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Alk-2-ynyl Trimethylsilyl Chalcogenoethers by Nucleophilic Substitution of Propargyl Bromides

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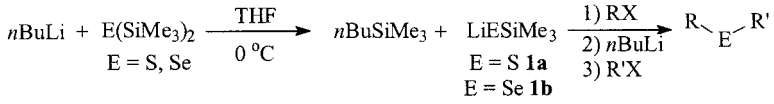
Lithium (trimethylsilyl)chalcogenolates have been generated and used to prepare a series of alk-2-ynyl trimethylsilyl chalcogenoethers from the corresponding propargyl bromides in good yield. The thermal decomposition of the telluroethers has also been studied.

Introduction

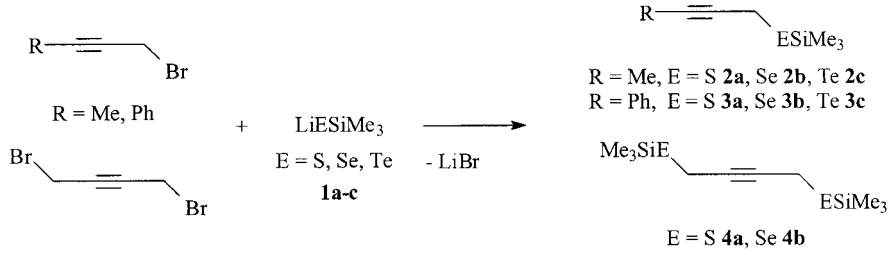
Trimethylsilyl chalcogenoethers of the general formula $RESiMe_3$ (R = alkyl or aryl, E = S, Se, Te) are a powerful class of reagents due to their demonstrated ability to react smoothly with metal salts (M–X) to form metal chalcogenolate cluster and nanocluster complexes $(M–ER)_x$, through the thermodynamically favorable elimination of $XSiMe_3$.[1–9] This includes their use in nanoparticle chemistry, where silylated reagents have been utilized to passivate the surface of metal chalcogenide cores.[10,11]

Despite their wide ranging utility, only a relatively limited number of $RESiMe_3$ reagents of the heavier congeners Se and Te have been reported, and this can likely be attributed to the difficulty of introducing the Me_3Si moiety onto RE^-. For the elements Se and Te, this typically involves silylation reactions of salts RE-M[12–29] (M = Li, Na) or REMgX (X = Cl, Br) with $ClSiMe_3$.[30–33]

Segi and co-workers have reported a general route to asymmetric thio- and selenoethers by the in situ generation of Me_3SiE^- nucleophiles from the silylated chalcogenides $E(SiMe_3)_2$ and alkyllithium reagents (Scheme 1).[34] Utilizing this methodology, we set out to combine the reactive lithium (trimethylsilyl)chalcogenolates with a series of propargyl bromides (Scheme 2). The coordination chemistry of both the chalcogen group(s) and the propargyl functionality could provide for a wide variety of structural types when complexed to metal centers.[35] In this paper, we report the preparation and spectral characterization of the series of



Scheme 1. Route to asymmetric chalcogenoethers as reported by Segi et al.[34]



Scheme 2.

Li[$ESiMe_3$] and its utility for the synthesis of propargyl chalcogenoethers. The chalcogenoethers have been characterized by nuclear magnetic resonance spectroscopy and

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mass spectrometry, along with decomposition studies of the highly unstable tellurium congeners.

Results and Discussion

The reagents $LiESiMe_3$ **1a**–**c**, provide ready access to reactive trimethylsilyl chalcogenolate fragments. Reported by Segi as reactive intermediates as part of a catalytic cycle,[39] the use of *n*BuLi and bis(trimethylsilyl) chalcogenide as the starting materials yields the desired product $[Me_3SiE]Li$ through reductive cleavage of the E–Si bond, without any complications due to formation of Li_2E.[40] The NMR chemical shifts of **1a**–**c** are reported in Table 1. In compounds **1a**–**c**, the chalcogen centers produce a downfield trend in the ^1H and ^{13}C chemical shifts and an upfield trend in the ^{29}Si NMR going from S < Se < Te. The ^{77}Se and ^{125}Te chemical shifts values of **1b** and **1c** are similar to those reported for related alkylsilylchalcogenolates[41] and are also close to the values reported for phosphane-stabilized copper trimethylsilylchalcogenolates.[42,43]

Table 1. NMR spectroscopic data for **1a**–**c** in C_6D_6. Chemical shifts are reported in ppm.

	$-Si(CH_3)_3$ ^1H	^{13}C	^{29}Si	$^{77}Se/^{125}Te$
1a	0.58	7.32	7.22	–
1b	0.70	7.87	4.10	–518.1
1c	0.88	9.71	–19.43	–1294.3[a]

[a] Recorded in $[H_8]$thf.

Chalcogen-substituted propargyl complexes can be prepared from propargyl bromides and metal chalcogenolates,[44–52] although demonstrated radical routes have recently been documented for the preparation of propargyl selenols from diselenides.[53] The demonstrated clean conversion of $E(SiMe_3)_2$ to $[Me_3SiE]Li$ using *n*-butyllithium has allowed for the successful preparation of a range of chalcogenoethers from alkyl bromides, including 1-bromo-2-propyne (propargyl bromide).[34] Our attempts to isolate pure $HC{\equiv}CCH_2ESiMe_3$ under a variety of reaction conditions with either **1a** or **1b** were unsuccessful. On occasion, the desired product was isolated but in extremely low yield, due to either the acidity of the alkynyl proton or the general instability of any $HC{\equiv}CCH_2ESiMe_3$ formed.[50] Indeed, with all propargyl bromides $RC{\equiv}CCH_2Br$ used as the starting materials in this study, the Me_3SiE^- anion proved to be too reactive under the conditions previously reported (thf, 0 °C) for the generation of selenoethers.[34] As nucleophilic displacements of this type are well known to proceed through the expected S_N2 reaction mechanism,[50] lower polarity solvents and low reaction temperatures were used to control the reaction. Propargyl–allenyl isomerization via a 1,3-hydride shift is quite common in chalcogen substituted propargyl complexes and in tellurium systems, the allenyl form is generally favored.[50] No evidence for isomerization was observed in this study. The lithium chalcogenolates **1a**–**c** are all soluble in hydrocarbon solvents, presumably due to the presence of the trimethylsilyl groups and the tightly bound thf molecules. Qualitatively, the reactivity of the lithium chalcogenolates increases on going from S < Se < Te and the reactivity of the propargyl bromides $RC{\equiv}CCH_2Br$ increases on going from R = Ph < Me < $BrCH_2$. Slight excesses of the lithium chalcogenolates were used in the preparation of **3a**,**b** and **4a**,**b** to ensure complete consumption of the starting propargyl bromides. The synthesis of **3a** and **4a** required refluxing temperatures of 65 °C and 35 °C, respectively, while the tellurium analogs **2c** and **3c** were not stable for extended periods of time at any accessible temperature, although dilute solutions maintained at –80 °C could be kept for 2 or 3 d before significant decomposition (as evidenced by the precipitation of tellurium metal) occurred. All of the compounds are highly water-, oxygen- and photosensitive. The sulfur and selenium derivatives are highly malodorous oils while the tellurium derivatives are obtained as yellow solids.

Selected NMR spectroscopic data are provided in Table 2. The ^1H chemical shifts of the methylene groups attached to the chalcogen centers show an upfield trend upon substitution by a heavier, less electronegative chalcogen while the trimethylsilyl resonances shift downfield. The chemical shifts of 3.05–3.25 ppm for the methylene group in the sulfur derivatives are upfield of those reported for S-aryl-substituted derivatives.[49,54] The ^{13}C chemical shifts of the methylene groups remain virtually constant upon varying R but are highly dependent on the chalcogen. The upfield shifts for the methylene carbons attached to selenium and tellurium are consistent with those observed previously[51,55] but were assigned conclusively by heteronuclear single-bond quantum correlation (HSQC) NMR spectroscopy techniques.

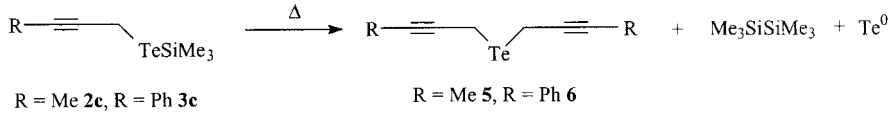
Table 2. Selected NMR spectroscopic data for **2**–**4** in C_6D_6. Chemical shifts are reported in ppm.

	^1H		^{13}C				$^{77}Se/^{125}Te$
	CH_2	$Si(CH_3)_3$	R–C≡C–	≡C–CH_2	CH_2	$Si(CH_3)_3$	
2a	3.10	0.25	77.97	78.42	14.44	0.79	–
2b	2.97	0.32	78.41	78.53	2.53	1.49	2.1
2c[a]	2.80	0.42	77.11	79.88	3.61	2.31	–80.9
3a	3.25	0.25	88.71	83.03	14.73	0.89	–
3b	3.14	0.34	89.39	83.18	2.55	1.51	12.4
3c[b]	2.89	0.42	91.27	81.67	5.00	2.21	–56.7
4a	3.05	0.24	81.13		14.29	0.83	–
4b	2.96	0.32	81.87		2.68	1.87	4.0

[a] Recorded at –50 °C in C_7D_8. [b] Recorded at –80 °C in C_7D_8.

Thermal Decomposition of 2c and 3c

Initial attempts at extending this chemistry to tellurium met with poor results as the reaction solutions rapidly decomposed to tellurium metal and colored tars. Maintaining the entire reaction at low temperatures resulted in beige-yellow solutions, which would decompose even at –25 °C. Although unstable, $RC{\equiv}CCH_2TeSiMe_3$ (**2c**, R = Me; **3c**, R = Ph) can be isolated provided reaction conditions are maintained below –40 °C. (Scheme 3) Although solid samples of **3c** decomposed significantly at –80 °C after 3 d, the



Scheme 3. Decomposition pathway of **2c** and **3c**.

slightly higher stability vs. **2c** allowed for its decomposition pathway to be studied. An aliquot of a reaction mixture of **3c** was isolated and dried (below –40 °C) and then, over a period of 5 d, the reaction flask was maintained at –25 °C and aliquots were taken and isolated at this temperature to monitor the reaction. ^{125}Te NMR spectra showed clearly that **3c** (δ = –56.7 ppm) was converting cleanly to a new compound **6** (δ = +679.7 ppm) and observation of the flask indicated the presence of Te^0. Due to the wide range of ^{125}Te chemical shifts for telluroethers (e.g. Me_2Te δ = 0 ppm, tBu_2Te δ = 999 ppm)[56] and ditellurides (Me_2Te_2 δ = 69 ppm, $MeTe_2tBu$ δ = 617 ppm)[57] a chemical shift value of +679.7 ppm is not diagnostic. The identity of the species as the telluroether $(PhC{\equiv}CCH_2)_2Te$ **6** could be inferred via the ^{125}Te-^{1}H spectrum which displayed a quintet at +679.7 ppm ($^2J_{Te-H}$ = 29 Hz) in addition to a multiplet at δ = –56.7 ppm assigned to **3c**. A $^2J_{TeH}$ value of 29 Hz observed for the peak centered at +679.7 ppm is consistent with this structural assignment.[58] Mass spectra of partially decomposed solutions of **2c** and **3c** were obtained and parent ions for the telluroethers **5** and **6**, respectively, were observed. If samples of **5** and **6** are exposed to the air, further deposition of Te^0 is observed and GC-MS analysis of the supernatant displays predominantly the corresponding propargyl alcohol $RC{\equiv}CCH_2OH$. Attempts to synthesize an authentic sample of **6** via the reaction of two equivalents of 1-bromo-3-phenyl-2-propyne with Na_2Te or Li_2Te[59] were unsuccessful in our hands due to the formation of the coupled product, 1,6-diphenylhexa-1,5-diyne. The ability of Te^{2-} to couple allyl halides has been reported by Clive and co-workers[60] and is thought to proceed via homolytic fission of the telluroether initially formed. In their study, high reaction temperatures were required to force the elimination of the Te^0 but they found that the stability of the organic radical thus generated was the primary thermodynamic barrier. In the case of **6**, both radicals would be extremely delocalized and thus the dissociation may proceed easily. Similar, but more complex reaction mixtures were observed for the attempted synthesis of **5** from M_2Te.

Experimental Section

All syntheses were carried out using standard inert atmosphere Schlenk and glovebox techniques. Bis(trimethylsilyl) sulfide,[36] bis(trimethylsilyl) selenide and bis(trimethylsilyl) telluride were synthesized according to the literature procedure reported for bis(trimethylsilyl) sulfide. 1-Bromo-3-phenyl-2-propyne, 1-bromo-2-butyne and 1,4-dibromo-2-butyne were synthesized from the corresponding propargyl alcohols using phosphorus tribromide.[37] *n*BuLi (1.6 M in hexanes) was used as received from Aldrich Chemical Co. Reaction solvents were dried by passing through packed columns of alumina using commercially available (MBraun) solvent drying towers. C_6D_6 was dried with Na/K alloy. Celite was dried under vacuum by heating at 100 °C for several days. NMR spectra were obtained with a Varian INOVA 400 MHz spectrometer. ^{1}H and ^{13}C spectra were referenced to internal solvent peaks relative to tetramethylsilane (TMS) at 0 ppm. ^{77}Se{^{1}H} and ^{125}Te{^{1}H} spectra were indirectly referenced to external $PhESiMe_3$ (+85.6, E = Se; +11.6, E = Te) relative to Me_2E at 0 ppm.[26,38] ^{29}Si spectra were obtained indirectly via a ^{1}H{^{29}Si} heteronuclear multiple bond correlation (HMBC) pulse sequence with a magnetization transfer time of 83 ms (coupling constant of 6 Hz) and were referenced to internal silicone grease at –21.5 ppm relative to TMS at 0 ppm. Chemical Analyses were performed by Chemisar Laboratories Inc. (Guelph Ontario). Due to their sensitivity, elemental analyses were not possible for the Se/Te derivatives **2b–c**, **3c** and **4b–c**. Mass spectra and precise mass determinations were performed with a Finnigan MAT 8200 instrument. Gas Chromatography-Mass Spectrometry measurements were performed on a Varian CP-3800 Gas Chromatograph with a Varian Saturn 2000 GC-MS analyzer.

Synthesis of $LiESiMe_3$ (1a–c): In a modification of the published procedure,[34] bis(trimethylsilyl) sulfide (0.20 mL, 0.953 mmol) was diluted in tetrahydrofuran (THF, 20 mL) and cooled to 0 °C. *n*-Butyllithium (1.6 M in hexanes, 0.60 mL, 0.953 mmol) was added dropwise causing a slight yellow color to develop which faded as the addition was completed. The cooling bath was removed after 30 min and the reaction was stirred for a further 30 min. Removal of the solvent in vacuo afforded an oily white solid, **1a**.

The syntheses of **1b** and **1c** were performed by the same method, although the preparation of **1c** required cooling the reaction solution to –40 °C. While **1a** and **1b** were relatively stable under an inert atmosphere at ambient temperatures, **1c** began to decompose within an hour after drying and so was used immediately in further reactions.

1a·0.84thf: ^{1}H NMR (C_6D_6): δ = 3.90 (thf), 1.50 (thf), 0.58 (–$SiMe_3$) ppm. ^{13}C{^{1}H} NMR: δ = 68.81 (thf), 25.45 (thf), 7.32 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 7.2 ppm.

1b·0.88thf: ^{1}H NMR (C_6D_6): δ = 3.93 (thf), 1.50 (thf), 0.70 (–$SiMe_3$) ppm. ^{13}C{^{1}H} NMR: δ = 68.99 (thf), 25.44 (thf), 7.87 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 4.10 ppm. ^{77}Se NMR: δ = –518.1 ppm.

1c·3.4thf: ^{1}H NMR (C_6D_6): δ = 3.76 (thf), 1.48 (thf), 0.88 (–$SiMe_3$) ppm. ^{13}C{^{1}H} NMR: δ = 68.69 (thf), 25.53 (thf), 9.71 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = –19.43 ppm. ^{1}H NMR ([H_8]thf): δ = 0.33 (–$SiMe_3$) ppm. ^{13}C{^{1}H} NMR: δ = 9.25 (–$SiMe_3$) ppm. ^{125}Te{^{1}H} NMR: δ = –1294.3 ppm.

Synthesis of 1-Trimethylsilylthio-2-butyne (2a): A freshly prepared sample of $LiSSiMe_3$ (2.38 mmol) was dissolved in pentane (50 mL). The flask was covered with aluminum foil and cooled to –78 °C. A cold (–78 °C) solution of 1-bromo-2-butyne (0.32 g, 2.38 mmol) in hexane (10 mL) was added dropwise and the solution was stirred at low temperature for 2 h and then the bath was warmed. After stirring at room temperature for 5 h, a ubiquitous white suspension had formed. Reaction completion was confirmed by monitoring via GC-MS and the reaction solution was filtered twice over celite to ensure removal of LiBr. The solvent was removed in vacuo from

the colorless filtrate to afford analytically pure **2a** as a colorless oil in 60% yield (0.23 g). ^{1}H NMR (C_6D_6): δ = 3.10 (q, ^5J = 2.6 Hz, 2 H, –CH_2–), 1.47 (t, ^5J = 2.6 Hz, 3 H, –CH_3,), 0.25 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR: δ = 78.42 (C≡C), 77.97 (C≡C), 14.44 (CH_2), 3.35 (CH_3), 0.79 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 16.25 ppm. $C_7H_{14}SSi$ (158.3): calcd. C 53.10, H 8.91; found C 52.86, H 9.11. Exact mass: calculated 158.058549, found 158.058489.

Synthesis of 1-Trimethylsilylseleno-2-butyne (2b): A freshly prepared sample of $LiSeSiMe_3$ (2.31 mmol) was dissolved in pentane (50 mL). The flask was covered with aluminum foil and cooled to –78 °C. A cold (–78 °C) solution of 1-bromo-2-butyne (0.31 g, 2.31 mmol) in hexane (10 mL) was added dropwise and the solution was stirred at low temperature for 2 h. The bath was warmed and after stirring at room temperature for 2 h, a ubiquitous white suspension had formed. Reaction completion was confirmed by monitoring via GC-MS and the reaction solution and the reaction solution was filtered twice over celite to ensure removal of LiBr. The solvent was removed in vacuo from the filtrate to afford **2b** as a pale yellow oil in 94% yield (0.45 g).^{1}H NMR (C_6D_6): δ = 2.97 (q, ^5J = 2.6 Hz, 2 H, –CH_2–), 1.49 (t, ^5J = 2.6 Hz, 3 H, –CH_3), 0.32 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR: δ = 78.53 (C≡C), 78.41 (C≡C), 3.55 (CH_3), 2.53 (CH_2), 1.49 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 14.3 ppm. $^{77}Se\{^1H\}$ NMR: δ = 2.1 ppm. Exact mass: calculated 206.002999, found 206.003044.

Synthesis of 1-Trimethylsilyltelluro-2-butyne (2c): A freshly prepared sample of $LiTeSiMe_3$ (2.34 mmol) was dissolved in pentane (50 mL) to give a beige solution due to slight decomposition of the $LiTeSiMe_3$. The flask was covered with aluminum foil and cooled to –78 °C. A cold (–78 °C) solution of 1-bromo-2-butyne (0.31 g, 2.34 mmol) in hexane (10 mL) was added dropwise and the solution was stirred at low temperature for 2 h to ensure reaction completion although a white solid was evident after 10 min. Attempts to confirm reaction completion by GC-MS failed as only a small amount of bis(trimethylsilyl) telluride was observed along with several unidentified organic compounds. The beige-yellow suspension was filtered at –78 °C through a cold bath jacketed filter and the receiver flask was also kept at low temperature. Removal of the solvent in vacuo at or below –40 °C afforded a **2c** as a yellow solid which decomposed significantly over a period of three days even when kept at –80 °C. ^{1}H NMR (C_7D_8, –50 °C): δ = 2.80 (q, ^5J = 2.7 Hz, 2 H, –CH_2–), 1.45 (t, ^5J = 2.7 Hz, 3 H, –CH_3), 0.42 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR: δ = 79.88 (C≡C), 77.11 (C≡C), 5.19 (CH_3), 3.61 (CH_2), 2.31 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = –2.44 ppm. $^{125}Te\{^1H\}$ NMR: δ = –80.9 ppm.

Synthesis of 3-Phenyl-1-trimethylsilylthio-2-propyne (3a): A freshly prepared sample of $LiSSiMe_3$ (2.38 mmol) was dissolved in hexane (50 mL). The flask was covered with aluminum foil and cooled to 0 °C. A cold (0 °C) solution of 1-bromo-3-phenyl-2-propyne (0.44 g, 2.26 mmol) in hexane (10 mL) was added dropwise and the solution was stirred at low temperature for 1 h and then the bath was warmed. After stirring at room temperature for 1 h, the reaction was heated to reflux for 5 h by which time a ubiquitous white suspension had formed. Reaction completion was confirmed by monitoring via GC-MS and the reaction solution and the reaction solution was filtered twice over celite to ensure removal of LiBr. The solvent was removed in vacuo from the colorless filtrate to afford **3a** as a pale yellow oil in 75% yield (0.37 g). ^{1}H NMR (C_6D_6): δ = 7.39 (m, 2 H, H_{ortho}), 6.97 (m, 3 H, $H_{meta/para}$), 3.25 (s, 2 H, –CH_2–), 0.25 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$: 131.81 (C_{ortho}), 128.55 (C_{para}), 128.20 (C_{meta}), 123.89 (C_{ipso}), 88.71 (C≡C), 83.03 (C≡C), 14.73 (CH_2), 0.89 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 17.72 ppm. $C_{12}H_{16}SSi$ (220.4): calcd. C 65.39, H 7.32; found C 65.19, H 7.76. Exact mass: calculated 220.074199, found 220.074223

Synthesis of 3-Phenyl-1-trimethylsilylseleno-2-propyne (3b): A freshly prepared sample of $LiSeSiMe_3$ (2.31 mmol) was dissolved in pentane (50 mL). The flask was covered with aluminum foil and cooled to –78 °C. A cold (–78 °C) solution of 1-bromo-3-phenyl-2-propyne (0.43 g, 2.19 mmol) in hexane (20 mL) was added dropwise and the solution was stirred at low temperature for 2 h and then the bath was warmed. After stirring at room temperature for 3 h, a yellow solution with a ubiquitous white solid had formed. Reaction completion was confirmed by monitoring via GC-MS and the reaction solution and the reaction solution was filtered twice over celite to ensure removal of LiBr. The solvent was removed in vacuo from the yellow filtrate to afford **3b** as a yellow oil in 80% yield (0.47 g). ^{1}H NMR (C_6D_6): δ = 7.41 (m, 2 H, H_{ortho}), 6.96 (m, 3 H, $H_{meta/para}$), 3.14 (s, 2 H, –CH_2–), 0.34 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR: δ = 131.78 (C_{ortho}), 128.54 (C_{para}), 128.11 (C_{meta}), 124.06 (C_{ipso}), 89.39 (C≡C), 83.18 (C≡C), 2.55 (CH_2), 1.51 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 13.84 ppm. $^{77}Se\{^1H\}$ NMR: δ = 12.4 ppm. $C_{12}H_{16}SeSi$ (267.3): calcd. C 53.92, H 6.03; found C 53.83, H 5.85. Exact mass: calculated 268.018649, found 268.018393

Synthesis of 3-Phenyl-1-trimethylsilyltelluro-2-propyne (3c): A freshly prepared sample of $LiTeSiMe_3$ (2.34 mmol) was dissolved in pentane (50 mL) to give a beige solution due to slight decomposition of the $LiTeSiMe_3$. The flask was covered with aluminum foil and cooled to –78 °C. A cold (–78 °C) solution of 1-bromo-3-phenyl-2-butyne (0.46 g, 2.34 mmol) in hexane (20 mL) was added dropwise and the solution was stirred at low temperature for 2 h to ensure reaction completion although a white solid was evident after 10 min. Attempts to confirm reaction completion by GC-MS failed as only a small amount of bis(trimethylsilyl) telluride, along with several unidentified organic compounds, was observed. The beige-yellow suspension was filtered at –78 °C through a cold bath jacketed filter and the receiver flask was also kept at low temperature. Removal of the solvent in vacuo at or below –40 °C afforded a **3c** as a yellow solid. Solutions of **3c** decomposed slowly at –25 °C but were more stable at lower temperatures. ^{1}H NMR (–80 °C, C_7D_8): δ = 7.39 (m, 2 H, H_{ortho}), 6.87 (m, 3 H, $H_{meta/para}$), 2.89 (s, 2 H, –CH_2–), 0.42 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR: δ = 131.49 (C_{ortho}), 127.86 (C_{para}), 125.01 (C_{meta}), 123.88 (C_{ipso}), 91.27 (C≡C), 81.67 (C≡C), 5.00 (CH_2), 2.21 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = –0.68 ppm. $^{125}Te\{^1H\}$ NMR: δ = –56.7 ppm.

Synthesis of 1,4-Bis(trimethylsilylthio)-2-butyne (4a): A freshly prepared sample of $LiSSiMe_3$ (2.38 mmol) was dissolved in pentane (50 mL). The flask was covered with aluminum foil and cooled to 0 °C. A solution of 1,4-dibromo-2-butyne (0.24 g, 1.13 mmol) in hexane (2 mL) was added dropwise and the solution was stirred at low temperature for 1 h. The bath was removed and after stirring at room temperature for 1 h, the reaction was heated to reflux for 3 h by which time a ubiquitous white suspension had formed. Reaction completion was confirmed by monitoring with GC-MS and the reaction solution and the reaction solution was filtered twice over celite to ensure removal of LiBr. The solvent was removed in vacuo from the colorless filtrate to afford **4a** as a light colored oil in 74% yield (0.22 g). ^{1}H NMR (C_6D_6): δ = 3.05 (s, 2 H, –CH_2–), 0.24 (s, 9 H, –$SiMe_3$) ppm. $^{13}C\{^1H\}$: 81.13 (C≡C), 14.29 (CH_2), 0.83 (–$SiMe_3$); ^{29}Si: 15.85 ppm. $C_{10}H_{22}S_2Si_2$ (262.6): calcd. C 45.74, H 8.44; found C 46.20. H 8.29. Exact mass: calculated 262.070150, found 262.070121.

Synthesis of 1,4-Bis(trimethylsilylseleno)-2-butyne (4b): A freshly prepared sample of $LiSeSiMe_3$ (2.31 mmol) was dissolved in pen-

tane (50 mL). The flask was covered with aluminum foil and cooled to –78 °C. A cold (–78 °C) solution of 1,4-dibromo-2-butyne (0.23 g, 1.09 mmol) in hexane (20 mL) was added dropwise and the solution was stirred at low temperature for 2 h. The bath was warmed and after stirring at room temperature for 2 h, a pale yellow solution with a ubiquitous white solid had formed. Reaction completion was confirmed by GC-MS and the reaction was filtered to remove the LiBr. The solvent was removed in vacuo from the colorless filtrate to afford **4b** as a pale yellow oil in 80% yield (0.31 g).

N.B. Extreme care to reduce exposure of this compound to ambient light is required as otherwise decomposition to an insoluble white solid occurs. ^{1}H NMR (C_6D_6): δ = 2.96 (s, 2 H, –CH_2–), 0.32 (s, 9 H, –$SiMe_3$) ppm. ^{13}C{^{1}H}: 81.87 (C≡C), 2.68 (CH_2), 1.87 (–$SiMe_3$) ppm. ^{29}Si NMR: δ = 13.69 ppm. ^{77}Se{^{1}H} NMR: δ = 4.0 ppm. Exact mass: calculated 357.959049, found 357.958961.

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