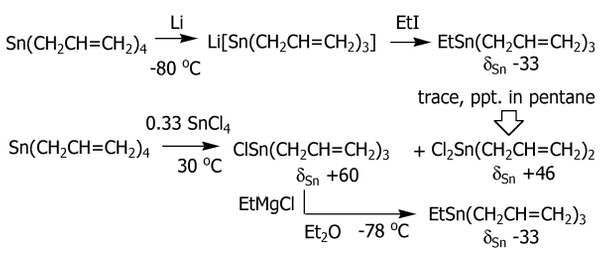
Table 1 Ketone allylation using $MTBH_2$ (20 mol%), water (40 mol%) and 1.1 equivalents of a 0.7 : 0.3 mol fraction mix of tetraallyltin : butyltriallyl tin[a]

Run	R^1	R^2	Time/h	Yield/%	Ee/%
3a	Ph	Me	17	97	87
3a[b]	Ph	Me	17	74	84
3b	Ph	Et	17	19	4
3c	1-Tetralone		18	9	<2
3d	2-Naphthyl	Me	18	>98	87
3e	4-NO_2Ph	Me	19	>98	86
3f	4-BrPh	Me	18	97	86
3g	3-BrPh	Me	16	>98	88
3h	2-BrPh	Me	17	21	45
3i	4-ClPh	Me	18	94	85
3j	4-MePh	Me	18	78	82
3k	4-MeOPh	Me	18	62	29
3l	*E*-PhCH=CH	Me	18	96	71
3m	EtC≡C	Me	16	97	5
3n	Cyclohexyl	Me	19	28	41
3o	1-Cyclohexenyl	Me	16	9	26
3p	*n*-Pentyl	Me	16	96	41
3q	Bu^t	Me	22	4	<2

[a] Reactions on 0.4 mmol (ketone) scale; isolated yields; ee determinations by chiral GC or HPLC (see Supplementary Data)†; (S_a)-$MTBH_2$ gives (*S*)-**3**. [b] Reaction conducted at 9 mol% $MTBH_2$ with 20 mol% water.

using this system and this formed the basis of our initial communication.[5]

In an attempt to further increase the reaction's selectivity we prepared $BuSn(CH_2CH{=}CH_2)_3$ and tetraallyltin completely devoid of even trace impurities. However, when mixed in a 0.7 : 0.3 molar ratio acetophenone was allylated to **3a** in only 63% ee. This result strongly suggested that $RSn(CH_2CH{=}CH_2)_3$ (R = Et, Bu) are *not* the only promoters in this chemistry and thus it became vital to reassess the composition of the initial impure tetraallyltin mixtures containing $EtSn(CH_2CH{=}CH_2)_3$. Finally, we found that we could attain the desired compound free of any other tin contaminant by reductive cleavage of tetraallyltin[19] followed by reaction with EtI (Scheme 2) or by very carefully controlling the conditions of the reaction of EtMgCl and $ClSn(CH_2CH{=}CH_2)_3$ at low temperature. Additionally, pure $ClSn(CH_2CH{=}CH_2)_3$ was attained by controlled reaction of tetraallyltin with $SnCl_4$.[20] The only tin containing by-product was $Cl_2Sn(CH_2CH{=}CH_2)_2$ which was essentially removed by its precipitation in pentane (Scheme 2).



Scheme 2 Routes to high purity $YSn(CH_2CH{=}CH_2)_3$ (Y = Et, Cl) compounds.

Using these pure compounds the dosing effect on pure tetrallyltin was studied in allylations leading to **3a** (Table 2).

From these studies it is clear that species of the type $RSn(CH_2CH{=}CH_2)_3$ (R = Et, Bu) promote the enantioselectivity if they are present in higher concentrations (0.5 mol fraction) while the chloro species has a stronger effect at lower concentrations (0.2 mol fraction). The observation that low levels of chlorotin species are important for the formation of a selective catalyst could be confirmed by washing of the initial impure tetraallyl tin sample (see Fig. 1c) with aqueous KF and drying followed by distillation. These processes reduced the

Table 2 Variation of enantioselectivity in the allylation of acetophenone using $MTBH_2$ (20 mol%) and mixtures of $YSn(CH_2CH{=}CH_2)_3$ (Y = Et, Cl) and tetraallyltin.[a]

Run	Mol Fraction[b]	Conv./%	Ee/%
A. With $EtSn(CH_2CH{=}CH_2)_3$			
1	0.1	>98	42
2	0.2	84	50
3	0.3	>98	58
4	0.5	>98	69
5	0.6	91	29
6	0.8	>98	23
7	1.0	0	—
B. With $ClSn(CH_2CH{=}CH_2)_3$			
8	0.1	>98	57
9	0.2	>98	72
10	0.3	>98	53
11	0.5	>98	34
12	0.6	>98	30
13	0.8	>98	13
14	1.0	>98	13
15	0.0[c]	>97	50

[a] Reactions on 0.4 mmol (ketone) scale; "wet" conditions; conversions by NMR; ee determinations by chiral GC; (S_a)-$MTBH_2$ gives (*S*)-**3a**. [b] Of $YSn(CH_2CH{=}CH_2)_3$ component Y = Et (A) or Y = Cl (B), remainder tetraallyltin. [c] Only tetraallyltin used.

Table 3 Variation of enantioselectivity in the allylation of acetophenone using $MTBH_2$ (20 mol%) and mixtures of $ClSnEt(CH_2CH{=}CH_2)_2$ and tetraallyltin.[a]

Run	Mol fraction[b]	Conv./%	Ee/%
1	0.05	>98	50
2	0.13	80	69
3	0.20	>98	70
4	0.5	>98	69
5	0.06[c]	>98	72

[a] Reactions on 0.4 mmol (ketone) scale; "wet" conditions; conversions by NMR; ee determinations by chiral GC; (S_a)-$MTBH_2$ gives (*S*)-**3a**. [b] Of $ClSnEt(CH_2CH{=}CH_2)_2$ component allowing for 80% purity, reminder tetraallyltin. [c] In presence of additional $EtSn(CH_2CH{=}CH_2)_3$ (mol fraction 0.21), remainder tetraallyltin.

enantioselectivity from 71% to 50% initially and 38% finally in the allylation of acetophenone. The presence of organotin chlorides is important as simple addition of alternative inorganic chloride salts to the reaction mixture had no effect. When mixed together in appropriate ratios mixtures of pure tetraallyltin and $YSn(CH_2CH{=}CH_2)_3$ (Y = Et, Cl) [molar ratios: 0.8 (tetraallyltin) : 0.06 (triallyl, Y = Et) : 0.14 (triallyl, Y = Cl)] are able to effect the $MTBH_2$ catalysed allylation of acetophenone in 80–93% ee. The need for both components to be present suggested to us that the ethyl and chloro species might be participating in redistribution reactions during catalyst formation and that this might lead to the formation of $ClSnEt(CH_2CH{=}CH_2)_2$ and that this leads to the most selective catalysts. The latter compound could be prepared by reaction of $EtSn(CH_2CH{=}CH_2)_3$ with $PhICl_2$ in $CHCl_3$[21] and gave a ^{119}Sn NMR resonance at +92 ppm which had previously been observed, at trace levels, in our most active tetraallyltin samples. However, $ClSnEt(CH_2CH{=}CH_2)_2$ proved rather sensitive to hydrolysis and only material of 80% purity could be attained by prompt distillation, the mass balance being PhI and traces of a tetraorganodistanoxane (see later). This impure $ClSnEt(CH_2CH{=}CH_2)_2$ when tested also led to an improvement in the stereoselectivity for the allylation to **3a** (Table 3). Which also showed modest promotion by this compound.

Tagliavini has observed that halotin reagents are much more reactive in the allylation reactions of carbonyl compounds than

tetraallyltin alone.[22] The results obtained here strongly suggest that such compounds effect the formation of a very active and selective catalyst with $MTBH_2$ and that uses $Sn(CH_2CH{=}CH_2)_4$ as the terminal allyl source in the catalytic asymmetric allylation reaction. Indirect evidence supports this proposal. Firstly, the presence of the SH function in $MTBH_2$ is vital. Its alkylation to an SMe group completely deactivates the system. Tin(IV) has a high affinity for Sn–S bond formation (comparable to Sn–O based on literature values[23]). Thus, ligation of the MTB unit to tin is expected to be favoured by tin precursors containing suitable leaving groups. Secondly, monitoring catalytic allylation reactions by ^{1}H NMR spectroscopy reveals that the majority of the $MTBH_2$ ligand remains after mild heating with tetrallyltin (52 °C, 2 h, *c.f.* catalyst formation conditions).

Studies on potential catalyst structures

Attempts to isolate the actual species responsible for the high activity from the active catalytic reaction mixtures were not successful and so some investigations involving reactions of $MTBH_2$ with organotin reagents were made.

Modest heating of $MTBH_2$ with pure tetraallyltin in CH_2Cl_2, benzene or toluene leads to no apparent reaction over 2 h. Heating much more strongly (80–120 °C) in aromatic solvents leads to the slow consumption of the $MTBH_2$ ligand and the formation of a bright yellow solution similar to that observed in the catalytic reaction. On removal of the solvent a yellow powder is isolated. Mass spectroscopic evidence indicates the presence of $Sn(MTB)_2$ [*m*/*z* 719], however, the compound could not be isolated analytically pure nor could it be crystallised. While $Sn(MTB)_2$ was very active (down to 3 mol%) in catalysing the addition of $Sn(CH_2CH{=}CH_2)_4$ to acetophenone the selectivities shown are slight (<15% ee) indicating that it is not the active species in the reaction mixture.

While reaction of $EtSn(CH_2CH{=}CH_2)_3$ with $PhICl_2$ proved an effective route to $ClSnEt(CH_2CH{=}CH_2)_2$. It is impossible to completely dry $PhICl_2$ without decomposing it (the reagent is prepared in water route by using conc. HCl and rigorous drying under vacuum removes Cl_2). We noted that traces of water in the hypervalent iodine reagent lead to slow formation of a new organotin species showing two broadened ^{119}Sn NMR resonances at −129 and −178 ppm. On standing of the $ClSnEt(CH_2CH{=}CH_2)_2$ sample subsequent precipitation of colourless hexagonal plates was observed. Crystallographic analysis revealed the identity of the hydrolysis product as **4** whose structure is shown in Fig. 2. It is interesting that selective hydrolysis of the allyl groups takes place and that the Sn–Cl bonds are unaffected.

Molecular structure of bis(diallyl-diethyl-dichlorodistanoxane) 4

Hydrolysis of $EtSnCl(CH_2CH{=}CH_2)_2$ gave the compound bis(diallyldiethyldichlorodistanoxane) **4**. It is known, through the X-ray structural analysis of several such molecules, $[(R_2SnX)_2O]_2$, that predominance of "ladder" **I** or "staircase" **II** structures exist on crystallisation based on four-membered Sn_2O_2 rings.

These molecules are believed to form *via* a hydroxo-tin intermediate, $[R_2SnX(OH)]$.[24] In the ladder structure all the four tin atoms, the four X groups and the two oxygen atoms comprising the fused systems are more or less planar. Solution NMR spectra of both **I** and **II**, in general, exhibit two well separated ^{119}Sn NMR signals for endo- and exo-cyclic tin sites, and one and two sets of resonances for the X and R groups, respectively, attached to tin in the ^{1}H and ^{13}C NMR spectra.[25,26] Variable temperature NMR data of published tetraorganodistannoxane dimers indicate that both the "ladder" **I** and "staircase" **II** conformations often co-exist in solution and can show dynamic exchange behaviour.[25] Interconversion between the two structures **I** and **II** may occur readily in solution,

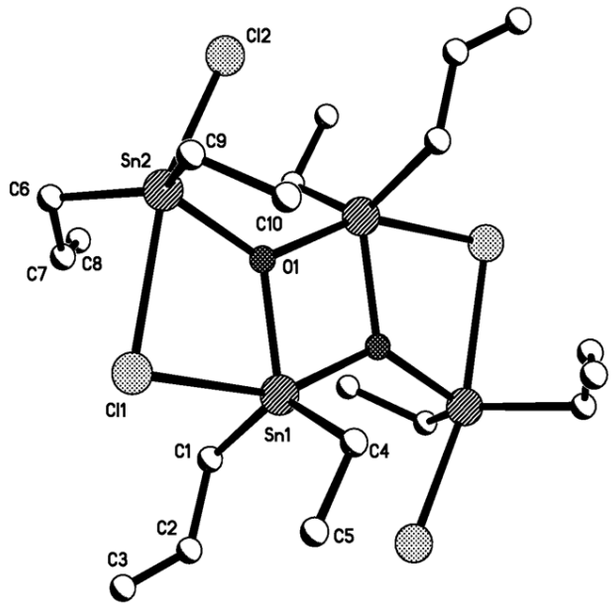
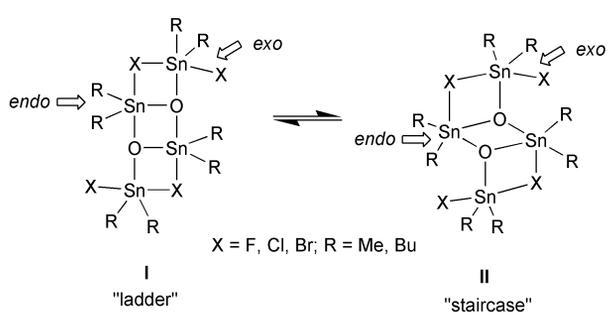


Fig. 2 View showing molecular structure of $Sn_4(\mu_3\text{-}O)_2(\mu_2\text{-}Cl)_2\text{-}Cl_2Et_4(CH_2CH{=}CH_2)_4$ **4**. Minor disorder components and hydrogen atom excluded for clarity. Selected bond distances and angles: Sn(1)–C(1) 2.141(4), Sn(1)–C(4) 2.116(5), Sn(1)–Cl(1) 2.6609(12), Sn(1)–O(1) 2.129(3), Sn(2)–C(6) 2.129(5), Sn(2)–C(9) 2.123(6), Sn(2)–Cl(1) 2.7537(13), Sn(2)–Cl(2) 2.4720(14) Å; Sn(1)–O(1)–Sn(2) 123.33(15), Sn(1)–Cl(1)–Sn(2) 83.21(4) (deg).



possibly owing to relatively small energy difference between the two forms, so that only one form is obtained on crystallisation. Interconversion between the two structures **I** and **II** in solution leads either to broadening or the observation of multiple signals in ^{119}Sn and ^{13}C NMR spectra.

The ^{119}Sn{^{1}H} NMR spectra of the compound **4** showed two well separated broadened resonances at −129 and −178 ppm, characteristic of disubstituted teraorganodistannoxane dimers.[26] The low (−129 ppm) and high (−178 ppm) field resonances have been attributed to the exo-cyclic and endocyclic tin atoms respectively. A $^2J(^{119}Sn–^{119/117}Sn)$ coupling was resolved for the exo-cyclic tin atom in our case. Due to the interconversion between the two structures, **I** and **II**, in the solution at RT the ^{119}Sn and ^{1}H NMR resonances of the compound **4** were broadened. Additionally, two sets of resonances for each of the allyl and ethyl, groups were observed in the ^{13}C{^{1}H} NMR spectra.

On crystallisation compound **4** showed the "staircase" **II** structure with a planar Sn_2O_2 ring as shown in Fig. 2. Each tin site has a five co-ordination number. The bridging Sn–Cl [2.7537(13)] bond distance is significantly longer than the non bridging Sn–Cl [2.4720(14)] bond distance as observed in a number of other teraorganodistannoxanes.[27]

The tetraorganodistannoxane **4** leads to the formation of a rather selective catalyst with $MTBH_2$ (20 mol%) at low mol fractions of tin (Table 4). At higher loadings of **4** only very low stereoselectivities are realised in the derived **4** implying that modification of **4** is facilitated by a higher relative

Table 4 Variation of enantioselectivity in the allylation of acetophenone using $MTBH_2$ (20 mol%) and mixtures of **4** and tetraallyltin.[a]

Run	Mol fraction[b]	Conv./%	Ee/%
1	0.20	>98	34
2	0.15	>98	31
3	0.10	>98	69
4	0.05	62 to >98[c]	80–85[c]
5	0.02	>98	59
6	0.01	50	55
7	0.005	>98	50

[a] Reactions on 0.4 mmol (ketone) scale; "wet" conditions; conversions by NMR; ee determinations by chiral GC; (S_a)-$MTBH_2$ gives (*S*)-**3a**. [b] Of **4** remainder tetraallyltin. [c] Range for multiple runs.

concentration of $MTBH_2$. This derived species appears to be responsible for our original observations.

Conclusion

Careful studies have revealed that the origin of the highly active and selective catalysts for the allylation of aryl/methyl ketones are formed from $MTBH_2$ and impure tetraalllyltin containing $EtSn(CH_2CH{=}CH_2)_3$, $ClSn(CH_2CH{=}CH_2)_3$ and especially $ClSnEt(CH_2CH{=}CH_2)_2$. The latter appears to lead to formation of the optimal catalyst through hydrolysis to the tetraorganodistanoxane **4**. This distanoxane ligates the $MTBH_2$ ligand and leads to a very selective catalyst of (presently) unknown structure. In reaction mixtures lacking $ClSnEt(CH_2CH{=}CH_2)_2$ small amounts of this species appear to be generated by Kocheshkov-type redistributions of $YSn(CH_2CH{=}CH_2)_3$ (Y = Cl and Et). The equivalent butyltin reagents presumably behave analogously. The exact nature of the species formed from the reaction of stanoxane **4** and $MTBH_2$ is under current investigation.

Experimental

General

Full details of the asymmetric allylation products are given in the supporting information. † Details of the preparation of the tin reagents is given here as some are poorly described and the route to the preparation can affect the catalysis due to the presence of minor impurities. Samples of $PhICl_2$ were prepared by literature procedures.[28]

Triallylethyltin

Method A. To a stirred mixture of tetraallyltin (1.415 g, 5.00 mmol) and lithium (87 mg, 12.54 mmol) cold THF (15 ml) was added dropwise at −45 °C over a period of 15 min, under argon atmosphere.[19] After the addition was completed the mixture was further stirred for 18 h at the same temperature to give a dark green solution. The complete disappearance of tetraallyltin was confirmed by TLC analysis. The above green solution was cooled at −80 °C and dry EtI (2.5 ml) was added drop wise through the wall of a reaction Schlenk over 25–30 min at the same temperature under an argon atmosphere. After being stirred for another 40 min at −80 °C, it was warmed to room temperature and then reaction was quenched with H_2O (10 ml). The organic layer was extracted with pentane (30 ml × 3) and the pentane layer was again washed with H_2O (20 ml × 3). The pentane layer was dried over Na_2CO_3 overnight and after filtration the solvent was removed under reduced pressure to give a colourless oily liquid. The crude product after fractional distillation (bp 110–112 °C, 0.7 mmHg) yielded a colourless oily liquid, $EtSn(CH_2CH{=}CH_2)_3$. Yield 95%. Elemental analysis, found: C 48.90, H 7.45%, Calculated for $C_{11}H_{20}Sn$: C 48.75, H 7.44%; δ_H (400 MHz, $CDCl_3$) 0.98 (2 H, q, *J* 8.0, CH_2), 1.21 (3 H, t, *J* 8.0, Me), 1.89 (6 H, ddd, *J* 8.6, 1.3, 0.7, CH_2), 4.72 (3 H, ddt, *J* 10.0, 1.9, 0.7, $=CH_{2\alpha}$), 4.86 (3 H, ddt, *J* 16.9, 1.9, 1.3, $=CH_{2\beta}$), 5.94 (3 H, ddt, *J* 16.9, 10.0, 8.6, =CH); δ_C (100.6 MHz, $CDCl_3$) 1.8, 10.9, 15.9, 110.6, 137.1; δ^{119}_{Sn} (149.2 MHz, $CDCl_3$) −32.8; *m*/*z* (EI) 271 (M^+, 1%), 231 (73), 161 (100); ν_{max} (thin film)/cm^{-1} 3077m, 2964br, 2910br, 1622s, 1421w, 1260w, 1188m.

The reliability of this route is critically dependent on the use of fresh lithium powder. Older samples led to capricious reactions yielding only mixtures containing tetraallyltin.

Method B. To a stirred solution of triallyltin chloride (1.3090 g, 4.72 mmol) in dry Et_2O, a solution of ethylmagnesium chloride in Et_2O (4.72 mmol, 2.36 ml of 2.0 M solution in Et_2O) was added dropwise at −78 °C over a period of 2 h, under argon atmosphere. The reaction mixture was stirred overnight in the same cold bath under argon during which time it was slowly warmed to room temperature. The reaction mixture was refluxed for two h under argon and $MgCl_2$ ppt. was filtered off and washed with dry Et_2O. The solvent was removed under reduced pressure to yield a colourless oily liquid (yield, 1.01 g, 80%). The crude product was further purified by fractional distillation (bp 110–115 °C, 0.6 mmHg), yielding a colourless oily liquid, $EtSn(CH_2CH{=}CH_2)_3$. The compound was characterised as per method A.

Triallylbutyltin

Neat $BuSnCl_3$ (2.76 g, 9.8 mmol) in dry Et_2O (10 mL) was added drop wise over 1 h to a stirred solution of allylmagnesium chloride in Et_2O (0.62 M in Et_2O; 75 ml, 46.8 mmol) under an inert atmosphere at −10 °C. The mixture was allowed to warm to room temperature and then refluxed for 8 h. The mixture was cooled to −10 °C and the excess Grignard reagent was quenched with H_2O followed by 2 M $HCl_{(aq)}$. The aqueous layer was extracted with Et_2O (× 2) and the combined organic layers were washed with H_2O and dried (4 Å molecular sieves). The solvent was removed to yield a pale yellow liquid (3.09 g). The crude product was distilled (bp 70–72 °C, 0.5 mmHg) to give a colourless liquid, (2.64 g, 90%); δ_H (400 MHz, $CDCl_3$) 0.91 (3 H, t, *J* 7.3, Me), 1.01 (2 H, apparent t, *J* 8.0, CH_2), 1.31 (2 H, sextet, *J* 7.3, CH_2), 1.49–1.57 (2 H, m, CH_2), 1.88 (6 H, ddd, *J* 8.6, 1.3, 0.8, CH_2), 4.72 (3 H, ddt, *J* 10.0, 1.9, 0.8, $=CH_{2\alpha}$), 4.84 (3 H, ddt, *J* 16.9, 1.9, 1.3, $=CH_{2\beta}$), 5.94 (3 H, ddt, *J* 16.9, 10.0, 8.6, =CH); δ_C (100.6 MHz, $CDCl_3$) 9.7, 13.8, 16.3, 27.2, 28.9, 110.5, 137.2; δ^{119}_{Sn} (149.2 MHz, $CDCl_3$) −35.4; ν_{max} (thin film)/cm^{-1} 3076w, 2960w, 2916br, 1622m, 1260w, 1188w.

When $BuSnCl_3$ (4.48 g, 15.9 mmol) was added drop wise over 5 min to allylmagnesium chloride (0.70 M in Et_2O; 70 mL, 47.6 mmol) and the reflux time reduced to 2 h, the distilled product was contaminated with minor traces of two other tin species; δ^{119}_{Sn} (149.2 MHz, $CDCl_3$) −22.4, +91.7 assigned to $Bu_2Sn(CH_2CH{=}CH_2)_2$ and $ClSnBu(CH_2CH{=}CH_2)_2$ respectively.

Triallyltin chloride

Neat $SnCl_4$ (0.8904 g, 3.42 mmol) was added drop wise over 15–20 min to a stirred solution of tetraallyltin (3.007 g, 10.63 mmol) in dry benzene (40 ml) under an atmosphere of argon at 30 °C.[20] After the addition was completed the mixture was further stirred for 15 min at 30 °C and allowed to cool to room temperature. The solvent was removed under reduced pressure to yield a colourless oily liquid (3.60 g, 92%). The crude product was distilled under reduced pressure (bp 100–103 °C, 0.5 mmHg) to give $ClSn(CH_2CH{=}CH_2)_3$ (3.4 g, 87%). The ^{119}Sn and ^1H NMR spectra of the distilled product revealed the presence of two species, a peak at +60 ppm (98%) which was assigned to $ClSn(CH_2CH{=}CH_2)_3$ and a trace impurity at +46 ppm (2%) assigned to $Cl_2Sn(CH_2CH{=}CH_2)_2$ based on literature data.[29] The diallyltin dichloride impurity was removed by precipitation in dry pentane at −20 °C giving pure $ClSn(CH_2CH{=}$

$CH_2)_3$. Elemental analysis, found: C, 38.32; H, 5.12%. Calculated for $C_9H_{15}SnCl$: C, 38.97; H, 5.45%. δ_H (400 MHz, $CDCl_3$) 2.30 (6 H, ddd, *J* 8.4, 1.3, 0.8, CH_2), 4.94 (3 H, ddt, *J* 10.0, 1.8, 0.8, $=CH_{2\alpha}$), 5.04 (3H, ddt, *J* 16.9, 1.8, 1.3, $=CH_{2\beta}$), 5.90 (3 H, ddt, *J* 16.9, 10.0, 8.4, =CH); δ_C (100.6 MHz, $CDCl_3$) 22.9 (J^{117}_{Sn} 284, J^{119}_{Sn} 298), 114.6 (J_{Sn} 67), 133.4 (J_{Sn} 56.9); δ^{119}_{Sn} (149.2 MHz, $CDCl_3$) +60.2; *m*/*z* (EI) 243 (M^+, 13%), 201, 161, 123, 109, 69 (100); ν_{max} (thin film)/cm^{-1} 3079m, 2971m, 2916w, 1800w, 1625s, 1420s, 1390m, 1296w, 1187s.

Diallylchloroethyltin

To a stirred solution of triallylethyltin (1.01 g, 3.73 mmol) in $CDCl_3$ (4 ml) crystals of $PhICl_2$ (1.08 g, 3.92 mmol) were added quickly under argon atmosphere at RT and the Schlenk tube closed quickly to avoid any loss of Cl_2 gas from the reaction mixture. The solution was stirred for 2–3 h while being monitored by ^{1}H NMR spectroscopy. The reaction mixture was filtered by cannula under argon atmosphere and the solvent removed under reduced pressure. A colourless oily liquid was left behind with some white crystalline solid. The white solid was filtered off by cannula and the crude liquid was further purified (for removal of PhI and any unreacted triallylethyltin) by fractional distillation (bp 100–120 °C, 1.5 mmHg), yielding a colourless, reactive, oily liquid, $EtSnCl(CH_2CH{=}CH_2)_2$ (0.69 g, 70%); δ_H (400 MHz, $CDCl_3$) 1.31 (2 H, q, *J* 8.1, CH_2Me), 1.36 (3 H, t, *J* 8.1, CH_2*Me*), 2.28 (4 H, ddd, *J* 8.7, 1.8, 0.8, CH_2), 4.90 (2 H, ddt, *J* 10.1, 1.8, 0.8, $=CH_{2\alpha}$), 5.02 (2 H, ddd, *J* 16.9, 1.8, 1.5, $=CH_{2\beta}$), 5.95 (2 H, ddt, *J* 16.9, 10.1, 8.7, =CH); δ^{119}_{Sn} (149.2 MHz, $CDCl_3$) +92 (>85%) assigned to $EtSnCl(CH_2CH{=}CH_2)_2$, −178 and −129 (<10%), assigned to $([(CH_2CH{=}CH_2)EtSnCl]_2O)_2$. Accurate elemental analyses and mass spectroscopic characterisation were prevented by the compound's reactivity. On standing, $EtSnCl(CH_2CH{=}CH_2)_2$ hydrolyses readily to white crystalline $([(CH_2CH{=}CH_2)EtSnCl]_2O)_2$, bis(diallyl-diethyl-dichlodistannoxane) **4** due to the presence of water in the reaction route through $PhICl_2$. Therefore, an alternative route for the synthesis of diallylchloroethyltin, which could avoid the hydrolysis of this compound, is under investigation.

Bis(diallyl-diethyl-dichlorodistanoxane) 4

To a stirred solution of triallylethyltin (0.689 g, 2.54 mmol) in $CDCl_3$ (4 ml) crystals of $PhICl_2$ (0.767 g, 2.79 mmol) were added quickly under argon atmosphere at RT and the reaction Schlenk was closed quickly to avoid any loss of Cl_2. The solution was stirred for overnight at RT under argon atmosphere and was then filtered with the help of a cannula. The solvent was removed under vacuum leaving behind colourless oily liquid [crude $EtSnCl(CH_2CH{=}CH_2)_2$]. This crude product was dissolved in wet Et_2O (undried, 5 ml) to facilitate hydrolysis of the $EtSnCl(CH_2CH{=}CH_2)_2$. The solution was left overnight at RT and solvent was removed under vacuum. The white crystalline solid was washed with pentane (4 × 4 ml) to remove PhI and any unreacted triallylethyltin. The residue was recrystallised from cold $CDCl_3$ and pentane to yield colourless hexagonal plates of $([(CH_2CH{=}CH_2)EtSnCl]_2O)_2$ **4**. (1.01 g, 85%). Mp 109 °C. Elemental analysis, Found: C, 25.81; H, 4.33; Cl, 15.70%. Calculated for $C_{20}H_{40}Sn_4Cl_4O_2$: C, 25.85; H, 4.35; Cl, 15.26%; δ_H (400 MHz, $CDCl_3$) 1.42–1.49 (12 H, m, Me), 1.80–1.89 (8 H, br m, $J(^{119/117}Sn–^1H)$ unresolved, CH_2), 2.52–2.89 (8 H, broad m, $J(^{119/117}Sn–^1H)$ unresolved), 5.02–5.09 (4 H, m, $=CH_{2\alpha}$), 5.19–5.24 (4 H, m, $=CH_{2\beta}$), 6.08–6.15 (4 H, m, =CH); δ_C (100.6 MHz, $CDCl_3$) 10.1, 10.5, 24.6, 26.5, 26.9, 36.9, 37.6, 37.9, 116.5, 116.9, 132.7 (due to presence of ladder and staircase isomers in solution); δ^{119}_{Sn} (149.2 MHz, $CDCl_3$) −178 (br, endo-cyclic Sn(1)), −129 (br, exo-cyclic Sn(2), $J(^{119}Sn–^{119/117}Sn)$ ~295); ν_{max} (thin film)/cm^{-1} 3050m, 2922br, 2869br, 1626s, 1500w, 1420m, 1390w, 1250w, 1187s, 1130w, 1033s, 879s, 757m, 680s. No acceptable mass spectrum could be attained with the techniques tried (EI, CI, ES, FAB).

Representative catalytic allylation for acetophenone, (*S*)-(−)-2-phenyl-pent-4-en-2-ol (3a)

Solid (S_a)-(+)-$MTBH_2$ (24.0 mg, 0.08 mmol) was treated with tetraallyltin (75 µl, 0.31 mmol) and $YSn(CH_2CH{=}CH_2)_3$ (Y = Et, Bu, Cl) (0.15 mmol) and H_2O (3 µl, 0.16 mmol) followed by the addition of toluene (1 mL) under an atmosphere of argon. The resulting mixture was stirred at ambient temperature for 5 min then heated at 52 °C for 2 h. The mixture was allowed to cool to room temperature and acetophenone (47 µl, 0.4 mmol) was added and the mixture stirred at room temperature for 16 h. Hexane (2–4 ml) was added to the reaction mixture and the precipitated catalyst was filtered off (Celite). The filtrate was concentrated and the residue chromatographed on silica (hexane then Et_2O) to yield (*S*)-(−)-2-phenyl-pent-4-en-2-ol (**3a**)[2,4] (64 mg, 98%) (83–89% ee); δ_H (400 MHz, $CDCl_3$) 1.57 (3 H, s, Me), 2.12 (1 H, s, OH), 2.53 (1 H, dd, *J* 13.7, 8.3, plus unresolved couplings to $=CH_2$, $CH_{2\alpha}$), 2.72 (1 H, ddt, *J* 13.7, 6.4, 1.1, $CH_{2\beta}$), 5.12–5.14 (1 H, m, $=CH_{2\alpha}$), 5.15–5.18 (1 H, m, $=CH_{2\beta}$), 5.64 (1 H, dddd, *J* 14.7, 10.2, 8.3, 6.4, =CH), 7.26 (1 H, tt, *J* 7.3, 1.3, Ar), 7.34–7.38 (2 H, m, Ar), 7.44–7.47 (2 H, m, Ar); δ_C (100.6 MHz, $CDCl_3$) 29.9, 48.5, 73.7, 119.5, 124.8 (2 C), 126.7, 128.2 (2 C), 133.7, 147.7; ν_{max} (thin film)/cm^{-1} 3428br, 3074m, 2977s, 2930m, 1639m, 1494m, 1446s, 1374m, 1069m; *m*/*z* (EI) 144 (13%), 129 (16), 121 (100). "Dry" procedures were identical except that water was not added. Equivalent runs were carried out with many different organotin reagents and varying ratios. Similar results were attained using catalysis by **4** (5 mol%) and $MTBH_2$ (20 mol%). Other ketones were reacted by related procedures under the conditions given in Tables 1–4.

Crystallographic structure determination of 4

Hexagonal colourless plates of $Sn_4(\mu_3\text{-}O)_2(\mu_2\text{-}Cl)_2Cl_2Et_4(CH_2CH{=}CH_2)_4$ **4** were grown from $CHCl_3$ at low temperature. A crystal of dimension 0.19 × 0.16 × 0.06 mm was mounted in perfluoropolyether oil. Data were collected at 150 K on a Bruker APEX CCD area detector diffractometer equipped with an Oxford Cryosystem opened-flow nitrogen cryostat. Data were corrected for Lorentz and polarization effects and for absorption, using a semi-empirical method (Bruker SADABS v2.03), (*T* min/max 0.589 and 0.810 respectively). The structure was solved by direct methods (SHELXS-97) and refined using full-matrix least squares refinement against F^2 (SHELXTL). Only fully occupied non-H atoms were refined with anisotropic atomic displacement parameters and H atoms placed in geometrically calculated positions and refined as part of a riding model, with $U(H)_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl hydrogen atom. Disorder was present in one of the ethyl and both the allyl groups. The methyl carbon atom (C10) and the central carbon atoms of the allyl groups were modelled over two sites with occupancies 0.75 and 0.25, and suitable distance restraints were applied.

$C_{20}H_{40}Cl_4O_2Sn_4$, M = 929.08, monoclinic, a = 18.525(3), b = 10.4917 (15), c = 15.695(2) Å, β = 95.085(2)°, U = 3038.4(13) Å^3, T = 150 K, space group *C*2/*c* (no. 15), Z = 4, μ(Mo-Kα) = 3.62 mm^{-1}, 7619 reflections measured, 3674 unique (R_{int} = 0.023) which were used in all calculations. The final w$R(F^2)$ was 0.089 for all data, $R_1(F)$ was 0.033 for 2780 observed data were $I > 2\sigma(I)$.§

§ CCDC reference number 222923. See http://www.rsc.org/suppdata/ob/b3/b313384b/ for crystallographic data in.cif or other electronic format.

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