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STANNYLMETALLATION OF CONJUGATED ENYNES

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Abstract: *Additions of lower order and higher order mixed and homostannylcuprates, as well as the Cu(I) catalyzed additions of $Bu_3SnBBN(OMe)^-Li^+$, $Bu_3SnAlEt_2$, and $Bu_3SnMgMe$ to conjugated 1,3-enynes were investigated Regioselective additions (> 90% of one isomer) of these bimetallic reagents to the alkyne moiety of 2-methyl-1-buten-3-yne, 2-methyl-1-hexen-3-yne and 2-penten-4-yn-1-ol were obtained The direction of the addition of the mixed HO cuprates could be affected by changing the size of the ligands bound to tin and copper The regioselectivity of addition of Sn-Al and Sn-Mg reagents was influenced by solvent and reaction conditions*

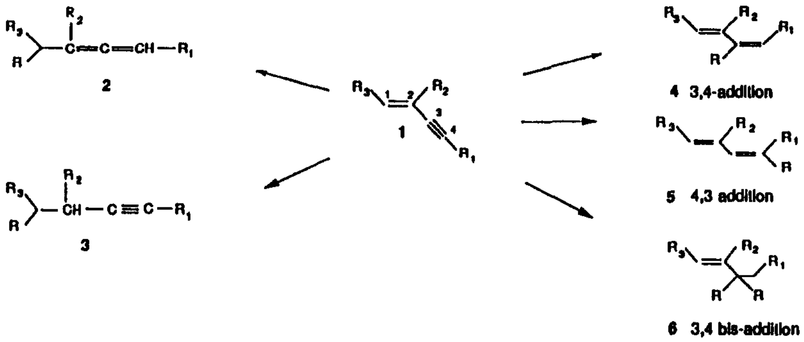
Reactions of 1,3-enynes with organometallics offer efficient routes to 1,3-dienes and allenes (Scheme 1) Organolithium (RLi), calcium, strontium or barium reagents react with conjugated enynes with internal triple bonds (**1a**) by 1,4-addition initiated by nucleophilic attack of the olefin[1] at C-1 to produce allenes (**2a**) When the triple bond is terminal (**1b**) this reaction with alkyllithiums proceeds by 1,2-addition to the olefin to give only alkynes (**3b**) [2] This is presumably due to the initial formation of an alkynyl anion which inhibits the 1,4-addition Organomagnesium reagents add to internal conjugated enynes by both 1,2- and 1,4-addition also initiated by attack on the olefin

Attenuation of the reactivity of benzyl magnesium halides by addition of $NiCl_2$ promotes nucleophilic attack on C-1 of the alkyne of conjugated 1,3-enynes to produce 1-substituted-1,3-dienes (**5a**) [3] Similarly, homocuprates ($R_2CuMgBr$), heterocuprates [(RCuBr)MgX] and di-t-butylzinc react with enynes possessing α-hydroxy, alkoxy and amino groups (**1c**,**1d**) to produce 1,3-dienes (**5c**,**5d**) [4] Stoichiometric zirconium chemistry[5] also provides efficient routes to 1-phenylseleno-, 1-phosphino and 1-bora-1,3-dienes [6,7]

With allylmagnesium halides additions proceed by attack of the nucleophile at the internal carbon of the alkyne (**1d**) to produce 2-substituted-1,3-dienes (**4d**) [8] Additions of allylic organozincs to enynes with terminal triple bonds (**1b**) also give 2-substituted-1,3-dienes (**4b**) [1,2,9] When excess organozinc reagent is used, alkenes (**6b**) resulting from double addition are produced As well, silanes,[10] germanes,[10,11] stannanes,[12] (R_3MH) and alanes (R_2MH)[1] react to give 2-substituted-1,3-dienes

Recently, methods have been developed for metallometalation of 1-alkynes [13] Bimetallic reagents reported to date that add to 1-alkynes include Sn-B[14], Sn-Al[15],Sn-Cu[16], Sn-Zn[15], Sn-Sn[17], Si-Al[18], Si-Sn[19], Si-Si[20] and Si-Cu[21] reagents Metallometallations of 1-alkynes involving these organometallics produce 1,2-dimetalloalkenes in which the metal accompanying Sn or Si yields a C-M bond more reactive than the simultaneously formed Si-carbon or Sn-carbon bond The reactivities of the bimetallic adducts produced in these reactions usually require electrophilic consumption of the more reactive organometallic centre prior to isolation Methods are available to react the C-M bonds of these adducts with a wide variety of electrophiles [13,22] Since several methods have been developed for replacement of the Si-C bond by electrophilic reagents[23] and for the transmetalation of the Sn-carbon bond with organopalladium[24] or organocopper reagents[25] the synthetic opportunities emanating from metallometallation of alkynes are appreciable

Scheme 1 Reactions of Organometallic Reagents with 1,3- Enynes.



	R_1	R_2	R_3
1a,2a,3a,4a,5a,6a	alkyl	H	alkyl
1b,2b,3b,4b,5b,6b,	H	H	alkyl
1c,2c,3c,4c,5c,6c	H	H	CH_2Y
1d,2d,3d,4d,5d,6d	CH_2Y	H	alkyl

Y= OH, OR, NH_2

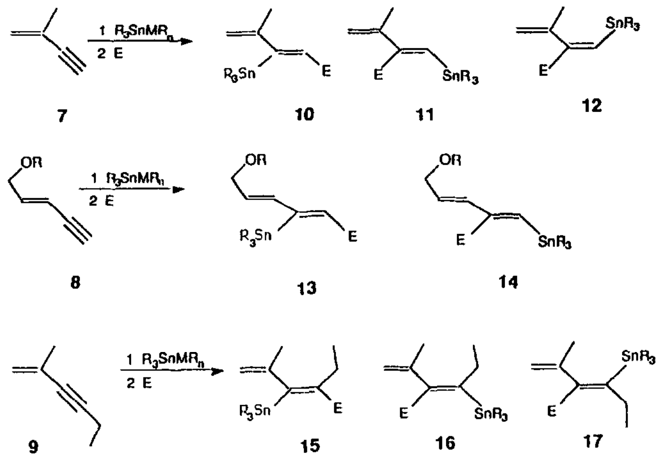
Encouraged by the efficiency of previous stannylmetallations of 1-alkynes in our laboratory we have now examined additions of several Sn-Cu, Sn-B, Sn-Al and Sn-Mg reagents to enynes In the case of 1,3-enynes these reactions would be expected to occur at the π-system perpendicular to the conjugated diene system to yield alkyne addition products [26] Such additions would produce bimetallic adducts that are 1,2-dianion equivalents of 1,3-dienes and could be elaborated to polysubstituted 1,3-dienes

We envisioned that cuprous ion catalyzed stannylmetallation of enynes would produce bimetallic 1,3-dienes which would easily be functionalized at the C-metal bond to yield either 1 or 2-stannyl-1,3-dienes Since 2-trialkylsilyl,[27] 2-trialkystannyl,[28] and 1-phenylseleno-1,3-dienes[7] as well as 1,3-dienylboronates[29] have been reported to undergo Diels-Alder additions with typical dienophiles, stannylmetallation of conjugated enynes could also be envisioned to produce bimetallic dienes which would undergo Diels- Alder reactions *in situ* Here we report regiocontrolled synthesis and reactions of bimetallic 1,3-dienes

Previous studies in our laboratory[13,30] suggest that cuprous ion catalyzed stannylmetallations proceed *via* stannylcupration followed by *in situ* transmetallation of the vinyl copper-carbon bond formed by the electrophilic metal partner of the stannylmetallic reagent Since the transition state involved in the reaction of the Sn-Cu reagents with alkynes was considered to be of low polarity, we expected that steric factors would play a significant role in regiochemical control With this in mind we studied the addition of stannylcuprates of the constitution $(Bu_3Sn)_{1-2}CuCNLi_{1-2}$ and $(R^1)_3Sn(R^2)CuCNLi_2$ to 1,3- enynes varying R^1 from methyl to butyl and R^2 from methyl to t-butyl From the array of stannylmetalloid reagents available that add to 1-alkynes, we chose Sn-B, Sn-Al and Sn-Mg reagents because it is known that the stannylmetal adducts these reagents produce can be efficiently consumed with electrophiles at the more reactive carbon-metal bond

Three readily available enynes, 2-methyl-1-buten-4-yne (7), 2-penten-4-yn-1-ol (8a), and 2-methyl-1-hexen-3-yne (9) were studied (Scheme 2) In most cases the more reactive C-M bond was protonolyzed to facilitate determination of the regiochemistry of the addition In selected cases the C-Cu bond was transmetallated with Et$_2$AlCl,[15a] an alanate prepared and reacted with allyl bromide Vinyl stannanes were separated from stannyl containing by-products by column chromatography In the cases where non-polar reaction products were produced, hexabutylditin was converted to tributyltin chloride by treatment with AgOAc in ethyl acetate[31] coupled with treatment by brine, prior to purification by column chromatography Structures of the vinyl stannanes were deduced by infrared, GC-MS as well as ^{1}H NMR Evidence for their structure and stereochemistry was provided by the magnitude of the coupling between the ^{117}Sn and ^{119}Sn isotopes and ^{1}H ($^3J_{\text{Sn-Htrans}}$ ~ 140Hz, $^3J_{\text{Sn-Hcis}}$ ~70 Hz and $^3J_{\text{Sn-Hgem}}$ ~ 60Hz) When mixtures of isomers were obtained, the ratios of the isomers were determined by GLC or by ^{1}H NMR The ^{1}H NMR spectra of **10a** and **11a** matched the previously obtained 60 MHz ^{1}H NMR data of these compounds[32] The reaction conditions given in Tables 1 and 2 are optimized

Scheme 2 Reactions of Stannyl Cuprates with 1,3 -Enynes



	R3Sn	E
10a,11a,12a,13a,14a,15a, 16a,17a	Bu$_3$Sn	H
10b,11b,13b,14b,15b,16b	Bu$_3$Sn	allyl
10c,11c,13c,14c,	Me$_3$Sn	H
10d,11d,13d,14d	Me$_3$Sn	allyl
13e,14e	Bu$_3$Sn	H
8a,13a-c,14a-c,	OR=OH	
8b,13e,14e	OR=OTHP	

Addition of stannylcopper reagents to enynes: Since stannylmetallations are considered to proceed *via* stannylcupration we initially undertook a study of the addition of stannyl copper reagents to 1,3-enynes We examined the addition of "lower order" stannylcuprates R$_3$SnCuCNLi as well as "higher order " (R$_3$Sn)$_2$CuCNLi$_2$ and "mixed" stannylcuprates R$^1{}_3$Sn(R^2)CuCNLi$_2$ to enynes **7**, **8a** and **9** The homostannylcuprates were prepared by reaction of

Bu$_3$SnLi with CuCN[30] The higher order mixed stannylcuprates were prepared by the reaction of Bu$_3$SnH with R$_2$CuCNLi$_2$[33] The recent discovery, made in our laboratory, that HO alkylcuprates cleave Sn-Sn bonds,[34] allowed another convenient method for the preparation of Me$_3$Sn(R)CuCNLi$_2$ Lipshutz *et al* have also developed a convenient method for preparation of this reagent from Me$_3$SnH[35] The by-product in both preparations, tetramethyltin, is volatile and can easily be distilled from the crude reaction mixture

Reaction of Bu$_3$SnCuCNLi with enynes **7**, **8a** and **9** produced only moderate yields of mixtures of stannylated 1,3-dienes Although there was a bias toward formation of the 1-stannyl isomer, regioselectivity was not synthetically useful (Table 1, entries 1, 14 and 23) Reactions of the homostannyl cuprate (Bu$_3$Sn)$_2$CuCNLi$_2$ with **7** and **8a** (Table 1, entries 2, 16) gave good yields of stannylated 1,3-dienes in which the regioselectivity for the 1-stannylated isomer was synthetically useful (97 3) only in the addition to **7** Reaction of the "mixed" stannylcuprate Bu$_3$Sn(Bu)CuCNLi$_2$ with **7**, **8a** and **9** (Table 1, entries 3, 17, 24) gave very good yields of 1-stannyl product (>97 3) in the cases of **7** and **9**
To determine the role of steric factors in the control of regioselectivity in the addition of "mixed" stannylcuprates to **7**, **8a** and **9** we systematically varied the size of the stannyl and copper bound ligands Since addition of Bu$_3$Sn(Bu)CuCNLi$_2$ to **7** gave mixtures rich in 1-stannylated product (**11a**, 97 3) it was expected that use of Me$_3$Sn(Bu)CuCNLi$_2$ would lead to mixtures enriched in 2-stannylated product (**10a**) Inspection of Table 1 (entries 9 - 12) reveal that reaction of Me$_3$Sn(Bu)CuCNLi$_2$ with **7** indeed gives mixtures enriched in **10a** but the ratio of **11a** to **10a** is dependent on the temperature of the solution during addition of the proton source is added as well as on the nature of the proton source In a similar fashion the reaction of Me$_3$Sn(Me)CuCNLi$_2$ with **7** (Table 1, entries 6, 7, 8) gave mixtures of **10c** and **11c** which were not synthetically useful Reaction of this cuprate with **8a** (Table 1, entry 22) gave a mixture of **13c** and **14c** in which the 2-stannylated product (**13c**) was favored (73 27) This bias could be increased to 81 19 by use of Me$_3$Sn(t-Bu)CuCNLi$_2$ (Table 1, entry 21)

The above results lead to the conclusion that regioselectivity in the additions of "mixed" stannyl cuprates to **7**, **8a** and **9** are influenced, but not entirely controlled by, steric factors For example, widely differing regioselectivities were obtained in the addition of Me$_3$Sn(Bu)CuCNLi$_2$ to **7** depending on whether the reaction was quenched with methanol at -60°C (**10c 11c**, 62 38, Table 1, entry 9) or at room temperature (**10c 11c**, 13 87, Table 1, entry 10) Indeed, addition of methanol to this cuprate prior to **7** caused normal yellow color to become dark red (Table 1, entry 13) This solution reacted with **7** to yield a 1 1 mixture of **10c 11c**. In reactions of Me$_3$Sn(Bu)CuCNLi$_2$ with alcoholic enyne **8a**, the reaction mixture turned red immediately after addition of the latter Both of these observations suggest formation of new, possibly alkoxy, ligated Cu(I) derivatives[36] of this cuprate prior to reaction with alkyne NMR spectra of solutions of Me$_3$Sn(Me)CuCNLi$_2$ and Me$_3$Sn(Bu)CuCNLi$_2$ to which alcohols have been added also suggest the formation of new reagents The formation of these new reagents generally occurs at temperatures below that at which stannylcupration occurs Furthermore, we have determined in related work that these mixed stannyl cuprates remove the acidic hydrogen of 1-alkynes This process explains the lower yields generally obtained in reactions of these reagents with **7** and **8a**. At least the "lower order" cuprates used in this study have been shown to react with 1-alkynes at appreciable rates only above -35°C by a completely reversible reaction[37] Thus, the regiochemistry observed in reactions of alkynes with stannyl cuprates is a result of several competing processes (reaction with protonic co-reactant, reversible addition and vinyl cuprate hydrolysis) whose relative rates would be expected to vary with reagent and reactant

Table 1. Stannylcupration of enynes **7**, **8a** and **9**

Entry	enyne	Reagent	Reaction time & Temp (°C)	Electrophile	Products[a] 3,4-vs 4,3-addn prd	Chem[b] yield %
1	7	$Bu_3SnCuCNLi$	- 40, 1 5 h	NH_4Cl at -40°C	19 / 81	56
2	7	$(Bu_3Sn)_2CuCNLi_2$	- 40, 2 h	MeOH at -40°C	3 / 97	72
3	7	$Bu_3Sn(Bu)CuCNLi_2$	- 40, 20 min	NH_4Cl at -40°C	3 / 97	>95
4	7	$Bu_3Sn(Bu)CuCNLi_2$	- 60, 20 min	MeOH at -60°C	4 / 96	93
5	7	$Bu_3Sn(Bu)CuCNLi_2$	- 40 to RT, 10 h	1 Et_2AlCl 2 BuLi 3 allyl bromide	8 / 92	86
6	7	$Me_3Sn(Me)CuCNLi_2$	- 78 to RT, 10 h	MeOH at RT	67 / 33	49
7	7	$Me_3Sn(Me)CuCNLi_2$	- 78 to RT, 10 h	NH_4Cl at RT	25 / 75	69
8	7	$Me_3Sn(Me)CuCNLi_2$	- 78, 1h	NH_4Cl at -78°C	49 / 51	57[c]
9	7	$Me_3Sn(Bu)CuCNLi_2$	- 60, 2h	MeOH at -60°C	62 / 38	66
10	7	$Me_3Sn(Bu)CuCNLi_2$	- 60 to RT, 3h	MeOH at RT	13 / 87	25
11	7	$Me_3Sn(Bu)CuCNLi_2$	- 60 to RT, 3h	NH_4Cl at RT	19 / 81	27
12	7	$Me_3Sn(Bu)CuCNLi_2$	- 60, 2 h	NH_4Cl at - 60°C	32 / 68	41
13	7	$Me_3Sn(Bu)CuCNLi_2$ + 1 eq MeOH	- 60, 2 h	NH_4Cl at - 60°C	50 / 50	32
14	8 a	$Bu_3SnCuCNLi$	-60, 30 min	NH_4Cl at - 60°C	38/62	58
15	8 a	$Bu_3SnCuCNLi$	-40, 30 min	1 Et_2AlCl 2 BuLi 3 allyl bromide	11/89	58
16	8 a	$(Bu_3Sn)_2CuCNLi_2$	-40, 2h	MeOH at -40°C	39/61	77
17	8 a	$Bu_3Sn(Bu)CuCNLi_2$	-50, 30 min	NH_4Cl at -50 °C	18/82	91
18	8 a	$Bu_3Sn(Bu)CuCNLi_2$	-50, 30 min	MeOH at -60°C	40/60	73
19	8 a	$Bu_3Sn(Bu)CuCNLi_2$	-50, 30 min	MeOH at RT	22/78	67
20	8 a	$Me_3Sn(^tBu)CuCNLi_2$	-60, 3h	MeOH at -60°C	81/19	64
21	8 a	$Me_3Sn(^tBu)CuCNLi_2$	-60 to RT 10 h	MeOH at RT	78/22	58
22	8 a	$Me_3Sn(Me)CuCNLi_2$	-78 to RT 16 h	NH_4Cl at RT	73/27	49
23	9	$Bu_3SnCuCNLi$	-60, 30 min	MeOH at -60 °C	28/80	45
24	9	$Bu_3Sn(Bu)CuCNLi_2$	-50 to RT, 2h	MeOH at RT	-/100	82
25	9	$Bu_3Sn(Bu)CuCNLi_2$	-50 to RT, E addn at -10	1 Et_2AlCl 2 BuLi 3 allyl bromide	-/100	75

a) For numbering of the enynes and the products, see Scheme 2 b) Isolated yields c) Yield calculated based on GC analysis using internal standard method

We have shown in previous studies that the vinyl cuprates formed during stannylcuprations of 1-alkynes are easily quenched by addition of electrophilic reagents such as Et_2AlCl[13] Addition of Et_2AlCl to the stannylcuprate adducts derived from stannylcupration of **7**, **8a** and **9** would be expected to result in transmetallation of the vinyl copper bond to a vinyl aluminum Reaction of the derived stannylaluminum adducts with butyllithium should yield alanates which could then be captured by electrophilic reagents This sequence was shown to be efficient for the reaction of $Bu_3Sn(Bu)CuCNLi_2$ with **7** and **9** which yielded **11b** and **16b**, respectively, in excellent yield and regiochemical purity when allyl bromide was the electrophile (Table 1, entries 5 and 25) When this sequence was performed on stannyl cuprations which usually gave mixtures of regioisomers, such as the reaction of $Bu_3SnCuCNLi$ with **8a** (Table 1, entry 15), mixtures of regioisomeric vinyl stannanes were obtained No significant change in the regiochemistry compared to the previous experiments, where the carbon-copper bond was protonolyzed, was observed

Additions of $Bu_3SnBBN(OMe)^-Li^+$ to enynes: Our previously developed method for addition of tributylstannyl methoxy-9-borabicyclo-(3,3,1)-nonane, $Bu_3SnBBN(OMe)^-Li^+$, to 1-alkynes[14b] was applied to **7**, **8a** and **9** Reaction of this organometallic with **7** in the presence of catalytic amount of $CuBr\ Me_2S$ gave a mixture of **10a-12a** in low yield (Table 2, entry 1) When one equivalent of copper catalyst was used, **10a** was obtained in high yield and good regiochemical purity (Table 2, entry 2) Likewise stannylboration of **8b** and **9** were successful only when an equimolar amount of catalyst was used Regioselectivity was good in both these cases but chemical yields were low

Table 2. Reactions of $Bu_3SnBBN(OMe)^-Li^+$ (**A**), $Bu_3SnAlEt_2$ (**B**) and $Bu_3SnMgMe$ (**C**) with enynes **7**, **8a**, **8b** and **9**

Entry	Enyne[a]	Reagent	Catalyst & Reaction Conditions	Electrophile	Products[a] 3,4-cis/4,3-cis /4,3-trans addn	Chem [b] yield (%)
1	7	A	$CuBr\ Me_2S$, 1 0 eq, -50°C, 3h, THF	1M HCl in MeOH at -50 °C	34 / 48 / 18	21
2	7	A	$CuBr\ Me_2S$, 1 0 eq -40 °C, 2 5 h, THF	1M HCl in MeOH at -40 °C	89 / 11 / -	74
3	8b	A	$CuBr\ Me_2S$, 1 0 eq -40 °C, 3 h, THF	1M HCl in MeOH at -40 °C	95/5/-	19
4	9	A	$CuBr\ Me_2S$ 1 0 eq -40 °C, 2 5 h, THF	1M HCl in MeOH at -40 °C	84/16/-	~10
5	7	B	CuCN, 0 1 eq, -40 °C, 5h, THF	NH_4Cl at 0 °C	44/56/-	90
6	7	B	CuCN, 1 0 eq, -40 °C, 3h, THF	NH_4Cl at 0 °C	34/66/-	73
7	7	B	CuCN, 1 0 eq, -40 °C, 3h, THF HMPA 1 1[c]	NH_4Cl at 0 °C	21/79/-	56
8	8a	B	CuCN, 0 1eq, -40 °C, 5h, THF	1M HCl in MeOH at -40 °C	85/15/-	52
9	8a	B	CuCN, 1 0 eq, -40 °C, 3h, THF HMPA 1 1[c]	NH_4Cl at 0 °C	-/100/-	54
10	9	B	CuCN, 1 0 eq, -40 °C, 3h, THF	NH_4Cl at 0 °C	16/84/-	19
11	9	B	CuCN, 0 1eq, -40 °C, 3h, THF HMPA 1 1[c]	NH_4Cl at 0°C	6 / - /94	29
12	7	C	CuCN, 0 1eq, -40 °C, 3h, THF	MeOH at -40 °C	-/71/25	85
13	7	C	CuCN, 0 1eq, -40 °C, 3h, THF HMPA 1 1[c]	MeOH at -40 °C	10/90/-	70
14	8a	C	CuCN, 1 0 eq, -60 °C, 5h, THF	MeOH at -60 °C	9/91/-	57

a) For numbering, see Scheme 2 b) Isolated yields c) HMPA was added into the reaction mixture after the reagent preparation, prior to the enyne addition

Addition of $Bu_3SnAlEt_2$ to enynes: Regiochemistry of the stannylalumination of 1-alkynes can be controlled by a proper choice of solvent, electrophile and reaction conditions[15a] The addition of $Bu_3SnAlEt_2$ to **7** in the presence of catalytic or equimolar amounts of CuCN resulted in good chemical yields of 2 3 mixtures of **10a** and **11a**, whereas similar addition to the α–functional enyne, **8a**, and **9** gave a moderate regiochemical bias in favor of **13a** and **16a** (Table 2, entries 8 and 10) The addition of hexamethylphosphorous triamide (HMPA) to the reaction of this organometallic with **7** as well as its reaction with **8a** yielded major amounts of **11a** and **14a** (Table 2, entries 7 and 9) Interestingly, the trans-addition product was obtained in good regiochemical purity in the addition of this reagent to **9** in the presence of HMPA (Table 2, entry 11) This is proposed to be due to intervention of an allene intermediate or to the steric requirements of the internal triple bond

We have previously suggested that Cu^{+1} catalyzed addition of $Bu_3SnAlEt_2$ to 1-alkynes occurs *via* a stannyl-copper intermediate[13] According to ^{13}C NMR studies in this laboratory, HMPA sharpens the signals of lower order stannylcuprates, suggesting less aggregation in THF/HMPA solvent[21] In this light, the change in the regiochemistry could be due to a lower steric requirement for the copper center in this solvent compared to THF HMPA could also change the electronic environment in the stannyl-copper-aluminum intermediate by complexation with the aluminum[30] The π-electron density on the terminal carbon of an alkyne is known to be higher than on the terminal carbon[38] When aluminum is complexed with HMPA, the electron density in copper is presumed to increase favoring formation of 1-stannyl product

Addition of $Bu_3SnMgMe$ to enynes. Addition of $Bu_3SnMgMe$ to enynes **7**, **8a** and **9** was conducted according to the procedure we have prevously used for its addition to 1-alkynes[27] With catalytic amounts of CuCN the reaction of this organometallic with **7** yielded a 3 1 mixture of **11a** and **12a** With HMPA as a co-solvent **12a** was not obtained and the reaction produced major amounts of **11a** contaminated with minor amounts of **10a** (Table 2, entries 12 and 13) This result was also obtained when $Bu_3SnMgMe$ was reacted with **8** (Table 2, entry 14)

Experimental

^1H NMR spectra were recorded on a Bruker WM-400 spectrometer in $CDCl_3$ using residual $CHCl_3$ (δ 7 25) as internal standard The Sn-H coupling constants (J_{Sn-H}) are given as an average of the ^{117}Sn and ^{119}Sn values Low resolution mass spectra were obtained on a Hewlett-Packard 5985B GC/MS system operating at 70 eV High resolution GC/MS spectra were recorded on a Kratos MS80 instrument For compounds containing Bu_3Sn groups, molecular mass measurements are based on ^{120}Sn (M^+-Bu) fragment Gas chromatographic analyses were conducted on a Hewlett-Packard 5880A instrument equipped with a flame-ionization detector and employing J/W fused silica capillary columns (15 m x 0 25 mm or 7 m x 0 25 mm) using linear temperature gradient IR spectra were recorded as neat film on NaCl on a Perkin-Elmer 599B instrument

Tetrahydrofuran was freshly distilled over sodium or potassium benzophenone ketyl Hexamethylphosphorous triamide and diisopropylamine were distilled over calcium hydride and stored over activated 3A molecular sieves 2-Methylbut-1-en-3-yne, 2-methylhex-1-en-3-yne, and 2-penten-4-yn-1-ol were purchased from Farchan, distilled and stored under nitrogen prior to use The latter was also prepared according to the procedure of Brandsma[39] Tributyltin hydride was prepared by reduction of Bu_3SnCl with $LiAlH_4$[40] or purchased from Aldrich Hexabutylditin and hexamethylditin were purchased from Aldrich and used without further purification All organometallic reactions were conducted in flame-dried glassware under a positive pressure of argon or nitrogen

Preparation of 1-Tetrahydropyranyloxy-2-penten-4-yne **8b**· 3,4-Dihydro-2H-pyran (1 45 g, 1 6 mL, 17 25 mmol) was added dropwise to **8a** (0 95 g, 11 5 mmol) in 10 mL of dry ether at 0 °C A few crystals of p-toluenesulfonic acid were added and the reaction mixture was stirred for 14 h at rm temp , quenched by addn of aq , satd $NaHCO_3$ (2x 20 mL), separated and dried over anhyd $MgSO_4$ Distillation of the crude product (bp 38-40°C/ 0 1 mm Hg) gave 1 54 g of **8b** (93% pure by GLC, 75% yield) ^1H NMR δ 1 46-1 90 (m, 6H), 2 87 (d, 1H, J< 2Hz), 3 50 and 3 82 (2 x m, 2H, $OCH_2C{=}$), 4 03 and 4 28 (2 x ddt, 2 x 1H), 4 62 (t, 1H, J=4Hz), 5 74 (ddt, 1H, J=16 Hz, J=2Hz, J=2 Hz), 6 29 (dtd, 1H, J=16 Hz, J=5 Hz, J<1Hz), GC/MS (Chemical ionization, isobutane) m/z (rel intensity) 167 (100, M^++1)

Reaction of $Bu_3SnCuCNLi$ with **7** Bu_3SnLi, (2 2 mmol) in 10 mL of dry THF, was prepared at - 30°C Thus, Bu_3SnH (0 67 g, 0 72 mL, 2 3 mmol) was added dropwise to a soln containing lithium diisopropylamide which was prepared by dropwise addn of n-BuLi (2 5 M in hexane, 0 96 mL, 2 4 mmol) to a soln of diisopropylamine (0 24 g, 0 34 mL, 2 4 mmol) in 10 mL of dry THF at -30°C The soln was cooled to -60°C and CuCN (0 197 g, 2 2 mmol) was added The resulting yellow soln was stirred for 10 min and enyne **7**, (0 20 mL, 0 132 g, 2 0 mmol) was added in 1 mL of dry THF The reaction mixture was stirred at -40°C for 1 5 h, quenched with MeOH (2 mL) and warmed to rm temp Ether (20 mL) was added and the reaction mixture was stirred with aq , satd NH_4Cl (25 mL), washed with aq , satd NH_4Cl (2 x 25 mL) and brine (2 x 25 mL) The crude product was stirred for 1 h with 1 g of silver acetate in 10 mL of ethyl acetate, filtered through a pad of Celite, washed with brine (2 x 25 mL), dried over anhyd $MgSO_4$ and concentrated *in vacuo* Column chromatography (Silica Gel 60, E Merck, 230-400 mesh, 35 cm x 2 5 cm column made basic with a 3% soln of Et_3N in hexanes, hexanes as eluent) yielded 0 24 g (56%) of a 19 81 mixture of **10a** and **11a**, 93% pure by GLC The isomer ratio obtained after the column chromatography (basic conditions) was within a few percent that obtained prior to purification For ^1H NMR analysis,**10a** and **11a** were separated by preparative TLC (Silica Gel 60, E Merck, 0 25mm, hexanes) Pure **10a** was isolated from TLC plates not treated with Et_3N under which conditions **11a** decomposed The latter compound was isolated from preparative TLC separation using hexanes containing Et_3N

2-Methyl-3-tributylstannyl-1,3-butadiene **10a** ^1H NMR δ 0 88 (m, 15H), 1 34 (m, 6H,) 1,40 (m, 6H), 1 88 (s, 3H), 4 79 and 4 96 (2 x s, 2 x 1H, $C{=}\underline{CH}_2$), 5 27 (s, 1H, $^3J_{Sn\text{-}Hcis}$=65 Hz), 5 88 (s, 1H, $^3J_{Sn\text{-}Htrans}$=135 Hz), GC/MS m/z (rel intensity %) 301 (M^+-57, 52), 245 (10), 235 (15), 177 (100), 121 (45), high resolution GC/MS calcd for $C_{13}H_{25}{}^{120}Sn$ (M^+-57) 301 0978, found 301 1008, IR (cm^{-1}) 2970 s, 2940 s, 2885 s, 2865 s, 1570 w, 1470 m, 1380 w, 995 w, 895 w

3-Methyl-1(E)-tributylstannyl-1,3-butadiene **11a**: ^1H NMR ($CDCl_3$) δ 0 88 (m, 15H,), 1 34 (m, 6H), 1,40 (m, 6H), 1 84 (s, 3H), 4 93 and 5 0 (2 x s, 2 x 1H, $C{=}\underline{CH}_2$), 6 19 (d, 1H, J=20 Hz, $^3J_{SnHcis}$=69 Hz), 6 62 (d, 1H, J=20 Hz, $^3J_{Sn\text{-}Hgem}$=63 Hz), GC/MS m/z (rel intensity %) 301 (65), 245 (80), 189 (100), 121 (15), high resolution GC/MS calcd for $C_{13}H_{25}{}^{120}Sn$ $(M\text{-}57)^+$301 0978, found 301 0998, IR (cm^{-1}) 2970 s, 2940 s, 2885 s, 2865 s, 1465 m, 1380 w, 920 w, 890 w

Reaction of $Bu_3SnCuCNLi$ with **8a** The reaction of this cuprate with enyne **8a** was conducted by the same procedure used above for its reaction with **7** The alcoholic products **13a** and **14a** were separated from the crude reaction product by column chromatography using the column conditions described above but with hexanes EtOAc 90 10 for the first 100 mL of eluant and hexanes EtOAc 1 1 thereafter

2-Tributylstannyl-1(E),3(E)-pentadien-5-ol **13a**· ^1H NMR δ 0 88 (m, 15H), 1 31 (m, 6H), 1 49 (m, 6H), 4 18 (d, 2H, J=6 0 Hz), 5 31 (d, 1H, J=3 Hz, $^3J_{Sn\text{-}Hcis}$=59 Hz), 5 70 (dt, 1H, J= 6 Hz, J=11 Hz, $C{=}C\underline{H}\text{-}CH_2O$), 5 85 (d, 1H, J= 3 Hz,$^3J_{Sn\text{-}Htrans}$=128 Hz), 6 48 (d, 1H, J=11 Hz, $^3J_{Sn\text{-}H}$=73 Hz), GC/MS m/e (rel intensity %) 317 (M^+-57,15), 251 (100), 234 (15), 177 (55), High resolution GC/MS calcd for $C_{13}H_{25}O^{118}Sn$ $(M\text{-}57)^+$ 315 0921, found 315 0891, IR (cm^{-1}) 3320 s (br), 2970 s, 2935 s, 2880 s, 2860 s, 1720 w, 1570 m, 1470 m, 1420 w, 1380 w, 1290 w, 1185 w, 1080 m, 1010 s, 970 w, 880 w, 870 w

1-Tributylstannyl-1(E),3(E)-pentadien-5-ol **14a** ^{1}H NMR δ 0 87 (m, 15H), 1 31 (m, 6H), 1 49 (m, 6H), 4 18 (d, 2H, J=6 0 Hz), 5 77 (dt, 1H, J=15Hz, J=6 0 Hz), 6 21 (dd, 1H, J=15 Hz, J=10 Hz), 6 24 (d, 1H, J=19 Hz, $^3J_{Sn\text{-}Hgem}$=52 Hz), 6 52 (dd, 1H, J=19 Hz, J=10 Hz, $^3J_{Sn\text{-}Hcis}$=58Hz), high resolution GC/MS calcd for $C_{13}H_{25}O^{118}Sn$ $(M\text{-}57)^+$ 315 0921, found 315 0921, IR (cm^{-1}) 3320 s (br), 2970 s, 2935 s, 2880 s, 2860 s, 1570 m, 1470 m, 1420 w, 1380 w, 1290 w, 1185 w, 1080 m, 1010 s, 970 m, 880 w, 870 w

Reaction of $Bu_3SnCuCNLi$ with **8a** and addition of allyl bromide. The reaction of $Bu_3SnCuCNLi$ with **8a** was conducted as described above One equivalent of Et_2AlCl (1M soln in hexanes) was added dropwise *via* syringe After stirring for 15 min at -40 °C, 1 eq of BuLi (2 5M soln in hexanes) was added and the reaction mixture was stirred for 15 min Allyl bromide (1 5 eq) was added and the reaction mixture was warmed over 16 h to rm temp while stirring Ether was added and the reaction mixture was subjected to the usual workup The alcoholic products **13b** and **14b** were separated by column chromatography using conditions described above but with hexanes EtOAc 90 10 for the first 100 mL of eluant and gradually changing the hexanes EtOAc ratio to 1 1 thereafter

4-Tributylstannyl-2E,4(Z),7-octatrien-1-ol. **13b**. ^{1}H NMR δ 0 88 (m, 15H), 1 30 (m, 6H), 1 47(m, 6H), 2 85 (t, 2H, J=6 5 Hz), 4 26 (t, 2H, J=6 5 Hz), 5 00-5 08 (d of d, 2H, $=CH_2$), 5 67(dt, 1H, J=16 Hz, J=6 5 Hz, $=C\underline{H}CH_2O$), 5 80 (ddt, 1H, J=18 Hz, J=10 Hz, J=6 Hz, $=C\underline{H}CH_2C=$), 6 26 (t, 1H, J=8 0 Hz,$^3J_{Sn\text{-}Htrans}$=140 Hz), 6 42 (d, 1H, J=15 Hz), GC/MS m/z (rel intensity %) 357 (M-57$^+$, 100), 301 (55), 177 (45), high resolution GC/MS calcd for $C_{16}H_{29}O^{118}Sn$ $(M\text{-}57)^+$ 355 1235, found 355 1264

1-Tributylstannyl-2-propenyl-1(E),3(E)-pentadien-6-ol. **14b** ^{1}H NMR δ 0 88 (m, 15H), 1 30 (m, 6H), 1 44 (m, 6H), 3 02 (d, 2H, J=6 5 Hz), 4 18 (t, 2H, J=6 0 Hz), 5 02 (dd, 1H, J=17 Hz, J= 2 Hz,), 5 07 (dd, 1H, J= 24 Hz, J=2 Hz), 5 72-5 85 (m, 2H, $=C\underline{H}CH_2O$ and $=C\underline{H}CH_2C=$), 6 05 (s,1H, $^3J_{Sn\text{-}Hgem}$=62 Hz), 6 26 (d, 1H, J=16 Hz), GC/MS m/z (rel intensity %) 357 (M-57, 15), 251 (100), 177 (55), high resolution GC/MS calcd for $C_{16}H_{29}O^{118}Sn$ $(M\text{-}57)^+$ 355 1235, found 355 1215, IR (cm^{-1}) 3320 s (br), 2975 s, 2940 s, 2885 s, 2860 s, 1642 s, 1568 m, 1470 m, 1420 w, 1380 w, 1080 m, 1010 s, 970 m, 920 m, 870 w, 850w

Reaction of $Bu_3SnCuCNLi$ with **9** The reaction of this cuprate with enyne **9** was conducted by the same procedure used above for its reaction with **7** The stannyl products **15a** and **16a** were obtained in enriched isomeric purity by column chromatography using conditions described above for the separation of **10a** and **11a**

2-Methyl-3-tributylstannyl-1(E),3(E)-hexadiene. **15a**· ^{1}H NMR δ 0 88 (m, 15H,), 1 00 (t, 3H, J=6 5 Hz), 1 34 (m, 6H), 1,40 (m, 6H), 1 84 (s, 3H), 2 38 (q, 2H, J=6 5 Hz), 4 70 and 4 78 (2 x s, 2 x 1H, $H_2C=$), 5 36 (t,1H, J=7 Hz, $^3J_{Sn\text{-}Hcis}$=68 Hz), GC/MS m/z (rel intensity %) 386 (1), 329 (100), 217 (15), 177 (20)

2-Methyl-4-tributylstannyl-1(Z),3(E)-hexadiene. **16a** ^{1}H NMR ($CDCl_3$) δ 0 88 (m, 15H), 1 00 (t, 3H, J=6 5 Hz), 1 34 (m, 6H), 1 40 (m, 6H), 1 84 (s, 3H), 2 38 (q, 2H, J=6 5 Hz), 4 74 and 4 92 (2 x s, 2 x 1H), 5 90 (s, 1H, $^3J_{Sn\text{-}Hcis}$=75 Hz), GC/MS m/z (rel intensity %), 386 (M$^+$, 2), 329 (100), 273 (55), 217 (50), 177 (35), high resolution GC/MS calcd for $C_{15}H_{29}{}^{120}Sn$ $(M\text{-}57)^+$ 329 1291, found 329 1292, IR (cm^{-1}) 2975 s, 2940 s, 2880 s, 2860 s, 1470 s, 1425 w, 1380 m, 1080 m, 970 w, 900 m

Reaction of $(Bu_3Sn)_2CuCNLi_2$ with **7** Bu_3SnLi, (2 0 mmol) in 5 mL of dry THF) was prepared at -40°C by dropwise addn of BuLi (2 5 M in hexanes, 0 8 mL, 2 0 mmol) to a soln of $Bu_3SnSnBu_3$ (1 01 mL, 1 16 g, 2 0 mmol) in THF (5 mL) After stirring 30 min CuCN

(90 mg, 1 0 mmol) was added and the yellow soln was stirred at -40°C for 15 min and cooled to -78°C Enyne **7** (0 95 mL, 66 mg, 1 0 mmol) in 1 mL of dry THF was added dropwise and the reaction mixture was stirred for 2 h at -78°C The reaction was quenched by addn of MeOH (2 mL) at -78°C, warmed to rm temp and subjected to the usual workup and purification

Reaction of $(Bu_3Sn)_2CuCNLi$ with **8a**· The reaction of this cuprate with enyne **8a** was conducted by the same procedure used above for its reaction with **7** The reaction product was purified by column chromatography using conditions described above for the separation of **13a** and **14a**

Reaction of $Bu_3Sn(Bu)CuCNLi_2$ with **7** and addition of allyl bromide The mixed stannyl cuprate was prepared according to the procedure of Lipshutz *et al*[41] Thus, BuLi (2 5 M soln in hexanes, 0 84 mL, 2 1 mmol) was added dropwise into a suspension of CuCN (95 mg, 1 05 mmol) in 5 mL of THF at -40°C and the resulting soln was stirred for 15 min Bu_3SnH (0 56 mL, 0 61 g, 2 1 mmol) was added dropwise and the soln was stirred for 30 min Enyne **7** (0 10 mL, 69 5 mg, 1 05 mmol) in 1 mL of dry THF was added dropwise and the reaction mixture was stirred for 15 min at -40°C The addn of allyl bromide was conducted by the same procedure used above for the reaction of $Bu_3SnCuCNLi$ with **8a** The stannyl products **10b** and **11b** were obtained by column chromatography using column conditions described above for the separation **10a** and **11a**

2-Methyl-3-tributylstannyl-1,3(Z),6-heptatriene, **10b**. ^1H NMR δ 0 88 (m, 15H), 1 34 (m, 6H), 1,40 (m, 6H), 1 80 (s, 3H), 2 80 (t, 2H, J=7 8 Hz), 4 54 and 4 70 (2 x s, 2 x 1H, $\underline{H_2}C{=}CCH_3$-), 5 00 and 5 05 (2xdq, 2H, J=10 Hz, J=17 Hz, J=2 Hz, $H_2C{=}$), 5 80 (ddt, 1H, J=17 Hz, J=10 Hz, J=6 Hz), 6 11 (t,1H, J=7 8 Hz, $^3J_{Sn\text{-}Htrans}$=130 Hz), GC/MS *m/z* (rel intensity %) 341 ($M\text{-}57^+$, 100), 285 (35), 227 (15), 177 (40), high resolution GC/MS calcd for $C_{16}H_{29}O^{120}Sn$ $(M\text{-}57)^+$ 341 1291, found 341 1258

3-methyl-2-propenyl-1-tributylstannyl-1(E),3-butadiene, **11b**. ^1H NMR δ 0 88 (m, 15H), 1 34 (m, 6H), 1 40 (m, 6H), 1 90 (s, 3H), 3 98 (d, 2H, J=6 5 Hz), 4 95-5 07 (m, 4H), 5 80 (ddt, 1H, J=17 Hz, J=10 Hz, J=6 Hz, $=C\underline{H}CH_2$-), 6 07 (s, 1H, $^3J_{Sn\text{-}Hgem}$=60 Hz), GC/MS m/z (rel intensity %) 341 ($M\text{-}57^+$, 100), 285 (80), 227 (45), 177 (20), high resolution GC/MS calcd for $C_{16}H_{29}O^{120}Sn$ $(M\text{-}57)^+$ 341 1291, found 341 1320, IR (cm^{-1}) 2970 s, 2940 s, 2885 s, 2865 s, 1563 s, 1465 m, 1450 s, 1380 m, 920 w, 900 m, 840 m

Reaction of $Bu_3Sn(Bu)CuCNLi_2$ with **8a** The reaction of this mixed cuprate with **8a** was conducted by the same procedure used above for the reaction with **7** The reaction products **13a** and **14a** were separated by column chromatography using conditions described above

Reaction of $Bu_3Sn(Bu)CuCNLi_2$ with **9** and addition of allyl bromide The reaction of this cuprate with **9** was conducted by the same procedure used above for its reaction with **7** The reaction was quenched by addn of MeOH at -50 °C, warmed to rm temp and subjected to the usual workup Pure **16a** was obtained after column chromatography using conditions described above for the separation of **10a** and **11a** The addn of allyl bromide was conducted by the same procedure used above for the reaction of **19** with **8a** and isomerically pure **16b** was obtained after the usual workup and purification

2-Methyl-3-propenyl-4-tributylstannyl-1,3-heptadiene **16b** ^1H NMR δ 0 88 (m, 15H,), 1 00 (t,3H, J=6 5 Hz), 1 34 (m, 6H), 1 40 (m, 6H), 1 84 (s, 3H), 2 38 (q, 2H, J=6 5 Hz), 4 70 and 4 78 (2x m, 2H, $\underline{H_2}C{=}CCH_3$-), 4,95 and 5 00 (2x dq, 2x 1H, J=10 Hz, J=2 Hz, J=16 Hz, J=2 Hz, $\underline{H_2}C{=}$), 5 73 (ddt, 1H, J= 16 Hz, J=10 Hz, J= 6 5 Hz), GC-MS m/z (relative intensity %) 369 (100), 313 (45), 179 (48), High resolution GC-MS calculated for $C_{15}H_{29}{}^{120}Sn$ $(M\text{-}57)^+$ 369 1604, found 369 1585

Reaction of $Me_3Sn(Me)CuCNLi_2$ with **7** Methyllithium (1 26 M soln in hexanes, 1 74 mL, 2 2 mmol) was added dropwise into a vigorously stirred suspension of CuCN (98 mg, 1 1 mmol) in 5 mL of dry THF while the temperature was maintained below -40°C The resulting colourless soln was stirred for 20 min at which point hexamethylditin (0 360 g, 1 1 mmol) was added and the soln gradually turned yellow The soln was stirred for 1h at -40°C, cooled to -78°C and enyne **7** (0 10 mL, 69 5 mg, 1 05 mmol) in 1 mL of dry THF was added dropwise The reaction mixture was stirred for 1 5 h at -78°C warmed to rm temp overnight and quenched by addn of aq , satd NH_4Cl/1M NaOH (pH=8) The aq soln was extracted with ether (2 x 10 mL), backwashed with aq , satd NH_4Cl/1M NaOH (pH=8), dried over anhyd $MgSO_4$ and the extract concentrated *in vacuo* The concentrate was passed through a short column of silica gel (10 cm x 1 2 cm, hexanes basified with a 3% soln of Et_3N in hexanes) to yield a mixture of **10c** and **11c**

2-Methyl-3-trimethylstannyl-1,4-butadiene, **10c:** ^1H NMR δ 0 20 (s, 9H), 0 84 (s, 3H), 4 84 and 4 97 (s+s, 2x1H), 5 32 (s, 1H,$^3J_{Sn\text{-}Hcis}$=75 Hz), 5 89 (s, 1H, $^3J_{Sn\text{-}Htrans}$=150 Hz), GC/MS m/z (rel intensity %) 232 (15), 217 (100), 189 (25), 165 (85, 151 (25), 135 (42), high resolution GC/MS calcd for $C_8H_{16}{}^{120}Sn$ (M^+) 232 0274, found 232 0286

3-Methyl-1-trimethylstannyl-1,3-butadiene, **11c.** ^1H NMR δ 0 15 (s, 9H), 1 92 (s, 3H), 4 97 and 5 03 (2 s, 2 x 1H), 6 25 (d, 1H, J=20 Hz, $^3J_{Sn\text{-}Hcis}$=64 Hz), 6,64 (d, 1H, J=20 Hz, $^3J_{Sn\text{-}Hgem}$=73 Hz), GC/MS m/e (rel intensity %) 232 (2), 217 (100), 165 (18), 151 (65), 135 (63), high resolution GC/MS calcd for $C_8H_{16}{}^{120}Sn$ (M^+) 232 0274, found 232 0260

Reaction of $Me_3Sn(Me)CuCNLi_2$ with **8a** The reaction of this mixed cuprate with **8a** was conducted by the same procedure used above for its reaction with **7** A mixture of the reaction products **13c** and **14c** was separated by filtration through a short column of silica gel using conditions described above but with hexanes EtOAc 90 10 for the first 20 mL of eluant and hexanes EtOAc 1 1 thereafter

2-Trimethylstannyl-1,3(E)-pentadien-5-ol **13c.** ^1H NMR ($CDCl_3$) δ 0 21 (s, 9H), 4 20 (d, 2H, J=5 2 Hz), 5 34(s, 1H, $^3J_{SnHcis}$=63 Hz), 5 71 (dt, 1H, J=16 Hz, J=5 2 Hz, =C$\underline{H}$$CH_2O$), 5 86 (s, 1H,$^3J_{Sn\text{-}Htrans}$=137 Hz), 6 48 (d,1H, J= 16 Hz, C$\underline{H}$=$CHCH_2O$), GC/MS m/z (rel intensity %) 233 (M^+, 100), 167 (50), 135 (45), high resolution GC/MS calcd for $C_7H_{13}O^{120}Sn$ $(M-15)^+$ 232 9988, found 232 9983

1-Trimethylstannyl-1(E),3(E)-pentadien-5-ol **14c:** ^1H NMR δ 0 15 (s, 9H), 4 20 (d, 2H, J=5 2 Hz), 5 80 (dt, 1H, J=16 Hz, J=5 2 Hz), 6 22 (dd, 1H, J= 16 Hz, J=10 Hz), 6,24 (d, 1H, J=19 Hz, $^3J_{Sn\text{-}Hcis}$=68 Hz), 6 52 (dd, 1H, J= 19 Hz, J= 10Hz, $^3J_{Sn\text{-}Hgem}$=58 Hz), GC/MS m/z (rel intensity %) 233 (M^+, 3), 165 (100), 135 (45), high resolution GC/MS calcd for $C_7H_{13}O^{120}Sn$ (M^+) 232 9988, found 232 9971, IR (cm^{-1}) 3400 s (br), 2975 s, 2980 s, 2940 s, 2860 s, 1720 s, 1460 m, 1380 w, 1280 m, 1195 s, 885 m, 860 m, 780 w, 745w, 660

Reaction of $Me_3Sn(t\text{-}Bu)CuCNLi_2$ with **8a** The reaction of this mixed cuprate with **8a** was conducted by the same procedure used above for its reaction with **8a** A mixture of the reaction products **13c** and **14c** was separated by filtration through a short column of silica gel using conditions described above

Reaction of $Me_3Sn(Bu)CuCNLi_2$ with **7** To HO cuprate $Bu_2CuCNLi_2$ (2 1 mmol) in 10 mL of dry THF, prepared as described above, was added $Me_3SnSnMe_3$ (0 688 g, 2 1 mmol) at -40°C and the mixture was stirred for 30 min Enyne **7**, (0 20 mL, 0 132 g, 2 0 mmol) in 1 mL of dry THF was added and the soln was stirred for 2h The reaction was quenched by addn of 2 mL of MeOH and was subjected to the usual workup and purification

Reaction of $Bu_3SnBBN(OMe)^-Li^+$ with **7** Lithium diisopropylamide was prepared by adding n-BuLi (2 4 mmol) to diisopropylamine (0 243 g, 0 33mL, 2 4 mmol) in 10 mL if dry THF at -30 °C After stirring 15 min Bu_3SnH (0,669 g, 0 720 mL, 2 3 mmol) was added dropwise maintaining the temperature below -30 °C The soln was stirred for 30 min at -30 °C and cooled to -50 °C β–Methoxy-9-BBN (0 365 g, 2 4 mmol, prepared by addn of methanol to 9-BBN at 0 °C)[42] was added dropwise to the reaction mixture After stirring for 30 min enyne **7** (0 132 g, 0 189 mL, 2 0 mmol) was added dropwise in 1 mL of THF, followed by CuBr Me_2S (0 420 g, 2 04 mmol) The resulting light brown soln was stirred at -40 °C for 2 5 h The reaction was quenched by addition of 2 mL of 1M HCl in MeOH at -40 °C After warming the resulting black soln to rm temp , ether was added and the reaction mixture was filtered through a pad of Celite and washed with aq , satd NH_4Cl (2 x 25 mL) and brine (2 x 25 mL) After drying over anhyd $MgSO_4$, the solvent was evaporated *in vacuo* to give1 13 g of product The crude product was treated with AgOAc as described above and subjected to the usual purification

Reactions of $Bu_3SnBBN(OMe)^-Li^+$ with **8b** and **9**: The reactions of this metallometallic reagent with **8b** and **9** were conducted by the same procedure used above for its reaction with **7** A mixture of the reaction products **13e** and **14e** were separated using column conditions described above but with hexanes EtOAc 90 10 for the first 100 mL of eluant and hexanes EtOAc 1 1 thereafter The crude reaction mixture from this reaction was subjected to usual purification

5-Tetrahydropyranyloxy-2-tributylstannyl-1,3(Z)-pentadiene, **13e**: ^1H NMR δ 0 88 (m, 15H,), 1 31 (m, 6H), 1 46-1 90 (m,12H), 3 49 and 3 85 (2 x m, 2H,), 4 05 and 4 25 (2 x ddd, 2 x 1H), 5 29 (d, 1H, J=3Hz, $^3J_{Sn\text{-}Hcis}$=59 Hz), 5 61 (dt, 1H, J= 6Hz, J=16 Hz), 5 88 (d, 1H, J= 3 Hz,$^3J_{Sn\text{-}Htrans}$=130 Hz), 6 52 (d, 1H, J=16 Hz,$^3J_{Sn\text{-}H}$=74 Hz), GC/MS m/z (rel intensity %) 459 (23), 291 (100) , IR (cm^{-1}) 2975 s, 2940 s, 2880 m, 2865 m, 1470 m, 1380 w, 1210 m, 1125 m, 1080 m, 1035 s, 970 w, 915 m, 820 w, anal calcd for $C_{22}H_{42}O_2Sn$ C 57 61, H 9 24, found C 57 74, H 9 44

5-Tetrahydropyranyloxy-1-tributylstannyl-1(E),3(E)-pentadiene **14e** ^1H NMR δ 0 88 (m, 15H), 1 31 (m, 6H), 1 46-1 90 (m,12H), 3 49 and 3 85 (2 x m, 2H), 4 05 and 4 25 (2 x ddd, 2 x 1H), 5 77 (dt, 1H, J=15 Hz, J=6 0 Hz), 6 21 (dd, 1H, J=15 Hz, J=10 Hz), 6 24 (d, 1H, J=19 Hz, $^3J_{Sn\text{-}Hgem}$ =52 Hz), 6 52 (dd, 1H, J=19 Hz, J=10 Hz, $^3J_{Sn\text{-}Hcis}$ =58Hz), GC/MS m/z (rel intensity %) 459 (63), 401 (18), 357 (100), 291 (80)

Reaction of $Bu_3SnAlEt_2$ with **7** Bu_3SnH (1 13g, 3 9 mmol) was added dropwise to 6 mL of THF containing lithium diisopropylamide (4 0 mmol, prepared as above) maintaining the temperature below -30°C After stirring for 30 min, Et_2AlCl (1 M soln in hexanes, 3 9 mL, 3 9 mmol) was added dropwise *via* syringe at -30°C The clear soln was stirred for further 30 min at which time enyne **7** (92 mg, 0 13 mL, 1 4 mmol) in 1 mL of THF was added dropwise followed by CuCN (30 mg, 0 33 mmol) The orange soln was stirred at -30 °C for 2 h, warmed to 0 °C, quenched by addn of satd NH_4Cl and extracted with ether (2 x 10 mL) which was washed with aq , satd NH_4Cl (2 x 25 mL) and brine (2 x 25 mL) before drying over anhyd $MgSO_4$ Concentration of the extract *in vacuo* followed by column chromatography yielded **10a** and **11a** When HMPA was used as co-solvent, a mixture of **10a** and **12a** was obtained

3-Methyl-1(Z)-tributylstannyl-1,3-butadiene, **12a** ^1H NMR δ 0 88 (m, 15H), 1 34 (m, 6H,), 1 40 (m, 6H), 1 84 (s, 3H), 4 93 and 5 0 (2 x s, 2 x 1H), 6 88 (d, 1H, J=14 Hz, $^3J_{Sn\text{-}Hgem}$=56 Hz), (d,1H, J=14 Hz, $^3J_{Sn\text{-}Htrans}$=138 Hz), GC/MS m/z (rel intensity %) 301 (40), 245 (65), 185 (100)

Reactions of $Bu_3SnAlEt_2$ with **8a** and **9** The reactions of this stannylaluminum reagent with **8a** and **9** were conducted by the same procedure used above for its reaction with **7** A mixture of the reaction products **13a** and **14a** were separated using column conditions described above but with hexanes EtOAc 90 10 for the first 100 mL of eluant and hexanes EtOAc 1 1 thereafter The crude product from the reaction $Bu_3SnAlEt_2$ with **9** was subjected to usual purification When HMPA was used as co-solvent, a mixture of **15a** and **17a** was obtained

2-Methyl-4-tributylstannyl-1,3(Z)-hexadiene **17a** ^1H NMR δ 0 88 (m, 15H,), 1 00 (t, 3H, J=6 5 Hz), 1 34 (m, 6H), 1 40 (m, 6H), 1 77 (s, 3H), 2 23 (q, 2H, J=6 5 Hz), 4 70 and 4 77 (2 x s, 2 x 1H), 6 48 (s, 1H, $^3J_{Sn\text{-}Htrans}$=150 Hz), GC/MS m/z (rel intensity %) 329 (100), 273 (55), 217 (65), 177 (68)

Reaction of $Bu_3SnMgMe$ with **7**: Bu_3SnH (0 944 g, 0 91 mL, 3 2 mmol) was added dropwise to 6 mL of THF containing lithium diisopropylamide (3 4 mmol, prepared as above) maintaining the temperature below -30°C After stirring for 30 min, MeMgI (3M in hexane, 1 1 mL, 3 2 mmol) was added dropwise and the soln was stirred at -30°C for another 30 min After cooling to -40°C, enyne **7** (86 mg, 0 12 mL, 1 2 mmol) in 1 mL of THF was added dropwise *via* syringe followed by CuCN (18 mg, 0 2 mmol) The resulting yellow soln was stirred at -40°C for 2 h and was quenched by addn of 2 mL of MeOH The reaction was warmed to rm temp and was subjected to the workup used for stannylalumination to yield **11a** and **12a**

Reactions of $Bu_3SnMgMe$ with **8a** and **9**: The reactions of $Bu_3SnMgMe$ with **8a** and **9** were conducted by the same procedure used above for its reaction with **7** A mixture of the reaction products **13a** and **14a** were separated using column conditions described above but with hexanes EtOAc 90 10 for the first 100 mL of eluant and hexanes EtOAc 1 1 thereafter The crude reaction mixture from the reaction of $Bu_3SnMgMe$ with **9** was subjected to the usual purification

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