143 (100), 127 (13), 89 (69), 73 (25).

Anal. Calcd for $C_7H_{14}O_2Si$: C, 53.12; H, 8.92. Found: C, 53.09; H, 9.20.

Methyl (*E*)-3-(dimethylphenylsilyl)propenoate (1c): yield 69%; bp 160-168 °C (30 mmHg); IR (neat) 1730 (C=C), 1600 cm^{-1} (C=C); NMR (CCl_4) δ 0.39 (s, 6 H), 3.66 (s, 3 H), 6.18 (d, J = 19 Hz, 1 H), 7.17-7.50 (c, 6 H); mass spectrum, m/e (relative intensity) 220 (44), 219 (48), 205 (77), 189 (23), 177 (24), 151 (23), 145 (31), 135 (48), 121 (47), 89 (100).

Anal. Calcd for $C_{12}H_{16}O_2Si$: C, 65.41; H, 7.32. Found: C, 65.42; H, 7.53.

Methyl (*E*)-3-(triethoxysilyl)propenoate (1d): yield 47%; bp 130-138 °C (50 mmHg); IR (neat) 1730 (C=O), 1605 cm^{-1} (C=C); NMR (CCl_4) δ 1.27 (t, J = 7 Hz, 9 H), 3.73 (s, 3 H), 3.83 (t, J = 7 Hz, 6 H), 6.32 (d, J = 19 Hz, 1 H), 6.87 (d, J = 19 Hz, 1 H).

Ethyl (*E*)-3-(diethylmethylsilyl)propenoate (1e): yield 76%; bp 116-118 °C (20 mmHg); IR (neat) 1730 (C=O), 1605 cm^{-1} (C=C); NMR (CCl_4) δ 0.09 (s, 3 H), 0.45-0.75 (m, 4 H), 0.84-1.08 (m, 6 H), 1.26 (t, J = 8 Hz, 3 H), 4.14 (q, J = 8 Hz, 2 H), 6.15 (d, J = 19 Hz, 1 H), 7.11 (d, J = 19 Hz, 1 H); mass spectrum, m/e (relative intensity) 185 (3), 171 (95), 143 (100), 115 (9), 113 (11).

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.82; H, 10.32.

Butyl (*E*)-3-(diethylmethylsilyl)propenoate (1f): yield 86%; bp 145-150 °C (20 mmHg); IR (neat) 1730 (C=O), 1600 cm^{-1} (C=C); NMR (CCl_4) δ 0.09 (s, 3 H), 0.45-0.75 (m, 4 H), 0.81-1.08 (m, 9 H), 1.20-1.71 (c, 4 H), 4.05 (t, J = 7 Hz, 2 H), 6.12 (d, J = 19 Hz, 1 H), 7.07 (d, J = 19 Hz, 1 H); mass spectrum, m/e (relative intensity) 213 (2), 199 (100), 185 (4), 171 (73), 143 (37), 115 (15).

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.74; H, 10.79.

Methyl 4-(diethylmethylsilyl)butanoate (3): bp 125-135 °C (10 mmHg); IR (neat) 1740 cm^{-1} (C=O); NMR (CCl_4) δ 0.07 (s, 3 H), 0.40-0.80 (m, 6 H), 0.80-1.17 (m, 6 H), 1.47-1.94 (c, 2 H), 2.37 (t, J = 7 Hz, 2 H), 3.74 (s, 3 H); mass spectrum, m/e (relative intensity) 187 (5), 174 (95), 117 (8), 113 (14), 103 (100), 75 (30), 73 (30).

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.43; H, 10.87.

Methyl 3-(diethylmethylsilyl)-2-methylpropanoate (4): bp 90-100 °C (10 mmHg); IR (neat) 1740 cm^{-1} (C=O); NMR (CCl_4) δ -0.07 (s, 3 H), 0.43-0.77 (m, 6 H), 0.77-1.07 (m, 6 H), 1.20 (d, J = 7 Hz, 3 H), 2.33-2.77 (m, 1 H), 3.70 (s, 3 H); mass spectrum, m/e (relative intensity) 187 (11), 173 (97), 117 (11), 103 (100), 75 (50), 73 (33).

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.23; H, 10.89.

Methyl 2-[(diethylmethylsilyl)methyl]propenoate (5): IR (neat) 1720 (C=O), 1620 cm^{-1} (C=C); NMR (CCl_4) δ 0.08 (s, 3 H), 0.57-0.93 (m, 4 H), 0.93-1.27 (m, 6 H), 1.90 (s, 2 H), 3.77 (s, 3 H), 5.33 (br s, 1 H), 5.97 (d, J = 2 Hz, 1 H); mass spectrum, m/e (relative intensity) 200 (10), 185 (37), 171 (70), 157 (7), 117 (10), 103 (70), 101 (33), 75 (40), 73 (100).

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.69; H, 10.20.

Reaction of Methyl Acrylate with $DSiEt_2Me$ in the Presence of $Co_2(CO)_8$. A solution of 15 mmol methyl acrylate, 6 mmol of $DSiEt_2Me$, 0.24 mmol of $Co_2(CO)_8$, and 10 mL of toluene was heated at 25 °C for 3 h with stirring. Analysis of the reaction mixture by GLC (90 °C, n-heptane as an internal standard) showed it to contain 3.5 mmol of methyl acrylate and 5.5 mmol of methyl propionate. $DSiEt_2Me$ was completely consumed. Analysis of the reaction mixture (110 °C, n-tridecane as an internal standard) showed **1a** and **2a** in 92% and 6% yields, respectively. Distillation of the reaction mixture and preparative GLC afforded analytical samples of methyl acrylate, methyl propionate, and **1a**. The deuterium content in the products (**1a** and methyl propionate) and the starting material (methyl acrylate) were calculated from NMR and mass spectra as shown in Table IV and V.

Registry No. **1a**, 88761-81-3; **1b**, 42201-68-3; **1c**, 88761-82-4; **1d**, 110434-16-7; **1e**, 110434-17-8; **1f**, 110434-19-0; **2a**, 110434-15-6; **2b**, 18296-04-3; **2c**, 59344-04-6; **2d**, 104564-46-7; **2e**, 110434-18-9; **2f**, 110434-20-3; **3**, 110434-21-4; **4**, 17962-96-8; **5**, 110434-22-5; $Co_2(CO)_8$, 15226-74-1; $RhCl(PPh_3)_3$, 14694-95-2; $RhCl(CO)(PPh_3)_2$, 13938-94-8; $IrCl(CO)(PPH_3)_2$, 14871-41-1; $Et_2MeSiCo(CO)_4$, 69897-17-2; $CH_3CH{=}CHCOOMe$, 18707-60-3; $HSiEt_2Me$, 760-32-7; $CH_2{=}CHCOOMe$, 96-33-3; $CH_2{=}CHCOOEt$, 140-88-5; $CH_2{=}CHCOO$-n-C_4H_9, 141-32-2; $HSiMe_3$, 993-07-7; $HSiMe_2Ph$, 766-77-8; $HSi(OEt)_3$, 998-30-1; $CH_2{=}C(CH_3)COOMe$, 80-62-6.

Formation and Reactions of Olefins with Vicinal Silyl and Stannyl Substituents

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The silicon-tin bond in Me_3SiSnR_3 (R = Me, n-Bu) adds regio- and stereospecifically to 1-alkynes and also to a limited number of nonterminal alkynes when $Pd(PPh_3)_4$ is added as a catalyst. The use of the (Z)-silylstannylalkenes thus formed in synthesis either via organolithiums or via palladium-catalyzed carbon-carbon bond formation has been investigated. Halodestannylation using halogens is nonstereospecific, while that using N-bromosuccinimide is stereospecific except in the styryl system. Halodemethylation at tin occurs readily and leads to allene formation when a hydroxy group is present β to the tin moiety.

Introduction

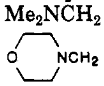
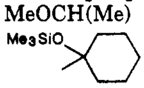
Following our discovery[2] that hexamethylditin adds stereospecifically cis to 1-alkynes (and also to allenes[3]) under the influence of $Pd(PPh_3)_4$ as catalyst, we were able to show that this compound also catalyzes the stereo- and regiospecific addition of (trimethylsilyl)trimethylstannane to 1-alkynes and that it also adds regiospecifically to 1,1-dimethylallene.[4] After our preliminary communication[4] had appeared, Chenard et al. reported[5] on the addition of t-$BuMe_2SnSiMe_3$ to 1-alkynes: they have since shown[6]

† In part.

(1) The work reported here is taken mainly from the Dissertation of R. Wickenamp (Univ. Dortmund, 1987).
(2) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45; **1986**, *304*, 257.
(3) Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318.
(4) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354.
(5) Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666.

0022-3263/87/1952-4868$01.50/0

Table I. Addition to Terminal Alkynes: Reaction Conditions, Yields, and Boiling Points of Products of the Type (Z)-RC(SnR′3)=CHSiMe3[a]

R	R′	reactn condtns (°C/h)	isoltd yield (%)	bp (°C/mmHg)
Bu	Bu	80/20	52	107–110/0.001
t-Bu	Bu	20/240[b]	46	115–118/0.005
$PhCH_2$	Me	75/170	48	90–92/0.04
Me_2NCH_2	Bu	80/96	57	115/0.01
	Me	20/96	63	95–98/0.001
$HOCH_2$	Me	20/72[c]	51	94/0.1
HOCH(Me)	Me	70/140[c]	49	58–60/0.007
$HOCMe_2$	Me	70/22	89	56–58/0.025
HOC(Me)Et	Me	20/45	63	72–75/0.05
HOCH(Me)CH_2	Me	20/192	44	72–73/0.07
HOCH(Me)	Bu	80/41[d]	50	120–128/0.001
$MeOCH_2$	Me	20/140	52	39/0.002
$PhOCH_2$	Me	75/18	70	106–108/0.02
$MeOCH_2CH_2$	Me	20/98	59	47–48/0.03
MeOCH(Me)	Me	20/22	72	39–41/0.1
	Me	80/460	19	89–91/0.09
$EtOCMe_2$	Me	20/66	74	78–80/0.85
EtOOC	Me	20/40	75	55–57/0.002

[a] No solvent used unless otherwise indicated. [b] UV irradiation. [c] In THF. [d] In dimethoxyethane (DME).

that vicinal silylstannylalkenes react with acid chlorides in the presence of $Pd(PPh_3)_4$. Ito et al. demonstrated that isonitriles insert into the Si–Sn bond in the presence of $Pd(PPh_3)_4$,[7] while Piers has found that hexamethylditin adds to nonterminal alkynes if they are activated by ester or amide groups.[8]

Chenard has very recently published a more detailed paper[9] dealing with Si–Sn addition, in which a few reactions of the vicinal (Z)-silylstannylalkenes are reported. The developments outlined above in this area of high synthetic potential have prompted us to publish in detail some of the results that we have obtained in the past 2 years concerning the chemistry of the vicinal (Z)-silylstannylalkenes.

Results and Discussion

(a) Addition of the Si–Sn Bond to Terminal and Nonterminal Alkynes. Like Chenard,[9] we have not been able to improve on our original choice[4] of $Pd(PPh_3)_4$ as catalyst. We have carried out reactions of 22 1-alkynes with $Me_3SiSnMe_3$ and in addition added $Me_3SiSnBu_3$ successfully to seven of these: isolated yields lie generally between 40% and 70%. Table I gives details, but excludes those systems also reported by Chenard. The functional groups OH, OR, NR_2, and ester C=O were tolerated in this reaction. The (Z)-alkenes formed in this addition reaction undergo only partial isomerization to their E isomers on UV irradiation; this isomerization is catalyzed by the addition of R_3SnH as a source of stannyl radicals.

The number of nonterminal alkynes that underwent reaction was more limited (Table II): while $MeOCH_2C\equiv CCH_2OMe$ and EtOOCC≡CCOOEt reacted with both $Me_3SiSnMe_3$ and $Me_3SiSnBu_3$, alkynes RC≡CR with R = $HOCH_2$, HOCH(Me), MeOCH(Me), and $MeOCMe_2$ did

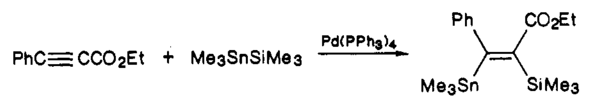
(6) Chenard, B. L.; Van Zyl, C.; Sanderson, D. R. *Tetrahedron Lett.* **1986**, *27*, 2801.
(7) Ito, Y.; Bando, T.; Matsuura, T.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 980.
(8) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1986**, 626.
(9) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561.

Table II. Addition to Nonterminal Alkynes: Reaction Conditions, Yields, and Boiling points of Products of the Type (Z)-RC(SnR″3)=CR′(SiMe3)

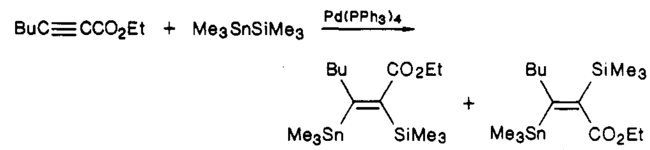
R	R′	R″	reactn condtns	isoltd yield	bp (°C/mmHg)
$MeOCH_2$	$MeOCH_2$	Me	80/240	48	75–77/0.3
$MeOCH_2$	$MeOCH_2$	Bu	80/72	32	140–145/0.005
EtOOC	EtOOC	Me	50/90	17	90–95/0.01
EtOOC	EtOOC	Bu	80/144[b]	14	158/0.005
Ph	EtOOC	Me	75/45[c]	84	97–98/0.001

[a] No solvent used unless otherwise stated. [b] In DME. [c] In THF.

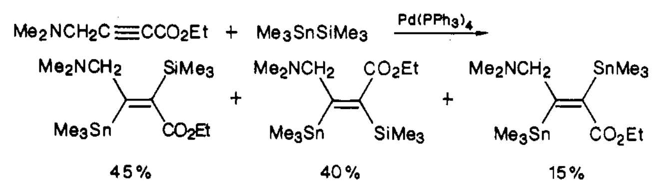
not react. A number of alkynes of the type RC≡CR′ were also reacted with $Me_3SiSnMe_3$, but with only limited success:

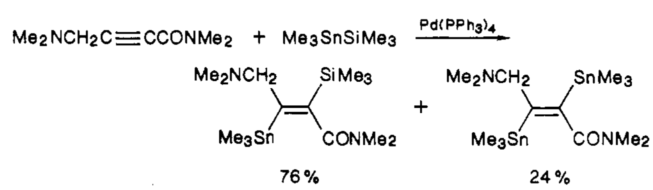


while PhC≡CCOOEt reacted to give the Z adduct in 84% yield (the byproduct being the Z distannane adduct), $PhC\equiv CCO_2Ph$ was unaffected. $BuC\equiv CCO_2Et$, however, gave a 1:1 mixture of Z and E isomers:

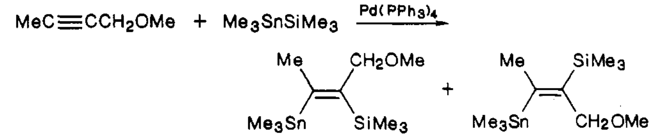


Replacement of the ester group by an amide group prevented reaction (in the case of $PhC\equiv CCONMe_2$); the presence of an ester and an amide functionality ($Me_2NCH_2C\equiv COOEt$) gave a complex mixture, while the combination amide/amine ($Me_2NCH_2C\equiv CCONMe_2$) gave a mixture of two products. In both cases a distannane adduct (distannane is formed by disproportionation of the silylstannane[9]) was obtained as well as adducts of the silylstannane:





The presence of only one ether functionality (in $CH_3C\equiv CCH_2OMe$) decreases alkyne reactivity greatly: after 14 days at 80 °C, only 12% of a mixture of E and Z products was obtained.

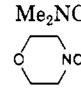


It is not clear why in some cases after long reaction times at high temperatures distannane adducts are observed while in other cases they are not formed. In the reactions studied by us, they were only observed where stated. The fact that no disilane adducts are observed is however readily explained by the low reactivity of Me_6Si_2 compared

Table III. Vinylsilanes $PhCR{=}CHSiMe_3$ from Reactions of Electrophiles with Vinyllithiums Prepared in THF from (*Z*)-$PhC(SnMe_3){=}CHSiMe_3$ and Methyllithium

electrophile	R	reactn temp (°C)	yield (%)	*Z*/*E* ratio	bp (°C/mmHg)
H_2O	H	−78	51	20/80	85–87/12
Me_2SO_4	Me	−20	68	83/17	90–92/12
EtBr	Et	0	44	82/18	100–102/12
MeCOMe	$HOCMe_2$	0	60	26/74	58–62/0.02
EtCHO	HOCH(Et)	0	42	15/85	72–75/0.005
Me_2NCHO	CHO	0	44	10/90	54–56/0.002
Me_3SiCl	Me_3Si	−78	52	16/84	110–112/12
Me_3GeCl	Me_3Ge	0	29	12/88	58–64/0.5
Me_3PbCl	Me_3Pb	−78	44	18/82	75–78/0.02

Table IV. Vinylsilanes $RR''C{=}CHSiMe_3$ from Vinyllithiums Prepared in THF from (*Z*)-$RC(SnR'_3){=}CHSiMe_3$ and Methyllithium

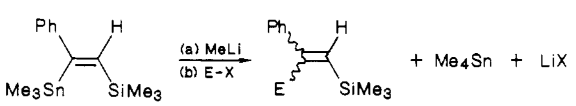
R	R′	R″	reactn temp (°C)	yield (%)	*Z*/*E* ratio	bp (°C/mmHg)
Bu	Bu	H	0	64	0/100	42–43/12
t-Bu	Bu	H	0	26	0/100	25–27/12
Me_2NCH_2	Bu	H	0	32	0/100	76–80/12
	Me	H	0	60	0/100	94–96/12
Bu	Bu	Me	0	65	0/100	62–65/12
Bu	Bu	CHO	0	43	93/7	68–80/1
Bu	Bu	HOCH(Et)	0	47	100/0	90–96/2
Bu	Bu	Me_3Si	0	40	100/0	54–64/1
Me_2NCH_2	Bu	Me_3Si	0	39	100/0	80–90/12
t-Bu	Bu	Me_3Si	20	35	100/0	40–42/0.005
Ph[a]	Me	Me_3Si	−78	32	100/0	80–90/0.001
Bu	Bu	Me_3Ge	0	51	100/0	75–90/1
Me_2NCH_2	Bu	Me_3Ge	0	41	100/0	93–101/12
Bu	Bu	Me_3Pb	0	20	100/0	58–60/0.005

to that of Me_6Sn_2 or $Me_3SnSiMe_3$.

The results discussed above show clearly that $Me_3SiSnMe_3$ is less reactive than Me_6Sn_2 with respect to nonterminal alkynes.[8]

(b) Replacement of Tin by an Organic or Organometallic Residue via an Intermediate Vinyllithium. Since we had previously carried out experiments involving the formation, characterization, and reactions of α-silyl-[10] and α-stannylvinyl anionoids,[11] we felt it of interest to extend our studies to include systems involving β-silylvinyl anionoids. We shall not include spectral data on the latter here, but merely comment on reaction sequences in which they are formed as intermediates.

A number of our experiments were carried out on the styryl system:



Like Chenard,[9] we observed a clear tendency for isomerization of the *E* anionoid formed by lithiodestannylation: although on quenching with water at −78 °C the product consisted of (*Z*)- and (*E*)-styrylsilanes in the ratio of 20:80, reactions with other electrophiles at this or higher temperatures (see Table III) showed the product isomer formed by vinyl inversion to predominate. However, such a configurative instability of vinyllithiums bearing an α-phenyl substituent is not new, having been described by Seyferth over 20 years ago.[12] Further experiments showed the vinyllithium species obtained from systems $RC(SnMe_3){=}CHSiMe_3$ with R = Bu, *t*-Bu, and Me_2NCH_2 to be completely or almost completely configurationally stable, as expected (Table IV): when R = Me_2NCH_2 there is however a tendency to decompose before it can react with the added electrophile.

(c) Palladium-Catalyzed C–C Bond Formation. In view of the successful use by Stille and others[13] of vinyltins for carbon–carbon bond formation, we expected that the vicinal silylstannylalkenes would also be suitable for such

Table V. Palladium-Catalyzed Coupling Reactions between (*Z*)-$PhC(SnR_3){=}CHSiMe_3$ and Organic Halides[a]

R	halide	reactn time (h)	yield (%)	bp (°C/mmHg)
Me	$BrCH_2CH{=}CH_2$	170	51	48–50/0.001
Bu	$BrCH_2CH{=}CH_2$	45	75	47–49/0.001
Me	$BrCH_2CH{=}CHPh$	120	49	100–140/0.001
Bu	$BrCH_2Ph$	340	19	105–112/0.05
Me	PhBr	200	79	87–92/0.3
Me	$ClCOCH_3$	300	62	120–123/12
Bu	$ClCOCH_3$	320	47	119–121/12
Me	ClCOPh	18	75	114–115/0.01
Me	$ClCOCH{=}CHPh$	0.25	85	140/0.001
Me	$ClCOCH{=}CMe_2$	3	35	82–84/0.07

[a] Reaction temperature 80 °C, catalyst $PhCH_2PdCl(PPh_3)_2$.

Table VI. Palladium-Catalyzed Coupling Reactions between Allyl Bromide and (*Z*)-$R'C(SnR_3){=}CHSiMe_3$[a]

R	R′	reactn time (h)	yield (%)	*Z*/*E* ratio	bp (°C/mmHg)
Bu	Bu	55	61	0/100	26–30/0.001
Me	*t*-Bu	450	48	90/10	38–42/0.005
Me	$HOCH_2$	72	20	0/100	31–32/0.005
Bu	$HOCH_2$	240	40	0/100	31–32/0.005
Bu	HOCHMe	48	41	20/80	36–38/0.005
Bu	$MeOCH_2$	48	55	0/100	37–40/0.04
Me	$PhOCH_2$	48	50	0/100	68–70/0.005
Me	EtOOC	36	61	0/100	47–48/0.005

[a] Reaction temperature 80 °C, catalyst $PhCH_2PdCl(PPh_3)_2$.

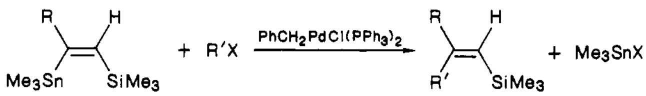
(10) Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1985**, *281*, 163.
(11) Mitchell, T. N.; Amamria, A. *J. Organomet. Chem.* **1983**, *252*, 47. Mitchell, T. N.; Reimann, W. *J. Organomet. Chem.* **1987**, *322*, 141.
(12) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 833. Seyferth, D.; Vaughan, L. G.; Suzuki, R. *J. Organomet. Chem.* **1964**, *1*, 437.
(13) Stille, J. K. *Angew. Chem.* **1986**, *98*, 504.

Table VII. Products (*E*/*Z*)-RC(Hal)═CHSiMe$_3$ of Halodestannylation of (*Z*)-RC(SnMe$_3$)═CHSiMe$_3$

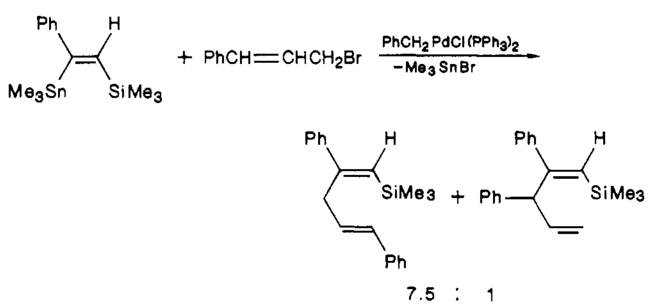
R	halogenating agent	reactn temp (°C)	yield (%)	*Z*/*E* ratio	bp (°C/mmHg)
Ph	Br$_2$	−78[b]	89	71/29	60–70/0.005
Ph	Br$_2$	−25[b]	72	70/30	60–70/0.005
Ph	Br$_2$	25[c]	81	65/35	60–70/0.005
Ph	I$_2$	−78[b]	93	16/84	90–92/0.001
Ph	NBS[a]	−78[b]	58	42/58	60/0.001
Bu	Br$_2$	0[c]	77	31/69	35–43/0.75
Bu	I$_2$	−78[b]	92	29/71	37–44/0.001
Bu	NBS[a]	−20[d]	46	0/100	65–69/1
Me$_2$NCH$_2$	I$_2$	−78[b]	25	0/100	78–83/0.25
Me$_2$NCH$_2$	NBS[a]	−78[b]	21	0/100	45–50/0.001

[a] *N*-Bromosuccinimide. [b] In CH$_2$Cl$_2$. [c] In CHCl$_3$. [d] In CCl$_4$.

coupling reactions, provided that the trimethylsilyl group did not cause problems because of its size.



We first carried out a number of experiments using the styryl system (R = Ph): as can be seen from Table V, allyl bromide and bromobenzene reacted better than benzyl bromide. The reaction with cinnamyl bromide gave two products, that involving allyl inversion being the minor product:



The reactions with acid chlorides were interestingly nonstereospecific, the *Z* product isomer predominanting. There is thus a considerable and unexpected difference between our system and that of Chenard,[9] who observed considerable desilylation when reacting Me$_3$SiSnBu$_3$ and using bis(acetonitrile)palladium(II) chloride as catalyst in CHCl$_3$ at 60 °C.[14] We used benzylchlorobis(triphenylphosphine)palladium which is thus apparently more selective.

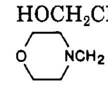
In order to check the sensitivity of the coupling reaction to the presence of other groups R on the sp^2 carbon we then reacted allyl bromide with a number of substrates (Table VI): the presence of hydroxy, alkoxy, or ester functions had no effect on the reaction, though with R = Me$_2$NCH$_2$ no reaction was observed.

(d) Halodestannylation Reactions. Chenard[9] reports iododestannylation using iodine and indirect fluorodestannylation (using *N*-alkyl-*N*-fluorosulfonamide to fluorinate the vinyl anionoid); although mixtures of cis and trans products are formed, the amounts of these are not stated.

We have in addition carried out bromodestannylation using bromine and *N*-bromosuccinimide: the latter (which we have already used successfully in selective monobromodestannylation of 1,1-distannyl-1-alkenes[14]) appears to show more promise as a reagent for stereoselective introduction of bromine, as can be seen from the product ratios recorded in Table VII. However, even at −78 °C

(14) A referee has suggested that the chloroform solvent used by Chenard acts as a source of HCl, which causes desilylation.

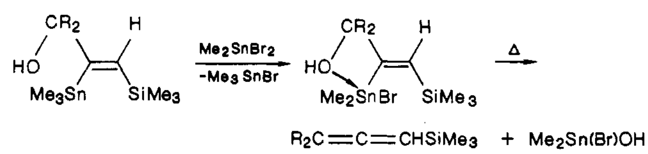
Table VIII. Products (*Z*)-RC(SnMe$_2$Br)═CHSiMe$_3$ from Bromodemethylation of (*Z*)-RC(SnMe$_3$)═SiMe$_3$ with Me$_2$SnBr$_2$ at 80–100 °C

R	reactn time (h)	isoltd yield (%)
Ph	144	62
HOCH$_2$CH$_2$	24	70
	20	81[a]
EtOCMe$_2$	15	30[b]
N≡C(CH$_2$)$_3$	20	65

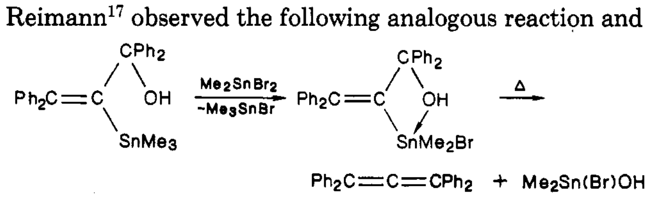
[a] mp 85–87 °C. [b] mp 49–53 °C. The remaining compounds were obtained as viscous oils and could not be crystallized.

this reagent also gives a cis/trans product mixture in the styryl system, presumably due to the configurative instability of the intermediate vinyl radical.

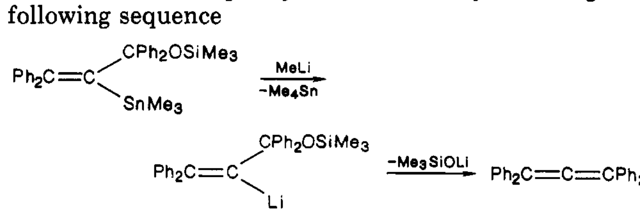
(e) Halodemethylation at Tin. We have previously shown[15] that vinylic trimethylstannyl residues as well as alkyltrimethylstannanes[16] readily undergo bromodemethylation. This functionalization at tin is also possible in the vicinal silylstannylalkenes, as can be seen from Table VIII. However, one potentially useful complication has been noted here as well as in the parallel reaction of β-stannyl allylic alcohols:[17] the presence of a hydroxy group β to tin leads to allene formation, presumably via prior intramolecular coordination of the hydroxy oxygen to tin:



Reimann[17] observed the following analogous reaction and



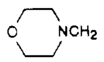
also obtained tetraphenylallene in 60% yield using the following sequence



which is in principle also applicable to the chemistry described in the present paper. Such methodologies for

(15) Mitchell, T. N.; Reimann, W. *Organometallics* **1986**, *5*, 1991.
(16) Mitchell, T. N.; Fabisch, B.; Wickenkamp, R.; Kuivila, H. G.; Karol, T. J. *Silicon, Germanium, Tin Lead Compd.* **1986**, *9*, 57.
(17) Reimann, W. Dissertation, Univ. Dortmund, 1985.

Table IX. Selected NMR Data for Compounds of the Type (*Z*)-$RC(SnMe_3){=}CHSiMe_3$[a]

R	δ(=CH)	^3J_t(Sn,H)	δ(C_1)[b]	δ(C_2)[b]	δ(*Sn*Me_3)	δ(*Si*Me_3)	^3J_c(Sn,Si)
H	7.06	192	152.20	153.72	−63.1	−9.06	47.4
n-Bu	6.40	201	166.19	143.17	−53.6	−10.96	39.0
t-Bu	6.32	219	176.49	135.94	−64.7	−10.46	48.3
Ph	6.58	184	166.08	148.24	−50.0	−9.68	36.0
$PhCH_2$	6.46	192	163.61	146.09	−48.8	−10.60	39.1
Me_2NCH_2	6.29	198	166.72	143.65	−57.3	−10.84	40.0
	6.48	194	164.65	145.12	−57.0	−10.72	39.2
$NC(CH_2)_3$	6.45	190	162.51	145.81	−51.1	−10.44	39.2
$MeOCH_2$	6.57	186	162.27	144.35	−52.4	−10.07	38.4
$PhOCH_2$	6.70	182	160.79	145.12	−50.6	−9.57	36.7
MeOCH(Me)	6.48	194	169.07	142.57	*c*	−10.14	39.8
$EtOCMe_2$	6.23	210	176.02	138.15	−66.3	−10.01	45.8
$MeOCH_2CH_2$	6.48	198	162.01	146.01	−52.1	−10.72	40.4
EtOOC	7.65	165	155.58	158.71	*c*	−8.07	32.3
$HOCH_2$	6.71	188	164.04	140.96	−53.1	−9.64	38.7
$HOCMe_2$	6.33	204	175.58	136.90	−64.4	−9.92	44.5
HOC(Me)Et	6.33	208	174.40	138.30	−64.7	−10.01	45.2
$HOCH_2CH_2$	6.49	194	161.52	147.80	−51.2	−10.67	39.2
$HOCH(Me)CH_2$	6.43	192	162.71	148.26	−51.1	−10.66	39.1

[a] Chemical shifts referenced to TMS or Me_4Sn in ppm, *J* in Hz. [b] C_1 is the tin-bearing vinyl carbon, C_2 that bearing silicon. [c] Not measured.

Table X. Selected NMR Data for Compounds of the Type (*E*/*Z*)-$RC(SnMe_3){=}CR'(SiMe_3)$[a]

R	R′	*E*/*Z*	δ(C_1)[b]	δ(C_2)[b]	^3J(Sn,$C_{3'}$)	δ(*Sn*Me_3)	δ(*Si*Me_3)	^3J(Sn,Si)
$MeOCH_2$	$MeOCH_2$	*Z*	161.91	150.22	82.7	−52.9	−5.32	42.2
EtOOC	EtOOC	*Z*	169.28	148.00	39.8	−27.2	−4.45	45.2
Me	$MeOCH_2$	*E*	157.74	149.52	63.5	−48.5	−5.88	65.1
Me	$MeOCH_2$	*Z*	155.18	149.96	80.1	−55.9	−5.40	46.8
Bu	EtOOC	*E*	163.49	149.08	54.7	−42.4	*c*	63.1
Bu	EtOOC	*Z*	162.83	148.44	113.2	−40.3	*c*	38.7
Ph	EtOOC	*Z*	163.59	151.05	103.0	−39.3	−5.76	32.6
Me_2NCH_2	EtOOC	*E*	163.24	153.71	*c*	−61.7	−5.90	69.0
Me_2NCH_2	EtOOC	*Z*	153.16	148.74	106.8	−50.8	−7.15	36.6
Me_2NCH_2	$Me_2NC(O)$	*E*	157.32	149.22	52.1	−69.7	−6.34	73.3

[a] Chemical shifts referenced to TMS or Me_4Sn in ppm, *J* in Hz. [b] C_1 is the tin-bearing vinyl carbon, C_2 that bearing silicon. [c] Not measured.

allene formation require a more detailed study.

Experimental Section

General Procedures. Manipulations involving organotin or organolithium species were carried out in an argon atmosphere. Melting points were taken with a Buchi capillary melting point apparatus and are uncorrected. Proton NMR spectra were generally obtained at 60 MHz on a Varian EM-360 instrument, carbon-13, silicon-29, tin-119, and lead-207 data on a Bruker AM-300 spectrometer. Chemical shifts are reported in ppm (δ) downfield from either tetramethylsilane (proton, carbon-13, and silicon-29), tetramethyltin (tin-119), or tetramethyllead (lead-207). Satisfactory microanalyses (carried out in this department) were obtained for all new compounds isolated.

Addition of Stannylsilanes to Alkynes. Equimolar amounts of the alkyne and stannylsilane (10 mmol) were mixed and ca. 1 mol % of $Pd(PPh_3)_4$ addded: if the reactants were not miscible, THF or DME (ca. 1 mL) was added to give a homogeneous mixture. The stirred reaction mixture was subjected to the conditions given in Tables I and II: the reaction was followed by proton NMR spectroscopy (disappearance of the acetylene proton, appearance of the vinyl proton with satellites due to tin–proton coupling). The product was if necessary freed from solvent and then distilled at reduced pressure by using a short-path distillation apparatus. The palladium catalyst was decomposed and could not be reisolated.

Formation of Vinyllithiums and Their Reaction with Electrophiles. The silylstannylalkene (10 mmol) was added dropwise to a solution of methyllithium (10 mmol) in THF (ca. 1 M) at the temperature shown in Tables III and IV. The anionoid was generally formed instantaneously, its formation being accompanied by the development of an intense color. After 30 min the electrophile was added, the reaction mixture becoming light yellow: it was allowed to warm to room temperature, hydrolyzed with water (10 mL), and extracted with ether (3 × 30 mL). The organic phase was dried over $MgSO_4$, the solvent removed on a rotary evaporator, and the residue fractionated by using a short-path distillation apparatus.

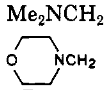
Palladium-Catalyzed C–C Bond Formation. To an equimolar mixture of the silylstannylalkene and the halide or acid chloride (10 mmol) was added ca. 1 mol % $ClPd(PPh_3)_2CH_2Ph$. The reaction mixture was heated and the reaction monitored by proton NMR spectroscopy. The volatiles (R_3SnCl) were removed under reduced pressure and the residue was fractionated by using a short-path distillation apparatus. Details are given in Tables V and VI.

Halodestannylation. (a) Using Bromine or Iodine. A solution of 10 mmol of silylstannylalkene in $CHCl_3$ or (for reactions at −78 °C) CH_2Cl_2 (15 mL) was treated at the temperature shown in Table II with a solution of bromine (10 mmol) in $CHCl_3$ (20 mL) or of iodine (10 mmol) in CH_2Cl_2 (150 mL). After 1 h, the solvent and the trimethyltin halide formed were removed under reduced pressure. The residue was fractionated by using a short-path distillation apparatus.

(b) Using *N*-Bromosuccinimide. A solution of the silylstannylalkene (10 mmol) in CH_2Cl_2 (10 mL) was cooled to −78 °C and a solution of *N*-bromosuccinimide (10 mmol) in CH_2Cl_2 (120 mL) added dropwise. The reaction mixture was allowed to warm to room temperature and the solvent removed under reduced pressure. To the residue was added ether (15 mL); the insoluble stannyl succinimide was filtered off, the ether removed from the filtrate, and the residual oil fractionated under reduced pressure (for boiling points see Table VII.

Halodemethylation at Tin. Equimolar amounts of the silylstannylalkene and dimethyltin dibromide were heated to 70–80 °C, the reaction being monitored by proton NMR spectroscopy. When the reaction was complete, the trimethyltin bromide formed was removed under reduced pressure. The purity of the bromodemethylated silylstannylalkenes was such (98%) that no

Table XI. Selected NMR Data for Compounds of the Type (*E*/*Z*)-RR′C=CHSiMe$_3$[a]

R	R′	*E*/*Z*	δ(Si*Me*$_3$)	δ(=C*H*)	δ(C$_1$)[b]	δ(C$_2$)[b]	δ(^{29}Si)
Ph	H	*E*	0.05	5.82,7.35[c]	143.65	140.07	−6.25
Ph	H	*Z*	0.13	6.60[d,i]	146.62	132.73	−9.85
Ph	Me	*E*	−0.17	5.58	152.0	143.0	−10.09
Ph	Me	*Z*	0.20	5.88	155.29	144.71	−10.57
Ph	Et	*E*	−0.18	5.55	159.07	144.40	−10.16
Ph	Et	*Z*	0.20	5.72	161.21	143.0	−10.57
Ph	HOCH(Et)	*E*	−0.18	5.82	160.45	141.09	−9.29
Ph	HOCH(Et)	*Z*	0.22	5.80	*i*	*i*	−10.92
Ph	HOCMe$_2$	*E*	−0.25	5.98	164.53	146.47	−9.05
Ph	HOCMe$_2$	*Z*	0.15	6.01	164.63	141.12	−9.97
Ph	CHO	*E*	−0.02	7.33	156.11	135.30	−6.78
Ph	CHO	*Z*	0.30	*i*	153.83	143.46	−8.01
Bu	H	*E*	0.03	5.57, 6.07[e]	147.32	129.55	−8.22
Bu	Me	*E*	0.10	5.17	155.47	122.76	−11.56
Bu	CHO	*E*	0.05	6.35	151.22	138.0	−9.13
Bu	CHO	*Z*	0.27	6.87	151.09	141.79	*i*
Bu	HOCH(Et)	*Z*	0.12	5.38	160.39	125.39	−11.54
Me$_2$NCH$_2$	H	*E*	0.00	5.75, 6.12[f]	143.49	133.09	−7.79
	H	*E*	0.06	5.92,6.17[g]	141.92	133.51	−7.94
t-Bu	H	*E*	0.04	5.48,6.08[h]	*i*	*i*	*i*

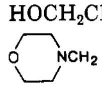
[a] Chemical shifts referenced to TMS in ppm, *J* in Hz. [b] C$_1$ is the silicon-bearing vinyl carbon, C$_2$ the second vinyl carbon. [c] *J*(H,H) = 16 Hz. [d] ^3J(H,H) = 12 Hz. [e] ^3J(H,H) = 18 Hz. [f] ^3J(H,H) = 17 Hz. [g] ^3J(H,H) = 17 Hz. [h] ^3J(H,H) = 19 Hz. [i] Not determined.

Table XII. Selected NMR Data for Compounds of the Type (*E*/*Z*)-RC(MMe$_3$)=CHSiMe$_3$[a]

R	M	*E*/*Z*	δ(=CH)	δ(C$_1$)[b]	δ(C$_2$)[b]	δ(*M*Me$_3$)	δ(*Si*Me$_3$)
Ph	Si	*E*	6.27	166.59	143.80	−4.19	−10.01[d]
Ph	Si	*Z*	6.40	164.0	148.0	−7.19	−10.69
Ph	Ge	*E*	6.17	167.18	140.97	*i*	−10.35
Ph	Pb	*E*	6.10[c]	173.03	142.56	−27.9	−10.20[f]
Bu	Si	*Z*	6.28	162.59	143.54	−7.27	−11.89
Bu	Ge	*Z*	6.18	164.41	140.53	*i*	−11.71
Bu	Pb	*Z*	6.38[d]	173.21	140.59	−82.7	−10.22[g]
t-Bu	Si	*Z*	6.33	170.85	137.62	−8.08	−10.98
Me$_2$NCH$_2$	Si	*Z*	6.35	159.93	145.32	−6.97	−11.55
Me$_2$NCH$_2$	Ge	*Z*	6.32	162.29	142.49	*i*	−11.35
Me$_2$NCH$_2$	Pb	*Z*	6.55[e]	173.29	141.62	−86.2	−10.10[h]

[a] Chemical shifts referenced to TMS or Me$_4$Pb in ppm, *J* in Hz. [b] C$_1$ is the vinyl carbon bearing R, C$_2$ the second vinyl carbon. [c] ^3J_c(Pb,H) = 188 Hz. [d] ^3J_t(Pb,H) = 384 Hz. [e] ^3J_t(Pb,H) = 362 Hz. [f] ^3J(Pb,Si) = 138.9 Hz. [g] *J*(Pb,Si) = 71.2 Hz. [h] ^3J(Pb,Si) = 65.6 Hz. [i] Not measured.

Table XIII. Selected NMR Data for Compounds of the Type (*Z*)-RC(SnMe$_2$Br)=CHSiMe$_3$[a]

R	δ(=CH)	^3J_t(Sn,H)	δ(C$_1$)[b]	δ(C$_2$)[b]	δ(*Sn*Me$_2$Br)	δ(*Si*Me$_3$)	^3J_c(Sn,Si)
Ph	6.70	264	162.4	150.9	35.9	−8.76	46.9
HOCH$_2$CH$_2$	6.55	280	160.6	148.3	−35.1	−9.28	*c*
	6.51	286	162.7	146.4	−5.6	−9.10	49.7
EtOCMe$_2$	6.47	291	174.5	139.8	−21.4	−8.61	52.0
NC(CH$_2$)$_3$	6.53	280	160.3	147.4	53.7	−9.64	52.0

[a] Chemical shifts referenced to TMS or Me$_4$Sn in ppm, *J* in Hz. [b] C$_1$ is the tin-bearing vinyl carbon, C$_2$ the other vinyl carbon. [c] Not measured.

Table XIV. Selected NMR Data for Compounds of the Type (*E*/*Z*)-RC(Hal)=CHSiMe$_3$[a]

R	Hal	δ(=CH)	δ(C$_1$)[b]	δ(C$_2$)[b]	δ(*Si*Me$_3$)
Ph	Br	6.23/6.76	*c*/150.0	141.3/138.8	−5.79/−2.33
Ph	I	6.83/6.87	145.1/157.0	141.3/147.0	−4.23/−0.80
Bu	Br	5.93/6.58	143.5/146.4	128.2/114.3	−7.18/−2.97
Bu	I	6.32/6.65	136.4/153.5	123.5/*c*	−5.64/−1.29
Me$_2$NCH$_2$	Br	6.28/*c*	139.2/*c*	130.9/*c*	−6.51/*c*
Me$_2$NCH$_2$	I	6.68/*c*	138.5/*c*	120.2/*c*	−5.12/*c*

[a] Chemical shifts referenced to TMS in ppm, *J* in Hz. The first value in each pair refers to the *E* isomer. [b] C$_1$ is the vinyl carbon bearing the halogen atom, C$_2$ the second vinyl carbon. [c] Not measured.

further purification was necessary. The following two reactions result in allene formation: compounds Me$_3$SiCH=C(SnMe$_3$)-CMe(R)OH (R = Me, Et) (6.5 and 5.4 mmol, respectively) were heated at 80 °C for 4 days with an equimolar amount of Me$_2$SnBr$_2$. Volatile compounds were pumped off and condensed in a trap cooled with liquid nitrogen. The product mixture (0.9 and 0.7 g, respectively) consisted of Me$_3$SiCH=C=CMe(R) (90% and 74%, respectively) and Me$_3$SnBr; mixture compositions were determined by GLPC on a 25-m capillary column (CP-SIL-5 CB(5)).

Me$_3$SiCH=C=CMe$_2$: IR ν_{max} 1925 cm^{-1}; ^{1}H NMR 0.28 (s, 9 H, Me$_3$Si), 1.83 (d, 6 H, CH$_3$, ^5J (HH) = 3 Hz), 4.97 (septet, 1 H, ^5J (HH) = 3 Hz); ^{13}C NMR −0.81 (Me$_3$Si), 19.56 (Me), 80.93 (=CHSiMe$_3$, ^1J(SiC) = 64.8 Hz), 87.21 (=CMe$_2$), 209.23 (=C=); ^{29}Si NMR −5.68 ppm.

Me$_3$SiCH=C=CMeEt: IR ν_{max} 1925 cm^{-1}; ^{1}H NMR 0.08 (s, 9 H, Me_3Si), 1.00 (t, 3 H, CH_3CH_2, ^3J (HH) = 7 Hz), 1.66 (d, 3 H, Me), 1.91 (m, 2 H, CH_3CH_2), 4.90 (sextet, 1 H, =CH, ^5J (HH) = 4 Hz); ^{13}C NMR −0.77 (Me_3Si), 12.40 (CH_3CH_2), 18.13 (CH_3CH_2), 26.06 (Me), 82.71 (=$CHSiMe_3$), 93.61 (=CMeEt), 208.37 (=C=); ^{29}Si NMR −5.94 ppm.

NMR Studies. Complete multinuclear NMR characterization of all new compounds was carried out. Since however the complete data are of less interest in the present preparatively oriented paper, only those directly relevant to the characterization of the compounds are reported here. The data are contained in Tables IX–XIV. In all cases "Sn" denotes ^{119}Sn. The silylstannylalkenes derived from 1-alkynes (Table IX) are well characterized by the large tin–proton coupling exhibited by the vinylic proton. The most relevant carbon-13 parameters are the chemical shifts for the olefinic carbons, while the metal(loid) spectra afford the value for the cis tin–silicon coupling. This coupling permits the determination of the geometry of the adducts obtained from nonterminal alkynes (Table X).

Compounds in which tin is replaced by an organic residue (Table XI) are best characterized by the shift of the methylsilyl protons or of the vinylic proton. The latter shift is also diagnostic for the geometry of the compounds in which tin is replaced by another organometal residue (Table XII). Bromodemethylation at tin occurs without affecting the stereochemistry at the olefinic bond, as shown by the data in Table XIII. Finally, the data for the halodestannylated compounds appear in Table XIV: since in several cases both isomers could be observed, the pairs of values indicate the usefulness of the various parameters in determining product geometry.

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Registry No. (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = R′ = Bu), 110509-66-5; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = *t*-Bu, R′ = Bu), 110509-67-6; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $PhCh_2$, R′ = Me), 97607-45-9; (*Z*)-RC(SnR'_3 =$CHSiMe_3$ (R = Me_2NCH_2, R′ = Bu), 110509-68-7; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $CH_2CH_2OCH_2CH_2NCH_2$, R′ = Me), 110509-69-8; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $HOCH_2$, R′ = Me), 97607-48-2; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = HOCH(Me), R′ = Me), 97607-49-3; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $HOCME_2$,R′ = Me), 97607-50-6; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = HOC(Me)Et, R′ = Me), 110509-70-1; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $HOCH(Me)CH_2$,R′ = Me), 110509-71-2; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = HOCH(Me), R′ = Bu), 110509-72-3; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $MeOCH_2$, R′ = Me), 97607-47-1; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $PhOCH_2$, R′ = Me), 110509-73-4; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $MeOCH_2CH_2$, R′ = Me), 110509-74-5; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = MeOCH(Me), R′ = Me), 110509-75-6; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $Me_3SIOC(CH_2)_4CH_2$, R′ = Me), 110509-76-7; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = $EtOCMe_2$, R′ = Me), 110509-77-8; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = EtOOC, R′ = Me), 110509-78-9; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = Ph, R′ = Me), 97607-44-8; (*Z*)-RC(SnR'_3)=$CHSiMe_3$ (R = Ph, R′ = Bu), 103731-37-9; (*Z*)-PhCR=$CHSiMe_3$ (R = H), 19319-11-0; (*E*)-PhCR=$CHSiMe_3$ (R = H), 19372-00-0; (*Z*)-PhCR=$CHSiMe_3$ (R = Me), 68669-67-0; (*E*)-PhCR=$CHSiMe_3$ (R = Me), 68669-68-1; (*Z*)-PhCR=$CHSiMe_3$ (R = Et), 68669-61-4; (*E*)-PhCR=$CHSiMe_3$ (R = Et), 68669-62-5; (*Z*)-PhCR=$CHSiMe_3$ (R = $HOCMe_2$), 110509-84-7; (*E*)-PhCR=$CHSiMe_3$ (R = $HOCMe_2$), 110509-85-8; (*Z*)-PhCR=$CHSiMe_3$ (R = HOCH(Et), 110509-86-9; (*E*)-PhCR=$CHSiMe_3$ (R = HOCH(Et), 110509-87-0; (*Z*)-PhCR=$CHSiMe_3$ (R = CHO), 110509-88-1; (*E*)-PhCR=$CHSiMe_3$ (R = CHO), 110509-89-2; (*Z*)-PhCR=$CHSiMe_3$ (R = Me_3Si), 53511-11-8; (*E*)-PhCR=$CHSiMe_3$ (R = Me_3Si), 53511-10-7; (*Z*)-PhCR=$CHSiMe_3$ (R = Me_3Ge), 110509-90-5; (*E*)-PhCR=$CHSiMe_3$ (R = Me_3Ge), 110509-91-6; (*Z*)-PhCR=$CHSiMe_3$ (R = Me_3Pb), 110509-92-7; (*E*)-PhCR=$CHSiMe_3$ (R = Me_3Pb), 110509-93-8; PhCR=$CHSiMe_3$ (R = CH_2CH=CH_2), 110510-02-6; PhCR=$CHSiMe_3$ (R = CH_2CH=CHPh), 110510-03-7; PhCR=$CHSiMe_3$ (R = CH_2Ph), 110510-04-8; PhCR=$CHSiMe_3$ (R = Ph), 51318-07-1; PhCR=$CHSiMe_3$ (R = $COCH_3$), 110510-05-9; PhCR=$CHSiMe_3$ (R = COPh), 110529-46-9; PhCR=$CHSiMe_3$ (R = COCH=CHPh), 110510-08-2; PhCR=$CHSiMe_3$ (R = COCH=CMe_2), 110510-06-0; PhCR=$CHSiMe_3$ (R = CH(Ph)CH=CH_2), 110510-07-1; (*E*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = H), 54731-58-7; (*E*)-RR″C=$CHSiMe_3$ (R = *t*-Bu, R″ = H), 20107-37-3; (*E*)-RR″C=$CHSiMe_3$ (R = Me_2NCH_2, R″ = H), 110529-44-7; (*E*)-RR″C=$CHSiMe_3$ (R = $CH_2CH_2OCH_2CH_2NCH_2$, R″ = H), 110509-94-9; (*E*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = Me), 94286-32-5; (*Z*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = CHO), 110509-95-0; (*E*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = CHO), 110509-96-1; (*Z*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = HOCH(Et)), 110529-45-8; (*Z*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = Me_3Si), 79424-14-9; (*Z*)-RR″C=$CHSiMe_3$ (R = Me_2NCH_2, R″ = Me_3Si), 110509-97-2; (*Z*)-RR″C=$CHSiMe_3$ (R = *t*-Bu, R″ = Me_3Si), 110509-98-3; (*Z*)-RR″C=$CHSiMe_3$ (R = Ph, R″ = Me_3Si), 53511-11-8; (*Z*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = Me_3Ge), 110509-99-4; (*Z*)-RR″C=$CHSiMe_3$ (R = Me_2NCH_2, R″ = Me_3Ge), 110510-00-4; (*Z*)-RR″C=$CHSiMe_3$ (R = Bu, R″ = Me_3Pb), 110510-01-5; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = Bu), 88083-70-9; (*Z*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = *t*-Bu), 110510-09-3; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = *t*-Bu), 110510-10-6; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = $HOCH_2$), 70338-41-9; (*Z*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = HOCHMe), 110510-11-7; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = HOCHMe), 110510-12-8; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = $MeOCH_2$), 110510-13-9; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = $PhOCH_2$), 110510-14-0; (*E*)-R′C(CH_2CH=CH_2)=$CHSiMe_3$ (R′ = EtOOC), 110510-15-1; (*Z*)-RC(Hal)=$CHSiMe_3$ (Hal = Br, R = Ph), 110510-16-2; (*E*)-RC(Hal)=$CHSiMe_3$ (Hal = Br, R = Ph), 110510-17-3; (*Z*)-RC(Hal)=$CHSiMe_3$ (Hal = I, R = Ph), 110510-18-4; (*E*)-RC(Hal)=$CHSiMe_3$ (Hal = I, R = Ph), 110510-19-5; (*Z*)-RC(Hal)=$CHSiMe_3$ (Hal = Br, R = Bu), 110510-20-8; (*E*)-RC(Hal)=$CHSiMe_3$ (Hal = Br, R = Bu), 110510-21-9; (*Z*)-RCl(Hal)=$CHSiMe_3$ (Hal = I, R = Bu), 110510-22-0; (*E*)-RCl(Hal)=$CHSiMe_3$ (Hal = I, R = Bu), 110510-23-1; (*E*)-RC(Hal)=$CHSiMe_3$ (Hal = I, R = Me_2NCH_2), 110510-24-2; (*E*)-RC(Hal)=$CHSiMe_3$ (Hal = Br, R = Me_2NCH_2), 110510-25-3; (*Z*)-RC($SnMe_2Br$)=$CHSiMe_3$ (R = Ph), 110510-26-4; (*Z*)-RC($SnMe_2Br$)=$CHSiMe_3$ (R = $HOCH_2CH_2$), 110510-27-5; (*Z*)-RC($SnMe_2Br$)=$CHSiMe_3$ (R = $CH_2CH_2OCH_2CH_2NCH_2$), 110510-28-6; (*Z*)-RC($SnMe_2Br$)=$CHSiMe_3$ (R = $EtOCMe_2$), 110510-29-7; (*Z*)-RC($SnMe_2Br$)=$CHSiMe_3$ (R = N≡C$(CH_2)_3$), 110510-30-0; (*Z*)-RC($SnMe_3$)=$CHSiMe_3$ (R = Bu), 97607-43-7; (*Z*)-RC($SnMe_3$)=$CHSiMe_3$ (R = Me_2NCH_2), 97607-46-0; (*Z*)-RC($SnMe_3$)=$CHSiMe_3$ (R = $HOCH_2CH_2$), 97607-51-7; (*Z*)-RC($SnMe_3$)=$CHSiMe_3$ (R = N≡C$(CH_2)_3$), 110510-35-5; (*Z*)-RC($SnMe_3$)=$CHSiMe_3$ (R = H), 110510-36-6; (*Z*)-RC(SnR''_3)=CR′($SiMe_3$) (R = R′ = $MeOCH_2$, R″ = Me), 110509-79-0; (*Z*)-RC(SnR''_3)=CR′($SiMe_3$) (R = R′ = $MeOCH_2$, R″ = Bu), 110509-80-3; (*Z*)-RC(SnR''_3)=CR′($SiMe_3$) (R = R′ = EtOOC, R″ = Me), 110509-81-4; (*Z*)-RC(SnR''_3)=CR′($SiMe_3$) (R = R′ = $MeOCH_2$, R″ = Bu), 110509-82-5; (*Z*)-RC(SnR''_3)=CR′($SiMe_3$) (R = Ph, R′ = EtOOC, R″ = Me), 110509-83-6; (*E*)-RC(SnR''_3)=CR′($SiMe_3$) (R = Me, R′ = $MeOCH_2$, R″ = Me), 110510-37-7; (*Z*)-RC(SnR''_3)=CR′ ($SiMe_3$) (R = Me, R′ = $MeOCH_2$ R″ = Me), 110510-38-8; (*E*)-RC(SnR''_3)=CR′ ($SiMe_3$) (R = Bu, R′ = EtOOC, R″ = Me), 110510-39-9; (*Z*)-RC(SnR''_3)=CR′($SiMe_3$) (R = Bu, R′ = EtOOC, R″ = Me), 110510-40-2; (*E*)-RC(SnR''_3)=CR′ ($SiMe_3$) (R = Me_2NCH_2, R′ = EtOOC, R″ = Me), 110510-41-3; (*Z*)-RC(SnR''_3)=CR′ ($SiMe_3$) (R = Me_2NCH_2, R′ = EtOOC, R″ = Me), 110510-42-4; (*E*)-RC(SnR''_3)=CR′($SiMe_3$) (R = Me_2NCH_2, R′ = $Me_2NC(O)$, R″ = Me), 110510-43-5; (*Z*)-RC($PbMe_3$)=$CHSiMe_3$ (R = Me_2NCH_2), 110510-44-6; BuC≡CH, 693-02-7; *t*-BuC≡CH, 917-92-0; $PhCH_2C$≡CH, 10147-11-2; Me_2NCH_2C≡CH, 7223-38-3; $CH_2CH_2OCH_2CH_2NCH_2C$≡CH, 5799-76-8; $HOCH_2C$≡CH, 107-19-7; HOCH(Me)C≡CH, 2028-63-9; $HOCH(Me)_2C$≡CH, 115-19-5; HOC(Me)(Et)C≡CH, 77-75-8; $HOCH(Me)CH_2C$≡CH, 2117-11-5; $MeOCH_2C$≡CH, 627-41-8; $PhOCH_2C$≡CH, 13610-02-1; $MeOCH_2CH_2C$≡CH, 36678-08-7; MeOCH(Me)C≡CH, 18857-02-8; $Me_3SiOC(CH_2)_4CH_2C$≡CH, 62785-90-4; $EtOC(Me)_2C$≡CH, 7740-69-4; EtOOCC≡CH, 623-47-2; PhC≡CH, 536-74-3; $Bu_3SnSiMe_3$, 17955-46-3; $Me_3SnSiMe_3$, 16393-88-7; $BrCH_2CH$=CH_2, 106-95-6; $BrCH_2CH$=CHPh, 4392-24-9; $BrCH_2Ph$, 100-39-0; PhBr, 108-86-1; $ClCOCH_3$, 75-36-5; ClCOPh, 98-88-4; ClCOCH=CHPh, 102-92-1; ClCOCH=CMe_2, 3350-78-5.