Recent advances in the chemistry of the organotin hydrides

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Advances in the chemistry of the organotin hydrides during the last decade are reviewed.

Keywords: organotin, stannane, tin hydride

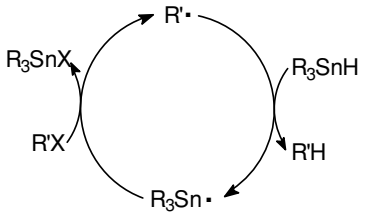
Much of the interest in the organotin hydrides results from their many applications in organic synthesis in the hydrostannolysis of halides or related molecules, and the hydrostannation of alkenes and alkynes. These reactions usually involve stannyl radicals in chain mechanisms.[1] The basic processes are shown in Schemes 1 and 2, but the secondary radicals R'• and R_3SnXY• (or $R_3SnX{=}Y$•) are often diverted through a cascade of reactions before they rejoin the cycle and are quenched by abstracting hydrogen from the tin hydride. An extreme example of this behaviour is shown in Scheme 3, where, between the initial formation of the stannyl radical and the removal of the resulting organic radical, a heptacyclic system is generated in a single step by seven sequential cyclisations.[2] Numerous further examples can be found in recent reviews.[3-7]

With the stimulation of these applications in synthesis, a lot of work has been reported recently on basic organotin hydride chemistry. This review will survey the advances that have been made in the last ten years, with some reference to earlier work to put the the recent work into context. It indicates the importance of organotin hydrides in synthetic chemistry, but does not look in any detail at their applications.

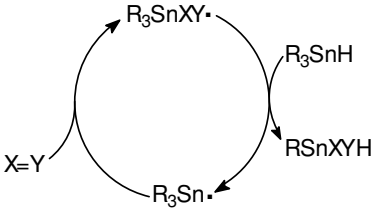
Preparation of the organotin hydrides

The hydrides were first prepared by reducing the corresponding chlorides with lithium aluminium hydride,[8] and this method is still widely used. Other reducing agents that have been used include R_2AlH, $NaBH_4$, $NaBH_3CN$, B_2H_6, LiH, $(MeSiHO)_n$ (PMHS), and Et_3SiH.[1,7]

Tributyltin hydride is used most frequently in synthesis because it is cheaper, less volatile, and less toxic than the lower homologues, and, for a long time, has been commercially available. In the laboratory, the most convenient preparation is probably by the distillation of tributyltin oxide and poly (methylhydrosiloxane) (PMHS) under reduced pressure, when the hydride (b.p. 80 °C/0.4 mm Hg) distils over in good yield (equation (1)).[9]



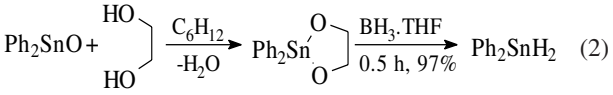
Scheme 1 Hydrostannolysis. X = Cl, Br, I, OC(=S)R', OC(O)SePh, SPh, SePh *etc.*



Scheme 2 Hydrostannation. X =Y = alkene, alkyne, carbonyl, *etc.*

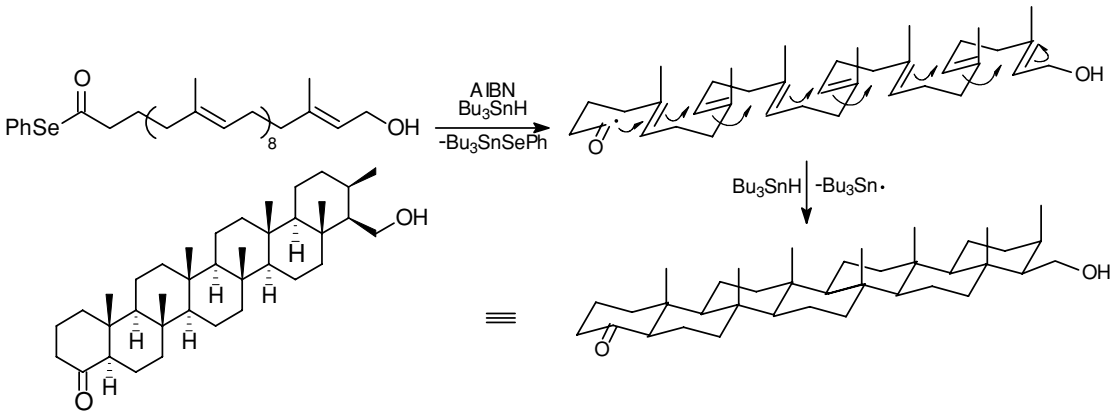
$$n(Bu_3Sn)_2O + 2(MeSiHO)_n \xrightarrow[79\%]{} 2nBu_3SnH + 2(MeSiO_{1\cdot5})_n \quad (1)$$

Dibutyltin oxide is an insoluble polymer, but it can be reduced with PHMS to dibutyltin hydride if it is first heated with butanol to convert it into the soluble distannoxane, $(BuO)Bu_2SnOSnBu_2(OBu)$.[10] The dioxastannolanes are also soluble, and provide an alternative (equation (2)).[11]



(2)

The organotin deuterides can be prepared by similar methods, and Bu_3Sn^3H has been obtained by reduction of the chloride



Scheme 3 Hydrostannolysis involving a cascade of intervening reactions.

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with NaB^3H_4 or Li^3H, or by hydrolysis of Bu_3SnLi with ^3H_2O.[12,13]

A novel approach to unsymmetrical tin hydrides, $R_2R'SnH$, is provided by the lithiation of R_2SnH_2 with lithium di-isopropylamide, then *in situ* treatment of the lithium stannide with an alkyl halide, *e.g.* equation (3).[14] This method has been used for attaching a stannyl hydride group to a polymer chain (equation (11)).

$$Bu_2SnH_2 + Pr^i_2NLi \longrightarrow [Bu_2SnHLi] \xrightarrow[45\%]{MeI} MeBu_2SnH \quad (3)$$

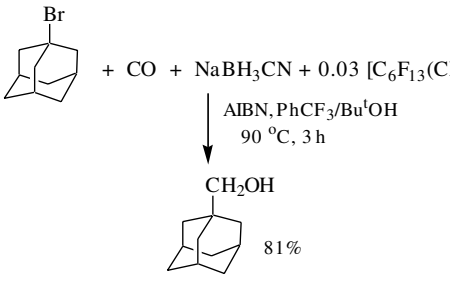
Hydroxy- or alkoxy-hydrides have been prepared by oxidative addition of water or an alcohol to a persistent stannylene (equation (4)).[15] When dimethylstannylene is generated in the presence of methanol, it shows a transient absorption spectrum which suggests that reaction occurs only to the stage of the Lewis acid-base complex, but, in the presence of Me_3SnH, the stannylene reacts to give the stable pentamethyldistannane (equation (5)).[16]

$$[(Me_3Si)_2CH]_2Sn: + H_2O \xrightarrow[0\ ^oC]{THF} \underset{98\%}{[(Me_3Si)_2CH]_2Sn(OH)H} \quad (4)$$

$$SnMe_2 \xrightarrow[C_6H_{14}]{h\nu} Me_2Sn: \xrightarrow{Me_3SnH} Me_3SnSnMe_2H \quad (5)$$

One factor that has limited the use of the simple tin hydrides in synthesis is the problem they present in separating and disposing of toxic organotin residues,[1] and the danger that traces may remain in pharmaceuticals. Very little has been published on the toxicity of the hydrides themselves, but the mammalian toxicity appears to be less than that of the corresponding organotin halides.[17,18-22]

The problem for hydrostannolysis reactions is reduced if a catalytic amount of the trialkyltin hydride (or its chloride or oxide precursor) is used in the presence of one of the metal hydrides that are listed above, so that the tin hydride is continually regenerated *in situ*, *e.g.* equations (6) and (7).[23,24]



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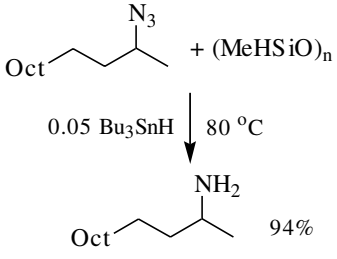
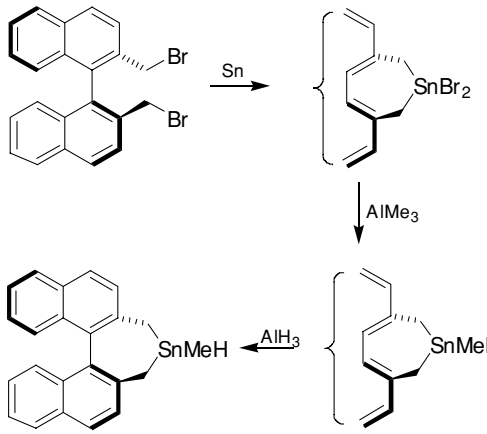


(7)

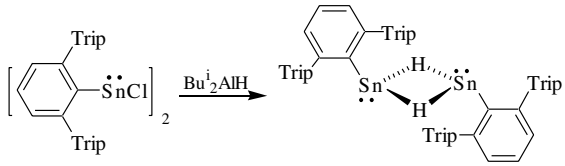
Alternatively, the reduction can be carried out with a dialkyltin hydride, R_2SnH_2 or R_2SnXH (see below), when the dialkyltin by-product can readily be hydrolysed to give the insoluble dialkyltin oxide $(R_2SnO)_n$, which can easily be separated.

A number of tin hydrides with chiral groups, particularly menthyl groups, have been prepared with the aim of asymmetric hydrostannation or hydrostannolysis.[25-28] Optically active tin hydrides containing the chiral 2,2'-binaphthyl group have been prepared,[29,30] *e.g.* equation (8).[29] With bulkier alkyl groups, such as *t*-butyl or neopentyl, on the tin, the highest enantioselectivity that has been reported in the reduction of a bromide is 68%.[30]



(8)

All the hydrides discussed above are based on Sn(IV). As yet, only one Sn(II) hydride has been reported, where the sterically protected 2,6-bis(2,4,6-triisopropylphenyl) phenyltin(II) chloride is reduced with diisobutylaluminium hydride (equation (9)). It is blue in solution, but separates out as orange crystals.[31] The structure has been determined by X-ray diffraction,[31] and, more accurately, by neutron diffraction, and exists of a hydrogen-bridged dimer, with *r*SnH 194 pm, at 20 K.[32]



(9)

Trip = 2,4,6-triisopropylphenyl

Tin hydrides designed for easy separation of residues

A variety of tin hydrides with special structures have been designed to facilitate the removal of tin residues (Fig. 1).

The first six hydrides in Fig. 1 contain basic nitrogen,[33-36] and by-products can be washed out with aqueous acid. The ketal lactone gives by-products that can be hydrolysed to give acids that are readily soluble in aqueous base.[37] The pyrenylpropylstannane can be removed by adsorption on activated carbon.[38] The by-products from the fluorous hydride can be extracted from an organic solvent into a fluorous solvent,[39-41] and the hydrides with a polyethylene oxide tail give derivatives that can be washed out with water.[42,43] Tin hydride-cyclodextrin complexes can be used for carrying out reactions in water.[44]

Polymer-supported tin hydrides provide an alternative solution to the problem of avoiding toxic residues.[45-47] The base is usually polystyrene, cross-linked with divinylbenzene to the degree that leaves the polymer sufficiently porous but insoluble. The hydrostannyl group is introduced by conventional organotin methodology, *e.g.* equations (10)[48] and (11).[49]

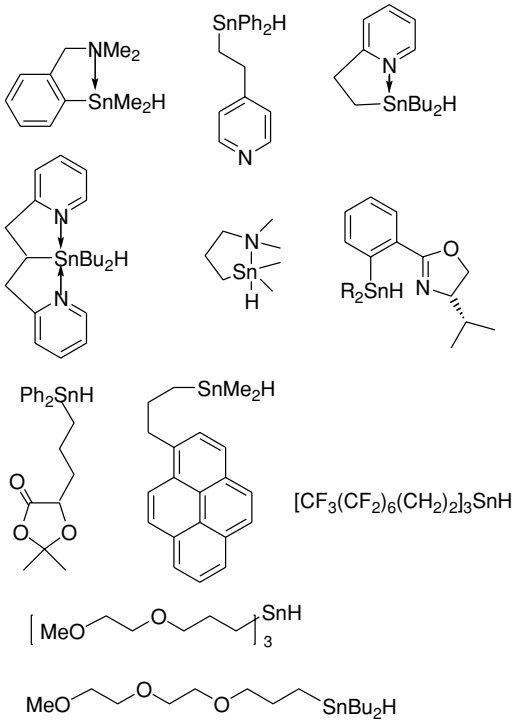
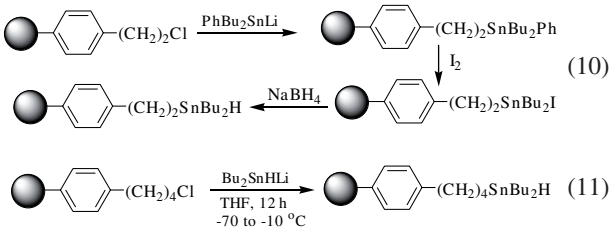


Fig. 1 Tin hydrides designed for easy separation of residues.

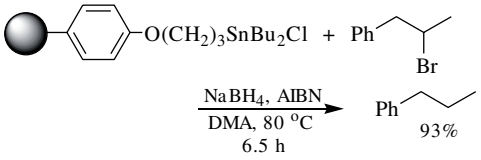


(10)

(11)

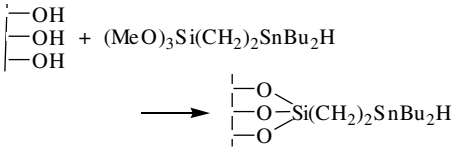
These polymer-supported hydrides show the same reactions as tributyltin hydride, including use in a catalytic amount in the presence of another metal hydride, and Nicolaou has used palladium-catalysed hydrostannolysis to bring about the cleavage of allyl esters[50] (see Table 1). The reactions, however, are slower than with the unsupported hydrides, because of the limiting rate of diffusion of the reactants into the polymer. A representative selection of reactions is given in Table 1.

An interesting alternative is to use a non-cross-linked polymer support, so that the reaction can be carried out in homogeneous solution in a solvent such as benzene, after which the catalyst can be recovered by precipitation with methanol (*e.g.* equation (12)). This has the advantage that the reaction may be 100 times faster than with a cross-linked polymer.[54]



(12)

Tin hydrides can also be grafted onto inorganic oxides. Grafting onto silica (equation (13)) gives a hydride with a loading of up to 0.8 milliequivalents per gramme, and which can be regenerated with $NaBH_4$ *in situ*, for reducing organic bromides and iodides.[55]

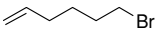
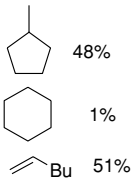
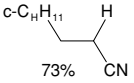
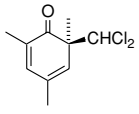
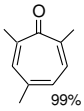


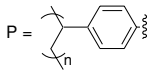
(13)

In a related technique, a fluorous surface layer has been grafted onto the silica surface, then the reduction carried out with a catalytic amount of the fluorous stannane, $(C_6F_{13}CH_2CH_2)_3SnH$, in the presence of $NaBH_4$ and the organic reactant in butanol. At the reaction temperature, the stannane partitions itself between the flourous surface and the butanol solvent and brings about the hydrostannolysis, but, when the system is cooled, the partition coefficient for the fluorous product and any residual reagent favours completely the fluorous phase, and the organotin by-product can be filtered off with the silica support.[56]

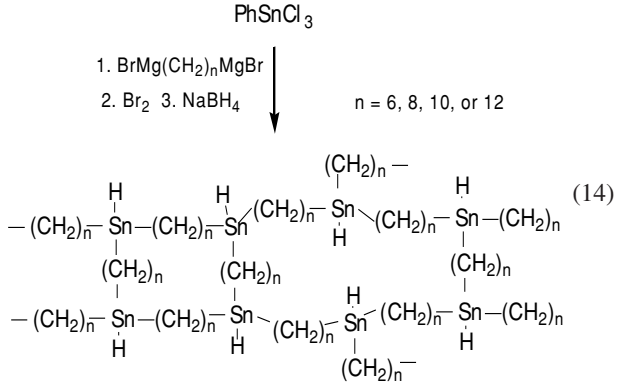
A hydride which itself is an insoluble polymer can be prepared by cross-linking $PhSnCl_3$ with a diGrignard reagent,

Table 1 Reactions of polymer-supported organotin hydrides

Resin	Reactant	Conditions	Product	Ref.
P-$(CH_2)_2SnBu_2H$		Heptane, hν 14 h, 44 °C	 48% 1% Bu 51%	51
P-$(CH_2)_2SnBu_2H$	c-C_6H_{11}I CH_2=CHC≡N	$NaBH_4$, AIBN EtOH, 18 h, 80 °C	 c-C_6H_{11} H 73% CN	52
P-$(CH_2)_4SnBu_2H$	1-Adamantyl Br	$NaBH_4$, AIBN EtOH, 12 h, 65 °C	Adamantane 93%	48
P-$(CH_2)_4SnBu_2D$	PhCHO	AIBN, THF 6 h, 70 °C	PhCHDOH 73%	49
P-$(CH_2)_2SnBu_2H$		AIBN, PhMe 9 h, 80 °C	 99%	53
P-$(CH_2)_2SnBu_2H$	CH_2=$CHCH_2OCOAr$	[$Pd(Ph_3)_4$] CH_2Cl_2, 0.5 h, rt	CH_2=$CHCH_2OCOH$	50

P = 

$BrMg(CH_2)_nMgBr$, then replacing the phenyl groups with hydrogen (equation (14)).[57]

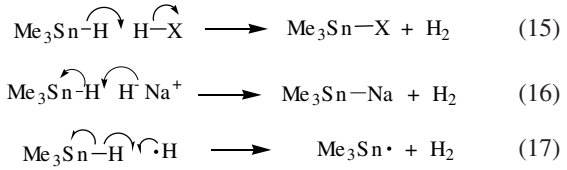


(14)

A loading of up to 3.07 milliequivalents of SnH per gramme can be achieved when n = 6, with H/Sn ratios approaching unity. The polymers swell in organic solvents, and appear capable of bringing about the usual reactions of soluble tin hydrides, and of being recovered and regenerated without loss of tin.

Reaction mechanism and the polar character of the SnH bond

The versatility of the tin hydrides in their reactions is due in part to the low polarity of the SnH bond which, on the demand of an appropriate reagent and the environment, can provide nucleophilic hydrogen (*e.g.* equation (15)), electrophilic hydrogen (*e.g.* equation (16)), or homolytic hydrogen (*e.g.* equation (17)).



The reactivity of tin hydrides towards carboxylic acids by the reaction shown in equation (15) follows the order of acid strength, *e.g.* $CH_3CO_2H < ClCH_2CO_2H < Cl_2CHCO_2H < Cl_3CCO_2H$. The reaction of R_2SnH_2 or $RSnH_3$ with acids can be used for preparing new hydrides R_2SnXH or $RSnXH_2$, for example HBr reacts with $EtSnH_3$ at –78 °C to give $EtSnBrH_2$. The rate constants for the reduction of the $(4\text{-}MeOC_6H_4)PhCH^+$ ion, which are shown in Table 2, provide a measure of the nucleophilicity of the Group 14 hydrides, which increases down the Group.[58,59]

A variety of bases (LiR, MgRX, NaH, KH, $LiNPr^i_2$) will abstract a proton from a tin hydride (*e.g.* equation (16)). Organolithium compounds, LiR, react with tetraalkylstannanes, R'_4Sn, to a give pentacoodinate stannate, $R'_4SnR^-Li^+$, in equilibrium with its factors and with R'_3SnR and LiR'. There is no evidence for the formation of the analogous hydrido-compounds, *e.g.* $R'_3SnH_2^-Li^+$, as intermediates, but the possible reaction of MH with R_4Sn to give R_4SnH^- does not seem to have been investigated.

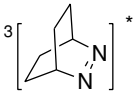
In both hydrostannolysis and hydrostannation reactions (Schemes 1 and 2), one propagation step involves the abstraction of a hydrogen atom from a tin hydride by a carbon- or hetero-centred radical and it is important to know the rates of these reactions in designing organic syntheses. Many measurements have therefore been made of the rate constants of these reactions, and the results up to 1999 have been thoroughly reviewed by Chatgilialoglu and Newcomb.[60] Recent values, together some earlier key figures, are given in Table 3. In many cases, activation energies and pre-exponential factors are known, so that the rate constants at other temperatures can be calculated.

In an attempt to bypass the toxity of the organotin compounds, hydrides alternative to tributylstannane have been sought. The reactivity of trialkylsilanes towards radicals is too low to propagate long radical chain reactions of the type required, but tris(trimethylsilyl)silane and tributylgermane are more reactive. Chatgilialoglu and Newcomb give the approximate rate constants that are shown in Table 4.

Table 2 Rate constants ($M^{-1}\ s^{-1}$) for the reaction of Group 14 hydrides with the $(4\text{-}MeOC_6H_4)PhCH^+$ ion

R	HCR_3	$HSiR_3$	$HGeR_3$	$HSnR_3$
Bu		3.9×10^2	2.8×10^4	2×10^6
Ph	2×10^{-7}	8.3	1.1×10^2	5×10^3

Table 3 Rate constants for the reaction X• + $Bu_3SnH \rightarrow XH + R_3Sn$•

X•	Solvent	R_3SnH	T(°C)	$k(M^{-1}s^{-1})$	Ref.
MeC• =O	PhMe	Bu_3SnH	23	3.9×10^5	61
EtC• =O	C_6H_{12}	Bu_3SnD	23	3.0×10^5	62
$^3Me_2CO$*	MeCN	Bu_3SnH	rt	5.4×10^8	63
$^1Me_2CO$*	MeCN	Bu_3SnH	rt	1.0×10^9	63
^{1}(MeCO)*	C_6H_{12}	Bu_3SnH	rt	2.7×10^7	63
TEMPO[a]	PhH	Bu_3SnH	60	0.025	64
C_6H_5•	THF	Bu_3SnH	25	7.8×10^8	65
C_8F_{17}•	PhH	Bu_3SnH	25	2.0×10^8	66
$Ph_2C{=}CH(CH_2)_4CH$•(OMe)	THF	Bu_3SnH	25	3.5×10^5	67
$Ph_2C{=}CH(CH_2)_3C$•Me(CO_2Et)	THF	Bu_3SnH	20	1.9×10^5	68
$Ph_2C{=}CH(CH_2)_3C$•Me(CN)	THF	Bu_3SnH	20	3.4×10^5	68
$Ph_2C{=}CH(CH_2)_4C$•Me(CO_2Et)	THF	Bu_3SnH	20	3.2×10^6	68
RR′N•	THF	Bu_3SnH	20	4.3×10^5	69
$Ph_2C{=}CH(CH_2)_2CMe{=}N$•	PhMe	Bu_3SnH	25	ca. 3×10^3	70
$Ph_2C{=}CH(CH_2)_2CO$ N•Me	MeCN	Bu_3SnH	20	1.3 ×. 10^9	71
$Ph_2CHCH_2N^{\bullet+}$ EtH	MeCN	Ph_3SnH	22	2.4×10^8	72
	MeCN	Bu_3SnH	21	6.2×10^7	73
$Ph_2C{=}CH(CH_2)_4C$• H_2	$PhCF_3$	[b]	20	3.8×10^6	40

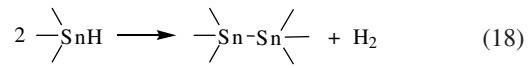
[a]2,2,6,6-tetramethylpiperidinooxyl [b]With $(C_6F_{13}CH_2CH_2)_3SnH$

Table 4 Rate constants ($M^{-1}s^{-1}$) for the reaction of radicals with Group 14 hydrides

	Et_3SiH	Bu_3GeH	Bu_3SnH	$[(Me_3Si)_3Si]_3H$
Me_3CO•	4.6×10^6	9.2×10^7	2.0×10^8	4.6×10^6
R_fCF_2•	5.0×10^5	1.5×10^7	2.0×10^8	4.6×10^6
RCH_2•	3.2×10^2	9.5×10^4	2.5×10^6	4.6×10^6
$PhCMe_2OO$•	0.1	19	1.6×10^3	4.6×10^6

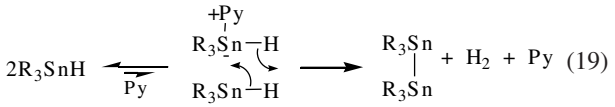
Reaction to give Sn–Sn bonds

Organotin hydrides, R_3SnH, react with the corresponding alkoxides, oxides, amides, or halides, R_3SnX, to give HX and the corresponding distannanes, R_3SnSnR_3, presumably by a heterolytic mechanism.[74] The metathetical reaction of tin hydrides to give dihydrogen and Sn-Sn bonded compounds (equation (18)) is also well established, but has recently come to the fore in a variety of modifications.



(18)

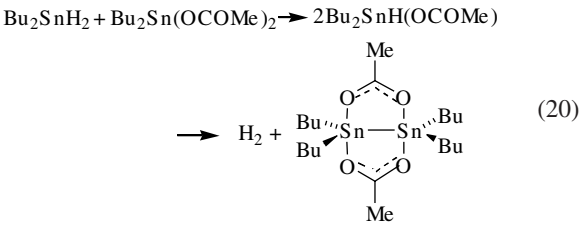
It was initially shown that amines or sodium alkoxides catalysed the decomposition of trialkyltin hydrides. The mechanism of the reaction has not been established, but one that was sometimes discussed involved heterolytic reduction of a coordinated hydride by a second hydride molecule, with opposite polarities in the two Sn-H bonds (equation (19)).



(19)

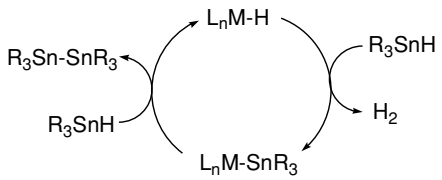
One convenient route to hexabutylditin is the reduction of bis(tributyltin) oxide with sodium borohydride in ethanol at room temperature; after 5 min, the only organotin compound present is tributyltin hydride, then, in 2 h, the ethoxide ion that is present causes the hydride to decompose into dihydrogen and the distannane in 83% yield.[75]

The hydride halides, R_2SnHX, similarly react with amines to give dihydrogen and the dihalogenodistannanes, XR_2SnSnR_2X,[76] but the hydride carboxylates spontaneously decompose at room temperature, *e.g.* equation (20).[77]



(20)

Studies of these reactions of the hydrides R_2SnXH, however, bring into question the mechanism illustrated in equation 19.[78] Alkynes quench the evolution of hydrogen, and may give the products of both hydrostannation and dihydrogenation in a reaction that can be catalysed by triethylborane, and the evolution of hydrogen is quenched also by 2,6-di-*t*-butyl-4-methylphenol[78] or galvinoxyl (see below).[79] The decomposition thus appears to follow a radical mechanism, but the details are not clear. These systems deserve further attention.



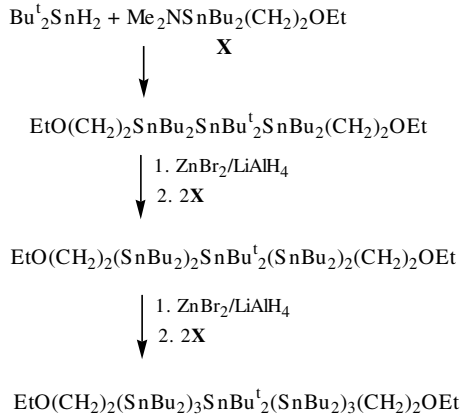
Scheme 4 Formation of distannanes from tin hydrides, catalysed by transition metals.

The metathesis of tin hydrides can also be catalysed by transition metals,[80] particularly palladium, often as $[Pd(PPh_3)_4]$.[81-83] A convenient preparation of hexaalkyldistannanes on a large scale (200 g) is provided by the reaction of the corresponding hydrides with $[Pd(PPh_3)_4]$; the reactions are exothermic, and yields are practically quantitative.[81,82]

Other metals that have been used are chromium, molybdenum, tungsten, gold,[84] yttrium, ruthenium,[85] rhodium,[86] platinum,[87] and hafnium.[88] The most active catalysts appear to be the heterobimetallic Fe/Pd complexes, such as $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-dppm})Pd(\eta^3\text{-allyl})]$, in which both metals are believed to be involved in the catalysis.[80]

The most likely mechanism for the metathesis catalysed by transition metals appears to be a cyclic process involving an intermediate in which tin is bonded to the metal (Scheme 4).

Any of the common routes to hexaalkyldistannanes can be extended to the preparation of cyclic or acyclic oligomeric or polymeric dialkylstannanes, $(R_2Sn)_n$, from the dihydrides R_2SnH_2. These polymers are attracting interest because of their potential in electronic and optical devices, comparable to those that have been found for the polysilanes. Interaction of the Sn sp^3 orbitals in the chain gives rise to a delocalised electronic structure, leading to electrical conduction and a low-energy (σ-σ^*) optical absorption maximum which shifts to the red as the chain length increases. Specific oligostannanes have been prepared with the aim of deconvoluting steric and electronic effects on these properties; the example in equation (21) builds up the chain by the reaction of a tin hydride with a tin amide.[89,90]



(21)

Dialkyltin dihydrides react with various transition metal catalysts with the elimination of hydrogen and the formation of Sn–Sn bonded compounds, which may be dehydrodimers, cyclic oligomers, acyclic oligomers, or linear or branched polymers, depending on the nature of the alkyl groups and of the catalyst.[80] The results are summarised in Table 5.

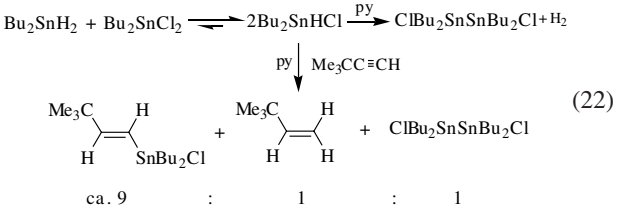
Table 5 Catalytic dehydropolymerisation of diorganotin dihydrides

R_2SnH_2	Catalyst	Polymer	Ref.
Bu_2SnH_2 Oct_2SnH_2	$[PdCl_2(PPh_3)_2]$	Cyclo pentamers and hexamers	83
Bu_2SnH_2, Hex_2SnH_2, Oct_2SnH_2	Zirconocene derivatives	High polymers $(Bu_2Sn)_n$ M_W/M_N 66,900/20,300 $(Oct_2Sn)_n$ M_W/M_N 149,000/17,000	91
Me_2SnH_2, $PhMeSnH_2$, Ph_2SnH_2	Zirconocene derivatives	Lower polymers	91
Bu_2SnH_2	$[RhH(CO)(PPh_3)_2]$	M_W/M_N 50,240/35,130	92
Bu_2SnH_2	$[MCp_2Cl_2]$/Red-Al (M = Ti, Zr, Hf)	Both linear and crosslinked polymers	93
Bu_2SnH_2	$[M(CO)_6]$/Red-Al (M = Cr, Mo, W)	Both linear and crosslinked polymers	93
$(4\text{-}Bu^tC_6H_4)_2SnH_2$ $(4\text{-}HexC_6H_4)_2SnH_2$	Zirconocene derivatives	Helical polymers, M_W/M_N 148,000/20,000	94
Bu_2SnH_2	Fe-Pd silyl complexes	Cyclic and linear polymers	95
Ph_2SnH_2	Fe-Pd silyl complexes	$(Ph_2Sn)_4$ and $(Ph_2Sn)_6$	95
$(Me_3C_6H_2)_2SnH_2$	$[HfCp_2ClH]$	$HMes_2SnSnMe_2H$	88
Me_2SnH_2	Various stannyl-hafnocene complexes	Oligo- and poly-stannanes	96
Bu_2SnH_2 Ph_2SnH_2	$[(PhMe_2P)_2PtMe_2]$	Linear oligomers then cyclostannanes	87
Bu_2SnH_2 Ph_2SnH_2	$[\{Ph_2PC_2H_4NMe_2\}PtMe_2]$	Only polystannanes	87
Bu_2SnH_2	$[RhCl(PPh_3)_3]$	Linear polymers, MW 20×10^3	86

Dialkyltin hydrides R_2SnXH

Dialkyltin dihydrides, R_2SnH_2, readily react with the corresponding compounds R_2SnX_2, where X is a relatively electronegative group such as halide, carboxylate, or sulfonate, to give new families of hydrides R_2SnXH. This provides a large family of new hydrides that are more reactive, both heterolytically and homolytically, than the simple hydrides, and with properties that can be modulated by varying the group X; this family is further expanded by the fact that their Lewis acidity makes available further novel neutral or anionic hydrides with the composition R_2SnXHL. Any organotin by-products arising from their use in synthesis can readily be removed by hydrolysing them to the insoluble dialkyltin oxides, R_2SnO. Although these hydrides have been known since the 1960s (Table 6), their potential is only now being exploited, and the mechanisms of their reactions are still largely a matter of speculation.

Dibutyltin dihydride comes into equilibrium with dibutyltin dichloride in about 60 minutes at room temperature, to give 97% of the hydride chloride, Bu_2SnHCl. This can be distilled under high vacuum, b.p. 35–40 °C at 0.03 mm Hg, but, at higher pressures and temperatures, the dihydride distils as the most volatile component in the equilibrium. In air, it is oxidised to the distannoxane, $ClBu_2SnOSnBu_2Cl$. It reacts with bipyridyl to give Bu_2SnCl_2.bipy, but pyridine reacts to give the dichlorodistannane with the evolution of hydrogen, and the same products are formed on thermal decomposition at 100 °C.[97] The evolution of hydrogen is quenched, and the hydride chloride is stabilised, by 2,6-di-*t*-butyl-4-methylphenol. 2-Methyl-3-butyne-2-ol also quenches the evolution of hydrogen, and diverts the decomposition into *trans*-hydrostannation of the triple bond. 3,3-Dimethylbut-1-yne undergoes hydrostannation with some dehydrogenation (equation (22)). The metathesis of the tin hydride therefore appears to follow a homolytic rather than a heterolytic mechanism.



(22)

The halide hydrides R_2SnHF, R_2SnHBr, and R_2SnIH can similarly be prepared from the dihydride and the appropriate dihalide.

Dibutytin dicarboxylates react with the dihydride to give the hydride carboxylates in lower equilibrium concentration, perhaps because the dicarboxylates achieves some extra stability from their intramolecular hexacoordination, but the detailed structure of the hydride carboxylates is not known.[77,78] They decompose spontaneously at room temperature to give molecular hydrogen and the dicarboxylatodistannanes, $(RCO_2)Bu_2SnSnBu_2(O_2CR)$; the decomposition can be interrupted by the addition of a small amount of 2,6-di-*t*-butyl-4-methylphenol, and the period of interruption is proportional to the amount of inhibitor added. Again, therefore, the decomposition appears to follow a homolytic process.

The simple hydrides, R_2SnH_2, show no obvious Lewis acid characteristics, but the hydrides R_2SnHX, where X is an electronegative ligand, do form 5-coordinate complexes, though none as yet appears to have been isolated and subjected to X-ray diffraction. Complexes such as Bu_2SnHCl.HMPA (Table 6) and $Bu_2SnHCl.Bu_3PO$ can be detected by NMR and IR spectroscopy, and there is no mention of the metathetical decomposition that is observed with pyridine. Presumably these adducts have a trigonal bipyramidal structure with the halogen and the added ligand in the apical positions.[98] Halide ions can similarly be added to give complexes such as $Bu_2SnHClF^-$ Bu_4N^+, $Bu_2SnHBrI^-$ $MgBr^+$, and $Bu_2SnHI_2^-$ Li^+.[99,100]. Again, the halide ions are assumed to occupy the

Table 6 Dibutyltin hydrides, Bu_2SnH_2, Bu_2SnXH and Bu_2SnXHL

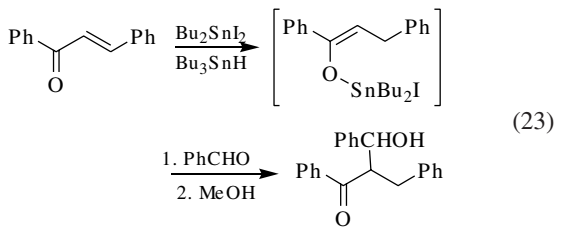
Hydride	δH	δSn	$^1J(^{117,119}SnH)$	νSnH (cm^{-1})	Ref.
Bu_2SnH_2	4.76	-205.4	1595/1669	1825	79
Bu_2SnHF				1869	97, 101
Bu_2SnHCl	7.21[a]	47.8[a]	1898/1986[a]	1857	79
Bu_2SnHBr	6.87		1875/1964	1845	102
Bu_2SnHI	6.41	-76.3	1968/2060	1846.1	99
$Bu_2SnH(OAc)$	7.6			1875	77,78
$Bu_2SnH(O_3SCF_3)$	8.99	22.7	2233/2336	–	79
$Bu_2SnHCl.HMPA$	7.19	-139.3	2283/2389	1861.5	98
$Bu_2SnHClF^-$ Bu_4N^+	7.21	-159.8	2329/2438	1859.6	98
$Bu_2SnI_2H^-$ Li^+	7.10	-177.9	/2318	1846.1	99

[a]In C_6D_6 7.42 and 1875/1963 Hz

apical positions in a trigonal bipyramid. Some characteristics are included in Table 6.

Part of the interest in these new types of hydride lies in the special characteristics that they have in hydrostannation and hydrostannolysis. The carbonyl group of α,β-epoxyketones is selectively reduced by Bu_2SnFH,[101] and α-alkoxyketones react with Bu_2SnClH to give mainly the α-alkoxyalcohols.[103]

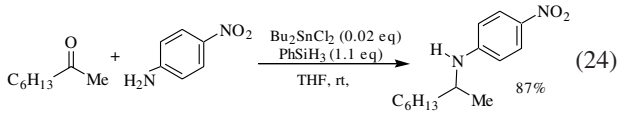
Both reactions are selective for the product *of anti* addition, probably because the tin is ligated by both functional groups. Enones can be reduced with Bu_2SnIH in the presence of aldehyde groups, and then, *in situ*, subjected to an aldol addition (equation (23)). 1,4-Dinitrobenzene has little effect on the reduction, suggesting that it follows a heterolytic mechanism.[104]



(23)

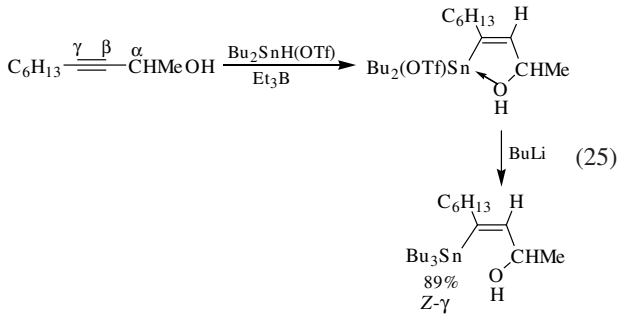
Enals are similarly reduced by $Bu_2SnHI_2^- Li^+$ to the corresponding saturated aldehydes under mild neutral conditions, but it is suggested that here the initial attack on the β-position is by nucleophilic iodide.[99]

The complex Bu_2SnClH/HMPA will selectively reduce imines in the presence of aldehydes,[105] and secondary amines can be prepared by reducing a mixture of carbonyl compound and amine with Bu_2SnClH (equation (24)).[106]



(24)

Terminal propargylic alcohols and ethers, $HC{\equiv}CCR_2OR'$, with Bu_2SnClH give virtually quantitative yields of the γ–stannyl compounds by *anti* addition by a free radical mechansim.[79,107,108] Non-terminal propargylic alcohols give a mixture of the products of β- and γ-addition of Bu_2SnClH, but the trifluoromethanesulfonate, $Bu_2Sn(OTf)H$, again gives a good yield of the γ-isomer (equation (25)).[79]



(25)

There is an obvious possible extension of this field of research to the monoalkyl analogues $RSnXH_2$ and $RSnX_2H$, but such work does not appear to have been reported as yet.

References

1 A.G. Davies, *Organotin Chemistry, 2nd Edn*, Wiley-VCH, 2004.
2 S. Handa and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, 1999, 843.
3 W.B. Motherwell and D. Crich, *Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, 1992.
4 B. Giese, B. Kopping, T. Göbel, J. Dickhaut, G. Thoma, K.J. Kulicke and F. Trach, *Org. Synth.*, 1996, **48**, 301.
5 A.-L. Dhimane, L. Fensterbank and M. Malacria, in *Radicals in Organic Synthesis*, ed. P. Renaud and M.P. Sibi, Wiley-VCH, Weinheim, 2001, p. 350.
6 D.J. Hart, in *Radicals in Organic Synthesis*, ed. P. Renaud and M.P. Sibi, Wiley-VCH, Weinheim, 2001, p. 279.
7 A.J. Clark, in *Science of Synthesis. Vol. 5. Compounds of Group 14 (Ge, Sn, Pb)* ed. E.J. Thomas, Thieme, Stuttgart, 2003, p. 205.
8 A.F. Finholt, A.C. Bond, K.E. Wilzbach and H.I. Schlesinger, *J. Am. Chem. Soc.*, 1947, **69**, 2692.
9 K. Hayashi, J. Iyoda and I. Shiihara, *J. Organomet. Chem.*, 1967, **10**, 81.
10 R. Knocke and W.P. Neumann, *Annalen*, 1974, 1486.
11 H. Deleuze and B. Maillard, *J. Organomet. Chem.*, 1995, **490**, C14.
12 H. Parnes and J. Pease, *J. Org. Chem.*, 1979, **44**, 151.
13 D.K. Jaiswal, H. Andres, H. Morimoto and P.G. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 907.
14 M.F. Connil, B. Jousseaume and M. Pereyre, *Organometallics*, 1996, **15**, 4469.
15 F. Schager, R. Goddard, K. Seevogel and K.-R. Pörschke, *Organometallics*, 1998, **17**, 1546.
16 R. Becerra, P.P. Gaspar, C.R. Harrington, W.J. Leigh, I. Vargas-Baca, R. Walsh and D. Zhou, *J. Am. Chem. Soc.*, 2005, **127**, 17469.
17 Anon, *Toxicity of organotin compounds*, NDCrc-132, Prog. Repts. Tox. Lab., Univ. Chicago, Chicago, 1942.
18 F. Caujolle, M. Lesbre, D. Meynier and G. d. Saqui-Sannes, *Compt. Rend. Hebd. Seances Acad. Sci. (Paris)*, 1956, **243**, 987.
19 Anon, *Documentation of the Threshold Limit Values for Chemical Substances*, 7th Edn., American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 2001.
20 O.R. Klimmer and I.U. Nebel, *Arzneimittel-Forschung*, 1960, **10**, 44.
21 S. Trapp, G. Ciucani and M. Sismilich, *Environmental Science and Pollution Research International*, 2004, **11**, 327.
22 G. Ciucani, H. Mosbaek and S. Trapp, *Environmental Science and Pollution Research International*, 2004, **11**, 267.
23 I. Ryu, T. Niguma, S. Minakata, M. Komatsu, S. Hadida and D.P. Curran, *Tetrahedron Lett.*, 1997, **38**, 7883.
24 D.S. Hays and G.C. Fu, *J. Org. Chem.*, 1998, **63**, 2796.
25 C. Lucas, C.C. Santini, M. Prinz, M.-A. Cordonnier, J.-M. Basset, M.-F. Connil and B. Jousseaume, *J. Organomet. Chem.*, 1996, **520**, 101.
26 L. Zeng, V.T. Perchyonok and C.H. Schiesser, *Tetrahedron: Asymmetry*, 2004, **15**, 995.
27 D. Dakternieks, V.T. Perchyonok and C.H. Schiesser, *Tetrahedron: Asymmetry*, 2003, **14**, 3057.
28 M.B. Faraoni, A.D. Ayala, V. Vetere, M.L. Casella, O.A. Ferretti and J.C. Podestá, *Appl. Organomet. Chem.*, 2005, **19**, 465.
29 D. Nanni and D.P. Curran, *Tetrahedron Asymmetry*, 1996, **7**, 2417.
30 M. Blumenstein, M. Lemmler, A. Hayen and J.O. Metzger, *Tetrahedron: Asymmetry*, 2003, **14**, 3069.
31 B.E. Eichler and P.P. Power, *J. Am. Chem. Soc.*, 2000, **122**, 8785.
32 T.F. Koetzle, A.J. Schultz, R. Henning, A. Albinati, W.T. Klooster, B.E. Eichler and P.P. Power, *Comptes Rendus Chimie*, 2005, **8**, 1487.
33 E. Vedejs, S.M. Duncan and A.R. Haight, *J. Org. Chem.*, 1993, **58**, 3046.
34 D.L.J. Clive and W. Yang, *J. Org. Chem.*, 1995, **60**, 2607.
35 S. Suga, T. Manabe and J.-i. Yoshida, *Chem. Commun.*, 1999, 1237.
36 X. Han, G.A. Hartmann, A. Brazzale and R.D. Gaston, *Tetrahedron Lett.*, 2001, **42**, 5837.
37 D.L.J. Clive and J. Wang, *J. Org. Chem.*, 2002, **67**, 1192.
38 S. Gastaldi and D. Stien, *Tetrahedron Lett.*, 2002, **43**, 4309.
39 D.P. Curran, S. Hadida, S.-Y. Kim and Z. Luo, *J. Am. Chem. Soc.*, 1999, **121**, 6607.
40 J.H. Horner, F.N. Martinez, M. Newcomb, S. Hadida and D.P. Curran, *Tetrahedron Lett.*, 1997, **38**, 2783.
41 D.P. Curran and Z. Luo, Fluorous tin compounds and methods of using fluorous tin compounds, WO 01/98312, 2001.
42 J. Light and R. Breslow, *Tetrahedron Lett.*, 1990, **31**, 2957.
43 F. Ferkous, D. Messadi, B. de Jeso, M. Degueil-Castaing and B. Maillard, *J. Organomet. Chem.*, 1991, **420**, 315.

44 F. Ortega-Caballero and M. Bols, Abstracts of Papers, 228th ACS National Meeting, Philadelphia, PA, United States, August 22-26, 2004, ORGN-076.
45 W.P. Neumann, *J. Organomet. Chem*, 1992, **437**, 23.
46 B. Delmond and G. Dumartin, in *Solid State Organometallic Chemistry; Methods and Applications*, ed. M. Gielen, R. Willem and B. Wrackmeyer, Wiley Chichester, 1999, p. 445.
47 S.V. Ley, I.R. Baxendale, R.N. Bream, P.S. Jackson, A.G. Leach, D.A. Longbottom, M. Nesi, J.S. Scott, R.I. Storer and S.J. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 2000, 3815.
48 G. Dumartin, M. Pourcel, B. Delmond and M. Pereyre, *Tetrahedron Lett.*, 1998, **39**, 4663.
49 G. Dumartin, G. Ruel, J. Kharboutli, B. Delmond, M.F. Connil, B. Jousseaume and M. Pereyre, *Synlett*, 1994, 952.
50 K.C. Nicolaou, N. Wissinger, R. Hughes, C. Smethurst and S.Y. Cho, *Angew. Chem. Int. Ed.*, 2000, **39**, 1084.
51 U. Gerigk, M. Gerlach, W.P. Neumann, R. Vieler and V. Weintritt, *Synthesis*, 1990, 448.
52 C. Bokelmann, W.P. Neumann and M. Peterseim, *J. Chem. Soc., Perkin Trans 1*, 1992, 3165.
53 D.P. Dygutsch, W.P. Neumann and M. Peterseim, *Synlett*, 1994, 363.
54 E.J. Enholm, M.E. Gallagher, K.M. Moran, J.S. Lombard and J.P. Schulte, *Org. Lett.*, 1999, **1**, 689.
55 Q.J. Fu, A.M. Steele and S.C. Tsang, *Green Chem.*, 2001, **3**, 71.
56 P.M. Jenkins, A.M. Steele and S.C. Tsang, *Catalysis Commun.*, 2003, **4**, 45.
57 P.M. Jenkins and S.C. Tsang, *Green Chem.*, 2004, **6**, 69.
58 H. Mayr and N. Basso, *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 1046.
59 H. Mayr and M. Patz, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 938.
60 C. Chatgilialoglu and M. Newcomb, *Adv. Organomet. Chem.*, 1999, **44**, 67.
61 C. Chatgilialoglu, C. Ferreri, M. Lucarini, P. Pedrielli and G.F. Pedulli, *Organometallics*, 1995, **14**, 2672.
62 C.E. Brown, A.G. Neville, D.M. Rayner, K.U. Ingold and J. Lusztyk, *Aust. J. Chem.*, 1995, **48**, 363.
63 W.M. Nau, F.L. Cozens and J.C. Scaiano, *J. Am. Chem. Soc.*, 1996, **118**, 2275.
64 M. Lucarini, E. Marchesi, G.P. Pedulli and C. Chatgilialoglu, *J. Org. Chem.*, 1998, **63**, 1687.
65 S.J. Garden, D.V. Avila, A.L.J. Beckwith, V.W. Bowry, K.U. Ingold and J. Lusztyk, *J. Org. Chem.*, 1996, **61**, 805.
66 D.V. Avila, K.U. Ingold, J. Lusztyk, W.R. Dolbier, H.-Q. Pan and M. Muir, *J. Am. Chem. Soc.*, 1994, **116**, 99.
67 C.C. Johnson, J.H. Horner, C. Tronche and M. Newcomb, *J. Am. Chem. Soc.*, 1995, **117**, 1684.
68 M. Newcomb, J.H. Horner, M.A. Filipkowski, C. Ha and S.-U. Park, *J. Am. Chem. Soc.*, 1995, **117**, 3674.
69 O.M. Musa, J.H. Horner, H. Shahin and M. Newcomb, *J. Am. Chem. Soc.*, 1996, **118**, 3862.
70 M.-H. Le Tadic-Biadatti, A.-C. Callier-Dublanchet, J.H. Horner, B. Quiclet-Sire, S.Z. Zard and M. Newcomb, *J. Org. Chem.*, 1997, **62**, 559.
71 J.H. Horner, O.M. Musa, A. Bouvier and M. Newcomb, *J. Am. Chem. Soc.*, 1998, **120**, 7738.
72 J.H. Horner, F.N. Martinez, O.M. Musa, M. Newcomb and H.E. Shahin, *J. Am. Chem. Soc.*, 1995, **117**, 11124.
73 W. Adam, J.N. Moorthy, W.M. Nau and J.C. Scaiano, *J. Org. Chem.*, 1997, **62**, 8082.
74 W.P. Neumann, *The Organic Chemistry of Tin*, Wiley, London, 1970.
75 H. McAlonan and P.J. Stevenson, *Organometallics*, 1995, **14**, 4021.
76 W.P. Neumann and J. Pedain, *Tetrahedron Lett.*, 1964, 2461.
77 A.K. Sawyer and H.G. Kuivila, *J. Am. Chem. Soc.*, 1960, **82**, 5958.
78 A.G. Davies and D.K. Osie-Kissi, *J. Organomet. Chem.*, 1994, **474**, C8.
79 K. Miura, D. Wang, Y. Matsumoto and A. Hosomi, *Organic Letters*, 2005, **7**, 503.
80 P. Braunstein and X. Morise, *Chem. Rev.*, 2000, **100**, 3541.
81 N.A. Bumagin, Y.V. Gulevich and I.P. Beletskaya, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1137.
82 T.N. Mitchell, A. Amamria, H. Killing and D. Rutschow, *J. Organomet. Chem.*, 1986, **304**, 257.
83 B. Jousseaume, N. Noiret, M. Pereyre and A. Saux, *Organometallics*, 1994, **13**, 1034.
84 H. Ito, T. Yajima, J.-i. Tateiwa and A. Hosomi, *Tetrahedron Lett.*, 1999, **40**, 7807.
85 S.M. Maddock and M.G. Finn, *Angew. Chem. Int. Ed.*, 2001, **40**, 2138.
86 F. Choffat, P. Smith and W. Caseri, *J. Mater. Chem.*, 2005, **15**, 1789.
87 S.M. Thompson and U. Schubert, *Inorg. Chim. Acta*, 2004, **357**, 1959.
88 Sita, L.R., *Adv. Organomet. Chem*., 1995. **38**, 189.
89 L.R. Sita, K.W. Terry and K. Shibata, *J. Am. Chem. Soc.,* 1995, **117**, 8049.
90 K. Shibata, C.S. Weinhert and L.R. Sita, *Organometallics*, 1998, **17**, 2241.
91 T. Imori, V. Lu, H. Cai and T.D. Tilley, *J. Am. Chem. Soc.*, 1995, **117**, 9931.
92 J.R. Babcock and L.R. Sita, *J. Am. Chem. Soc.*, 1996, **118**, 12481.
93 H.-G. Woo, J.-M. Park, S.-J. Song, S.-Y. Yang, I.-S. Kim and W.-G. Kim, *Bull. Korean Chem. Soc.*, 1997, **18**, 1291.
94 V. Lu and T.D. Tilley, *Macromolecules*, 1996, **29**, 5763.
95 P. Braunstein and X. Morise, *Organometallics*, 1998, **17**, 540.
96 N.R. Neale and T.D. Tilley, *Tetrahedron*, 2004, **60**, 7247.
97 A.K. Sawyer, J.E. Brown and E.L. Hanson, *J. Organomet. Chem.*, 1965, **3**, 464.
98 T. Kawakami, T. Sugimoto, I. Shibata, A. Baba, H. Matsuda and N. Sonoda, *J. Org. Chem.*, 1995, **60**, 2677.
99 T. Suwa, I. Shibata and A. Baba, *Organometallics*, 1999, **18**, 3965.
100 I. Shibata, T. Suwa, K. Ryu and A. Baba, *J. Am. Chem. Soc.*, 2001, **123**, 4101.
101 T. Kawakami, I. Shibata, A. Baba and H. Matsuda, *J. Org. Chem.*, 1993, **58**, 7608.
102 K. Kawakami, T. Saito and R. Okawara, *J. Organomet. Chem.*, 1967, **8**, 377.
103 I. Shibata, T. Yoshida, T. Kawakami, A. Baba and H. Matsuda, *J. Org. Chem.*, 1992, **57**, 4049.
104 T. Kawakami, M. Miyatake, I. Shibata and A. Baba, *J. Org. Chem.*, 1996, **61**, 376.
105 I. Shibata, T. Moriuchi-Kawakami, D. Tanizawa, T. Suwa, E. Sugiyama, H. Matsuda and A. Baba, *J. Org. Chem.*, 1998, **63**, 383.
106 R. Apodaca and W. Xiao, *Org. Lett.*, 2001, **3**, 1745.
107 T.N. Mitchell and S.-N. Moschref, *Chem. Commun.*, 1998, 1201.
108 C.M. Thiele and T.N. Mitchell, *Eur. J. Org. Chem.*, 2004, 337.