1,1-Distannyl-1-alkenes: A New Method of Formation and Some Further Reactions†

T. N. Mitchell* and W. Reimann

Fachbereich Chemie, Universität Dortmund, Postfach 500 500, 4600 Dortmund 50, FRG

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1,1-Distannyl-1-alkenes of the type $RR'C{=}C(SnMe_3)_2$ can be readily prepared from (trimethylstannyl)lithium and geminal dibromoalkenes. An extension of this method to include the preparation of vicinal distannylalkenes is in general not possible. Hydrostannation of the geminal distannylalkenes gives tristannylalkanes; bromodestannylation using *N*-bromosuccinimide occurs readily, as does halodemethylation at tin using dimethyltin dihalides. Palladium-catalyzed coupling reactions between geminal distannylalkenes and organic halides are possible, but stereoselective monocoupling is probably not realizable. Selected multinuclear NMR data for the compounds prepared are presented.

Introduction

We have been interested for some time in the chemistry of 1,1-distannyl-1-alkenes, particularly as precursors for α-metalated vinyl carbanionoids. The method of preparation used[1] involves hydrostannation of 1-stannyl-1-alkynes (eq 1). Although this method is extremely useful,

$$RC{\equiv}CSnR'_3 + R'_3SnH \rightarrow \underset{\mathrm{I}}{RCH{=}C(SnR'_3)_2} \qquad (1)$$

it of course leads to the formation of a trisubstituted rather than a tetrasubstituted olefin. Since we have observed that α-stannylated vinyl anionoids prepared from I are thermally labile,[1] we felt that it might be possible to increase their stability by using a precursor of the type $R_2C{=}C(SnR'_3)_2$. We report here on the method used to form such precursors and on some hitherto unreported chemistry of geminal distannylalkenes.

Results and Discussion

1. Formation of 1,1-Distannyl-1-alkenes. The reaction of a triorganostannyl derivative of an alkali metal with a geminal dihaloalkene should provide the required distannylalkene. The dihaloalkene can be prepared from an appropriate ketone by means of a Wittig-type reaction (eq 2 and 3).[2-4] This method had previously only been

$$CX_4 + 2PPh_3 \rightarrow X_2C{=}PPh_3 \qquad (2)$$

$$X_2C{=}PPh_3 + RR'C{=}O \rightarrow X_2C{=}CRR' + OPPh_3 \qquad (3)$$

used for dialkyl ketones, and we found it to have serious limitations. Steric hindrance already precludes the reaction of methyl isopropyl ketone, and halogenated ketones react with instantaneous formation of an intractable solid mass. Ketones with electron-withdrawing substituents (alkoxy, dimethylamino, trifluoromethyl, phenyl) react well, however. 1,1-Diphenyldibromoethylene was prepared in 67% yield by using a different literature procedure.[5]

Geminal dichloroalkenes are, however, unsuitable for the planned reaction with (trimethylstannyl)lithium, reacting to form hexamethylditin and an alkyne (eq 4 and 5). The

$$PhCH{=}CCl_2 + 2\ Me_3SnLi \rightarrow PhC{\equiv}CH + Me_6Sn_2 + 2LiCl \qquad (4)$$

$$PhC(Me){=}CCl_2 + 2Me_3SnLi \rightarrow PhC{\equiv}CMe + Me_6Sn_2 + 2LiCl \qquad (5)$$

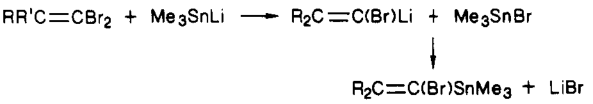
dibromoalkenes, however, afford the required distannylalkenes when the reaction is carried out below −70 °C (eq 6). Details of the results of the reactions carried out are given in Table I.

$$RR'C{=}CBr_2 + 2\ Me_3SnLi \rightarrow \underset{\mathrm{II}}{RR'C{=}C(SnMe_3)_2} + 2LiBr \qquad (6)$$

At temperatures above −70 °C the formation of hexamethylditin is the dominant reaction. We have observed that addition of only 1 equiv of the lithium reagent to $Ph_2C{=}CBr_2$ gives the monobromostannylalkene (eq 7).

$$Ph_2C{=}CBr_2 + Me_3SnLi \rightarrow Ph_2C{=}CBrSnMe_3 + LiBr \qquad (7)$$

We assume[6] that this reaction proceeds as follows (eq 8).



$$\begin{tikzcd} RR'C{=}CBr_2 + Me_3SnLi \arrow[r] & R_2C{=}C(Br)Li + Me_3SnBr \arrow[d] \\ & R_2C{=}C(Br)SnMe_3 + LiBr \end{tikzcd} \qquad (8)$$

Decomposition of the vinyllithium species[7] prior to tin-carbon bond formation will lead to the formation of the alkyne and ditin as observed. However, we cannot exclude the possibility that free radical intermediates are also formed. The reactions of Bu_3SnLi and Ph_3SnLi with $Me_2C{=}CBr_2$ yielded the ditins as the sole organotin products.

2. Formation of Vicinal Distannylalkenes. The palladium-catalyzed reaction between alkynes and ditins to give 1,2-distannylalkenes normally proceeds only for 1-alkynes,[8] and it was thus of interest to react vicinal dihaloalkenes (*E*)-$RCX{=}CXR$ with Me_3SnLi. When R = Ph, the vicinal distannylalkene is formed when X = I but not when X = Br; in the latter case, diphenylacetylene and the ditin are isolated. When X = Br the required product can, however, be prepared by using Me_3SnK.

In contrast, the reactions of $PhCI{=}CHI$ with Me_3SnLi and $PhCBr{=}C(CH_3)Br$ with Me_3SnK yield only ditin and alkyne. The principle of intramolecular coordination ap-

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† Dedicated to Prof. Wilhelm Neumann on the occasion of his 60th birthday (October 29, 1986).

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Table I. Isolated Yields, Boiling Points, and Elemental Analysis Values for 1,1-Distannylalkenes of the Type $RR'C{=}C(SnMe_3)_2$

R	R′	yield, %	bp, °C (*p*, torr)	anal. calcd (found) C	anal. calcd (found) H
Me	Me	69	110 (12)	31.4 (31.1)	6.3 (6.6)
Me	Et	61	120 (12)	33.4 (33.1)	6.6 (6.5)
Me	$EtOCH_2$	76	85–89 (0.001)	33.8 (33.4)	6.6 (6.7)
Me	MeO(Me)CH	71	70 (0.2)	33.8 (34.2)	6.6 (6.4)
Me	$MeOCH_2CH_2$	64	88 (0.001)	33.8 (33.9)	6.6 (6.7)
Me	Ph	62	105–110 (0.02)	40.6 (40.6)	5.9 (6.2)
CF_3	Ph	36	102 (0.01)	36.2 (36.6)	4.7 (5.0)
Ph	Ph	63	120[a]	47.5 (47.3)	5.6 (5.6)
$MeOCH_2$	$MeOCH_2$	78	90–95 (0.02)	32.6 (32.2)	6.4 (6.4)
$MeOCH_2$	$MeOCH_2CH$	50	102 (0.03)	34.2 (34.2)	6.6 (6.6)
$-CH_2(CH_2)_2CH_2-$		70	80 (0.001)	35.3 (35.7)	6.4 (6.4)
$-CH_2(CH_2)_3CH_2-$		64	90 (0.001)	36.8 (37.2)	6.7 (6.7)

[a] Melting point.

Table II. Isolated Yields, Melting Points, and Elemental Analysis Values for Tristannylalkanes of the Type $RR'CH\text{-}C(SnMe_3)_3$

R	R′	yield, %	mp, °C	anal. calcd (found) C	anal. calcd (found) H
Me	Me	90	281–284[a]	28.6 (28.5)	6.3 (6.3)
Et	Me	76	293[b]	30.0 (30.4)	6.4 (6.8)
$EtOCH_2$	Me	89	132–134[c]	30.5 (30.1)	6.5 (6.8)
MeO(Me)CH	Me	57	220[b]	30.5 (30.9)	6.5 (6.7)
$MeOCH_2CH_2$	Me	48	120–125[b]	30.5 (30.5)	6.5 (6.7)
Ph	Me	43	214–217[b]	35.5 (35.2)	6.0 (6.4)
$MeOCH_2$	$MeOCH_2$	73	230–235[b]	29.7 (30.1)	6.3 (6.6)
$-CH_2(CH_2)_2CH_2-$		87	275–280[b]	31.5 (31.8)	6.3 (6.7)
$-CH_2(CH_2)_3CH_2-$		80	248–250[a]	32.8 (33.1)	6.5 (6.8)

[a] After drying. [b] After sublimation. [c] After recrystallization from CCl_4.

Table III. Isolated Yields, Boiling Points, Composition, and Elemental Analysis Values for Compounds of the Type $RR'C{=}C(Br)SnMe_3$

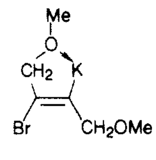
R	R′	yield, %	bp, °C (*p*, torr)	% *E* isomer[b]	anal. calcd (found) C	anal. calcd (found) H
t-Bu	H	43	47 (0.01)	5 (77[c])	33.2 (33.3)	5.8 (5.9)
Ph	H	87	74–81 (0.005)	11 (54[d])	38.4 (38.0)	4.5 (4.5)
Ph	H[a]	58	75 (0.005)	23	44.0 (43.7)	5.0 (4.7)
Me	Me	60	82 (12)		24.5 (24.1)	4.4 (4.0)
Ph	Me	40	70–75 (0.01)	5	42.0 (42.1)	4.6 (4.4)
Ph	Ph	66	80–100 (0.03)		48.4 (48.1)	4.6 (4.4)

[a] Chloroalkene. [b] From proton NMR spectrum. [c] After UV irradiation for 3 days. [d] After UV irradiation for 7 days.

pears to be useful for carrying out reactions of this type: reaction 9 yields the required product in good yield,

$$MeOCH_2CBr{=}CBrCH_2OMe + 2\ Me_3SnK \rightarrow MeOCH_2C(SnMe_3){=}C(SnMe_3)CH_2OMe \quad (9)$$

probably via species such as



or the dianion.

3. Hydrostannation of 1,1-Distannyl-1-alkenes. We have previously shown[1] that 1,1-distannyl-1-alkenes (I) readily undergo hydrostannation to give 1,1,1-tristannylalkanes (eq 10). Introduction of a further substituent R′

$$RCH{=}C(SnMe_3)_2 + Me_3SnH \rightarrow RCH_2C(SnMe_3)_3 \quad (10)$$

at the olefinic carbon does not prevent the occurrence of such a reaction except when R and R′ = Ph. However, the reactions only proceed under the influence of UV irradiation. Isolated yields are 40–90%: formation of byproducts was not observed. Table II gives details of products formed.

4. Halodestannylation of 1,1-Distannyl-1-alkenes. Monoiododestannylation of geminal distannylalkenes is always accompanied by the cleavage of both stannyl residues, while monobromodestannylation using bromine is not possible.[9] In contrast, *N*-bromosuccinimide reacts at room temperature in methylene chloride with a fair degree of stereoselectivity but without formation of dibromoalkene (eq 11). The main product is the *E* isomer; the stereoselectivity is not increased by lowering the temperature. *N*-Chlorosuccinimide also reacts, but only very slowly on heating (e.g., $PhCH{=}C(SnMe_3)_2$, 150 h at 50 °C).

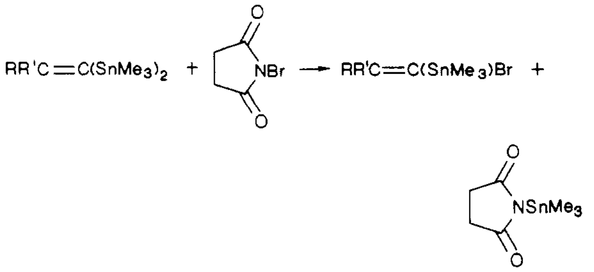


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Table IV. Isolated Yields, Melting Points, and Elemental Analysis Values for Compounds of the Type $RR'C{=}C(SnMe_2X)_2$

R	R′	X	yield, %	mp, °C	anal. calcd (found) C	anal. calcd (found) H
n-Bu	H	Br	55	*c*	22.3 (22.0)	4.1 (3.9)
c-Hex	H	Br	60	70	21.2 (21.4)	4.3 (4.0)
t-Bu	H	Br	79	86	22.3 (22.1)	4.1 (4.2)
$MeOCH_2CH_2$	H	Br	53	70–75	20.0 (19.7)	3.7 (3.7)
$MeO(C_6H_{10})^a$	H	Br	65	221	25.2 (25.3)	4.3 (4.4)
Ph	H	Br	75	82	25.8 (25.9)	3.2 (3.3)
Ph	H	Cl	90	75	30.6 (30.3)	3.8 (3.6)
Ph	Ph	Br	95	148	34.0 (34.1)	3.5 (3.5)
$MeO(C_6H_{10})^{a,b}$	H	Br	92	52	31.7 (31.5)	5.5 (5.2)

[a] 1-Methoxycyclohexyl. [b] $MeO(C_6H_{10})CH{=}C(SnMe_3)SnMe_2Br$. [c] Viscous oil.

Since the reaction is not affected by the addition of an equimolar amount of hydroquinone, it seems likely that (as postulated for reactions between aryltins and *N*-halosuccinimides)[10] ionic rather than free radical intermediates are involved.

As previously observed for α-iodostannyl alkenes,[9] UV irradiation leads over several days to isomerization and partial decomposition: the amount of *E* isomer increases steadily with concomitant formation of Me_3SnBr and alkyne (20–30% after 7 days). Table III gives details of the haloalkenes formed.

5. Halodemethylation of 1,1-Distannyl-1-alkenes. The introduction of a functionality at tin in the form of a halide residue opens wide preparative possibilities. Kuivila et al.[14] demonstrated that chlorodemethylation at tin occurs readily for bis(trimethylstannyl)alkanes using dimethyltin dichloride (eq 12). We have since observed[12]

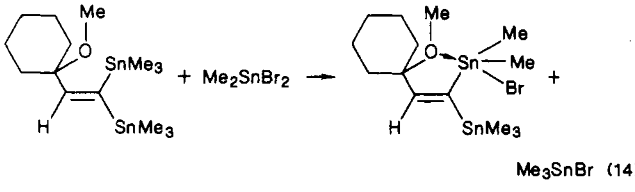
$$RR'C(SnMe_3)_2 + 2Me_2SnCl_2 \rightarrow RR'C(SnMe_2Cl)_2 + 2Me_3SnCl \quad (12)$$

that bromodemethylation using Me_2SnBr_2 proceeds more readily, while the use of bromine[13,14] and trimethyltin chloride[15] for halodestannylation has been reported.

We find that (in analogy to Kuivila's results) the use of a 1:1 molar ratio of distannylalkene and Me_2SnCl_2 yields a statistical mixture containing starting material and mono- and bis-demethylated products. However, a 1:2 reaction using Me_2SnX_2 (X = Cl, Br) gives the bis-demethylated product in isolated yields of 50–95% (eq 13). The

$$RR'C{=}C(SnMe_3)_2 + Me_2SnX_2 \rightarrow RR'C{=}C(SnMe_2X)_2 + 2Me_3SnX \quad (13)$$

presence of a suitable ether functionality in one of the substituents decreases the reaction time and permits stereospecific monodemethylation (eq 14). Tin-119 NMR spectra demonstrate the postulated intramolecular coordination: both tin resonances for the mono(bromodimethylstannyl) compound occur near 0 ppm, while in the bis(bromodimethylstannyl) compound one signal (that for the noncoordinated tin) lies at over 80 ppm.



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Reaction of $PhCH{=}C(SnMe_2Cl)_2$ with 1 or 2 equiv of tin tetrachloride leads to the introduction of trichlorostannyl residues: the products are thermally labile and cannot be isolated in a pure state (eq 15 and 16). Table IV gives details of the compounds formed.

$$PhCH{=}C(SnMe_2Cl)_2 + SnCl_4 \rightarrow (E)\text{-}PhCH{=}C(SnMe_2Cl)SnCl_3 + Me_2SnCl_2 \quad (15)$$

$$PhCH{=}C(SnMe_2Cl)_2 + 2SnCl_4 \rightarrow PhCH{=}C(SnCl_3)_2 + 2Me_2SnCl_2 \quad (16)$$

6. Palladium-Catalyzed Coupling Reactions between 1,1-Distannyl-1-alkenes and Allyl Bromide. Carbon–carbon bond formation using organotins and palladium catalysts has been the subject of considerable investigation in recent years.[16] Coupling between vinyltins and various organic halides has been reported,[17] and we felt it necessary to determine whether a stereospecific monocoupling was possible starting from geminal distannylalkenes: if so, this would provide a viable alternative to coupling via organolithium reagents.[1]

The 1:1 reaction between allyl bromide (a typical substrate for such coupling reactions) and $PhCH{=}C(SnMe_3)_2$ using $PhCH_2PdCl(PPh_3)_2$ (or other catalysts[18]) in THF (or other solvents[18]) gave a mixture containing starting material and the product of double allyl substitution as well as the required monosubstitution product (*E* and *Z* isomers).

Replacement of one of the trimethylstannyl groups by a trimethylsilyl residue[19] apparently increases the steric hindrance to the vinyl–allyl coupling to such an extent that only a methyl–allyl coupling takes place (eq 17). The 1:2 coupling reaction between allyl bromide and the distannyl alkene gives a 54% yield of 4-benzylidenehepta-1,6-diene.

$$PhCH{=}C(SiMe_3)SnMe_3 + CH_2CH{=}CH_2Br \rightarrow PhCH{=}C(SiMe_3)SnMe_2Br + CH_3CH_2CH{=}CH_2 \quad (17)$$

7. NMR Studies. All new compounds described have been characterized by multinuclear NMR (^1H, ^{13}C, ^{119}Sn) as well as by elemental analysis. A compilation of the complete data is not required here, but selected data are presented in Tables V–VII.

Three-bond proton–tin coupling constants are collected in Table V for compounds $RCH{=}C(X)SnMe_3$ and $RCH{=}C(SnMe_2X)_2$ (X = halogen), together with chemical shift values for the vinyl proton. It is clear that substitution of trimethylstannyl by halogen at the vinyl group leads to a drastic decrease in ^3J compared with values in the geminal distannylalkanes ($^3J_{cis}$ = ca. 100, $^3J_{trans}$ = ca. 200 Hz),[1] while substitution of methyl by halogen at tin leads to a marked increase in the values.

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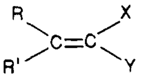
Table V. Chemical Shift Values for the Vinyl Proton and Three-Bond Tin-Proton Coupling Constants in Compounds of the Type RCH=CXY (X = Br, Cl, $SnMe_2Br$, $SnMe_2Cl$, $SnCl_3$; Y = $SnMe_3$, $SnMe_2Br$, $SnMe_2Cl$, $SnCl_3$)

R	X	Y	δ(H)	^3J_c(SnH)	^3J_t(SnH)
n-Bu	Br	$SnMe_3$	6.8 [6.1]	[40]	88
t-Bu	Br	$SnMe_3$	7.1 [6.2]	[44]	103
$MeO(C_6H_{10})^a$	Br	$SnMe_3$	7.1 [6.1]	[44]	96
Ph	Br	$SnMe_3$	8.0 [6.6]	[43]	88
Ph	Cl	$SnMe_3$	7.6 [6.5]	[39]	80
n-Bu	$SnMe_2Br$	$SnMe_2Br$	7.4	127	244
c-Hex	$SnMe_2Br$	$SnMe_2Br$	7.0	134	240
t-Bu	$SnMe_2Br$	$SnMe_2Br$	7.4	144	288
$MeO(CH_2)_2$	$SnMe_2Br$	$SnMe_2Br$	7.4	140	274
$MeO(C_6H_{10})^a$	$SnMe_2Br$	$SnMe_2Br$	7.9	133	268
Ph	$SnMe_2Br$	$SnMe_2Br$	8.3	121	241
Ph	$SnMe_2Cl$	$SnMe_2Cl$	7.9	120	244
Ph	$SnMe_2Cl$	$SnCl_3$	8.4	171	302
Ph	$SnCl_3$	$SnCl_3$	8.6	200	476

[a] 1-Methoxycyclohexyl. [b] Values for the *E* isomer in brackets; δ vs. internal Me_4Si; $^3J(^{119}Sn–H)$ in Hz.

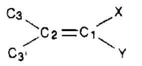
Table VI. Olefinic Carbon-13 NMR Chemical Shifts and Selected Tin-Carbon Coupling Constants for Compounds of the Type



X,Y=Br, $SnMe_3$, $SnMe_2Br$, $SnMe_2Cl$, $SnCl_3$

R	R′	X	Y	δ(C_1)	δ(C_2)	^3J(Sn–C_3)	^3J(Sn–$C_{3'}$)
Me	Me	$SnMe_3$	$SnMe_3$	138.4	160.0	71/95	71/95
$EtOCH_2$	Me	$SnMe_3$	$SnMe_3$	138.5	157.6	64/97	72/98
MeO(Me)CH	Me	SnMe	$SnMe_3$	138.9	163.5	73/103	72/95
$MeOCH_2CH_2$	Me	$SnMe_3$	$SnMe_3$	138.0	158.4	68/93	74/97
Ph	Me	$SnMe_3$	$SnMe_3$	143.4	163.6	53/94	67/88
Ph	CF_3	$SnMe_3$	$SnMe_3$	161.5	152.1	51/74	48/118
Ph	Ph	$SnMe_3$	$SnMe_3$	151.7	168.5	51/88	51/88
Bu	H	Br	$SnMe_3$	128.8	144.0		33
Bu	H	$SnMe_3$	Br	125.2	148.2	23	
t-Bu	H	Br	$SnMe_3$	125.0	151.5		38
t-Bu	H	$SnMe_3$	Br	124.5	159.4	a	
Me	Me	$SnMe_3$	Br	121.1	146.2	28	28
Ph	Me	$SnMe_3$	Br	126.8	152.1	25	18
Ph	Ph	$SnMe_3$	Br	127.7	156.2	34	17
Bu	H	$SnMe_2Br$	$SnMe_2Br$	142.0	162.6	90/110	
c-Hex	H	$SnMe_2Br$	$SnMe_2Br$	139.6	167.5	88/107	
t-Bu	H	$SnMe_2Br$	$SnMe_2Br$	134.4	172.5	46/97	
Ph	H	$SnMe_2Br$	$SnMe_2Br$	152.2	160.1	69/111	
Ph	Ph	$SnMe_2Br$	$SnMe_2Br$	152.5	170.6	56/95	56/95
$MeO(C_6H_{10})$	H	$SnMe_2Br$	$SnMe_2Br$	143.9	159.1	48/90	
$MeO(C_6H_{10})$	H	$SnMe_2Br$	$SnMe_3$	143.8	155.1	56/68	
Ph	H	$SnMe_2Cl$	$SnCl_3$	151.4	163.5	44/276	
Ph	H	$SnCl_3$	$SnCl_3$	142.1	168.6	97/188	

[a] Not determined. δ vs. Me_4Si; *J* in Hz. Numbering:



Three-bond tin–carbon coupling constants can be found in Table VI for compounds $RR'C=C(SnMe_3)_2$, $RR'C=C(X)SnMe_3$, and $RCH=C(SnMe_2X)_2$ (X = halogen), together with chemical shift values for the vinyl carbons.

The behavior of the coupling constants parallels that of the tin–proton coupling constants, extremely low values being observed for the bromoalkenes. In one case the cis and trans couplings are equal, while the cis/trans ratio varies widely, particularly extreme values being shown by the CF_3 group. The vinyl carbon chemical shifts lie in the expected ranges. Table VII contains tin-119 chemical shift and coupling constant data for the same group of compounds.

Experimental Section

All manipulations involving organotin compounds were carried out in an argon atmosphere. Routine proton NMR data were obtained by using a Varian EM 360 spectrometer and other data (^{13}C, ^{119}Sn) from a Bruker AM 300 spectrometer. $CDCl_3$ was generally used as solvent. All new compounds were characterized by elemental analysis unless otherwise stated: values not given in the text are collected in Tables I–IV and VIII. Organotin precursors were prepared as described in the following references: Me_3SnH, ref 20; Me_3SnLi, ref 21; Ph_3SnLi, ref 22; Me_3SnNa, ref 23; Me_3SnK, ref 24.

1,1-Dibromo-1-alkenes were prepared as follows: doubly sublimed CBr_4 (84.3 g, 0.254 mol) was dissolved under argon in dry benzene (600 mL) and PPh_3 (133.4 g, 0.508 mol) added in portions. After being stirred for a further 30 min, the deep orange solution was treated with a solution of the ketone (0.127 mol) in

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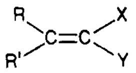
Table VII. Tin-119 Chemical Shifts and Tin-Tin Coupling Constants in Compounds of the Type



X, Y = Br, $SnMe_3$, $SnMe_2Br$, $SnMe_2Cl$, $SnCl_3$

R	R′	X	Y	δ(X)	δ(Y)	^2J(Sn–Sn)[b]
Me	Me	$SnMe_3$	$SnMe_3$	−42.4	−42.4	741
$EtOCH_2$	Me	$SnMe_3$	$SnMe_3$	−46.2[a]	−40.4	684
MeO(Me)CH	Me	$SnMe_3$	$SnMe_3$	−49.3[a]	−46.3	707
Ph	Me	$SnMe_3$	$SnMe_3$	−38.7[a]	−42.6	666
Ph	CF_3	$SnMe_3$	$SnMe_3$	−25.0[a]	−25.6	366
Ph	Ph	$SnMe_3$	$SnMe_3$	−33.8	−33.8	602
Bu	H	Br	$SnMe_3$		−21.8	
Bu	H	$SnMe_3$	Br	−11.3		
t-Bu	H	Br	$SnMe_3$		−16.3	
t-Bu	H	$SnMe_3$	Br	−6.6		
Me	Me	$SnMe_3$	Br	−20.5		
Ph	Me	$SnMe_3$	Br	−13.2		
Ph	Ph	$SnMe_3$	Br	−7.9		
Bu	H	$SnMe_2Br$	$SnMe_2Br$	75.7	88.0	1058
c-Hex	H	$SnMe_2Br$	$SnMe_2Br$	72.0	89.1	1088
t-Bu	H	$SnMe_2Br$	$SnMe_2Br$	77.9	94.4	1079
Ph	H	$SnMe_2Br$	$SnMe_2Br$	70.0	85.6	964
Ph	Ph	$SnMe_2Br$	$SnMe_2Br$	49.5	49.5	629
$MeO(C_6H_{10})$	H	$SnMe_2Br$	$SnMe_2Br$	−9.3	84.7	1405
$MeO(C_6H_{10})$	H	$SnMe_2Br$	$SnMe_3$	−9.8	−0.6	741
Ph	H	$SnCl_3$	$SnMe_2Cl$	−86.7	102.3	944
Ph	H	$SnCl_3$	$SnCl_3$	−101.2	−76.1	4530

[a] Assignment tentative. [b] $^2J(^{119}Sn–^{119}Sn)$. δ vs. Me_4Sn; *J* in Hz.

Table VIII. Isolated Yields, Boiling Points, and Elemental Analysis Values for 1,1-Dibromo-1-alkenes RR′C=CBr_2

				anal. calcd (found)	
R	R′	yield, %	bp, °C (*p*, torr)	C	H
Me	Me	48	38 (15)	22.5 (22.3)	2.8 (2.9)
Me	Et	22	58 (15)	26.3 (26.5)	3.5 (3.6)
Me	*i*-Pr	0			
Me	*t*-Bu	0			
Me	$PhCH_2$	0			
Me	$EtOCH_2$	64	81 (15)	27.9 (27.8)	3.9 (3.7)
Me	Et_2NCH_2	41	105 (15)	33.7 (34.0)	5.3 (5.0)
Me	$MeOCH_2CH_2$	41	95 (9)	37.9 (27.0)	3.9 (4.1)
Me	MeO(Me)CH	23	70 (15)	24.7 (24.3)	2.9 (2.5)
$MeOCH_2$	$MeOCH_2$	75	71 (0.6)	39.2 (39.1)	2.9 (3.1)
$MeOCH_2$	$MeOCH_2CH_2$	24	80 (0.7)	26.7 (26.7)	3.7 (3.6)
CF_3	Ph	80	60 (1)	37.0 (36.6)	1.7 (1.6)
$-CH_2(CH_2)_2CH_2-$		55	88 (15)	30.0 (30.3)	3.3 (3.6)
$-CH_2(CH_2)_3CH_2-$		50	105 (15)	33.1 (33.0)	3.9 (4.1)

benzene (30 mL). During the slightly exothermic reaction the mixture darkened in color. It was then refluxed overnight, allowed to cool, and filtered. The filter residue was extracted twice with benzene (150 mL), the extracts were combined with the filtrate, and the solvent was removed in vacuo. The residue was treated with *n*-hexane (300 mL) and stirred for 2 h, and the mixture was filtered. The filtrate was again freed from solvent and distilled. Table VIII gives details of the dibromoalkenes prepared. The two **1,1-dichloroalkenes** used (PhMeC=CCl_2 and PhCH=CCl_2) were prepared according to ref 2.

Reactions of 1,1-Dibromoalkenes with Organostannyl Alkalis (1:2). A solution of the dibromoalkane (0.03 mol) in THF (150 mL) was cooled to −78 °C. (Trimethylstannyl)lithium (0.06 mol of a THF solution) was added dropwise at a rate such that the temperature did not exceed −70 °C. The reaction mixture was allowed to warm to room temperature and hydrolyzed with water (100 mL). The aqueous phase was treated with ether (2 × 50 mL), and the combined ether phases were dried over $MgSO_4$. After removal of THF in vacuo, the residual oil was distilled. $Ph_2C=C(SnMe_3)_2$ was recrystallized from *n*-hexane. Table I contains experimental data for the 1,1-distannyl-1-alkenes prepared.

When the two **1,1-dichloro-1-alkenes** were reacted in the same way, hexamethylditin and the corresponding alkyne were obtained (together with byproducts). A solution of the vicinal dichloroalkene (35 mmol) in THF (150 mL) was cooled to −78 °C and treated with Me_3SnLi (70 mmol of a THF solution, 0.61 mol/L) in such a way that the reaction temperature did not exceed −70 °C. The mixture was warmed to room temperature and worked up as described above: according to its proton NMR spectrum, it consisted in each case of hexamethylditin and the alkyne. A number of byproducts were present in low yields (<10%); these were not investigated further.

The following reactions were carried out in an analogous manner: (a) $Ph_2C=CBr_2$ + Me_3SnLi (1:1), (b) $Ph_2C=C(Br)SnMe_3$ + Me_3SnLi (1:1), (c) $Me_2C=CBr_2$ + Bu_3SnLi (1:2), (d) $Me_2C=CBr_2$ + Ph_3SnLi (1:2). The products obtained are noted in the text.

Reactions of 1,2-Dihaloalkenes with Me_3SnLi (1:2). A solution of Me_3SnLi (10–40 mmol) was cooled to −78 °C. The (*E*)-alkenes (PhCBr=CBrPh,[25] PhCI=CIPh,[25] PhCI=CHI)[26] were added as a THF solution or (PhCI=CIPh) suspension. Workup as above yielded (quantitatively) tolan and hexamethylditin in the first case (the same result was obtained for inverse addition) and phenylacetylene and hexamethylditin in the third. In the second case, the (*E*)-bis(trimethylstannyl)stilbene was obtained in 75% isolated yield (7.9 g) as a colorless solid (from *n*-hexane), mp 125 °C. ^1H NMR ($CDCl_3$): δ −0.4 (s, 18 H, $SnMe_3$),

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7.1 (m, 10 H, Ph). ^{13}C NMR ($CDCl_3$): δ −7.4 ($SnMe_3$, ^1J(SnC) = 330 Hz), 125.6, 126.9, 128.2, 148.1 (aromatic C), 161.1 (olefin C, ^1J(SnC) = 497, ^2J(SnC) = 10 Hz). ^{119}Sn NMR ($CDCl_3$): δ −50.4 (^3J(^{119}Sn–^{119}Sn) = 697 Hz). MS (80 eV): *m/e* 506 (3, M^+). Anal. Calcd for $C_{20}H_{28}Sn_2$: C, 47.5; H, 5.6. Found: C, 47.8; H, 5.4.

Reaction of (*E*)-PhCBr═CBrPh with Me_3SnNa. A solution of Me_3SnNa in liquid ammonia (200 mL) was prepared from sodium (3.0 g, 0.13 mol) and Me_3SnCl (11.8 g, 0.06 mol, solution in 50 mL of ether) at −78 °C. The dibromostilbene (0.03 mol) in ether (100 mL) was added. After 1 h the reaction mixture was warmed to room temperature and filtered under argon, the ether removed, and the product characterized. Hexamethylditin (the sole organotin product) was characterized by NMR; tolan was isolated in 65% yield.

Reaction of 1,2-Dibromoalkenes with Me_3SnK. A solution of Me_3SnK (60 mmol) in glyme was prepared and treated at −78 °C with the (*E*)-alkene (PhCBr═CBrMe,[27] PhCBr═CBrPh,[25] $MeOCH_2CBr$═$CBrCH_2OMe$;[28] molar ratio 2:1 in each case), allowed to warm to room temperature, and worked up as described above. In the first case hexamethylditin and PhC≡CMe were formed quantitatively, and in the second case the (*E*)-distannylstilbene was prepared as previously described (isolated yield 54%). The third reaction also yielded the required distannylalkene (*E* isomer) as an oil: bp 105 °C (0.01 torr); isolated yield 25% (1.4 g). The low yields were due to losses during workup and distillation, as shown by NMR spectra of the raw product mixtures. ^{119}Sn NMR ($CDCl_3$): δ −59.3 (^3J(^{119}Sn–^{119}Sn) = 771 Hz). The identification as the *E* isomer follows from previous work[8] in which hexamethylditin was added to $MeOCH_2$≡CCH_2OMe by using $Pd(PPh_3)_4$ as the catalyst; the *Z* isomer so obtained has a ^3J(Sn–Sn) of 426 Hz. ^{1}H NMR ($CDCl_3$): δ 0.1 (s, 18 H, $SnMe_3$), 3.2 (s, 6 H, CH_3), 3.9 (s, 4 H, CH_2). ^{13}C NMR ($CDCl_3$): δ −6.8 ($SnMe_3$, ^1J(SnC) = 335 Hz), 57.4 (CH_3O), 79.4 (CH_2O, *J*(SnC) = 65 Hz), 154.0 (olefin C, ^1J(SnC) = 419 Hz). Anal. Calcd for $C_{12}H_{28}Sn_2O_2$: C, 30.4; H, 6.0. Found: C, 30.1; H, 5.7.

Hydrostannation of 1,1-Distannyl-1-alkenes. Equimolar amounts of Me_3SnH and the distannylalkene were irradiated without solvent at room temperature in a quartz tube, using a high-pressure mercury vapor lamp (Hanau TQ150), until the mixture became solid. The product was extracted with methylene chloride and filtered, the solvent removed, and the residue (generally) sublimed. Exceptions are noted in Table II. The structures follow from the NMR spectra and the elemental analysis data. The ^{119}Sn NMR data are particularly relevant: δ (Sn) lies between 17 and 23 ppm, ^2J(Sn–Sn) being in the range 259 ± 7 Hz.

Halodestannylation of 1,1-Distannyl-1-alkenes. The distannylalkenes were dissolved in CH_2Cl_2, the solution cooled to −78 °C, and an equimolar amount of a solution of *N*-bromosuccinimide in methylene chloride (ca. 20 g/L) added dropwise. The mixture was allowed to warm to room temperature and the solvent removed in vacuo. The residue was taken up in a little ether and filtered and the filter cake washed with water. The organic phase was dried over $MgSO_4$, the ether removed, and the remaining oil distilled. Table III gives details of the products formed. Addition of an equimolar amount of hydroquinone before the addition of the *N*-bromosuccinimide had no effect on the reaction.

Irradiation of the bromoalkenes was carried out at room temperature on a solution in $CDCl_3$ with a TQ150 lamp. The reaction was followed by proton NMR. After 7 days, 20–30% decomposition to Me_3SnBr and the alkyne was observed. The accompanying changes in the *E*/*Z* ratio are given in Table III. Longer irradiation times had no further effect on the *E*/*Z* ratio.

Halodemethylation of 1,1-Distannyl-1-alkenes. The distannylalkene was heated for 12–16 h with 2 molar equiv of Me_2SnX_2 (X = Cl, Br) at ca. 90 °C: methoxyalkyl substituents reduced the reaction time to ca. 2 h. No solvent was used. Trimethyltin halide was removed in vacuo (0.01 torr) at 40 °C, leaving the crystalline product in a pure state (recrystallization from *n*-hexane is possible). Details of the products are given in Table IV.

The 1:1 **reaction** was carried out successfully starting with ($MeOC_6H_{10}$)CH═C($SnMe_3$)$_2$ and Me_2SnBr_2; the mixture was heated at 80 °C until it solidified. After removal of Me_3SnBr in vacuo (0.01 torr) the product remains behind in a pure form. ^{1}H NMR ($CDCl_3$): δ 0.3 (s, 9 H, $SnMe_3$, ^2J(SnH) = 52 Hz), 0.7 (s, 6 H, $SnMe_2Br$, ^2J(SnH = 62 Hz), 1.7 (m, 10 H, c-C_6H_{10}), 3.3 (s, 3 H, MeO), 7.3 (s, 1 H, ═CH, $^3J_{cis}$(SnH) = 98, $^3J_{trans}$(SnH) = 293 Hz). ^{13}C NMR ($CDCl_3$): δ −7.0 ($SnMe_3$, ^1J(SnC) = 351 Hz), 3.4 ($SnMe_2Br$, ^1J(SnC) = 445 Hz), 23.2, 25.1, 33.3 (c-C_6H_{10}), 47.8 (MeO), 81.5 (c-C_6H_{10}, $^3J_{cis}$(SnC) = 56, $^3J_{trans}$(SnH) = 68 Hz), 143.8 (C═*C*Sn_2, ^1J(SnC) = 335, ^1J(SnC) = 433 Hz), 155.1 (*C*═CSn_2, ^2J(SnC) = 34 Hz). Anal. Calcd for $C_{14}H_{29}BrOSn_2$: C, 31.7; H, 5.5. Found: C, 31.5; H, 5.2.

Reactions of PhCH═C($SnMe_2Cl$)$_2$ with $SnCl_4$. (a) 1:1. A solution of PhCH═C($SnMe_2Cl$)$_2$ (2.4 g, 5.1 mmol) in methylene chloride (3 mL) was treated with $SnCl_4$ (0.6 mL, 1.3 g, 5.1 mmol). The reaction mixture turned black. Volatiles were removed in vacuo (0.01 torr, 40 °C). When the residue was treated with *n*-hexane, gray crystals precipitated out; these were filtered under argon and dried to give 1.1 g (42%) of (*E*)-PhCH═C($SnMe_2Cl$)$SnCl_3$, mp 91 °C dec. No elemental analysis could be obtained for this compound. ^{1}H NMR ($CDCl_3$): δ 0.7 (s, 6 H, $SnMe_2Cl$, ^2J(SnH) = 61 Hz), 7.5 (m, 5 H, Ph), 8.4 (s, 1 H, ═CH, $^3J_{cis}$(SnH) = 171, $^3J_{trans}$(SnH) = 302 Hz). ^{13}C NMR ($CDCl_3$): δ 7.2 ($SnMe_2Cl$, ^1J(SnC) = 421), ^3J(SnCSnC) = 27 Hz), 126.1, 129.6, 130.6 (C_{arom}); 139.6 (C_{arom}, $^3J_{cis}$(SnC) = 44, $^3J_{trans}$(SnC) = 276 Hz), 151.4 (C═*C*Sn_2, ^1J(SnC) = 351, 589 Hz), 163.5 (*C*═CSn_2, ^2J(SnC) = 50 Hz).

(b) $SnCl_4$ in Excess. A solution of PhCH═C($SnMe_2Cl$)$_2$ (2.0 g, 4.3 mmol) in methylene chloride (3 mL) was treated with $SnCl_4$ (3.3 g, 12.9 mmol) and the mixture heated under reflux for 5 h. $CDCl_3$ was added and the mixture characterized by NMR spectroscopy: workup was not possible as the distannylalkene decomposed. Apart from signals for Me_2SnCl_2, the following data were obtained. ^{1}H NMR: δ 7.68 (5 H, Ph), 8.6 (s, 1 H, ═CH, $^3J_{cis}$(SnH) = 200, $^3J_{trans}$(SnH) = 476 Hz). ^{13}C NMR = δ 126.9, 130.2, 132.4 (C_{arom}), 138.0 (C_{arom}, $^3J_{cis}$(SnC) = 97, $^3J_{trans}$(SnC) = 188 Hz), 142.1 (C═*C*Sn_2, ^1J(SnC) = 867 Hz), 168.6 (*C*═CSn_2, ^2J(SnC) = 18, 46 Hz).

Reactions of PhCH═C($SnMe_3$)$_2$ with Allyl Bromide Catalyzed by $PhCH_2$(Cl)Pd(PPh_3)$_2$. (a) 1:1. PhCH═C($SnMe_3$)$_2$ (5.3 g, 12.2 mmol) and allyl bromide (1.1 mL, 12.2 mmol) were heated for 48 h at 80 °C with a few crystals of the catalyst. After this time the allyl bromide was completely consumed. A coupled GLC/MS analysis (70 eV; column, OV 17, 4 m) permitted the identification of the following products: starting material (distannyl alkene), m/e 293 (33 and 34, respectively, M − Me; isomer identification by addition of a pure sample of the *E* compound obtained from (*E*)-PhCH═C(Li)$SnMe_3$[1] and allyl bromide); Me_3SnBr, *m/e* 245 (3, M^+); PhCH═C(CH_2CH═CH_2)$_2$, *m/e* 184 (14, M^+).

(b) With Excess Allyl Bromide. Distannylalkene (7.0 g, 16.2 mmol) and allyl bromide (4.7 mL, 6.0 g, 50 mmol) were heated for 5 days at 70 °C with a small amount of catalyst. The mixture was then taken up in ether (50 mL) and the solution so obtained shaken with 20 mL of an aqueous solution of KF (10% w/w). The white precipitate (Me_3SnF) was filtered; the aqueous phase and the precipitate each were extracted with ether (20 mL). The combined organic phases were dried, the solvent was removed, and the residue was distilled under vacuum. 4-Benzylidenehepta-1,6-diene was obtained as a colorless oil; yield 1.6 g (54%); bp 56–65 °C (0.005 torr). GLC (OV 17, 4 m) showed it to be 97% pure. ^{1}H NMR (neat): δ 2.5 (m, 4 H, CH_2), 5.4 (m, 7 H, ═CH), 6.8 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ 35.3, 41.5 (CH_2), 116.1, 116.5 (═CH_2), 126.3, 127.3, 128.2, 128.4, 135.8, 136.3 (aromatic CH), 137.9, 138.6 (aromatic quaternary C). Anal. Calcd for $C_{14}H_{16}$: C, 91.2; H, 8.8. Found: C, 90.9; H, 8.6.

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Registry No. II (R = R′ = Me), 103670-41-3; II (R = Me, R′ = Et), 103670-42-4; II (R = Me, R′ = $EtOCH_2$), 103670-43-5; II (R = Me, R′ = MeO(Me)CH), 103670-44-6; II (R = Me, R′ = $MeOCH_2CH_2$), 103670-45-7; II (R = Me, R′ = Ph), 103670-46-8; II (R = CF_3, R′ = Ph), 103670-47-9; II (R = R′ = Ph), 103670-48-0; II (R = R′ = $MeOCH_2$), 103670-49-1; II (R = $MeOCH_2$, R′ =

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Supplementary Material Available: Thirteen tables of ^{1}H, ^{13}C, and ^{119}Sn NMR and coupling constant data (14 pages). Ordering information is given on any current masthead page.

Chemistry of Chromium Chalcogen Complexes. Self-Condensation of $\mathrm{Cp_2Cr_2(CO)_4S}$ and $\mathrm{Cp_2Cr_2(CO)_5S_2}$ under Thermolytic Conditions. Crystal Structure of $\mathrm{Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2}$

Wei Chen and Lai Yoong Goh*

Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

Thomas C. W. Mak*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, NT., Hong Kong

Received December 3, 1985

Thermolysis of $\mathrm{Cp_2Cr_2(CO)_5S_2}$ (**2**) (Cp = η^5-$\mathrm{C_5H_5}$) in toluene at ca. 100 °C afforded initially $\mathrm{Cp_2Cr_2(CO)_4S}$ (**1**) and finally $\mathrm{Cp_4Cr_4S_4}$ (**4**) in 86% isolated yield. Similar decomposition of **1** for 1.5 h yielded a mixture of $\mathrm{Cp_4Cr_4(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2}$ (**3**) and **4**, which were separated by chromatography on silica gel. Compound **3** was isolated in 61% yield as brown-black air-stable cuboid crystals: monoclinic, space group $C2/c$, a = 17.557 (6) Å, b = 8.136 (3) Å, c = 18.009 (6) Å, β = 126.19 (2)°, Z = 4. The molecule adopts a cubane-like configuration with triply bridging S and CO ligands which are indistinguishable due to disorder. Thermolysis of **3** in benzene-d_6 over 6 h at 60 °C gave an equimixture of **4** and an unknown complex with δ(Cp) 5.13 in the ^{1}H NMR spectrum. Plausible mechanistic pathways are discussed in terms of self-condensation reactions wherein the linearly bridging multiply bonding S of **1**, the doubly bridging μ-$\mathrm{S_2}$ ligand of **2**, and the triply bridging μ_3-S ligand of **3** each plays an integral role in the initial dimerizations leading to the formation of the cubanes **3** and **4**.

Introduction

Systematic approaches toward a strategy for the synthesis of high nuclearity complexes are a recurring theme in recent research in cluster chemistry.[1-4] Many of the methods employed make use of main-group elements including sulfur, selenium, phosphorus, arsenic, carbon, nitrogen, and germanium. Of these elements, sulfur has featured most prominently[3-6] by virtue of its ability to act

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