ORGANOMETALLICS

Addition of Organometallic Reagents to a Stable Silene and Germene

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Supporting Information

ABSTRACT: A variety of alkyllithium (R = Me, Bu, *t*-Bu) reagents and potassium *tert*-butoxide were added to the highly reactive silene Mes₂Si=CHCH₂*t*-Bu (1) and the germene Mes₂Ge=CHCH₂*t*-Bu (4) in diethyl ether. 1,2-Addition products were obtained regioselectively and in good yield after treatment with a weak acid with no evidence for any rearrangement products and no polymerization observed. The reactivity of the silene 1 and germene 4 toward organometallic reagents is compared to previous studies of analogous silenes and germenes.



INTRODUCTION

After a quarter century of active research on the synthesis, characterization, and reactivity of silenes^{1,2} applications of this chemistry are now being explored in diverse areas such as organic synthesis,^{1f,3} polymer chemistry,^{4,5} and materials science.^{6,7} Pertinent to these applications is the study of the reactivity of silenes toward organometallic reagents for the purpose of creating new Si–C bonds either to increase functionality in molecular compounds for applications in synthesis or materials chemistry or to initiate anionic polymerizations. However, there are, for the most part, only isolated reports on the addition of organometallic reagents to silenes, and, furthermore, the types of substrates and conditions of the reactions are quite variable.

The reactions of Grignard reagents with stable Brook-type silenes $((Me_3Si)_2Si=(OSiMe_3)R)$ are complicated by the lability of the trimethylsilyl group,⁸ and the addition of MeLi/MgBr or *t*-BuLi to transient 1,1-dialkylsilenes often leads to side products due to loss or migration of hydride.^{9,10} In one instance, Ishikawa was able to isolate the simple products of addition (after hydrolysis of the initially formed organometallic adducts) of 1,1-dialkylsilenes in low yield (20–40%, GPC yields): MeLi (or MeMgBr) added to the transient $Me_2Si=CPh(CH_2SiMe_3)$ regioselectively with the organic group adding to the silicon atom of the silene (Scheme 1).⁹

Scheme 1. Addition of Organometallic Reagents to a Transient 1,1-Dialkylsilene⁹



reagents to silenes to date was reported by Oehme. His group studied the addition of organometallic reagents to transient 1,1bis(trimethylsilyl)silenes ((Me₃Si)₂Si=CR₂), generated by Petersen elimination of the corresponding carbinols upon treatment with organolithium reagents.^{11–15} In most cases, the excess organolithium reagent or the released lithium silanolate adds regioselectively to the silicon of the transient silene to give 1,2-addition products in moderate to good yields after hydrolysis (Scheme 2), although, on occasion, migration of

Scheme 2. Addition of Organometallic Reagents to Transient Bis(silyl)silenes¹¹⁻¹⁵



the silyl substituents was observed.¹⁴ Only a few studies of the addition of organometallic reagents to stable, naturally polarized silenes have been reported. When excess *t*-BuLi was added to 1,1-dimesitylneopentylsilene (Mes₂Si=CHCH₂*t*-Bu, 1)¹⁶ in diethyl ether at 0 °C, quantitative and regioselective formation of Mes₂Si(*t*-Bu)CH₂CH₂*t*-Bu (2) was observed.⁵ Interestingly, at room temperature in diethyl ether, a rearrangement took place to give 3 (Chart 1).⁵ In contrast, the addition of excess *t*-BuLi to 1,1-dimesitylneopentylgermene

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Chart 1



(Mes₂Ge=CHCH₂t-Bu, 4) at room temperature in diethyl ether gave Mes₂Ge(t-Bu)CH₂CH₂t-Bu regioselectively;¹⁷ no evidence for any rearrangement was noted. Alternatively, when t-BuLi (0.1 equiv) was added to silene 1 or germene 4 dissolved in pentane, polymeric material was formed in each case.^{5,18}

Given the potential usefulness of the addition of organometallic reagents to silenes in synthesis and materials chemistry, we wished to examine the reaction under a consistent set of reaction conditions to determine if addition products could reliably be obtained in good yields. Therefore, the addition of a variety of organometallic reagents to the solution-stable silene $Mes_2Si = CHCH_2t$ -Bu, 1, in diethyl ether at room temperature is reported, and, for comparison purposes, we have also examined the addition of the same organometallic reagents to the analogous solution-stable germene, Mes₂Ge=CHCH₂t-Bu, 4. We selected diethyl ether as the solvent since we previously reported that the addition of *t*-BuLi to 1 or 4 in a hydrocarbon solvent, pentane, leads to the formation of polymers,^{5,18} and THF is known to complex with silenes and reduce the rate of addition of alcohols.^{19,20} Given the well-known stability of aryland silvl-substituted silvl (or germyl) anions, we have always been intrigued by the exclusive regioselectivity of the isolated reports on the addition of organometallic reagents to transient and stable silenes and wished to determine if the same regiochemistry persisted with germenes as well. Finally, the addition of t-BuLi to the stable silene 1 has been re-examined in an effort to understand the different chemistry observed at low $(0 \ ^{\circ}C)$ and at room temperature in diethyl ether.

RESULTS AND DISCUSSION

Silene 1^{16} and germene 4^{17} were synthesized by the addition of *t*-BuLi to fluorodimesitylvinylsilane (5) or -germane (6) in diethyl ether in the cold (dry ice/acetone) prior to each reaction and used *in situ* without purification (Scheme 3).

Scheme 3. Preparation of Silene 1 and Germene 4 in Diethyl Ether

Mes ₂ M	< 1 eq. <i>t</i> -BuLi	H
	-78 °C to RT	Mes₂M≓
F	ether	✓ <i>t</i> -Bu
5: M = Si 6: M = Ge		1: M = Si 4: M = Ge

We have improved the overall yield for the synthesis of the precursor germane **6** from approximately $50\%^{17,21}$ to approximately 84% by synthesizing difluorodimesitylgermane, the required starting material for the synthesis of **6**, in one step from dichlorodimesitylgermane using silver tetrafluoroborate rather than in two steps via dimesityldimethoxygermane. Germane **6** is then made from the addition of vinylmagnesium bromide to Mes₂GeF₂ according to the published procedure.¹⁷ As a precaution, slightly less than 1 equiv of *t*-BuLi was used in

the addition of *t*-BuLi to fluorovinylsilane **5** (or -germane **6**) to prevent polymerization of the tetrelene. After addition of the organometallic reagent to the tetrelene and quenching of the reaction mixture with methanol, the products were purified by preparative thin-layer chromatography and characterized by IR and NMR spectroscopy and mass spectrometry.

As previously reported, to prepare Mes₂Si(*t*-Bu)CH₂CH₂*t*-Bu, **2**, the addition of *t*-BuLi to silene **1** was performed in cold diethyl ether (0 °C); however, at room temperature, the isomeric *tert*-butylsilane (**3**) was produced quantitatively (Chart 1).⁵ We reasoned that the initial α -silyl anion, formed by the regioselective addition of *tert*-butyllithium to silene **1**, removed a proton from an *o*-methyl group of the mesityl substituent to form a benzylic anion, followed by a 1,3-silyl shift to form intermediate 7 (Scheme 4). Anion 7 could abstract a hydrogen

Scheme 4. Proposed Mechanism for the Formation of 3



to form the more stable benzvlic. α -silvl-substituted anion 8. To test the validity of the hypothesis and to unequivocally determine the identity of the anion in solution immediately prior to quenching (i.e., 7 or 8), the reaction of silene 1 with excess tert-butyllithium in diethyl ether at room temperature was quenched with D_2O_3 ; silane 3 was isolated with a deuterium at the benzylic position (3D). The ¹H NMR spectrum of 3 contained an AB spin system (I = 15 Hz) at 2.61 and 2.65 ppm, which was assigned to the inequivalent hydrogens of the benzyl moiety.⁵ The AB pattern was not apparent in the ¹H NMR spectrum of 3D, and only a singlet was observed at approximately the same chemical shift (2.65 ppm). The ²H NMR spectrum of 3D also revealed a signal at 2.60 ppm. The results demonstrate that 8 is indeed the anion quenched in the reaction. The strain around silicon is likely the major driving force for the rearrangement. Conversely, the previously reported addition of t-BuLi to germene 4 in diethyl ether at room temperature does not yield any rearrangement products. Undoubtedly, the longer bonds to germanium ease the steric strain around the central metalloid, and thus, the driving force for rearrangement is diminished. We hypothesized that the use of less bulky organometallic reagents, such as MeLi, BuLi, and

even *t*-BuOK, may avoid rearrangement at room temperature by relieving the congestion at silicon in the initially formed anion.

The addition of MeLi, BuLi, or *t*-BuOK to silene 1 or germene 4 in diethyl ether results in the regioselective formation of simple 1,2-addition products, which, after treatment with a weak acid, gave the corresponding silanes 9-11 or germanes 12-14, respectively, in good to excellent yields (Scheme 5). Silanes 9-11 and germanes 12-14 were the *only* products derived from the tetrelenes isolated.

Scheme 5. Addition of Organometallic Reagents to Silene 1 and Germene 4



No rearrangement products were observed in the reactions, in contrast to the addition of organometallic reagents to some 1,1-bis(trimethylsily)silenes^{8,14} or the addition of *t*-BuLi to the same silene (1) at room temperature. The lack of rearrangement in the systems studied here is likely because of the absence of substituents that readily migrate, such as a silyl group. Although the previously reported addition of *t*-BuLi to silene 1 in diethyl ether did result in the formation of a rearranged product (3),⁵ our results now demonstrate that such a rearrangement can easily be avoided by the use of less sterically demanding organometallic reagents, which supports our earlier hypothesis that the driving force of the rearrangement to give 3 is indeed the relief of steric strain about the silicon.

Polysilene or polygermene was not formed in the addition of MeLi, BuLi, or t-BuOK to silene 1 or germene 4, respectively. Some comparative experiments are instructive. The addition of 0.1 equiv of t-BuLi to either the silene or germene in pentane results in the rapid formation of the polysilene,⁵ or -germene,¹⁸ respectively. In preliminary experiments, we have demonstrated that both silene 1 and germene 4 do polymerize under the same conditions in ether, and thus, the solvent does not appear to have much of an influence; however, we have not yet investigated the molecular weight of the polymers formed in ether. We have also added excess t-BuLi to silene 1 and germene 4 in pentane at room temperature and compared the results to those obtained in diethyl ether. For silene 1, where only the rearranged silane 3 is obtained after the addition of methanol in ether at room temperature,⁵ polysilene is the predominate product in pentane, with silane 2 also being present in small amounts.²² For germene 4, both $Mes_2Ge(t-$ Bu)CH₂CH₂t-Bu and polygermene are formed (after quenching) in pentane,²² whereas only $Mes_2Ge(t-Bu)CH_2CH_2t-Bu$ is

formed in ether at room temperature.¹⁷ In these cases, there is clearly an effect of solvent, although a clear understanding of the effect is difficult to discern. The changes observed may be due to the difference in the degree of aggregation of *t*-BuLi in pentane (tetramer) compared to diethyl ether $(dimer)^{23}$ and/ or a change in the energies of key transition states and intermediates along the reaction pathway due to solvation, especially of the initially formed α -silvl (or germyl) lithium species (Scheme 4). Further studies are required to understand the influence of the solvent in these reactions. In the addition of excess MeLi and BuLi to silene 1 or germene 4 in ether, in addition to the factors just mentioned, the use of an anionic reagent with a less bulky organic moiety may also increase the rate of addition of the reagent to the tetrelene relative to the subsequent dimerization (oligomerization), resulting in the lack of polymer formation. These are the kinetics needed to achieve a controlled anionic polymerization, and the use of less bulky anionic initiators in ether for the controlled polymerization of silenes and germenes will be the subject of further research in this laboratory.

In all reports of the addition of organometallic reagents to silenes and germenes, including the results presented in this study, the addition is completely regioselective, with the organometallic reagent adding to the silicon (or germanium) atom. We found the regioselectivity to be somewhat surprising since the reverse regiochemistry would result in the formation of relatively stable diaryl- or bis(silyl)-substituted silyl (or germyl) anions. There have been few mechanistic studies on the addition of nucleophiles to silenes. Water and alcohols have been shown to undergo nucleophilic addition.^{1h,i} Again, the reaction is regioselective, with the nucleophilic moiety adding to the silicon. The bond polarity of the Si=C bond is the most important factor governing the reactivity of the silene and plays a significant role in the regioselectivity of the addition of water and alcohols. For silenes of natural polarity, such as silene 1 or Me₂Si=CPh(CH₂SiMe₃) studied by Ishikawa,⁹ or even silenes of reduced polarity, such as the bis(silyl)-substituted silenes studied by Oehme, ¹¹⁻¹⁵ the regiochemistry might be expected. On the other hand, the complete regioselectivity of the addition of organometallic reagents to Brook silenes $((Me_3Si)_2Si =$ $C(OSiMe_3)R)$, which have reversed polarity, is, at first, surprising. Interestingly, it was noted in the addition of alcohols^{1h} or water²⁴ to silenes that the regiochemistry of the addition is substituent-independent and that the silicon atom is always the most electrophilic atom in the double bond of a range of substituted silenes. Thus, it appears as if the addition of organometallic reagents to silenes follows the same reactivity pattern, although the reaction may be further complicated by the influence of the solvent and the counterion on the nature and aggregation of the organometallic reagent. The same factors appear to govern the regiochemistry of the addition of organometallic reagents toward germenes.

The reactions shown in Scheme 5 are complicated because of the salt elimination method used to make silene 1 and germene 4. It can be difficult to achieve high conversions of fluorosilane 5 to silene 1 or fluorogermane 6 to germene 4 (Scheme 3) while, at the same time, avoiding polymerization of the tetrelenes. Therefore, the presence of residual fluorosilane and -germane in the reaction mixtures is unavoidable, and the amount present is directly related to the degree of conversion achieved in a given reaction. Not surprisingly, the residual fluorosilane and germane also react with the organometallic reagent (MeLi, BuLi, and t-BuOK), added in the second step of the reaction sequence, to give byproducts²⁵ that can be difficult to separate from the products derived from the silene (or germene) because of the similarities in the polarities of the two compounds. To unambiguously identify all possible products, the anticipated byproducts were synthesized directly by treatment of fluorosilane **5** and fluorogermane **6** with MeLi, BuLi, or *t*-BuOK (Scheme 6).

Scheme 6. Reaction of Fluorosilane 5 and Fluorogermane 6 with Organometallic Reagents

Mes ₂ M F	1. RM' ether 2. MeOH	Mes₂M─ ∣ R
5: M = Si 6: M = Ge	R = Me, Bu, <i>t</i> -BuO M' = Li, K	15: M = Si, R = Me 16: M = Ge, R= Me 17: M = Ge, R = Bu 18: M = Ge, R = O <i>t</i> -Bu

Indeed vinylsilane 15 and vinylgermanes 16-18 were present in the crude product mixtures. Vinylgermanes 16 and 17 could not be separated from the products derived from the germene (i.e., 12 and 13); however, in each of the other cases, separation was achieved. Interestingly, in the addition of excess BuLi to silene 1, derived from 5, in diethyl ether, butylhexyldimesitylsilane (19) (Chart 2) was formed in

Chart 2



addition to silane 10. Silane 19 was clearly formed by the reaction of 2 equiv of BuLi to fluorovinylsilane 5, as demonstrated by the direct synthesis of 19 from the addition of excess BuLi to silane 5 in diethyl ether. Interestingly, when an excess of BuLi was added to silane 5 in pentane, only 1 equiv of BuLi added to give Mes₂Si Bu(CH=CH₂). Finally, in the addition of *t*-BuOK to silene 1 (or germene 4), silanol 20 (or germanol 21) was also present in the crude reaction mixture and presumably arises from direct reaction of hydroxide present in the alkoxide reagent with residual 5 (or 6).

CONCLUSION

We have examined the reactivity of the naturally polarized silene 1 and germene 4 toward organometallic reagents in diethyl ether. The organometallic reagent adds regioselectively to the tetrelene, with the organic moiety always adding to the group 14 atom of the unsaturated bond. In combination with previously published results on silene chemistry, the addition is always regioselective despite a range of substituents on the silicon. As in the addition of oxygen nucleophiles to silenes, the electrophilicity of the unsaturated group 14 element appears to be the governing factor in the regiochemistry of the reaction. Rearrangements are possible after initial addition of the organometallic moiety if there is a substituent that readily undergoes migration, such as a silyl substituent, or if there is considerable congestion about the group 14 atom. The straightforward, selective addition of organometallic reagents to silenes and germenes makes this reaction synthetically useful and may be used to introduce functionality into the compound. However, as we and others have observed, the nature of the

cation, the solvent, and the reaction temperature may influence the reaction pathway followed, and thus, appropriate caution must be exercised.^{8,12,14} No polymer was observed during addition of MeLi, BuLi, and *t*-BuOK to silene 1 and germene 4 in diethyl ether, suggesting that the rate of addition to the tetrelene is significantly faster than the rate of propagation in this solvent. Further studies are needed to examine the effect of the use of MeLi and BuLi in comparison with *t*-BuLi as anionic initiators in the polymerization of silenes and germenes.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive reactions were carried out in flame-dried Schlenk tubes under an argon atmosphere. C_6D_6 was distilled from LiAlH₄, stored over 4 Å molecular sieves, and degassed prior to use. All other solvents were dried using a solvent purification system (Innovative Technology Ltd.) by passing the solvent through an alumina column. All reagents were purchased from the Aldrich Chemical Co. and were used as received. 1,1-Dimesitylneopentylsilene, 1,^{16b} fluorovinylsilane, 5,^{16b} 1,1-dimesitylneopentylgermene, 4,¹⁷ and fluorovinylgermane, 6,¹⁷ were prepared according to the previously reported procedures. *Caution: t-BuLi is highly pyrophoric and should be handled with the necessary precautions.*

¹H NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer, a Varian Inova 400 MHz spectrometer, or a Varian Inova 600 MHz spectrometer and are referenced to residual C_6D_5H (7.15 ppm) or CHCl₃ (7.25 ppm). IR spectra were recorded (cm⁻¹) from thin films on a Bruker Tensor 27 FT-IR spectrometer. Electron impact mass spectra were obtained using a MAT model 8400 mass spectrometer. Mass spectral data are reported in mass-to-charge ratios (*m/z*).

Synthesis of Difluorodimesitylgermane. Silver tetrafluoroborate (1.94 g, 9.96 mmol) was added to a solution of dichlorodimesitylgermane (1.0 g, 2.6 mmol) dissolved in dichloromethane (75 mL) under an inert atmosphere. The solid immediately dissolved, and a white precipitate was observed. The mixture was allowed to stir for 3– 4 min. Water (10 mL) was then added, and the mixture filtered. The organic layer and the aqueous layer were separated. The aqueous layer was washed with dichloromethane (3 × 10 mL). The combined organic phase was dried using MgSO₄. The solids were removed by filtration, and the solvent was removed on a rotary evaporator to give a white solid in quantitative yield. The isolated yield depends on the number of times the product is washed with water. The ¹H NMR data of Mes₂GeF₂: ¹H NMR (C₆D₆) δ 1.98 (s, 6 H, p-Me), 2.45 (s, 12 H, o-

Mes₂der₂. If NMR (C_6D_6) o 1.98 (s, 6 H, p-Me), 2.43 (s, 12 H, 0 Me), 6.58 (s, 4 H, Mes-H).

Synthesis of 3D. *tert*-Butyllithium (1.7 M in pentane, 0.10 mL, 0.17 mmol) was added to a solution of **5** (57 mg, 0.17 mmol) dissolved in pentane (3 mL) and cooled in a dry ice/acetone bath. The solution was allowed to warm to room temperature. After 10 min at room temperature, the pentane was removed under vacuum and the residue was dissolved in diethyl ether (3 mL). A second portion of *tert*-butyllithium (1.7 M in pentane, 0.30 mL, 0.54 mmol) was added to the solution, which was then allowed to stir at room temperature for 2 h. D₂O (1 drop) was added to the reaction mixture. The solution was washed with saturated ammonium chloride (3 × 10 mL). The combined aqueous solution was washed with diethyl ether (3 × 10 mL). The combined organic solution was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give a viscous, clear oil (58 mg, 85% yield). **3D** was purified by thin-layer chromatography (95:5 pentane/diethyl ether) (22 mg, 32% yield).

3D: ¹H NMR (CDCl₃) δ 0.70 (s, 9 H, C(C<u>H</u>₃)₃), 1.02 (s, 9 H, SiC(C<u>H</u>₃)₃), 0.79–0.84 (XX' portion of an AA'XX' spin system, 2 H, SiC<u>H</u>₂CH₂), 0.87–0.92 (AA' portion of an AA'XX' spin system, 2 H, SiCH₂C<u>H</u>₂), 2.20 (s, 6 H, ArC<u>H</u>₃), 2.27 (s, 3 H, Mes *p*-C<u>H</u>₃), 2.50 (s, 6 H, Mes *o*-C<u>H</u>₃), 2.63 (s, 1 H, SiC<u>H</u>DAr), 6.70 (s, 1 H, Ar *p*-<u>H</u>), 6.75 (s, 2 H, Ar *o*-<u>H</u>), 6.84 (s, 2 H, Mes-H); ²H NMR (CDCl₃) 2.60 (s, 1 H, SiCH<u>D</u>Ar).

Representative Procedure for the Addition of MeLi to 1. tert-Butyllithium (1.7 M in pentane, 0.09 mL, 0.15 mmol) was added to a solution of 5 (57 mg, 0.17 mmol) dissolved in diethyl ether (3 mL) and cooled in a dry ice/acetone bath. The solution was allowed to warm to room temperature and then stirred for 1.5 h. Methyllithium (1.6 M in diethyl ether, 0.30 mL, 0.48 mmol) was added to the solution, which was then allowed to stir for 10 min. Methanol (1 drop) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution $(3 \times 10 \text{ mL})$. The combined aqueous solution was washed with diethyl ether $(3 \times 10 \text{ mL})$. The combined organic solution was dried over MgSO4 and filtered. The solvent was removed under vacuum to give a viscous, light yellow oil consisting of a mixture of 9, 15, and the water adduct of the silene (53 mg). 9 (20 mg, 31% yield) and 15 (4 mg, 6% yield) were separated by thin-layer chromatography (80:20 hexanes/DCM) to give each as a clear oil.

*Mes*₂*Si*(*Me*)*CH*₂*CH*₂*t*-*Bu* (9): ¹H NMR (C₆D₆) δ 0.74 (s, 3 H, SiC<u>H</u>₃), 0.82 (s, 9 H, C(C<u>H</u>₃)₃), 1.25–1.31 (AA'XX' spin system, 4 H, SiC<u>H</u>₂C<u>H</u>₂), 2.09 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.34 (s, 12 H, Mes *o*-C<u>H</u>₃), 6.71 (s, 4 H, Mes-H); ¹³C NMR (C₆D₆) δ 4.3 (SiC_H₃), 15.62 (SiC_H₂CH₂), 20.93 (Mes *p*-C<u>H</u>₃), 24.36 (Mes *o*-C<u>H</u>₃), 28.97 (C(CH₃)₃), 31.09 (C(CH₃)₃), 39.03 (SiCH₂C<u>H</u>₂), 129.73 (Mes *m*-C), 134.78 (Mes *i*-C), 138.19 (Mes *p*-C), 143.36 (Mes *o*-C); ²⁹Si NMR (C₆D₆) δ -6.7; EI-MS *m*/*z* 366 (M⁺, 6%), 351 (M⁺ - CH₃, 4%), 281 (M⁺ - CH₂C_LC₂C(CH₃)₃, 100%), 246 (M⁺ - Mes, 44%); high-resolution EI-MS for C₂₅H₃₈Si *m*/*z* calcd 366.2743, found 366.2732.

 $\begin{aligned} & \textit{Mes}_{2}Si(\textit{Me})CH = CH_{2} (15): \text{IR} (\text{cm}^{-1}) 793 (\text{m}), 847 (\text{m}), 1285 (\text{m}), \\ & 1449 (\text{m}), 1605 (\text{m}), 2978 (\text{s}); {}^{1}\text{H} \text{NMR} (C_{6}\text{D}_{6}) \delta 0.76 (\text{s}, 3 \text{H}, \\ & \text{SiC}\underline{H}_{3}), 2.10 (\text{s}, 6 \text{H}, \text{Mes} p\text{-C}\underline{H}_{3}), 2.29 (\text{s}, 12 \text{H}, \text{Mes} o\text{-C}\underline{H}_{3}), 5.63 \\ & (\text{dd}, J = 5, 20 \text{ Hz}, 1 \text{H}, \text{SiCH} = C\underline{H}_{2}), 5.86 (\text{dd}, J = 4, 14 \text{ Hz}, 1 \text{H}, \\ & \text{SiCH} = C\underline{H}_{2}), 6.68 (\text{dd}, J = 5, 20 \text{ Hz}, 1 \text{H}, \text{SiCH} = CH_{2}), 6.70 (\text{s}, 4 \text{H}, \\ & \text{Mes-H}); {}^{13}\text{C} \text{NMR} (C_{6}\text{D}_{6}) \delta 4.18 (\text{SiC}\underline{H}_{3}), 21.00 (\text{Mes} p\text{-}\underline{C}\underline{H}_{3}), 24.63 \\ & (\text{Mes} o\text{-}\underline{C}\underline{H}_{3}), 129.64 (\text{Mes} m\text{-}C), 130.48 (\text{SiCH} = \underline{C}\underline{H}_{2}), 133.58 (\text{Mes} i\text{-}C), 138.43 (\text{Mes} p\text{-}C), 141.48 (\text{Si}\underline{C}\underline{H} = CH_{2}), 143.59 (\text{Mes} o\text{-}C); \text{EI-} \\ & \text{MS} m/z 308 (\text{M}^{+}, 28\%), 293 (\text{M}^{+} - \text{CH}_{3}, 24\%), 281 (\text{M}^{+} - \text{CH} = \\ & \text{CH}_{2}, 7\%), 188 (\text{M}^{+} - \text{MesH}, 100\%); \text{ high-resolution EI-MS for} \\ & \text{C}_{21}\textbf{H}_{28}\text{Si} m/z \text{ calcd } 308.1960, \text{ found } 308.1971. \end{aligned}$

In the addition of MeLi to 4, a viscous, colorless oil, identified as a mixture of 12 and 16, was obtained in a ratio of 1:0.03 (10 mg, 92% yield).

 $\begin{array}{l} \textit{Mes}_2\textit{Ge}(\textit{Me})\textit{CH}_2\textit{CH}_2\textit{t-Bu}~(12): \ ^{1}\textit{H}~\text{NMR}~(C_6D_6)~\delta~0.825~\text{and}~0.829} \\ (s, C(C\underline{H}_3)_3 \text{ and} s, GeC\underline{H}_3, 12~\text{H}), 1.23-1.33~(XX'~\text{of}~an~AA'XX'~\text{spin} \\ \text{system}, 2~\text{H}, GeC\underline{H}_2C\underline{H}_2), 1.46-1.50~(AA'~\text{of}~an~AA'XX'~\text{spin} \\ \text{system}, 2~\text{H}, GeC\underline{H}_2C\underline{H}_2), 2.10~(s,~6~\text{H}, \text{Mes}~p-C\underline{H}_3), 2.33~(s,~12~\text{H}, \text{Mes}~o-C\underline{H}_3), 6.72~(s,~4~\text{H}, \text{Mes-H}); \ ^{13}\text{C}~\text{NMR}~(C_6D_6)~\delta~4.16~(Ge\underline{C}H_3), 17.46~(Ge\underline{C}\underline{H}_2C\underline{H}_2), 20.93~(\text{Mes}~p-\underline{C}\underline{H}_3), 24.19~(\text{Mes}~o-\underline{C}\underline{H}_3), 28.96~(C(\underline{C}\underline{H}_3)_3), 31.21~(\underline{C}(CH_3)_3), 39.78~(GeC\underline{H}_2\underline{C}\underline{H}_2), 129.41~(\text{Mes}~m-C), 137.53~(\text{Mes}~p-C), 137.71~(\text{Mes}~i-C), 142.79~(\text{Mes}~o-C); EI-MS~m/z~411~(M^+,~11\%), ~397~(M^+~-CH_3,~41\%), 293~(M^+~-CH_2CH_2C(CH_3)_3), 100\%); \ \text{high-resolution}~\text{EI-MS}~\text{for}~C_{25}\underline{H}_{38}^{-70}\text{Ge}~m/z~\text{calcd}~407.2138, \ \text{found}~407.2130. \end{array}$

*Mes*₂*Ge*(*CH*=*CH*₂)*Me* (*16*): IR (cm⁻¹) 799 (s), 848 (s), 946 (m), 1009 (s), 1239 (m), 1261 (m), 1449 (m), 1603 (s), 2804 (w); ¹H NMR (C₆D₆) δ 0.84 (s, 3 H, GeC<u>H</u>₃), 2.11 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.29 (s, 12 H, Mes *o*-C<u>H</u>₃), 5.58 (dd, *J* = 3, 20 Hz, 1 H, GeCH=C<u>H</u>₂), 5.85 (dd, *J* = 3, 13 Hz, 1 H, GeCH=C<u>H</u>₂), 6.71 (s, 4 H, Mes-H), 6.78 (dd, *J* = 13, 20 Hz, 1 H, GeC<u>H</u>=CH₂); ¹³C NMR (C₆D₆) δ 4.53 (GeC_H₃), 20.98 (Mes *p*-C<u>H</u>₃), 24.42 (Mes *o*-C<u>H</u>₃), 128.18 (GeCH= CH₂), 129.38 (Mes *m*-C), 136.39 (Mes *i*-C), 137.94 (Mes *p*-C), 142.76 (GeCH=CH₂), 142.96 (Mes *o*-C); EI-MS *m/z* 354 (M⁺, 11%), 339 (M⁺ - CH₃, 70%), 327 (M⁺ - CH=CH₂, 33%), 234 (M⁺ - Mes, 81%), 219 (M⁺ - CH₃ - Mes, 100%); high-resolution EI-MS for C₂₁H₂₈⁷⁴Ge *m/z* calcd 354.1407, found 354.1402.

Synthesis of $Mes_2Si(CH=CH_2)CH_3$ (15). Methyllithium (1.6 M in diethyl ether, 0.40 mL, 0.64 mmol) was added to a solution of 5 (100 mg, 0.32 mmol) dissolved in diethyl ether (6 mL). The solution was allowed to stir overnight at room temperature. An ammonium chloride solution (2 mL) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3

 \times 10 mL). The combined aqueous solution was washed with diethyl ether (3 \times 10 mL). The combined organic phase was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give **15** as a viscous, colorless liquid (10 mg, 10% yield). Similarly, the addition of methyllithium to **6** gave **16** (58 mg, 59% yield).

Representative Procedure for the Addition of BuLi to 1. *tert*-Butyllithium (1.7 M in pentane, 0.10 mL, 0.17 mmol) was added to a solution of **5** (58 mg, 0.18 mmol) dissolved in diethyl ether (3 mL) and cooled in a dry ice/acetone bath. The solution was allowed to warm to room temperature and then stirred for 1.5 h. Butyllithium (1.6 M in hexane, 0.34 mL, 0.54 mmol) was added to the solution, which was then allowed to stir for 10 min. Methanol (1 drop) was added to the reaction. The solution was washed with a saturated ammonium chloride solution (3 × 10 mL). The combined aqueous solution was washed with diethyl ether (3 × 10 mL). The combined organic phase was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give a viscous, colorless oil (58 mg, 78% yield) identified as a mixture of **10** and **19** in a ratio of 1:1. The mixture was purified by thin-layer chromatography (70:30 hexane/ DCM) to give a clear oil (38 mg).

*Mes*₂*Si*(*Bu*)*CH*₂*CH*₂*t*-*Bu* (**10**): ¹H NMR (C₆D₆) δ 0.83 (t, 3 H, *J* = 7 Hz, Si(CH₂)₃C<u>H₃</u>), 0.84 (s, 9H, C(C<u>H₃</u>)₃), 1.46–1.15 (m, SiC<u>H₂CH₂CH₂CH₂CH₃), 2.09 (s, 6 H, Mes *p*-C<u>H₃</u>), 2.38 (s, 12 H, Mes *o*-C<u>H₃</u>), 6.71 (s, 4 H, Mes-H); ¹³C NMR (C₆D₆) δ 9.14, 13.15 (SiC<u>H₂CH₂CH₂CH₂ and SiCH₂CH₂CH₂CH₂CH₃), 18.70, 27.06, 27.43 (SiCH₂C<u>H₂CH₂CH₂CH₃), 24.52 (Mes *o*-C<u>H₃</u>), 28.97 (C(C<u>H₃</u>)₃), 31.13 (C(CH₃)₃), 39.14 (SiCH₂C<u>H</u>₂), 129.76 (Mes *m*-C), 134.30 (Mes *i*-C), 138.17 (Mes *p*-C), 143.59 (Mes *o*-C); ²⁹Si NMR (C₆D₆) δ –4.1; EI-MS *m/z* 408 (M⁺, 1%), 351 (M⁺ – (CH₂)₃CH₃, 14%), 323 (M⁺ – (CH₂)₅CH₃, 18%), 288 (M⁺ – MesH, 26%), 267 (Mes₂Si⁺, 100%); high-resolution EI-MS for C₂₈H₄₄Si *m/z* calcd 408.3212, found 408.3214.</u></u></u>

*Mes*₂*Si*(*Bu*)*Hex* (**19**): ¹H NMR (C₆D₆) δ 0.815 (t, *J* = 7 Hz) 0.821 (t, *J* = 7 Hz) (6 H, Si(CH₂)₃C<u>H</u>₃ and Si(CH₂)₅C<u>H</u>₃), 1.16–1.21 (br, 4 H, SiC<u>H</u>₂), 1.30–1.46 (m, SiCH₂(C<u>H</u>₂)₂CH₃ and SiCH₂(C<u>H</u>₂)₄CH₃), 2.10 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.37 (s, 12 H, Mes *o*-C<u>H</u>₃), 6.71 (s, 4 H, Mes-H); ¹³C NMR (C₆D₆) δ 13.90, 14.25 (SiC<u>H</u>₂CH₂CH₂CH₂CH₃ and SiC<u>H</u>₂(CH₂)₄CH₃), 18.98, 19.24 (SiCH₂C<u>H</u>₂CH₂CH₂CH₃ and SiC<u>H</u>₂(CH₂)₃CH₂CH₂CH₃), 20.95 (Mes *p*-C<u>H</u>₃), 22.98, 25.24 (Si(CH₂)₃C<u>H</u>₂CH₂CH₂CH₃, and Si(CH₂)₂C<u>H</u>₂(CH₂)₂CH₃), 27.48, 31.82 (SiCH₂C<u>H</u>₂CH₂CH₃ and Si(CH₂)₂C<u>H</u>₃), 129.75 (Mes *m*-C), 134.40 (Mes *i*-C), 138.14 (Mes *p*-C), 143.58 (Mes *o*-C); ²⁹Si NMR (C₆D₆) δ –5.1; EI-MS *m/z* 408 (M⁺, 1%), 351 (M⁺ – (CH₂)₃CH₃, 10%), 323 (M⁺ – (CH₂)₅CH₃, 13%), 288 (M⁺ – MesH, 13%), 267 (Mes₂Si⁺, 100%); high-resolution EI-MS for C₂₈H₄₄Si *m/z* calcd 408.3212, found 408.3205.

In the addition of BuLi to 4, a viscous, colorless oil identified as a mixture of 13 and 17 was obtained in a ratio of 1:0.2 (28 mg, 47% yield).

Synthesis of $Mes_2Si(Bu)Hex$ (19). Butyllithium (1.6 M in hexane, 0.5 mL, 0.8 mmol) was added to a solution of 5 (47 mg, 0.15 mmol) dissolved in diethyl ether (3 mL). The solution was allowed to stir for 2 h at room temperature. Methanol (1 drop) was added to the reaction mixture. The solution was washed with saturated ammonium chloride (3 × 10 mL). The combined aqueous solution was washed

with diethyl ether (3 \times 10 mL). The combined organic phase was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give a viscous, colorless liquid (55 mg, 90% yield). **19** was purified by thin-layer chromatography (70:30 hexanes/DCM) to give a colorless oil (37 mg, 61% yield).

Synthesis of Mes₂Si(CH=CH₂)Bu. Butyllithium (1.6 M in hexane, 0.50 mL, 0.80 mmol) was added to a solution of **5** (47 mg, 0.15 mmol) dissolved in pentane (3 mL). The solution was allowed to stir for 2 h at room temperature. Methanol (1 drop) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3×10 mL). The combined aqueous solution was washed with diethyl ether (3×10 mL). The combined organic phase was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give a viscous, colorless liquid (50 mg, 96% yield). Mes₂Si(CH=CH₂)Bu was purified by thin-layer chromatography (80:20 hexanes/DCM) to give a clear oil (38 mg, 72% yield). Vinylgermane 17 was synthesized in a similar manner to give a viscous, colorless oil (55 mg, 50% yield).

*Mes*₂*Si*(*CH*=*CH*₂)*Bu*: ¹H NMR (C₆D₆) δ 0.80 (t, *J* = 7 Hz, 3 H, SiCH₂CH₂CH₂CH₂C<u>H</u>₃), 1.29–1.43 (m, SiC<u>H₂CH₂CH₂CH</u>₂CH₃), 2.10 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.32 (s, 12 H, Mes *o*-C<u>H</u>₃), 5.65 (dd, *J* = 3, 20 Hz, 1 H, SiCH=C<u>H</u>₂), 5.91 (dd, *J* = 4, 14 Hz, 1 H, SiCH=C<u>H</u>₂), 6.71 (s, 4 H, Mes-H), 6.82 (dd, *J* = 14, 20 Hz, 1 H, SiC<u>H</u>=CH₂); ¹³C NMR (C₆D₆) δ 13.84 (SiC<u>H</u>₂CH₂CH₂CH₃), 20.03 (SiCH₂C<u>H</u>₂CH₂CH₂), 20.99 (Mes *p*-C<u>H</u>₃), 24.76 (Mes *o*-C<u>H</u>₃), 27.09 (SiCH₂C<u>H</u>₂C<u>H</u>₂CH₃), 27.58 (SiCH₂C<u>H</u>₂C<u>H</u>₂C<u>H</u>₃), 129.63 (Mes *m*-C), 130.83 (SiCH= C<u>H</u>₂), 133.05 (Mes *i*-C), 138.42 (Mes *p*-C), 140.11 (SiC<u>H</u>=C<u>H</u>₂), 143.87 (Mes *o*-C); ²⁹Si NMR (C₆D₆) δ –13.8; EI-MS *m/z* 350 (M⁺, 33%), 335 (M⁺ – CH₃, 10%), 293 (M⁺ – C₄H₉, 100%), 230 (M⁺ – MesH, 30%); high-resolution EI-MS for C₂₄H₃₄Si *m/z* calcd 350.2430, found 350.2441.

*Mes*₂*GeBu*(*CH*=*CH*₂) (**17**): IR (cm⁻¹) 697 (s), 847 (m), 1008 (m), 1289 (w), 1377 (m), 1392 (m), 1450 (s), 1603 (s), 2731 (w), 2858 (m), 2924 (s), 2957 (s); ¹H NMR (C₆D₆) δ 0.79 (t, *J* = 7 Hz, 3 H, GeCH₂CH₂CH₂C<u>H</u>₂C_H₃), 1.25–1.60 (m, GeC<u>H₂CH₂CH₂CH₂CH₃), 2.11 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.31 (s, 12 H, Mes *o*-C<u>H</u>₃), 5.60 (dd, *J* = 3, 19 Hz, 1 H, GeCH=C<u>H</u>₂), 5.90 (dd, *J* = 3, 13 Hz, 1 H, GeCH=C<u>H</u>₂), 6.72 (s, 4 H, Mes-H), 6.93 (dd, *J* = 13, 19 Hz, 1 H, GeCH=CH₂); ¹³C NMR (C₆D₆) δ 13.80 (GeCH₂CH₂CH₂C<u>H</u>₃), 20.97 (Mes *p* -<u>C</u>H₃), 22.00 (G e<u>C</u>H₂CH₂CH₂CH₃), 24.55 (Mes *o* -<u>C</u>H₃), 26.74 (GeCH₂CH₂C<u>H</u>₂CH₃), 28.43 (GeCH₂<u>C</u>H₂CH₂CH₃), 128.48 (GeCH=<u>C</u>H₂), 129.35 (Mes *m*-C), 135.91 (Mes *i*-C), 137.93 (Mes *p*-C), 141.49 (Ge<u>C</u>H=CH₂), 143.19 (Mes *o*-C); EI-MS *m/z* 396 (M⁺, 2%), 369 (M⁺ - CH=CH₂, 1%), 339 (M⁺ - C₄H₉, 100%), 276 (M⁺ - MesH, 11%); high-resolution EI-MS for C₂₄H₃₄⁻⁷⁴Ge *m/z* calcd 396.1877, found 396.1869.</u>

Representative Procedure for the Addition of KOt-Bu to 1. tert-Butyllithium (1.7 M in pentane, 0.1 mL, 0.2 mmol) was added to a solution of 5 (57.8 mg, 0.18 mmol) dissolved in diethyl ether (3 mL) and cooled in a dry ice/acetone bath. The solution was allowed to warm to room temperature and then stirred for 1.5 h. Potassium tertbutoxide (90 mg, 0.80 mmol) was added to the solution, which was then allowed to stir for 10 min. The potassium tert-butoxide did not dissolve completely. Methanol (1 drop) was added to the reaction. The solution was washed with a saturated ammonium chloride solution $(3 \times 10 \text{ mL})$. The combined aqueous solution was washed with diethyl ether $(3 \times 10 \text{ mL})$. The combined organic phase was dried over MgSO4 and filtered. The solvent was removed under vacuum to give a clear, colorless liquid (60 mg). The liquid consisted of 11 and 20 in a 1:2 ratio as determined by ¹H NMR spectroscopy. The mixture was separated twice by thin-layer chromatography (80:20 hexane/DCM) to give 11 (17 mg, 23% yield) and 20 (13 mg, 17%). Compound 11 remains contaminated with trace amounts of an unknown.

 $\begin{array}{l} \textit{Mes}_{2}\textit{Si}(\textit{Ot-Bu})\textit{CH}_{2}\textit{CH}_{2}\textit{t-Bu}~(11): \ ^{1}\textit{H}~\text{NMR}~(C_{6}D_{6})~\delta~0.87~(s,~9~\text{H},\\ C(C\underline{H}_{3})_{3}),~1.23~(s,~9~\text{H},~OC(C\underline{H}_{3})_{3}),~1.33-1.35~(XX'~\text{portion of an}\\ AA'XX'~\text{spin system},~2~\text{H},~\text{Si}C\underline{H}_{2}C\underline{H}_{2}),~1.48-1.50~(AA'~\text{portion of an}\\ AA'XX'~\text{spin system},~2~\text{H},~\text{Si}C\underline{H}_{2}C\underline{H}_{2}),~2.09~(s,~6~\text{H},~\text{Mes}~p-C\underline{H}_{3}),~2.48~(s,~12~\text{H},~\text{Mes}~o-C\underline{H}_{3}),~6.73~(s,~4~\text{H},~\text{Mes-H});~^{13}C~\text{NMR}~(C_{6}D_{6})~\delta\\ 18.53~(Si\underline{CH}_{2}CH_{2}),~21.02~(\text{Mes}~p-\underline{CH}_{3}),~24.29~(\text{Mes}~o-\underline{CH}_{3}),~29.08~\text{N} \end{array}$

 $(C(\underline{CH}_3)_3)$, 31.04 $(\underline{C}(CH_3)_3)$, 31.69 $(OC(\underline{CH}_3)_3)$, 38.31 $(SiCH_2\underline{CH}_2)$, 74.16 $(O\underline{C}(CH_3)_3)$, 129.89 (Mes *m*-C), 134.88 (Mes *i*-C), 138.46 (Mes *p*-C), 143.64 (Mes *o*-C); ²⁹Si NMR $(C_6D_6) \delta - 8.1$; EI-MS *m*/*z* 424 (M⁺, 0.1%), 339 (M⁺ - CH₂CH₂C(CH₃)₃, 55%), 283 (Mes₂SiO⁺, 100%); high-resolution EI-MS for C₂₈H₄₄OSi *m*/*z* calcd 424.3161, found 424.3156.

*Mes*₂*Si*(*OH*)*CH*=*CH*₂ (**20**): IR (cm⁻¹) 632 (m), 801 (m), 1179 (w), 1234 (m), 1263 (s), 1405 (m), 1448 (m), 1548 (m), 1605 (s), 2734 (w), 2860 (m), 2922 (s), 2965 (s); ¹H NMR (C_6D_6) δ 2.10 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.37 (s, 12 H, Mes *o*-C<u>H</u>₃), 5.81 (dd, *J* = 4, 20 Hz, 1 H, SiCH=C<u>H</u>₂), 5.91 (dd, *J* = 4, 14 Hz, 1 H, SiCH=C<u>H</u>₂), 6.57 (dd, *J* = 14, 20 Hz, 1 H, SiC<u>H</u>=CH₂), 6.70 (s, 4 H, Mes-H); ¹³C NMR (C_6D_6) δ, 21.05 (Mes *p*-<u>C</u>H₃), 24.18 (Mes *o*-<u>C</u>H₃), 129.56 (Mes *m*-C), 131.61 (SiCH=<u>C</u>H₂), 132.97 (Mes *i*-C), 139.06 (Mes *p*-C), 140.78 (Si<u>C</u>H=CH₂), 143.97 (Mes *o*-C); EI-MS *m*/*z* 310 (M⁺, 12%), 283 (M⁺ - CH=CH₂, 8%), 191 (M⁺ - Mes, 14%), 84 (100%); highresolution EI-MS for C₂₀H₂₆OSi *m*/*z* calcd 310.1753, found 310.1748.

In the addition of potassium *tert*-butoxide to **4**, a clear oil was obtained, which was identified as a mixture of **14**, **18**, and **21** (in a ratio of 1:0.5:0.5) and a trace of an unknown. The mixture was purified by thin-layer chromatography (80:20 hexanes/DCM) to give **14** as a clear oil contaminated with a minor impurity (15 mg, 12% yield).

 $\begin{array}{l} Mes_2Ge(Ot-Bu)CH_2CH_2t-Bu \ (14): \ IR \ (cm^{-1}) \ 848 \ (m), \ 1021 \ (m), \\ 1466 \ (m), \ 1604 \ (m), \ 2965 \ (s); \ ^{1}H \ NMR \ (C_6D_6) \ \delta \ 0.83 \ (s, \ 9 \ H, \\ C(C\underline{H}_3)_3), \ 1.19-1.21 \ (XX' \ portion \ of \ an \ AA'XX' \ spin \ system, \ 2 \ H, \\ GeC\underline{H}_2CH_2), \ 1.32 \ (s, \ 9 \ H, \ OC(C\underline{H}_3)_3), \ 1.6-1.62 \ (AA' \ portion \ of \ an \ AA'XX' \ spin \ system, \ 2 \ H, \\ GeC\underline{H}_2CH_2), \ 1.32 \ (s, \ 9 \ H, \ OC(C\underline{H}_3)_3), \ 1.6-1.62 \ (AA' \ portion \ of \ an \ AA'XX' \ spin \ system, \ 2 \ H, \ GeC\underline{H}_2CH_2), \ 2.10 \ (s, \ 6 \ H, \ Mes \ p-C\underline{H}_3), \\ 2.32 \ (s, \ 12 \ H, \ Mes \ o-C\underline{H}_3), \ 6.73 \ (s, \ 4 \ H, \ Mes-H); \ ^{13}C \ NMR \ (C_6D_6) \ \delta \ 14.82 \ (GeC\underline{H}_2CH_2), \ 20.87 \ (Mes \ p-C\underline{H}_3), \ 25.32 \ (Mes \ o-C\underline{H}_3), \ 28.99 \ (C(C\underline{H}_3)_3), \ 30.01 \ (C(CH_3)_3), \ 31.44 \ (OC(C\underline{H}_3)_3), \ 41.08 \ (GeCH_2CH_2), \ 84.06 \ (OC(CH_3)_3), \ 31.44 \ (Mes \ m-C), \ 137.31 \ (Mes \ p-C), \ 142.62 \ (Mes \ o-C); \ EI-MS \ m/z \ 395 \ (M^+ - \ Ot-Bu, \ 66\%), \ 312 \ (Mes_3Ge^+, \ 81\%), \ 84 \ (100\%). \end{array}$

Synthesis of Mes₂Ge(OH)CH=CH₂ (21). Aqueous sodium hydroxide (15%, 5.0 mL, 1.4 mmol) was added to a solution of 6 (50 mg, 0.14 mmol) dissolved in THF (20 mL), which was then allowed to stir for 1 h at room temperature. The aqueous solution was washed with diethyl ether (3×10 mL), and the organic layer was washed with water (3×10 mL). The combined organic phase was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give a viscous, colorless oil (25.0 mg, 50% yield). The oil consisted of 21 and 6 in a ratio of 1:0.04. The mixture was purified by thin-layer chromatography on silica gel (50:50 hexane/DCM) to give 21 as a clear oil (2.2 mg). Silanol 20 was synthesized using the same procedure (99 mg, 98% yield).

*Mes*₂*Ge*(*OH*)*CH*=*CH*₂ (21): IR (cm⁻¹) 848 (s), 962 (m), 1449 (s), 1602 (s), 2922 (s) 3430 (br, m); ¹H NMR (C₆D₆) δ 2.08 (s, 6 H, Mes *p*-C<u>H</u>₃), 2.40 (s, 12 H, Mes *o*-C<u>H</u>₃), 5.77 (dd, *J* = 3, 20 Hz, 1 H, GeCH=C<u>H</u>₂), 5.87 (dd, *J* = 3, 13 Hz, 1 H, GeCH=C<u>H</u>₂), 6.65 (dd, *J* = 13, 20 Hz, 1 H, GeC<u>H</u>=CH₂), 6.69 (s, 4 H, Mes-H). ¹³C NMR (C₆D₆) δ 20.99 (Mes *p*-<u>C</u>H₃), 23.77 (Mes *o*-<u>C</u>H₃), 129.43 (Mes *m*-C), 130.02 (GeCH=<u>C</u>H₂), 134.97 (Mes *i*-C), 138.99 (Mes *p*-C), 141.37 (Ge<u>C</u>H=CH₂), 143.25 (Mes *o*-C); EI-MS *m*/*z* 356 (M⁺, 7%), 338 (M⁺ − OH, 11%), 329 (M⁺ − CH=CH₂, 26%), 236 (M⁺ − Mes-H, 52%), 145 (100%); high-resolution EI-MS for C₂₀H₂₆O⁷⁴Ge *m*/*z* calcd 356.1200, found 356.1189.

Synthesis of Mes₂Si(CH=CH₂)Ot-Bu. Potassium *tert*-butoxide (153 mg, 1.37 mmol) was added to a solution of 5 (94 mg, 0.30 mmol) dissolved in THF (9 mL). The solution was allowed to stir for 24 h. Saturated ammonium chloride (1 drop) was added to the reaction mixture. The solution was washed with a saturated ammonium chloride solution (3×10 mL). The combined aqueous solution was washed with THF (3×10 mL). The combined organic phase was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give an orange powder (100 mg, 90% yield). The powder consisted of Mes₂Si(CH=CH₂)Ot-Bu and a small amount of an unknown. The mixture was purified by thin-layer chromatography on silica gel (70:30 hexane/DCM) to give Mes₂Si(CH=CH₂)Ot-Bu (59 mg, 53%). Vinylgermane 18 was synthesized in a similar manner

to give a viscous, colorless oil (106 mg, 92% yield) consisting of 18 and 21 in a ratio of 1:0.06.

 $\begin{aligned} & \textit{Mes}_{2}Si(CH=CH_{2})Ot\text{-}Bu: \text{ IR } (\text{cm}^{-1}) 632 \text{ (s)}, 697 \text{ (s)}, 848 \text{ (m)}, 959 \\ & \text{(m)}, 1021 \text{ (s)}, 1040 \text{ (s)}, 1189 \text{ (s)}, 1363 \text{ (m)}, 1450 \text{ (m)}, 1605 \text{ (m)}, \\ & 2799 \text{ (m)}, 2948 \text{ (m)}, 3100 \text{ (br, s)}; ^{1}\text{H } \text{NMR } (C_{6}\text{D}_{6}) \delta 1.20 \text{ (s, 9 } \text{H}, \\ & OC(C\underline{H}_{3})_{3}), 2.11 \text{ (s, 6 } \text{H}, \text{Mes } p\text{-}C\underline{H}_{3}), 2.44 \text{ (s, 12 } \text{H}, \text{Mes } o\text{-}C\underline{H}_{3}), \\ & 5.70 \text{ (dd, } J = 3, 20 \text{ Hz}, 1 \text{ H}, \text{SiCH}=C\underline{H}_{2}), 5.90 \text{ (dd, } J = 3, 14 \text{ Hz}, 1 \text{ H}, \\ & \text{SiCH}=C\underline{H}_{2}), 6.73 \text{ (s, 4 } \text{H}, \text{Mes-H}), 6.76 \text{ (dd, } J = 14, 20 \text{ Hz}, 1 \text{ H}, \\ & \text{SiCH}=CH_{2}); ^{13}\text{C} \text{ NMR } (C_{6}\text{D}_{6}) \delta 21.07 \text{ (Mes } p\text{-}\underline{C}H_{3}), 24.52 \text{ (Mes } o\text{-}\underline{C}H_{3}), \\ & 31.80 \text{ (C}(\underline{C}H_{3})_{3}), 74.20 \text{ (OC}(CH_{3})_{3}), 129.73 \text{ (Mes } m\text{-}C), \\ & 131.45 \text{ (SiCH}=\underline{C}H_{2}), 133.64 \text{ (Mes } i\text{-}C), 138.72 \text{ (Mes } p\text{-}C), 141.77 \text{ (SiCH}=CH_{2}), 144.08 \text{ (Mes } o\text{-}C); EI\text{-MS } m/z 366 \text{ (M}^{+}, 58\%), 190 \\ & (100\%), 293 \text{ (M}^{+} - C_{4}H_{9}\text{O}, 13\%), 246 \text{ (M} - \text{Mes-H}^{+}, 37\%); \text{ high-resolution EI-MS for } C_{24}H_{34}\text{OSi} m/z \text{ caled } 366.2379, \text{ found } 366.2389. \end{aligned}$

 $\begin{aligned} & \text{Mes}_2 Ge(CH = CH_2)Ot - Bu \ (18): {}^{1}\text{H} \text{ NMR } (C_6D_6) \ \delta \ 1.26 \ (s, 9 \ \text{H}, \\ & OC(C\underline{H}_3)_3), 2.09 \ (s, 6 \ \text{H}, \text{ Mes} \ p-C\underline{H}_3), 2.46 \ (s, 12 \ \text{H}, \text{ Mes} \ o-C\underline{H}_3), \\ & 5.64 \ (\text{dd}, J = 3, 20 \ \text{Hz}, 1 \ \text{H}, \text{GeCH} = C\underline{H}_2), 5.86 \ (\text{dd}, J = 3, 13 \ \text{Hz}, 1 \ \text{H}, \text{GeCH} = C\underline{H}_2), \\ & 5.64 \ (\text{dd}, J = 3, 20 \ \text{Hz}, 1 \ \text{H}, \text{GeCH} = C\underline{H}_2), \\ & 5.64 \ (\text{dd}, J = 3, 20 \ \text{Hz}, 1 \ \text{H}, \text{GeCH} = C\underline{H}_2), \\ & 5.86 \ (\text{dd}, J = 3, 13 \ \text{Hz}, 1 \ \text{H}, \\ & \text{GeCH} = C\underline{H}_2), \\ & 6.72 \ (s, 4 \ \text{H}, \text{Mes-H}), \\ & 6.88 \ (\text{dd}, J = 13, 20 \ \text{Hz}, 1 \ \text{H}, \\ & \text{GeCH} = CH_2); \\ & 1^3C \ \text{NMR} \ (C_6D_6) \ \delta \ 21.03 \ (\text{Mes} \ p-C\underline{H}_3), \\ & 24.05 \ (\text{Mes} \ m-CH), \\ & 130.10 \ (\text{GeCH} = \underline{CH}_2), \\ & 135.55 \ (\text{Mes} \ i-C), \\ & 138.69 \ (\text{Mes} \ p-C), \\ & 142.62 \ (\text{GeCH} = CH_2), \\ & 143.43 \ (\text{Mes} \ o-C); \\ & \text{EI-MS} \ m/z \ 412 \ (\text{M}^+, 0.5\%), \\ & 385 \ (\text{M}^+ - \text{CH} = CH_2, 4\%), \\ & 339 \ (\text{M}^+ - C_4H_9O, 100\%), \\ & 311 \ (\text{Mes}_2\text{Ge} - \text{H}^+, 24\%); \\ & \text{high-resolution} \ \text{EI-MS} \ \text{for} \ C_{24}H_{34}O^{70}\text{Ge} \ m/z \ \text{calcd} \\ \\ & 408.1852, \ \text{found} \ 408.1857. \end{aligned}$

Addition of Excess t-BuLi to Silene 1 in Pentane. tert-Butyllithium (1.7 M in pentane, 0.11 mL, 0.19 mmol) was added to a solution of 5 (60 mg, 0.19 mmol) dissolved in pentane (3 mL) and cooled in a dry ice/acetone bath. The cloudy, pale yellow solution was allowed to warm to room temperature to give an orange solution. After 10 min at room temperature, a second portion of tert-butyllithium (1.7 M in pentane, 0.35 mL, 0.60 mmol) was added to the solution, which was then allowed to stir at room temperature for 2 h. The color of the solution deepened. MeOH (1 drop) was added to the reaction mixture. The solution was washed with saturated ammonium chloride $(3 \times 10 \text{ mL})$. The combined aqueous solution was washed with diethyl ether $(3 \times 10 \text{ mL})$. The combined organic solution was dried over MgSO₄ and filtered. The solvent was removed under vacuum to give a white solid (64 mg) consisting of silane 2, polysilene, and unknown compounds. Similarly, excess t-BuLi was added to germene 4 in pentane to give a mixture of Mes₂(t-Bu)GeCH₂CH₂t-Bu and polygermene.

ASSOCIATED CONTENT

Supporting Information

A PDF file containing ¹H and ¹³C NMR spectra of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ acs.organomet.5b00423.

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Notes

The authors declare no competing financial interest.

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