J. Org. Chem. **2001,** *66,* 1961−1965

Regiospecific and Stereoselective Synthesis of Functionalized and Differently Metalated Alkenes by Silyl- or Stannylcupration of Metalated Acetylenes

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Received July 19, 2000

Differently metalated vinylcuprate intermediates resulting from silyl- or stannylcupration of silyl- and tin-containing acetylenes reacted with a range of electrophiles, including chlorosilanes and chlorostannanes, affording regio- and stereodefined differently metalated *vic* and *gem* silyl- and tin-trisubstituted alkenes. Some of these functionalized polymetalated olefins are interesting synthons in organic chemistry.

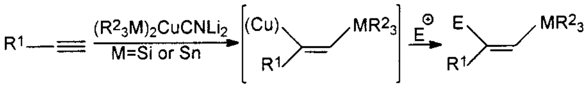
Introduction

The increasing importance of organosilicon and organotin compounds in organic synthesis has led to considerable interest in the formation of vinylsilanes[1] and vinylstannanes,[2] which are extremely useful synthetic intermediates. In previous papers the synthesis of vinylsilanes or vinylstannanes by silyl- or stannylcupration of acetylenes and quenching with electrophiles has been described. Higher-order cyano-silyl- or stannylcuprates, such as lithium bis(dimethylphenylsilyl),[3] bis(*tert*-butyldiphenylsilyl),[4] and bis(tributylstannyl) or mixed alkyltributylstannylcuprates,[5] react *syn*-stereospecifically with monosubstituted alkynes to place the silyl or stannyl group at C-1 and the copper atom on C-2. The vinylcuprate intermediate reacts regiospecifically with several electrophiles to give a range of silyl- or stannylalkenes (Scheme 1).

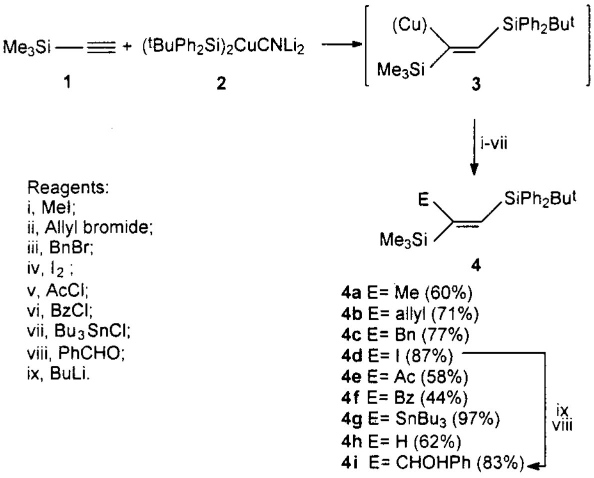
Moreover, since a silyl or stannyl group may be introduced as the electrophile (E=SiR_3,SnR_3) or may be the resident group (R^1= SiR_3, SnR_3), it was easy for us to prepare either *Z* or *E* stereoisomer of differentially silylated or stannylated 1,2-disilyl-,[4] 1,2-distannyl-[5] and differentially metalated 1,2-silylstannylethylenes.[4,5]

We have now studied the silyl- and stannylcupration of metalated acetylenes and subsequent reaction with a number of electrophiles, including silyl- and stannyl chlorides, with the purpose of preparing regio- and stereodefined functionally trisubstituted olefins bearing different silyl and stannyl groups.

Scheme 1



Scheme 2



Results and Discussion

The trimetalated intermediate **3** resulting from *syn tert*-butyldiphenylsilylcupration of trimethylsilylacetylene **1** reacts with other electrophiles, apart from protons, like methyl iodide, allyl bromide, benzyl bromide, iodine, acetyl chloride, benzoyl chloride and tributylstannyl chloride, to give a wide range of regio- and stereodefined di- or trimetalated alkenes **4**, resulting from retention of configuration (Scheme 2)

The regio- and stereochemistry assigned to disilylated alkenes **4** were confirmed with the aid of a single-crystal X-ray diffraction analysis of the crystalline **4c**.

The intermediate cuprate **3** does not react with carbonyl compounds. Attempts to trap this intermediate **3** with benzaldehyde led only to the vinyldisilane **4h** resulting from protodecupration. Nevertheless, we were able to prepare the β-hydroxyvinylsilane **4i** from the iodovinylsilane **4d** by metal−iodine exchange with but-

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(1) See for example: (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, Heidelberg, New York, 1983. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (c) Patai, S., Rappoport, Z., Eds. *Silicon Compounds*; Wiley: Chichester, 1989.

(2) For leading references to the transformation of organotin compounds, see: (a) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481−1487; **1977**, *99*, 4836−4838. (b) Pereyre, M.; Quintard, J. P.; Rahur, A. *Tin in Organic Synthesis*; Butterworth: London, 1987

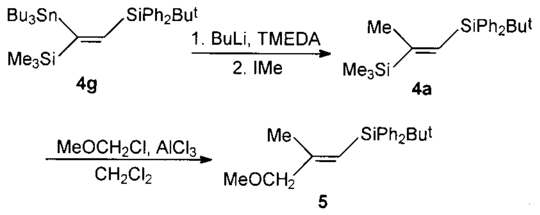
(3) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527.

(4) Barbero, A.; Cuadrado. P.; Fleming, I.; González, A. M.; Pulido, F. J.; Sánchez, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1525.

(5) (a) Barbero, A.; Cuadrado. P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1992**, 351. (b) Barbero, A.; Cuadrado. P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1657.

10.1021/jo0010983 CCC: $20.00

Scheme 3



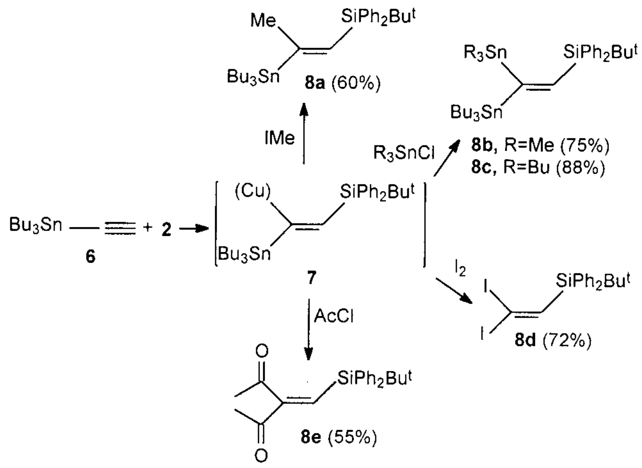
yllithium followed by reaction of the lithiated intermediate with benzaldehyde[6] (Scheme 2).

Some of these functionalized disilylalkenes **4** may be interesting synthons. For example, the differently silylated α,β-disilylenones **4e** and **4f** can be used as Michael acceptors in annelation reactions.[7] This methodology has also permitted us to prepare the regio- and stereodefined disilylated tin olefin[8] **4g.** Moreover, **4g** was selectively destannylated via transmetalation with BuLi in TMEDA/THF and reaction of the completely configurationally stable vinyllithium species with methyl iodide to yield the differently disilylated alkene **4a.** Subsequently, the trimethylsilyl group of **4a** was regioselectively substituted in the presence of the *tert*-butyldiphenylsilyl group to give **5** (Scheme 3). This is in accordance with the results obtained by us in disilylative acetylation of vinyldisilanes bearing both silyl groups.[4]

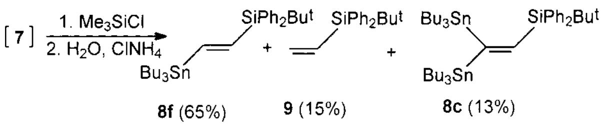
On the other hand, the intermediate cuprate **7**, resulting from *tert*-butyldiphenylsilylcupration of tributylstannylacetylene **6**, reacted with other electrophiles more interesting than a proton, such as methyl iodide and stannyl chlorides, giving silylstannylalkenes **8a**−**c** with good yields. The stereochemistry of vinylstannanes has been established by Sn−H coupling constants. The structure assigned to the tin-containing olefins was in accordance with the *J*(Sn−H) values for the vinyl protons in a *trans*-, *cis*-, or *gem*-coupling. When iodine and acetyl chloride was used, the electrophile reacted not only with the copper but also with the stannyl group, affording 2,2-diiodo- and 2,2-diacetylvinylsilanes **8d** and **8e**, respectively[9] (Scheme 4).

The reaction of intermediate **7** with trimethylsilyl chloride was even more puzzling. Together with the majority *E*-1-*tert*-butyldiphenylsilyl-2-tributylstannylethene **8f** resulting from protodecupration, we obtained as minor products the 1-*tert*-butyldiphenylsilylethene **9** resulting from the destannylation and the same distannylvinylsilane **8c** obtained by reaction of the intermediate **7** with tributylstannyl chloride. This result confirms the low reactivity of silyl chlorides as electrophiles toward vinylcuprate intermediates reported by us in a previous paper.[4] In the present case, the trimethylsilyl chloride was not trapped by the vinylcuprate intermediate **7**, which underwent protodecupration in the final hydrolysis to give the main product **8f** (65%). In a minor extension, the intermediate **7** underwent disproportionation affording the destannylated and distannylated product **9** (15%) and **8c** (13%), respectively (Scheme 5).

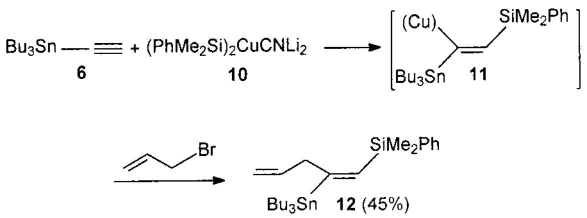
Scheme 4



Scheme 5



Scheme 6



Although the *tert*-butyldiphenylsilylcuprate **2** was the reagent normally used in our investigations, we verified that the intermediate **11** obtained from addition of the dimethylphenylsilylcuprate **10** to the tin-containing acetylene **6** could also be trapped by electrophiles. Thus, the intermediate **11** reacted with allyl bromide leading to the silylstannyldiene **12** (Scheme 6).

In a similar manner, the trimethylsilylacetylene **1** reacted with mixed higher-order cyano-alkyl-tributylstannylcuprates **13** giving the intermediates **14** and **15**, whose treatment with different electrophiles yielded, in general, the corresponding *E*-vinylsilylstannane **16a**−**d**. Only when methyl iodide was used was the reaction not very regioselective. We obtained the *E*-silylstannylalkene **16a**, together with its regioisomer **17a**, resulting from the intermediate **15**. This is a consequence of the known reversibility of the stannylcupration of 1-alkynes.[10] The addition of methyl propiolate occurred with concomitant loss of the trimethylsilyl group (Scheme 7).

These trans silyl tin olefins may serve as synthons for a variety of useful transformations. For example, they have been of great use as intermediates in Denmark's silicon-directed Nazarov cyclization.[11]

The bulky lithium bis(*tert*-butyldiphenylsilyl)cuprate **2**, whose reactivity toward dialkyl- or diphenylacetylenes is low,[4] did not react with bis-trimethylsilylacetylene **18**. Nevertheless, this deactivated acetylene showed a reac-

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[6] Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harpp, D. N. *J. Org. Chem.* **1978**, *43*, 1526.

[7] Fleming, I.; Newton, T. W.; Sabin, V.; Zammatio, F. *Tetrahedron* **1992**, *48*, 7793.

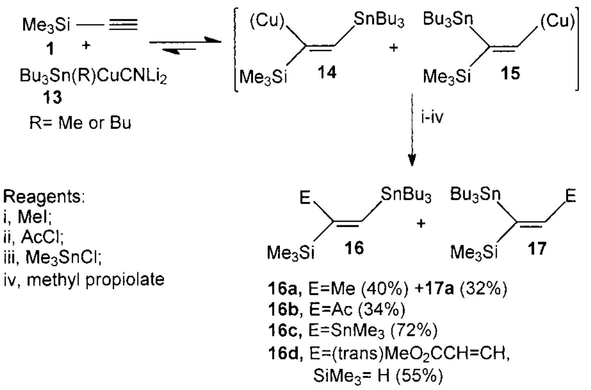
[8] Although an analogous 1,2-disilyl-1-stannylalkene was obtained by Chenard et al. by addition of corresponding silylstannane to trimethylsilylacetylene, they obtained a mixture of *Z* and *E* isomers. [Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561].

[9] The easy iodine−tin substitution had already been observed by Chenard et al. *(*see reference to note 8).

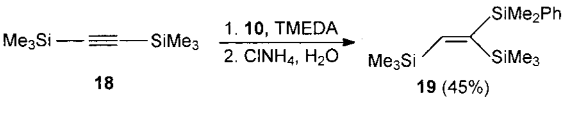
[10] Hutzinger, M. W.; Singer, R. D.; Oehlschlager, A. C. *J. Am. Chem. Soc.* **1990**, *112*, 9397.

[11] Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, 66, 2397−29411. *Ibid.* **1983**, *66*, 2377−2396.

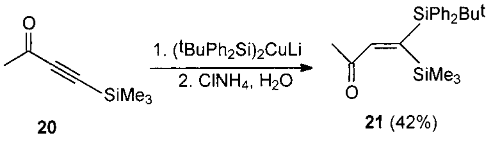
Scheme 7



Scheme 8



Scheme 9



tion with the dimethylphenylsilylcuprate reagent **10,** which was added to **18** in the presence of TMEDA to give the trisilylated alkene **19**. When TMEDA was omitted, the yield of **19** was only 20%. (Scheme 8).

On the other hand, we were able to add the *tert*-butyldiphenylsilylcuprate **2** to the disubstituted silylacetylene **20,** partially activated by a carbonyl group, affording the differently silylated β,β-disilylenone **21** regioisomer of α,β-disilylenone **4e** obtained from *tert*-butyldiphenylsilylcupration of trimethylsilylacetylene **1** and subsequent reaction with acetyl chloride. (Scheme 9).

In conclusion, we have developed a useful procedure for preparing geometrically defined trisubstituted alkenes bearing two different silyl groups or silyl and stannyl groups. Moreover, the checked minor electrofugacity of the hindered *tert*-butyldiphenylsilyl group versus the trimethylsilyl group has allowed us to impart regioselectivity to the desilylation of olefins substituted by both silyl groups and exclusively to remove the trimethylsilyl group. On the other hand, the known different reactivity of stannyl and silyl groups makes the selective destannylation in silyl tin olefins possible. In addition, the presence of other functional groups increases the interest of these polymetalated synthons.

Experimental Section

General. THF was distilled from sodium benzophenone ketyl in a recycling still. Dichloromethane was distilled from P_2O_5. All chromatographic and workup solvents were distilled prior to use. Copper(I) cyanide was dried in vacuo over P_2O_5. The starting acetylenes **1, 6, 18,** and **20** were purchased from Aldrich. Lithium *tert*-butyldiphenylsilylcuprate[4] **2**, lithium dimethylphenylsilylcuprate[3] **10**, and mixed alkyltributylstannylcuprates[5] **13** were prepared as previously described. All reactions involving organometallic reagents were carried out under nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on a precoated plate of silica gel 60 (nano-SIL-20, Macherey-Nagel). Flash chromatography was performed on silica gel 60 (230−400 mesh, M−N).

General Procedure for the Silyl- or Stannylcupration of the Metalated Acetylenes and Reactions of the Cuprate Intermediates with Electrophiles. To a stirred solution of lithium *tert*-butyldiphenylsilylcuprate[4] **2**, lithium dimethylphenylsilylcuprate[3] **10**, or lithium alkyltributylstannylcuprates[5] **13** (3 mmol) in THF (10 mL) at −78 °C was added the metalated acetylene **1**, **6**, **18**, or **20** (3 mmol) and the mixture stirred under nitrogen at this temperature for 30 min. The electrophile (usually 6 mmol) was then added at −78 °C. The mixture was slowly allowed to warm to 0 °C and stirred at that temperature until TLC indicated complete reaction. Quenching at 0 °C with aqueous ammonium chloride, aqueous workup with diethyl ether, drying ($MgSO_4$), and chromatography gave the following products.

(*E*)-1-(*tert*-Butyldiphenylsilyl)-2-(trimethylsilyl)prop-1-ene (4a): by reaction of vinylcuprate **3,** resulting from *tert*-butyldiphenylsilylcupration of trimethylsilylacetylene **1,** with methyl iodide; colorless oil (60%yield); $R_f = 0.35$ (hexane); IR (neat)1595, 1240, 1100, and 820 cm^{-1}; ^{1}H NMR δ 7.72−7.67 (m, 4H), 7.42−7.33 (m, 6H), 6.47 (q, J = 1.3 Hz, 1H), 1.56 (d, J = 1.3 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR δ 166.41, 136.12, 135.83, 135.34, 128.96, 127.60, 27.75, 27.54, 18.21, and 6.19; MS (EI) *m/z* 352 (M$^+$, 3%), 295 (100), 197 (80), 135 (56), 73 (62), and 57 (23). Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.93; H, 9.15. Found: C, 74.58; H, 9.21.

(*E*)-1-(*tert*-Butyldiphenylsilyl)-2-(trimethylsilyl)penta-1,4-diene (4b): by reaction of allyl bromide with **3**; colorless oil (71% yield); R_f = 0.51 (hexane); IR (CCl_4) 1640, 1610, 1250, and 1100 cm^{-1}; ^{1}H NMR δ 7.72−7.60 (m, 4H), 7.42−7.34 (m, 6H), 6.66 (s, 1H), 5.28 (ddt, J = 17.0, 10.0 and 6.8 Hz, 1H), 4.70 (ddt, J = 10.0, 1.8 and 1.3 Hz, 1H), 4.62 (ddt, J = 17.0, 1.8 and 1.7 Hz, 1H), 2.77 (ddd, J = 6.8, 1.7 and 1.3 Hz, 2H), 1.04 (s, 9H), and 0.18 (s, 9H); ^{13}C NMR δ 168.19, 136.02, 135.71, 135.32, 133.93, 129.40, 127.56, 115.67, 42.57, 27.44, 18.23, and −0.42; MS (EI) *m/z* 378 (M$^+$, 7%), 363 (10), 321 (100), 193 (38), 135 (81), 73 (42), and 41 (12). Anal. Calcd for $C_{24}H_{34}Si_2$: C, 76.12; H, 9.05. Found: C, 75.87; H, 9.13.

(*E*)-1-(*tert*-Butyldiphenylsilyl)-2-(trimethylsilyl)-3-phenylprop-1-ene (4c): by reaction of benzyl bromide with **3**; colorless crystals (77%), mp 79−80 °C (hexane−methanol); R_f = 0.23 (hexane); IR (neat) 1600, 1250, 1100, and 820 cm^{-1}; ^{1}H NMR δ 7.74−7.71 (m, 4H), 7.36−7.31 (m, 6H), 7.04−7.02 (m, 3H), 6.74−6.69 (m, 2H), 6.69 (s, 1H), 3.38 (s, 2H), 1.09 (s, 9H), and −0.05 (s, 9H); ^{13}C NMR δ 168.68, 139.68, 136.08, 135.94, 135.01, 129.06, 129.01, 127.60, 125.61, 43.91, 27.56, 18.33, and −0.62; MS (EI) *m/z* 428 (M$^+$, 1%), 413 (11), 371 (82), 351 (2), 293 (11), 259 (33), 221 (34), 197 (32), 183 (28), 135 (57), 73 (100), and 57 (72). Anal. Calcd for $C_{28}H_{36}Si_2$: C, 78.44; H, 8.46. Found: C, 78.56; H, 8.41.

(*Z*)-2-(*tert*-Butyldiphenylsilyl)-1-iodo-1-(trimethylsilyl)-ethene (4d): by adding iodine to **3**; colorless crystals (87%), m p 89−90 °C (MeOH); R_f = 0.23 (hexane); IR (neat) 1630, 1240, 1100, and 830 cm^{-1}; ^{1}H NMR δ 7.81 (s, 1H), 7.76−7.73 (m, 4H), 7.43−7.36 (m, 6H), 1.03 (s, 9H), and 0.26 (s, 9H); ^{13}C NMR δ 145.14, 140.09, 136.25, 131.98, 129.18, 127.65, 27.42, 18.54, and −1.40; MS (EI) *m/z* 464 (M$^+$, 1%), 449 (12), 407 (8), 387 (22), 337 (35), 239 (42), and 187 (100).). Anal. Calcd for $C_{21}H_{29}ISi_2$: C, 54.30; H, 6.29. Found: C, 54.42; H, 6.21.

(*E*)-4-(*tert*-Butyldiphenylsilyl)-3-(trimethylsilyl)but-3-en-2-one (4e): by adding acetyl chloride to **3**; colorless oil (58%); R_f = 0.4 (hexanes−EtOAc, 10:1); IR (neat) 1670, 1580, 1240, and 1110 cm^{-1}; ^{1}H NMR δ 7.60−7.57 (m, 4H), 7.42−7.34 (m, 6H), 6.69 (s, 1H), 1.40 (s, 3H), 1.06 (s, 9H), and 0.21 (s, 9H); ^{13}C NMR δ 208.83, 172.83, 136.89, 136.42, 133.38, 129.46, 127.60,30.66, 27.74, 18.41, and −1.32; MS (CI) *m/z* 381 (M+1, 2%), 365 (12), 323 (10), and 303 (100).). Anal. Calcd for $C_{23}H_{32}OSi_2$: C, 72.57; H, 8.47. Found: C, 72.15; H, 8.56.

(*E*)-3-(*tert*-Butyldiphenylsilyl)-1-phenyl-2-(trimethylsilyl)prop-2-enone (4f): by adding benzoyl chloride to **3**; colorless oil (44%), R_f = 0.25 (hexanes−EtOAc, 20:1); IR (neat)

1680, 1600, 1240, 1105, and 820 cm^{-1}; ^{1}H NMR δ 7.76−7.50 (m, 6H), 7.46−7.32 (m, 11H), 5.14 (s, 1H), 1.09 (s, 9H); and 0.18 (s, 9H); ^{13}C NMR δ 213.34, 172.94, 135.87, 134.72, 131.88, 130.22, 129.37, 128.83, 128.32, 127.57, 125.42, 27.24, 18.59, and −0.79; MS (EI) *m/z* 442 (M$^+$, 98%), 370 (38), 105 (100) and 73 (60). Anal. Calcd for $C_{28}H_{34}OSi_2$: C, 75.96; H, 7.74. Found: C, 76.24; H, 7.68.

(*Z*)-2-(*tert*-Butyldiphenylsilyl)-1-(tributylstannyl)-1-(trimethylsilyl)ethene (4g): by adding tributylstannyl chloride to **3**; colorless oil (97%); $R_f = 0.54$ (hexane); IR (neat) 1590, 1250, 1100, and 810 cm^{-1}; ^{1}H NMR δ 8.06 (s, $^3J_{\mathrm{Sn-Htrans}} = 222$,-233 Hz, 1H), 7.79−7.61 (m, 4H), 7.40−7.34 (m, 6H), 1.06 (m, 12H), 0.98 (s, 9H), 0.76 (t, $J = 7.1$ Hz, 9H), 0.36 (t, $J = 7.3$ Hz, 6H), and 0.27 (s, 9H); ^{13}C NMR δ 182.40, 156.77, 136.30, 134.54, 129.05, 127.51, 123.53, 29.06, 27.86, 27.50, 18.32, 11.72 and 0.23; MS (CI) *m/z* 629 (M + 1, 4%), 613 (11), 571 (31), 551 (21), and 291 (100). Anal. Calcd for $C_{33}H_{56}Si_2Sn$: C, 63.15; H, 8.99. Found: C, 63.42; H, 9.05.

(*E*)-1-(*tert*-Butyldiphenylsilyl)-2-(trimethylsilyl)ethene (4h): by adding benzaldehyde to **3**; clear colorless oil (62%); $R_f = 0.39$ (hexane); IR (neat) 1590, 1250, and 1010 cm^{-1};^{1}H NMR δ 7.66−7.54 (m, 4H), 7.32−7.20 (m, 6H), 7.08 (d, $J = 22.6$ Hz, 1H), 6.75 (d, $J = 22.6$ Hz, 1H), 1.09 (s, 9H), and 0.10 (s, 9H); ^{13}C NMR δ 157.49, 143.67, 135.77, 134.08, 129.14, 127.64, 27.96, 18.29, and −1.43; MS (EI) *m/z* 281 (M$^+$, 1%), 323 (1), 281 (100), 207 (64), 197 (81), 183 (96), 135 (98), and 73 (91). This compound is the same as that obtained by quenching of **3** with aqueous ammonium chloride.[4]

(*E*)-1-(*tert*-Butyldiphenylsilyl)-2-(tributylstannyl)prop-1-ene (8a): by reaction of the intermediate **7**, resulting from *tert*-butyldiphenylsilylcupration of tributylstannylacetylene **6** with methyl iodide; colorless oil (60%); $R_f = 0.55$ (hexanes−Et$_2$O, 9:1); IR (neat) 1590, 1100, 820 cm^{-1}; ^{1}H NMR δ 7.66−7.63 (m, 4H), 7.40−7.34 (m, 6H), 6.32 (s, $^3J_{\mathrm{Sn-Hcis}} = 98$ Hz, 1H), 1.72 (s, 3H), 1.58 (m, 6H), 1.39 (m, 12H), 1.06 (s, 9H), and 0.93 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR δ 170.02, 137.45, 136.22, 135.15, 129.07, 127.53, 29.32, 28.88, 27.54, 27.48, 17.88, 13.84, and 9.68; MS (EI) *m/z* 513 (M$^+$-^{t}Bu, 18%), 291 (8), 197 (22), 179 (25), 135 (77), 105 (21), and 57 (100). Anal. Calcd for $C_{31}H_{50}SiSn$: C, 65.38; H, 8.85. Found: C, 65.63; H, 8.79.

(*E*)-2-(*tert*-Butyldiphenylsilyl)-1-(tributylstannyl)-1-(trimethylstannyl)ethene (8b): by adding trimethyltin chloride to **7**; colorless oil (75%); $R_f = 0.70$ (hexane); IR (neat) 1630, 1100, and 815 cm^{-1};^{1}H NMR δ 7.91 (s, $^3J_{\mathrm{Sn-Hcis}} = 153$, 158 Hz and $^3J_{\mathrm{Sn-Htrans}} = 250$, 266 Hz, 1H), 7.80−7.77 (m, 6H), 1.58 (m, 6H),1.39 (m, 6H), 0.99 (m, 6H), 0.98 (s, 9H), 0.94 (t, $J = 7.2$ Hz, 9H), and −0.43 (s, 9H); ^{13}C NMR δ 183.89, 160.26, 136.49, 134.43, 129.15, 127.56, 29.44, 27.56, 27.07, 18.26, 13.85, 11.01, and −6.44; MS (EI) *m/z* 663 (M$^+$ − ^{t}Bu, 2%), 399 (17), 341 (12), 165 (42), 135 (100). Anal. Calcd for $C_{33}H_{56}SiSn_2$: C, 55.18; H, 7.86. Found: C, 54.82; H, 7.79.

1,1-Bis(tributylstannyl)-2-(*tert*-butyldiphenylsilyl)ethene (8c): by adding tributylstannyl chloride to **7**; colorless oil (88%); $R_f = 0.66$ (hexane); IR (neat) 1635, 1100, and 820 cm^{-1};^{1}H NMR δ 7.95 (s, $^3J_{\mathrm{Sn-Hcis}} = 160$, 165 Hz and $^3J_{\mathrm{Sn-Htrans}} = 230$, 240 Hz, 1H), 7.82−7.80 (m, 4H), 7.39−7.33 (m, 6H), 1.59 (m, 6H), 1.40 (m, 6H), 1.02 (m, 12H), 0.98 (s,9H), 0.93 (m, 12H), 0.73 (t, $J = 6.8$ Hz, 9H), and 0.28 (t, $J = 6.8$ Hz, 9H); ^{13}C NMR δ 185.18, 160.52, 136.43, 134.56, 128.99, 127.46, 29.42, 29.10, 27.62, 27.48, 26.95, 18.22, 13.83, 13.54, 11.45, and 11.14; MS (CI) *m/z* 847 (M$^+$ + 1, 13%), 789 (65), 523 (52), 498 (30), 291 (100), and 183 (25).

1-(*tert*-Butyldiphenylsilyl)-2, 2-diiodoethene (8d): by adding iodine to **7**; colorless oil (72%); $R_f = 0.73$ (hexanes−Et$_2$O, 9:1); IR (neat) 1620, 1100, 820 cm^{-1};^{1}H NMR δ 8.69 (s, 1H), 7.83−7.64 (m, 4H), 7.46−7.34 (m, 6H), and 1.00 (s, 9H); ^{13}C NMR δ 153.71, 136.22, 131.05, 129.55, 127.83, 28.08, 20.89 and 18.35; MS (EI) *m/z* 461 (M$^+$-Bu^t, 13%), 333 (20), 309 (100), 135 (36), and 57 (40). Anal. Calcd for $C_{18}H_{20}I_2Si$: C, 41.72; H, 3.89. Found: C, 41.53; H, 3.94.

3-Acetyl-4-(*tert*-butyldiphenylsilyl)-3-buten-2-one (8e): by adding acetyl chloride to **7**; colorless oil (55%); $R_f = 0.34$ (hexanes−Et$_2$O, 5:1); IR (neat) 1707, 1668, 1107 cm^{-1}; ^{1}H NMR δ 7.59−7.56 (m, 4H), 7.42−7.33 (m, 6H), 7.32 (s, 1H), 2.46 (s, 3H), 1.57 (s, 3H), and 1.11 (s, 9H); ^{13}C NMR δ 203.51, 197.43, 159.62, 139.53, 136.23, 131.98, 129.76, 127.71, 30.32, 27.68, 26.32 ,and 18.51; MS (EI) *m/z* 350 (M$^+$, 55%), 335 (12), 307 (24), 293 (58), 105 (41), and 43 (100). Anal. Calcd for $C_{22}H_{26}O_2Si$: C, 75.38; H, 7.48. Found: C, 75.12; H, 7.56.

(*E*)-1-(*tert*-Butyldiphenylsilyl)-2-(tributylstannyl)ethene (8f). The title compound (65% yield) together with the previously described 1,1-bis(tributylstannyl)-2-(*tert*-butyldiphenylsilyl)ethene **8c** (13%) and the *tert*-butyldiphenylsilylethene **9** (15%) was obtained by reaction of intermediate **7** with trimethylsilyl chloride. **8f** and **9** had spectroscopic properties identical to those earlier reported by us.[4]

(*E*)-1-(Dimethylphenylsilyl)-2-(tributylstannyl)penta-1,4-diene (12): by adding allyl bromide to intermediate **11** obtained from dimethylphenylsilylcupration of tributylstannylacetylene **6**; colorless oil (45%); $R_f = 0.60$ (hexane); IR (neat) 1650, 1640, 1600, 1250, 1110, 990, 910, and 830 cm^{-1};^{1}H NMR δ 7.57−7.54 (m, 2H), 7.37−7.30 (m, 3H), 6.06 (s,$^3J_{\mathrm{Sn-H\ cis}} = 96$, 110 Hz, 1H), 5.63 (ddt, $J = 7.5$, 16.8 and 6.5 Hz, 1H), 4.96 (dd, $J = 7.5$ and 1.8 Hz, 1H), 4.92 (dd, $J = 16.8$ and 1.8 Hz, 1H), 3.10 (d, $J = 6.5$ Hz,$^3J_{\mathrm{Sn-H\ cis}} = 50$, 54 Hz, 2H), 1.5 (m, 6H), 1.32 (m, 6H), 0.90 (t, $J = 7.2$ Hz, 9H), 0.89 (m, 6H), and 0.38 (s, 6H); ^{13}C NMR δ 168.98, 141.71, 140.09, 136.81, 133.73, 128.68, 127.70, 115.96, 44.97, 29.12, 27.39, 13.72, 10.24, and −0.37; MS (EI) *m/z* 492 (M$^+$, 5%), 435 (100), 377 (10), 321 (12), 235 (51), 179 (98), and 135 (99). Anal. Calcd. for $C_{25}H_{44}SiSn$: C, 61.10; H, 9.02. Found: C, 60.82; H, 9.09.

(*E*)-1-(Tributylstannyl)-2-(trimethylsilyl)prop-1-ene (16a) (40% yield) and (*Z*)-1-(tributylstannyl)-1-(trimethylsilyl)-prop-1-ene (17a) (32% yield): by reaction with methyl iodide of the intermediates **14** and **15**, resulting from tributylstannylcupration of trimethylsilylacetylene **1**; $R_f = 0.66$ (hexane); IR (CCl$_4$) 1620, 1450, 1250, and 840 cm^{-1};^{1}H NMR of **16a** δ 6.37 (q, $J = 1.2$ Hz, $^2J_{\mathrm{Sn-H}} = 75$, 83 Hz, 1H), 1.87 (d, $J = 1.2$ Hz, 3H), 1.60−1.43 (m, 6H), 1.40−1.20 (m, 6H), 1.00−0.70 (m, 15H), and 0.08 (s, 9H);^{1}H NMR of **17a** δ 6.84 (q, $J = 6.0$ Hz, $^3J_{\mathrm{Sn-H\ trans}} = 168$ Hz, 1H), 1.88 (d, $J = 6.0$ Hz, 3H), 1.60−1.43 (m, 6H), 1.40−1.20 (m, 6H), 1.00−0.70 (m, 15H), and −0.01 (s, 9H).

(*E*)-4-(Tributylstannyl)-3-(trimethylsilyl)but-3-en-2-one (16b): by adding acetyl chloride to **14**; colorless oil (34% yield); $R_f = 0.35$ (hexane−Et$_2$O, 20: 1); IR (neat) 1680, 1590, 1250, 1112, and 820 cm^{-1}; ^{1}H NMR δ 6.58 (s, 1H), 1.89 (s, 3H), 1.40 (m, 6H), 1.25 (m, 6H), 0.95 (m, 6H), 0.75 (t, $J = 7.5$ Hz, 9H), and 0.19 (s, 9H); ^{13}C NMR δ 205.53, 176.42, 135.13, 29.81, 29.19, 27.35, 13.68, 9.53, and −1.47; MS (EI) *m/z* 432 (M$^+$, 5%), 417 (15), 375 (100), 73 (54), and 43 (22).

(*Z*)-2-(Tributylstannyl)-1-(trimethylsilyl)-1-(trimethylstannyl)ethene (16c): by reaction of trimethyltin chloride with the intermediate **14**; colorless oil (72% yield); $R_f = 0.64$ (hexane); IR (neat) 1590, 1250, 1115, and 835 cm^{-1};^{1}H NMR δ 7.89 (s, 1H), 1.49 (m, 6H), 0.96 (m, 12H), 0.62 (t, $J = 7$ Hz, 9H), 0.14 (s, 3H), and −0.35 (s, 3H); ^{13}C NMR δ 172.06, 164.95, 29.18, 27.43, 13.56, 11.51, −0.31, and −5.26; MS (EI) *m/z* 554 (M$^+$, 1%), 497 (12), 440 (21), 399 (18), 291 (100), 263 (20), 165 (75), and 73 (39).

Methyl (*E,Z*)-5-(Tributylstannyl)penta-2,4-dienoate (16d): by reaction of **14** with methyl propiolate; yield 55%; $R_f = 0.2$ (hexane); IR (CCl$_4$) 1720, 1650, 1580, and 990 cm^{-1};^{1}H NMR δ 7.75 (d, $J = 19.36$ Hz, 1H) 7.12 (d, $J = 12.87$ Hz, $^2J_{\mathrm{Sn-H}} = 61$, 64,1H), 6.73 (d, $J = 12.87$ Hz, $^3J_{\mathrm{Sn-Htrans}} = 120$, 124, 1H), 6.30 (d, $J = 19.36$ Hz, 1H), 3.74 (s, 3H), 1.70−1.40 (m, 6H), 1.35−1.20 (m, 6H), 1.00−0.60 (m, 15H); ^{13}C NMR δ 167.96, 157.40, 153.83, 135.92, 134.91, 51.50, 29.11, 27.34, 13.72, and 10.95; MS (EI) *m/z* 402 (M$^+$, 1%), 345 (8), 319 (100), 263 (86), and 207 (83). Anal. Calcd for $C_{18}H_{34}O_2Sn$: C, 53.89; H, 8.54. Found: C, 54.17; H, 8.39.

(*E*)-1-(Dimethylphenylsilyl)-1,2-bis(trimethylsilyl)ethene (19): by dimethylphenylsilylcupration of bis-trimethylsilylacetylene **18** in the presence of TMEDA (1.2 equiv) and quenching with aqueous ammonium chloride; yield 45%; $R_f = 0.6$ (hexane); IR (neat) 1590, 1250, 1115, and 835 cm^{-1}; ^{1}H NMR δ 7.52−7.49 (m, 2H), 7.36−7.33 (m, 3H), 6.69 (s, 1H), 0.33 (s, 6H), and 0.06 (s, 18H); ^{13}C NMR δ 152.98, 147.93, 133.86, 128.85, 128.22, 127.73, −1.63, −2.39, and −2.91; MS (EI) *m*/*z* 306 (M^+, 2%), 232 (25), 217 (100), 135 (16), and 73 (18).

(*E*)-4-(*tert*-Butyldiphenylsilyl)-4-(trimethylsilyl)but-3-en-2-one (21): by *tert*-butyldiphenylsilyl-cupration of 4-(trimethylsilyl)-3-butyn-2-one **20** and quenching of the vinylcopper intermediate with ammonium chloride solution; yield 42%; R_f = 0.24 (hexane−Et_2O, 20: 1); IR (neat) 1722, 1251, 1113, and 816 cm^{-1};^1H NMR δ 7.74−7.69 (m, 4H), 7.41−7.35 (m, 6H), 6.58 (s, 1H), 2.03 (s, 3H), 1.07 (s, 9H), and 0.16 (s, 9H); ^{13}C NMR δ 217.81, 157.43, 135.87, 135.13, 134.37, 129.63, 127.69, 27.83, 26.52, 19.98, and 0.31; MS (EI) *m*/*z* 380 (M^+, 2%), 323 (24), 208 (5), 199 (100), 183 (12), 177 (59), and 43 (45). Anal. Calcd for $C_{23}H_{32}OSi_2$: C, 72.57; H, 8.47. Found: C, 72.31; H, 8.53.

(*E*)-1-(*tert*-Butyldiphenylsilyl)-3-hydroxy-3-phenyl-2-(trimethylsilyl)prop-1-ene (4i). The title compound was prepared by metal-iodine exchange of **4d** and reaction of the lithiated intermediate with benzaldehyde. A solution of **4d** (6 mmol) in THF (16 mL) was cooled at −78°C. BuLi (6 mmol) was added, and the mixture stirred under nitrogen for 30 min. Benzaldehyde (6 mmol) was then added at −78°C and the reaction progress monitored by TLC while the temperature was slowly warmed to 0 °C. After the reaction was complete, the mixture was hydrolyzed at 0 °C with aqueous ammonium chloride, extracted with ether, dried ($MgSO_4$), and chromatographed to give the alcohol **4i** (2.21 g; 83%); R_f = 0.54 (hexanes−Et_2O, 10:1); IR (neat) 3400, 1590, 1250, 1115, and 835 cm^{-1};^1H NMR δ 7.71−7.62 (m, 4H), 7.44−7.38 (m, 6H), 7.27−7.24 (m, 3H), 7.17−7.14 (m, 2H), 6.80 (d, *J* = 2.2 Hz, 1H), 5.71 (d, *J* = 2.2 Hz, 1H), 1.08 (s, 9H), 0.95 (s, br, 1H), and −0.08 (s, 9H); ^{13}C NMR δ 172.65, 141.77, 135.50, 135.09, 134.05, 129.42, 129.30, 128.37, 128.21, 127.87, 90.42, 25.95, 19.42, and −1.39; MS (EI) *m*/*z* 444 (M^+, 1%), 309 (100), 231 (19), 193 (32), 73 (28), and 57 (37). Anal. Calcd for $C_{28}H_{36}OSi_2$: C, 75.61; H, 8.16. Found: C, 75.43; H, 7.94.

Metalation of 4g and Reaction with Electrophiles. A THF solution of **4g** was cooled at −78 °C. TMEDA (1.2 equiv) and BuLi (1.2 equiv) were added, and the mixture was stirred for 30 min. Methyl iodide (2 equiv) was then added, and the mixture was slowly allowed to warm to 0 °C and stirred until TLC indicated complete reaction. Ammonium chloride solution was added and the mixture extracted with ether, dried ($MgSO_4$), and chromatographed to give (*E*)-1-(*tert*-butyldiphenylsilyl)-2-(trimethylsilyl)prop-1-ene **4a** (62%). The vinyldisilane **4a** (1 mmol), aluminum trichloride (1 mmol), and chloromethyl methyl ether (1 mmol) were stirred in dichloromethane (20 mL) at 0 °C for 90 min. The mixture was hydrolyzed with aqueous ammonium chloride, and the organic layer washed with a sodium hydrogen carbonate solution and brine, dried, and chromatographed to give (*E*)-1-(*tert*-butyldiphenylsilyl)-2-(methoxymethyl)prop-1-ene **5** (58%); R_f = 0.47 (hexane); IR (CCl_4) 1635, 1100, 1060 cm^{-1}; ^1H NMR δ 7.70−7.61 (m, 4H), 7.43−7.36 (m, 6H), 6.13 (s, 1H), 3.87 (s, 2H), 3.39 (s, 3H), 1.43 (s, 3H), and 1.02 (s, 9H); ^{13}C NMR δ 161.72, 136.21, 135.13, 129.08, 127.54, 124.67, 82.40, 58.15, 27.69, 22.41, and 18.02; MS (EI) *m*/*z* 324 (M^+, 2%), 267 (72), 235 (18), 105 (100), 59 (61), and 45 (32).

Acknowledgment. We thank Dr. Daniel Miguel (Universidad de Valladolid, Spain) for the X-ray structure determination of compound **4c**. This work was supported by the Junta de Castilla y León of Spain (Grant VA 73/99).

Supporting Information Available: ORTEP diagram, tables of X-ray crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0010983