Reactions of Allenyltri-*n*-butylstannane with Halides of Phosphorus, Arsenic, Antimony, Germanium, Tin, and Boron. Preparation of Propargylic and/or Allenic Derivatives

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The reaction of allenyltri-*n*-butylstannane with a phosphorus or arsenic trihalide and with germanium tetrachloride gave the corresponding propargylic halophosphine, arsine, or germane. When they were heated, the propargylic products partially (P, Ge) or completely (As) rearranged into the corresponding allenyl derivatives, the thermodynamic products. The allenic or propargylic stannane reacted with stronger Lewis acidic halides such as a boron halide, antimony trichloride, or tin tetrachloride to give only the allenic product, even when the reaction was performed and analyzed at low temperature (−80 °C). The propargylic intermediate was observed with the antimony and tin compounds when a substituted derivative (e. g. Vi_2SbCl, $ViSnCl_3$) was used. The reduction of the propargylic halide products prior to their isomerization gave the corresponding primary propargylic phosphine, arsine, germane, and stannane.

Introduction

In the past two decades, numerous homopropargylic alcohols and amines or their corresponding homoallenic isomers have been prepared by reaction of allenic stannanes with aldehydes or imines, respectively, in the presence of various Lewis acids.[1,2] Some mechanistic studies have been carried out,[3] but little has been done to characterize the products formed by reaction of an allenic stannane with a Lewis acidic element halide. Here we report the preparation of several propargylic compounds of phosphorus, arsenic, germanium, and tin by reaction of the propadienyltri-*n*-butylstannane with halides of these elements. The rearrangement of the products to the corresponding allenyl derivatives was studied. The reactivity of such compounds thus formed with benzaldehyde as well as the reduction of the propargylic element halides to the corresponding hydrides is also described.

Results and Discussion

Allenic stannanes $R_3SnCH{=}C{=}CH_2$ could have had a similar reactivity to that of α,β-unsaturated stannanes (vinylic derivatives)[4] or β,γ-unsaturated stannanes (allylic derivatives).[5] The answer was given by the reaction of propadienyltri-*n*-butylstannane (**1a**) with weak Lewis acidic halides. At room temperature, the reaction of stannane **1a** with phosphorus tribromide gave propargyldibromophosphine (**2a**) in 73% yield.[6] Small amounts of allenyldibromophosphine (**3a**; ∼10%) were observed after the crude mixture was heated for 2 h at 120 °C. The reaction of a mixture of arsenic trichloride and stannane **1a** at −20 °C gave propargyldichloroarsine (**2b**) in 85% yield.[7] The rearrangement in $CDCl_3$ of arsine **2b** in the allenylarsine **3b** occurred within a few hours at room temperature in 95% yield.[8] However, in the reaction of $SbCl_3$ with stannane **1a**, propargyldichlorostibine (**2c**) was not obtained, even when the reaction was carried out in CD_2Cl_2 and analyzed by ^1H NMR spectroscopy at −80 °C. Crude allenyldichlorostibine (**3c**) was formed in 33% yield.[8] A monochloro derivative, divinylchlorostibine (**4**),[8] reacted with stannane **1a** in $CDCl_3$ to give divinyl-2-propargylstibine (**2d**) in 87% yield. A distilled solution of **2d** very slowly rearranged at room temperature to give divinylallenylstibine (**3d**) in 90% yield (Scheme 1).[9,10]

(1) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987; pp 130−256.
(2) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
(3) (a) Marshall, J. A.; Perkins, J. *J. Org. Chem.* **1994**, *59*, 3509. (b) Yamamoto, Y.; Shida, N. *Adv. Detailed React. Mech.* **1994**, *3*, 1. (c) Marshall, J. A.; Perkins, J. F.; Wolf, M. A. *J. Org. Chem.* **1995**, *60*, 5556.
(4) (a) Guillemin, J.-C.; Lassalle, L. *Organometallics* **1994**, *13*, 1525. (b) Guillemin, J.-C.; Lassalle, L.; Dréan, P.; Wlodarczak, G.; Demaison, J. *J. Am. Chem. Soc.* **1994**, *116*, 8930. (c) Legoupy, S.; Lassalle, L.; Guillemin, J.-C.; Métail, V.; Sénio, A.; Pfister-Guillouzo, G. *Inorg. Chem.* **1995**, *35*, 1466. (d) Lassalle, L.; Legoupy, S.; Guillemin, J.-C. *Organometallics* **1996**, *15*, 3466. (e) Janati, T.; Guillemin, J.-C.; Soufiaoui, M. *J. Organomet. Chem.* **1995**, *486*, 57. (f) Lassale, L.; Janati, T.; Guillemin, J.-C. *J. Chem. Soc. Chem. Commun.* **1995**, 699.
(5) (a) Le Serre, S.; Guillemin, J.-C. *Organometallics* **1997**, *16*, 5844. (b) Le Serre, S.; Guillemin, J.-C.; Karpati, T.; Soos, L.; Nyulászi, L.; Veszprémi, T. *J. Org. Chem.* **1998**, *63*, 59.
(6) PBr_3 gave better results and higher yields than PCl_3. Several allenylhalophosphines or propargylic monohalophosphines have been prepared by other approaches. See for example: Simonnin, M.-P.; Charrier, C. *C. R. Acad. Sci. Paris, Ser. C* **1968**, *267*, 550.
(7) The presence of small amounts (3%) of allenyldichloroarsine (**3b**) in arsine **2b** cannot be avoided.
(8) The allenyldichloroarsine has been prepared previously by the same approach, but without identification of the propargylarsine **2b** intermediate. Lassalle, L.; Legoupy, S.; Guillemin, J.-C. *Inorg. Chem.* **1995**, *35*, 5694.

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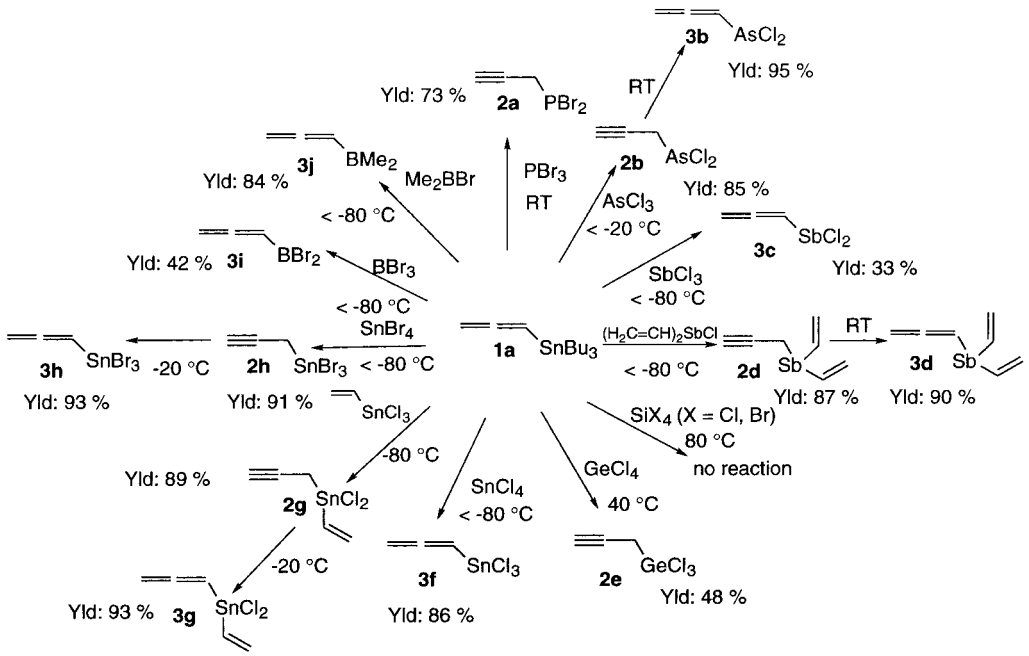
Scheme 1



The reactivity of stannane **1a** with group 14 element halides increases from silicon to tin halides. No reaction was observed between compound **1a** and $SiCl_4$ or $SiBr_4$ even at 80 °C. Propargyltrichlorogermane (**2e**) was prepared in 48% yield by reaction of $GeCl_4$ with stannane **1a** at 40 °C. Heating of germane **2e** at 120 °C for some hours led only to very small amounts of allenyltrichlorogermane (**3e**).[11] However, propargylgermane **2e** was obtained together with about 1% of germane **3e**, even starting from very pure stannane **1a**. As the temperature of the reaction is substantially lower than the temperature of isomerization, we can conclude that the formation of the propargylic compound occurs via an allenyl-propargyl transposition with more than 99% selectivity.

The reaction at −80 °C of $SnCl_4$ with stannane **1a** in CD_2Cl_2 gave allenyltrichlorostannane (**3f**)[4f] in 86% yield, as determined by low-temperature NMR spectroscopy. Propargyltrichlorostannane was not detected. On the other hand, vinyltrichlorostannane (**5**) reacted in CD_2Cl_2 with stannane **1a** at a temperature lower than −80 °C to give vinylpropargyldichlorostannane (**2g**) in 89% yield. At −20 °C, the isomerization of **2g** gave the corresponding allenyl derivative **3g** in 93% yield. Similarly, at −80 °C, stannane **1a** and tin tetrabromide in CD_2Cl_2 reacted to give propargyltribromostannane (**2h**) in 89% yield. It slowly rearranged around −20 °C to allenyltribromostannane (**3h**).

Boron trihalides are strong Lewis acidic species, and their addition to the carbon−carbon multiple bonds of allenes or alkynes occurs easily[12] and makes it difficult to effect clean exchange reactions. However, stannane **1a** in CD_2Cl_2 reacted with BBr_3 at a temperature lower than −80 °C to give allenyldibromoborane (**3i**), which was separated from *n*-Bu_3SnBr by codistillation with the solvent. Compound **3i** has low stability at room temperature, similar to allyldibromoborane,[5a] and is much less stable than vinylic dibromoboranes.[13] The addition of dimethylbromoborane to an excess of stannane **1a** gave allenyldimethylborane (**3j**) in 84% yield. Even when the reaction was performed at −80 °C in an NMR tube, propargyldimethylborane (**2j**) was not observed.[14] In the case of boron halides, we were not able to demonstrate the formation of a propargylborane intermediate.

Allenyl compounds **3a**−**j** also were prepared by reaction of the corresponding halide with propargyltriphenylstannane (**6**).[15] Yields ranged from 13 to 93% (Scheme 2). Partial rearrangement of propargylstannane **6** to the corresponding allenyltriphenylstannane (**1b**) was observed in the presence of weak Lewis acidic halides (PX_3, $GeCl_4$), and thus, mixtures of allenyl- and propargylphosphines or allenyl- and propargylgermanes, respectively, in low yields, resulted in reactions with stannanes **6** and **1b**. However, the reaction of compound **6** with stronger Lewis acidic halides ($AsCl_3$, $H_2C{=}CHSnCl_3$ **5**, SnX_4, BCl_3, ...) gave the allenic products **3b**,**f**−**j** exclusively in good yield. The propargylic derivatives **2b**,**g**,**h**, stable under the experimental conditions, were not observed, thus proving that the exchange reaction only occurs via a transposition reaction.

(9) The presence of small amounts (1−3%) of the propargylic isomer are observed in almost all the allenyl compounds.

(10) The preparation of a few pentavalent propargylstibines has been reported: Zhang, L.-J.; Mo, X.-S.; Huang, Y.-Z. *J. Organomet. Chem.* **1994**, *471*, 77. To our knowledge, compound **2d** is the first trivalent propargylstibine described to date.

(11) The preparation of compounds **2e** and **3e** has been reported: (a) Mironov, V. F.; Gar, T. K. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, 291. (b) Gar, T. K.; Nosova, V. M.; Kisin, A. V.; Mironov, V. F. *Zh. Obshch. Khim.* **1978**, *48*, 838.

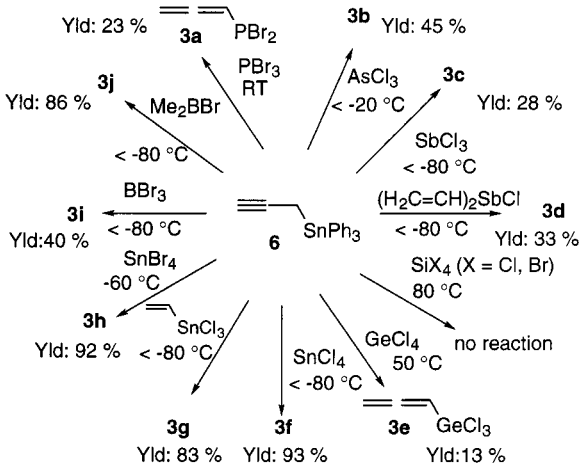
(12) Vaultier, M.; Carboni, B. Boron. *Comprehensive Organometallic Chemistry II*; Elsevier: Oxford, New York, Tokyo, 1995; Vol. 11, Chapter 5, pp 191−276.

(13) Hall, L. W.; Odom, J. D.; Ellis, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 4527.

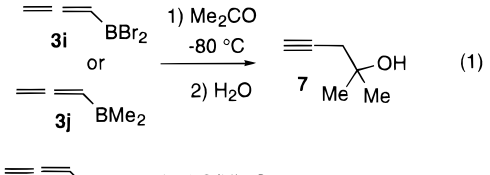
(14) An equilibrium between nonisolated allenyl- and propargylborane has already been proposed, but the latter was considered to be the thermodynamic product: (a) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1978**, *100*, 5561. (b) Zweifel, G.; Pearson, N. R. *J. Org. Chem.* **1981**, *46*, 829.

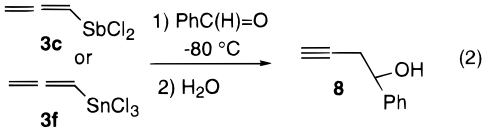
(15) Le Quan, M.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1965**, 45.

Scheme 2



The reactivity of propargylic and allenic compounds **2** and **3** with electrophiles is dependent on the heteroatom and the other substituents. As an example, reactions of boranes **3i**,**j** with acetone gave, after hydrolysis of the reaction mixture, 4-methyl-1-pentyn-4-ol (**7**)[16,17] (eq 1). At −78 °C, reactions of benzaldehyde with





stannane **1a** and compounds **3c**,**f**[18] gave the homopropargylic alcohol **8**[16] (eq 2). Under similar conditions, but using $SnBr_4$ or vinyltrichlorostannane **5** as the halide, the reaction occurred only at a temperature higher than −40 °C. At room temperature and after several hours of stirring, no product was observed in attempted reactions of benzaldehyde with compounds **2a**,**b**,**e**, **3a**,**b**,**e**, and stannane **1a**.

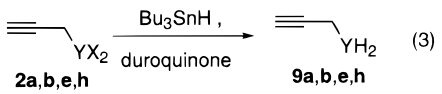
The formation of homoallenyl alcohols occurs when moderately strong Lewis acidic halides (**5**, $SnBr_4$, $BuSnCl_3$[19]) are used. With these Lewis acidic halides, the propargylic tin halide product, easily observed at low temperature, reacts with the electrophile at a temperature lower than that of isomerization. However, such trapping reactions have been performed using a stronger Lewis acidic halide such as $SnCl_4$ but at a lower temperature (−78 °C) and using allenylstannanes substituted on the C═C bonds;[19] the steric hindrance due to the presence of substituents inhibits the isomerization of the primary product.

$$BCl_3 > Me_2BBr \approx SbCl_3 > SnCl_4 > SnBr_4 \geq RSnCl_3 > AsCl_3 > R_2SbCl > GeCl_4 \approx PBr_3 > SiX_4$$

Figure 1.

The strong correlation between the temperature of reaction of Lewis acidic halides with stannanes **1a** and **6**, the temperature of rearrangement of the propargylic product in the allenyl derivative, and the chemical reactivity with electrophiles gives a new scale for the strength of Lewis acids (Figure 1). The major difference between this scale and the ones reported in the literature[20] is the particular role played by the Lewis acidic halides of group 15. In our approach, PCl_3 is more acidic than $SiCl_4$ or $SiBr_4$, $AsCl_3$ more so than $GeCl_4$, and $SbCl_3$ more so than any tin halide.[21] This scale is also consistent with reactions involving Lewis acidic halides and allylic stannanes[5] and corroborates postulated mechanisms reported elsewhere.[22]

The selective preparation of propargyl halo compounds (**2a**,**b**,**e**,**h**) in reactions of weak Lewis acidic halides provides a short route to the corresponding primary propargyl derivatives. Using Bu_3SnH in the presence of small amounts of duroquinone (a radical inhibitor),[23] we prepared the primary propargylphosphine **9a**,[24] arsine **9b**, germane **9e,** and stannane **9h** (eq 3). The latter was only obtained from a reaction with



2a: Y = P, X = Br, **2b**: Y = As, X = Cl,
2e: Y = GeCl, X = Cl, **2h**: Y = SnBr, X = Br
9a: Y = P, **9b**: Y = As, **9e**: Y = GeH, **9h**: Y = SnH

tribromostannane **2h** and the presence of the isomeric allenylstannane (∼30%) cannot be avoided. Compound **2h** can thus be considered as the strongest Lewis acidic halide that can be reduced using this approach before its isomerization. The yields of **9a**,**b**,**e**,**h** ranged from 22 to 78%. Arsine **9b**, in $CDCl_3$ solution, exhibited low stability at room temperature ($\tau_{1/2} \approx 3$ h), while solutions of compounds **9a**,**e**,**h** are stable under similar conditions. Only yellow-brown decomposition products were observed when **9b** was warmed to room temperature.

Conclusion

We have shown that the reaction of weak to moderately strong Lewis acidic halides with the allenyltri-*n*-butylstannane leads only to the corresponding propargylic derivative, the kinetic product via a transposition

(16) Compounds **7** and **8** have been identified by comparison with authentic samples. **7**: Gerard, F.; Miginiac, P. *J. Organomet. Chem.* **1976**, *111*, 17. **8**: Mondon, A. *Justus Liebigs Ann. Chem.* **1952**, *577*, 181.

(17) For the reaction of 9-allenyl-9-BBN with ketones see: Brown, H. C.; Khire, U. R.; Racheria, U. S. *Tetrahedron Lett.* **1993**, *34*, 15.

(18) The use of $SnCl_4$ in such reactions has been reported previously. See for example refs 1−3.

(19) *n*-$BuSnCl_3$ has been used as a Lewis acid to selectively prepare homoallenic alcohols: (a) Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995**, *60*, 5550. (b) Marshall, J. A.; Palovich, M. R. *J. Org. Chem.* **1997**, *62*, 6001.

(20) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(21) The effectiveness of antimony or bismuth halides as Lewis acids has already been reported previously; see for example: (a) Komatsu, N.; Uda, M.; Suzuki, H.; Takahashi, T.; Domae, T.; Wada, M. *Tetrahedron Lett.* **1997**, *38*, 7215. (b) Le Roux, C.; Mandrou, S.; Dubac, J. *J. Org. Chem.* **1996**, *61*, 3885.

(22) See for example: Masuyama, Y.; Ito, A.; Terada, K.; Kurusu, Y. *Chem. Commun.* **1998**, 2025.

(23) Numerous primary α,β-unsaturated compounds have been prepared using this reagent. See ref 4.

(24) Propargylphosphine **9a** can be synthesized by the reaction of $LiAl(PH_2)_4$ with propargyl bromide: Shay, R. H.; Diel, B. N.; Schubert, D. M.; Norman, A. D. *Inorg. Chem.* **1988**, *27*, 2378.

reaction. This latter species rearranges to the allenic isomer (the thermodynamic product) at a temperature dependent on this Lewis acid. This approach allows the synthesis of numerous propargylic derivatives. The reactivity and stability of propargylic or allenic heterocompounds can be attributed to a large interaction between the $C_\gamma C_\beta$ multiple bond and carbon−heteroatom bonds. Consequently, the allenic derivatives exhibit properties similar to those of allylic derivatives and not at all like those of α,β-unsaturated compounds.

The chemoselective reduction of these propargylic derivatives, before their isomerization, opens a general route to the synthesis of low-boiling primary propargylic arsines, germanes, and stannanes.

Experimental Section

General Considerations. ^{1}H (400 MHz), ^{31}P (125 MHz), and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker ARX400 spectrometer and ^{11}B NMR (96.3 MHz) or ^{119}Sn NMR (112 MHz) on a Bruker AC 300C spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (^{1}H) or to solvent (^{13}C, $CDCl_3$, δ 77.0 ppm), external Me_4Sn for ^{119}Sn NMR spectra, external H_3PO_4 for ^{31}P NMR spectra, and external $BF_3{\cdot}Et_2O$ for ^{11}B NMR spectra. The NMR spectra were recorded using $CDCl_3$ or CD_2Cl_2 as solvent. High-resolution mass spectra (HRMS) were obtained on a Varian MAT 311 instrument. To record the mass spectra, the propargylarsine **9b**, germane **9e**, and stannane **9h** were directly introduced from a cooled cell into the ionization chamber of the spectrometer. The yields and half-lives ($\tau_{1/2}$) of the unstabilized derivatives were determined by ^{1}H NMR with an internal reference. The spectroscopic characterization of compounds **3b**,[8] **3c**,[8] **3f**,[4f] **4**,[8] and **5**[4e] has been reported previously.

General Procedure for the Reaction of Stannane 1a with Lewis Acidic Halides. Into a two-necked flask equipped with a nitrogen inlet and a magnetic stirring bar, the Lewis acid (1 mmol) and 5 mL of CH_2Cl_2 were introduced. The flask was immersed in a cold bath (PBr_3, $AsCl_3$, and $GeCl_4$ at −20 °C; **4**, **5**, $SnCl_4$, Me_2BBr, and BCl_3 at −80 °C) and propadienyltri-*n*-butylstannane (**1a**; 1 equiv) in CH_2Cl_2 (2 mL) was slowly added. The mixture was stirred for 10 min (mixtures containing PBr_3 or $GeCl_4$ were stirred for 20 min at 40 °C). The flask was then fitted on a vacuum line and the product purified by trap-to-trap distillation at 0.1 mbar into a receiver at −30 °C.

With high-boiling Lewis acidic halides (antimony halides) or when the propargylic isomer was not observed after distillation (stannanes, boranes), the reaction was performed at −90 °C in an NMR tube using CD_2Cl_2 as solvent. The sample was analyzed by low-temperature (−90 °C) NMR spectroscopy. Thus, compounds **2g**,**h** were observed.

The allenyl derivatives **3d**,**g**−**j** were prepared by a similar procedure. The corresponding Lewis acidic halide was reacted with stannane **1a** or **6**. Phosphine **3a** and germane **3e** were prepared by reacting PBr_3 and $GeCl_4$, respectively, with stannane **6** at room temperature, followed by 2 h of stirring at 120 °C. Purification of **3a**,**d**,**e**,**f**−**j** was performed by distillation.

Propargylic Compounds 2a,b,d,e,g,h. Propargyldibromophosphine (2a). Yield: 168 mg (73%). Bp: 32 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$, room temperature): δ 2.39 (dt, 1H, $^4J_{PH}$ = 5.2 Hz, $^4J_{HH}$ = 2.8 Hz, CH_2); 3.59 (dd, 2H, $^2J_{PH}$ = 16.1 Hz, $^4J_{HH}$ = 2.8 Hz, CH). ^{13}C NMR ($CDCl_3$, room temperature): δ 30.6 (dt, $^1J_{CH}$ = 147.9 Hz, $^2J_{CP}$ = 48.0 Hz, CH_2); 73.8 (dd, $^1J_{CH}$ = 252.9 Hz, $^3J_{CP}$ = 7.8 Hz, CH); 76.8 (dd, $^2J_{CP}$ = 11.5 Hz, $^2J_{CH}$ = 49.9 Hz, HC≡*C*). ^{31}P NMR ($CDCl_3$): δ 164.1 (t, $^2J_{PH}$ = 16.1 Hz). HRMS: *m*/*z* calcd for $C_3H_3P^{79}Br_2$: 227.8339, found: 227.835. MS: *m*/*z* (%) 232 (11.5), 230 (23.1), 228 (11.9), 193 (45.1) $[PBr_2]^+$, 191 (97.7) $[PBr_2]^+$, 189 (46.0) $[PBr_2]^+$, 151 (77.1) $[C_3H_3PBr]^+$, 149 (79.0) $[C_3H_3PBr]^+$, 69 (100) $[C_3H_2P]^+$.

Propargyldichloroarsine (2b). Yield: 85%. At room temperature, compound **2b** slowly isomerized in **3b**. $\tau_{1/2}$ (5% in $CDCl_3$, room temperature): 3 h. Bp: 30 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$, −30 °C): δ 2.41 (t, 1H, $^4J_{HH}$ = 2.8 Hz, CH); 3.31 (d, 2H, $^4J_{HH}$ = 2.8 Hz, CH_2). ^{13}C NMR ($CDCl_3$, −30 °C): δ 32.6 (t, $^1J_{CH}$ = 144.7 Hz, CH_2); 74.4 (d, $^1J_{CH}$ = 253.2 Hz, CH); 75.8 (d, $^2J_{CH}$ = 51.1 Hz, HC≡*C*). HRMS: *m*/*z* calcd for $C_3H_3As^{35}Cl_2$, 183.8828; found, 183.883. MS: *m*/*z* (%) 186 (11.2), 184 (16.9), 149 (31.2) $[C_3H_3AsCl]^+$, 148 (27.3) $[C_3H_2AsCl]^+$, 147 (26.5) $[AsCl_2]^+$, 145 (46.6) $[AsCl_2]^+$, 113 (28.4) $[C_3H_2As]^+$, 39 (100) $[C_3H_3]^+$.

Propargyldivinylstibine (2d). Yield: 87%. Purity: >90%, contained 5−10% of stibine **3d**. At room temperature, compound **2d** slowly isomerized to **3d**. $\tau_{1/2}$ (5% in $CDCl_3$, room temperature): 12 h. Bp: ∼−50 °C (0.1 mmHg). ^{1}H NMR (CD_2Cl_2, −30 °C): δ 2.05 (t, 1H, $^4J_{HH}$ = 2.9 Hz, HC≡); 2.19 (d, 2H, $^4J_{HH}$ = 2.9 Hz, CH_2Sb); 5.87 (d, 1H, $^3J_{HHtrans}$ = 19.6 Hz, *H*CH=); 6.27 (d, 1H, $^3J_{HHcis}$ = 12.3 Hz, HC*H*=); 6.94 (dd, 1H, $^3J_{HHtrans}$ = 19.6 Hz, $^3J_{HHcis}$ = 12.3 Hz, CH=). ^{13}C NMR (CD_2Cl_2, −30 °C): δ 2.80 (t, CH_2); 68.9 (d, $^1J_{CH}$ = 248.7 Hz, H*C*≡C); 82.9 (d, $^2J_{CH}$ = 50.0 Hz, HC≡*C*); 133.6 (t, $^1J_{CH}$ = 157.5 Hz, HC=*C*H_2); 136.4 (d, $^1J_{CH}$ = 157.0 Hz, H*C*=CH_2).

Propargyltrichlorogermane (2e).[11a] Yield: 105 mg (48%). ^{1}H NMR ($CDCl_3$): δ 2.33 (t, 1H, $^4J_{HH}$ = 2.9 Hz, CH); 2.93 (d, 2H, $^4J_{HH}$ = 2.9 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 20.9 (t, $^1J_{CH}$ = 141.0 Hz, CH_2), 73.0 (d, $^2J_{CH}$ = 51.1 Hz, HC≡*C*); 73.7 (d, $^1J_{CH}$ = 254.0 Hz, CH).

Vinylpropargyldichlorostannane (2g). Yield: 89% (crude). Around −20 °C, compound **2g** slowly isomerized to **3g**. $\tau_{1/2}$ (5% in CD_2Cl_2, −15 °C): 15 min. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 2.26 (t, 1H, $^4J_{HH}$ = 2.9 Hz, $^4J_{SnH}$ = 50.8 Hz (d), CH); 2.70 (d, 2H, $^4J_{HH}$ = 2.9 Hz, $^2J_{SnH}$ = 88.8 Hz (d), CH_2); 6.20 (d, 1H, $^3J_{HHtrans}$ = 19.2 Hz, HC*H*=); 6.48 (d, 1H, $^3J_{HHcis}$ = 12.0 Hz, *H*CH=); 6.59 (dd, 1H, $^3J_{HHtrans}$ = 19.2 Hz, $^3J_{HHcis}$ = 12.0 Hz, HC=). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 14.5 (t, $^1J_{CH}$ = 141.9 Hz, $^1J_{SnC}$ = 518.6 Hz (d), CH_2); 75.4 (d, $^1J_{CH}$ = 252.3 Hz, $^2J_{SnC}$ = 108.6 Hz (d), CH); 76.3 (d, $^1J_{CH}$ = 51.2 Hz, $^3J_{SnC}$ = 86.2 Hz (d), C≡*C*); 134.2 (d, $^1J_{CH}$ = 170.3 Hz, $^1J_{SnC}$ = 733.1 Hz (d), =CH); 140.2 (t, $^1J_{CH}$ = 161.3 Hz, =CH_2). ^{119}Sn NMR ($CDCl_3$, −50 °C): −13.2.

Propargyltribromostannane (2h). Yield: 91% (crude). Around −20 °C, compound **2h** slowly isomerized into **3h**. $\tau_{1/2}$ (5% in CD_2Cl_2, −15 °C): 15 min. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 2.59 (t, 1H, $^4J_{HH}$ = 2.9 Hz, $^4J_{SnH}$ = 85.5 Hz (d), CH); 3.24 (d, 2H, $^4J_{HH}$ = 2.9 Hz, $^2J_{SnH}$ = 95.9 Hz (d), CH_2). ^{13}C NMR (CD_2Cl_2, −60 °C): δ 20.9 (t, $^1J_{CH}$ = 148.6 Hz, $^1J_{SnC}$ = 597.2 Hz (d), CH_2); 75.4 (d, $^1J_{CH}$ = 254.4 Hz, $^3J_{SnC}$ = 73.4 Hz (d), CH); 76.6 (s, $^2J_{SnC}$ = 100.0 Hz (d), C≡*C*). ^{119}Sn NMR ($CDCl_3$, −50 °C): δ −202.7.

Allenic Compounds 3a,d,e,g−j. Allenyldibromophosphine (3a). Yield: 53 mg (23%). Bp: 30 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$, room temperature): δ 5.30 (dd, 2H, $^4J_{PH}$ = 6.6 Hz, $^4J_{HH}$ = 3.3 Hz, CH_2); 6.45 (dt, 1H, $^2J_{PH}$ = 10.6 Hz, $^4J_{HH}$ = 3.3 Hz, CH). ^{13}C NMR ($CDCl_3$, room temperature): δ 78.1 (td, $^1J_{CH}$ = 171.0 Hz, $^3J_{CP}$ = 9.7 Hz, CH_2); 92.3 (dd, $^1J_{CH}$ = 181.6 Hz, $^1J_{CP}$ = 59.3 Hz, HC); 209.9 (d, $^2J_{CP}$ = 11.2 Hz, C=*C*=C). ^{31}P NMR ($CDCl_3$): δ 148.0 (d, $^2J_{PH}$ = 10.6 Hz). HRMS: *m*/*z* calcd for $C_3H_3PBr_2$, 227.8339; found, 227.834.

Allenyldivinylstibine (3d). Yield: 92% (starting from **2d**). Bp: ∼−50 °C (0.1 mmHg). ^{1}H NMR (CD_2Cl_2, room temperature): δ 4.40 (d, 2H, $^4J_{HH}$ = 6.8 Hz, H_2C=C=C); 5.40 (d, 1H, $^4J_{HH}$ = 6.8 Hz, C=C=CH); 5.82 (d, 1H, $^3J_{HHtrans}$ = 19.5 Hz, *H*CH=); 6.21 (d, 1H, $^3J_{HHcis}$ = 12.2 Hz, HC*H*=); 6.82 (dd, 1H, $^3J_{HHtrans}$ = 19.5 Hz, $^3J_{HHcis}$ = 12.2 Hz, =CH). ^{13}C NMR ($CDCl_3$): δ 67.8 (t, $^1J_{CH}$ = 168.1 Hz, CH_2=C=C); 74.4 (d, $^1J_{CH}$ = 173.1 Hz, CH_2=C=*C*H); 132.9 (t, $^1J_{CH}$ = 156.8 Hz, CH=*C*H_2); 133.5 (d, $^1J_{CH}$ = 158.1 Hz, H*C*=CH_2); 209.2 (s, C=*C*=C).

Allenyltrichlorogermane (3e).[11b] Yield: 13% (contained germane **2e**). ^{1}H NMR ($CDCl_3$): 5.15 (t, 1H, $^4J_{HH}$ = 6.9 Hz,

CH); 5.63 (t, 2H, $^4J_{HH}$ = 6.9 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 76.9 (t, $^1J_{CH}$ = 171.0 Hz, CH_2); 84.3 (d, $^1J_{CH}$ = 183.1 Hz, CH); 212.9 (s, C=*C*=C).

Allenylvinyldichlorostannane (3g). Yield: 228 mg (93%) (starting from **2g**). Bp: 44 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 4.85 (d, 2H, $^4J_{HH}$ = 6.6 Hz, C=C=CH_2); 5.50 (t, 1H, $^4J_{HH}$ = 6.6 Hz, HC=C=C); 6.18 (d, 1H, $^3J_{HHtrans}$ = 19.3 Hz, *H*CH=C−Sn); 6.47 (d, 1H, $^3J_{HHcis}$ = 11.2 Hz, *H*CH=CH−Sn); 6.53 (dd, 1H, $^3J_{HHtrans}$ = 19.3 Hz, $^3J_{HHcis}$ = 11.2 Hz, H_2C=C*H*−Sn). ^{13}C NMR ($CDCl_3$): δ 71.7 (t, $^3J_{CSn}$ = 101 Hz, C=C=*C*H_2); 79.9 (d, $^1J_{CSn}$ = 753 Hz, *C*=C=CH_2); 133.3 (d, H_2C=*C*H−Sn); 140.0 (t, $^2J_{CSn}$ = 69.4 Hz, H_2C=*C*−Sn); 212.9 (s, C=*C*=C). ^{119}Sn NMR ($CDCl_3$): δ −35.7. HRMS: *m*/*z* calcd for $C_5H_5{}^{35}Cl_2{}^{120}Sn$ ($[M - H]^+$), 254.8790; found, 254.879.

Allenyltribromostannane (3h). Yield: 329 mg (93%) (starting from **2h**). Bp: 48 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 5.16 (d, 2H, $^4J_{HH}$ = 6.7 Hz, $^4J_{SnH}$ = 120.1 Hz (d), CH_2); 5.82 (t, 1H, $^4J_{HH}$ = 6.7 Hz, $^2J_{SnH}$ = 151.4 Hz (d), CH). ^{13}C NMR ($CDCl_3$): δ 75.6 (t, $^1J_{CH}$ = 171.2 Hz, $^3J_{SnC}$ = 151.6 Hz (d), CH_2); 83.7 (d, $^1J_{CH}$ = 190.5 Hz, $^1J_{SnC}$ = 937.2 Hz (d), CH); 209.1 (s, $^2J_{SnC}$ = 57.5 Hz (d), C=*C*=C). ^{119}Sn NMR ($CDCl_3$): δ −251. HRMS: *m*/*z* calcd for $C_3H_3{}^{79}Br_3{}^{120}Sn$, 395.6808; found, 395.677.

Allenyldibromoborane (3i). Yield: 42%. Compound **3i** decomposes at room temperature into insoluble brown products. $\tau_{1/2}$ (5% in CD_2Cl_2, room temperature): 20 min. ^1H NMR (CD_2Cl_2, −30 °C): δ 4.90 (d, 2H, $^4J_{HH}$ = 6.4 Hz, CH_2); 5.96 (t, 1H, $^4J_{HH}$ = 6.4 Hz, CH). ^{13}C NMR (CD_2Cl_2, −30 °C): δ 73.1 (t, $^1J_{CH}$ = 170.5 Hz, CH_2); 94−96 (brd, CH); 224.1 (C=*C*=C). ^{11}B NMR (CD_2Cl_2): δ 57.5.

Allenyldimethylborane (3j). Yield: 67 mg (84%). Bp: ∼−65 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 0.82 (s, 6H, CH_3); 4.61 (d, 2H, $^4J_{HH}$ = 6.4 Hz, CH_2); 5.58 (t, 1H, $^4J_{HH}$ = 6.4 Hz, CH). ^{13}C NMR ($CDCl_3$): δ 8.4 (q brd, $^1J_{CH} \approx$ 127 Hz, CH_3); 68.1 (t, $^1J_{CH}$ = 167.9 Hz); 89−92 (brd, CH); 219.1 (s, C=*C*=C). ^{11}B NMR ($CDCl_3$): δ 76.5. HRMS: *m*/*z* calcd for $C_5H_9{}^{11}B$, 80.0797; found, 80.0795.

Reaction of an Allenylborane with Acetone. Solutions of compounds **3i**,**j** (1 mmol) in CH_2Cl_2 (10 mL) were cooled to −78 °C, and solutions of acetone (1 mmol) in CH_2Cl_2 (5 mL) were slowly added. The mixtures were stirred for 10 min at this temperature and then hydrolyzed with saturated aqueous $NaHCO_3$. The 4-methyl-1-pentyn-4-ol (**7**) produced was purified by column chromatography (hexane/ether) and characterized by comparison with an authentic sample.[16] Yields: 45 (**3i**) and 95% (**3j**).

Reaction of Allenylstibine 3c or -stannane 3f with Benzaldehyde. Solutions of compounds **3c**,**f** (1 mmol) in CH_2Cl_2 (10 mL) were cooled to −78 °C, and solutions of benzaldehyde (1 mmol) in CH_2Cl_2 (5 mL) were slowly added. The mixtures were stirred for 2 h at this temperature and then hydrolyzed with saturated aqueous $NaHCO_3$. The 1-phenyl-3-butyn-1-ol (**8**) produced was purified by column chromatography (hexane/ether) and characterized by comparison with an authentic sample.[16] Yields: 53% (**3c**), 78% (**3f**).

Addition of Benzaldehyde to Propargylic Compounds 2a,b,e or Allenic Compounds 3a,b,e. Compounds **2a**,**b**,**e** and **3a**,**b**,**e** (1 mmol) were prepared as reported above and diluted with CH_2Cl_2 (10 mL). A solution of benzaldehyde (1 mmol) diluted with CH_2Cl_2 (5 mL) was slowly added at 0 °C. The mixture was stirred for 2 h at room temperature and then hydrolyzed with saturated aqueous $NaHCO_3$. No product was detected.

General Procedure for the Preparation of the Propargylic Phosphine 9a, Arsine 9b, Germane 9e, or Stannane 9h.

Caution! Primary propargylic phosphine, arsine, germane, and stannane are pyrophoric and potentially highly toxic. All reactions and handling should be carried out in a well-ventilated hood.

The apparatus already described for the reduction of alkynyl- and allenylarsines was used.[4,5b] The flask containing the reducing mixture (20 mmol of Bu_3SnH containing about 5 mg of duroquinone (**2a**,**b**,**h**) or $LiAlH_4$ (20 mmol) in tetraglyme (10 mL) (**2e**)) was cooled to −30 °C, fitted on a vacuum line, and degassed. The pure (**2a**,**e**) or crude and cooled (**2b**,**h**) precursor (1 mmol) in decahydronaphthalene (5 mL) was then added with a short flex needle through the septum. During and after the addition, the product was distilled off in vacuo from the reaction mixture. A cold trap (−70 °C) selectively removed the less volatile products, and compounds **9a**,**b**,**e**,**h** were condensed in a second cold trap (−110 °C) to remove the most volatile products. After revaporization, the pure product was condensed on a cold finger (−196 °C) which was connected at the bottom to a flask or an NMR tube. A cosolvent was added at this step. After it was disconnected from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The product was collected and kept at low temperature (<−40 °C) before analysis. The boiling points of products **9b**,**e**,**h** have been approximately determined (±5 °C) from their temperature of condensation and revaporization in vacuo (0.1 mbar).

Propargylarsine (9b). Yield: 42%. Bp: ∼−85 °C (0.1 mmHg). $\tau_{1/2}$ (5% in $CDCl_3$, room temperature): 3 h. ^1H NMR ($CDCl_3$, −30 °C): δ 2.17 (t, 1H, $^4J_{HH}$ = 2.8 Hz, CH); 2.38 (td, 2H, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 2.8 Hz, CH_2); 2.87 (t, 2H, $^3J_{HH}$ = 6.2 Hz, AsH_2). ^{13}C NMR ($CDCl_3$, −30 °C): δ −0.9 (t, $^1J_{CH}$ = 140.4 Hz, CH_2); 69.0 (d, $^1J_{CH}$ = 249.5 Hz, CH); 84.9 (d, $^2J_{CH}$ = 46.4 Hz, HC≡*C*). HRMS: *m*/*z* calcd for C_3H_5As, 115.9607; found, 115.961. MS: *m*/*z* (%) 116 (32.6), 115 (18.7) $[M - H]^+$, 114 (11.1) $[M - 2H]^+$, 76 (88.2) $[AsH]^+$, 39 (100) $[C_3H_3]^+$.

Propargylgermane (9e). Yield: 78%. Bp: ∼−90 °C (0.1 mmHg). ^1H NMR ($CDCl_3$): δ 1.95 (t, 1H, $^4J_{HH}$ = 2.9 Hz, CH); 1.87 (dq, 2H, $^4J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 3.2 Hz, CH_2); 3.87 (t, 3H, $^3J_{HH}$ = 3.2 Hz, GeH_3). ^{13}C NMR ($CDCl_3$): δ −3.7 (t, $^1J_{CH}$ = 135.3 Hz, CH_2); 67.4 (d, $^1J_{CH}$ = 248.7 Hz, CH); 82.8 (s, $^2J_{CH}$ = 48.6 Hz, HC≡*C*). HRMS: *m*/*z* calcd for C_3H_5Ge $[M - H]^+$, 114.9603; found, 114.959. MS: *m*/*z* (%) 116 (11.8), 115 (36.0) $[M - H]^+$, 74 (71.4) $[Ge]^+$, 72 (55.4) $[Ge]^+$, 39 (100) $[C_3H_3]^+$.

Propargylstannane (9h). Yield: 22% (crude, contained allenylstannane). Bp: −80 °C (0.1 mmHg). ^1H NMR (CD_2Cl_2): 1.87 (qd, 2H, $^4J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 1.9 Hz, $^2J_{SnH}$ = 70.0 Hz, H_2C); 1.94 (t, 1H, $^4J_{HH}$ = 2.9 Hz, HC≡C); 4.90 (t, 3H, $^3J_{HH}$ = 1.9 Hz, SnH_3). ^{13}C NMR (CD_2Cl_2): δ −8.5 (q, CH_3); 67.0 (d, CH); 80.0 (s, *C*≡CH). ^{119}Sn NMR (CD_2Cl_2): δ −313 ($^1J_{SnH}$ = 1972 Hz). HRMS: *m*/*z* calcd for $[M - H]^+$ $(C_3H_5{}^{120}Sn)^+$, 160.9413; found, 160.941.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **2a**,**b**,**d**,**e**,**g**,**h**, **3a**,**d**,**g**−**j**, and **9b**,**e**,**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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