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Reactivity of sulfonyl-containing compounds with ditetrelenes†‡

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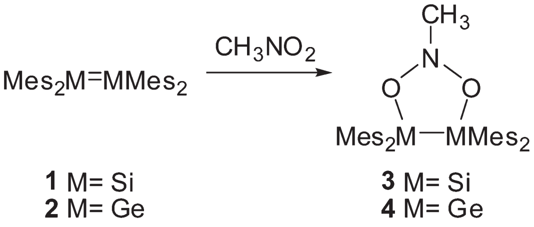
The addition of a variety of sulfones and a sulfoxide to ditetrelenes (a disilene and a digermene) was examined. The reaction of benzenesulfonyl chloride with tetramesityldisilene or tetramesityldigermene results in the formation of the 1,2-addition products, 2-chlorotetramesityldisilyl- or digermylbenzenesulfinate. The addition of *p*-toluenesulfonyl chloride to the disilene gave the analogous product, 2-chlorotetramesityldisilyl *p*-toluenesulfinate. In contrast, benzenesulfonyl fluoride, diphenyl and dimethyl sulfone did not react with either the disilene or the digermene. The unprecedented formation of the sulfinates reveals a selective 2-electron reduction of the sulfur centres using ditetrelenes. The addition reactions of sulfonyl compounds illustrates the potential of ditetrelenes to serve as reducing agents which react rapidly, at room temperature under mild conditions. The reaction of tetramesityldisilene with diphenyl sulfoxide resulted in the formation of tetramesityloxadisilirane and with benzene sulfonic acid resulted in the formation of 1,1,2,2-tetramesityldisilyl benzenesulfonate.

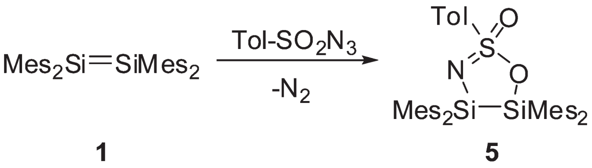
Introduction

The use of main group compounds as reducing agents is well-established and includes common reagents such as PR_3, R_3SnH, and $SnCl_2$. However, the notion of ditetrelenes as reducing agents, although known, has not been well-explored.[1] For example, Scheschkewitz *et al.* have reported the reductive cleavage of carbon monoxide by the addition of lithium disilenide $(Tip)_2Si{=}Si(Tip)Li(dme)_2$ (Tip = 2,4,6-triisopropylphenyl, dme = dimethoxyethane) to CO at room temperature.[2] We also reported the facile and clean, albeit unexpected, two electron reduction of nitromethane by both a disilene and a digermene (Scheme 1).[3]

Although other examples exist where a disilene has formally reduced a nitrogen in reaction with an unsaturated nitrogen-containing functional group,[4,5] we were interested in exploring whether other functional groups could also be readily reduced using ditetrelenes. Sulfur compounds, where the sulfur oxidation number can vary from +6 to −2, appeared to be excellent candidates to study in this regard. Thus, the reactivity of a variety of compounds with sulfur in higher oxidation states, *i.e.* sulfonyl compounds, RSO_2X where R = Ph or Tol and X = Cl, F, OH, or Ph, and a sulfoxide, towards ditetrelenes has been investigated. Notably, only one example of the addition of a sulfonyl derivative to a ditetrelene has been reported to date; the addition of *p*-toluenesulfonyl azide to tetramesityldisilene to give **5** was reported by West and co-workers (Scheme 2).[5] In this case, reduction of nitrogen, rather than sulfur, took place.



Scheme 1 Reduction of nitromethane using **1** and **2**.



Scheme 2 Reaction **1** with *p*-toluenesulfonyl azide.

Results

There was no reaction between diphenyl or dimethyl sulfone with disilene **1**. In contrast, the addition of benzene- or

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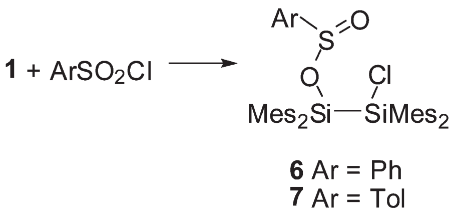
‡ Electronic supplementary information (ESI) available: Selected procedures, ^1H and $^{13}C\{^1H\}$ NMR spectra and crystallographic data for compounds **6**, **7**, **8** and **10**; atomic coordinates and energies for optimized geometries of compounds **6**, **10**, **12** and **13**. CCDC 1479171–1479174. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt02374j

p-toluenesulfonyl chloride to a bright yellow solution of disilene **1** dissolved in hexanes or C_6D_6 at room temperature gave a colourless solution and removal of the solvent gave a white solid. The products were purified by recrystallization from a saturated hexanes solution at low temperature to yield colourless solids which were characterized by multinuclear and multidimensional NMR spectroscopy and mass spectrometry. The structures of **6** and **7** in the solid state were unequivocally determined by single crystal X-ray diffraction as 2-chlorotetramesityldisilyl benzenesulfinate, **6**, and 2-chlorotetramesityldisilyl *p*-toluenesulfinate, **7** (Scheme 3 and Fig. 1; see the ESI‡ for the molecular structure of **7**).

The structural metrics of **6** and **7** are similar and the bond angles and bond lengths for both adducts are within expected ranges: the Si–Cl bond lengths (2.0981(13) Å for **6** and 2.0949(8) Å for **7**), the Si–O bond lengths (1.700(2) Å for **6** and 1.6953(14) Å for **7**) and the Si–Si bond distances (2.3993(14) Å for **6** and 2.3997(10) Å for **7**) are not significantly different from the average Si–Cl (2.065 ± 0.046 Å), Si–O (1.628 ± 0.032 Å) and Si–Si (2.363 ± 0.035 Å) bond lengths, respectively, found in similar four-coordinate silicon compounds on the basis of a search of the Cambridge Structural Database.[6] Both sulfur atoms exhibit pyramidal geometry (for example, the sulfur in **6** is displaced from the plane of the attached atoms by 0.6882(19) Å), indicating the presence of a stereochemically active lone pair. The non-bridging oxygen–sulfur bond distances are 1.462(3) and 1.4601(17) Å, for **6** and **7**, respectively, indicative of terminal oxygen–sulfur bonds, while the bridging oxygen–sulfur bonds have lengths of 1.637(2) and 1.6318(14) Å for **6** and **7**, respectively, that are longer, as expected, than the terminal oxygen–sulfur bonds. Compounds **6** and **7** are air- and moisture-sensitive and decompose upon exposure to air or upon chromatography.



Scheme 3 Synthesis of arylsulfinates **6** and **7**.

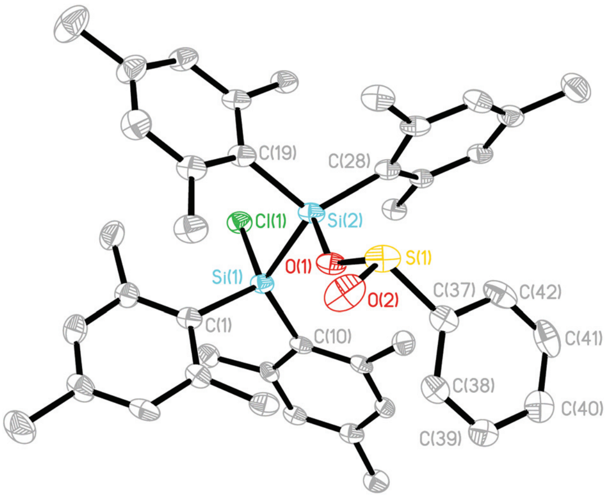


Fig. 1 Displacement ellipsoid plot of **6**. Ellipsoids are at the 50% probability level and hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–Cl1 = 2.0981(13), Si1–Si2 = 2.3993(14), S1–O2 = 1.462(3), S1–O1 = 1.637(2), Si2–O1 = 1.700(2); Cl1–Si1–Si2 = 99.86(5), O2–S1–O1 = 105.23(14), O2–S1–C37 = 105.88(16), O1–Si2–Si1 = 101.47(9), S1–O1–Si2 = 134.54(15).

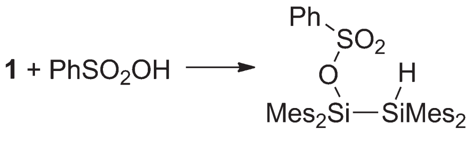
Due to the presence of the chiral sulfur centre, the two mesityl groups on each silicon of **6** and **7** are diastereotopic. Accordingly, the ^1H NMR spectra of **6** and **7** reveal the presence of four nonequivalent mesityl groups in addition to an aryl group. The signals assigned to the *o*-methyl groups on the mesityl groups in each spectrum are broad due to the slow rotation of the mesityl groups on the NMR time scale. Heating the sample to 70 °C resulted in sharpening of the signals in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **6** and **7**.

To explore the effect of the halide on the outcome of the reaction, the addition of benzenesulfonyl fluoride to disilene **1** was also examined; no reaction was observed.

The addition of benzenesulfonic acid to a yellow solution of disilene **1** in hexanes yielded a clear, colourless solution within a few minutes. The ^1H NMR spectrum of **8** showed two sets of mesityl signals and a singlet at 5.71 ppm, which was assigned to a Si–H moiety. Accordingly, the IR spectrum of **8** revealed an absorption at 2200 cm^{-1}, which is in the range typical for the stretching vibration of an Si–H bond. The strong absorption at 1349 cm^{-1} in the IR spectrum of **8** was assigned to the terminal SO bond stretching vibration, and the absorption at 909 cm^{-1} was assigned to the bridging S–O bond stretching vibration. The structure of **8** was confirmed by X-ray crystallography as 1,1,2,2-tetramesityldisilyl benzenesulfonate (Scheme 4 and Fig. 2). All bond lengths and angles are within normal ranges.

The addition of excess diphenyl sulfoxide to a bright yellow solution of disilene **1** in hexanes at room temperature gave a colourless solution. Removal of the solvent yielded a white solid, which revealed the presence of tetramesityloxadisilirane, Mes_4Si_2O, **9**,[7] and diphenylsulfide as confirmed by ^1H NMR spectroscopy (Scheme 5).

To compare the addition of sulfonyl compounds to tetramesityldisilene with a heavier congener, the reaction of sulfonyl compounds with tetramesityldigermene (**2**) was also examined.



8

Scheme 4 Synthesis of arylsulfonate **8**.

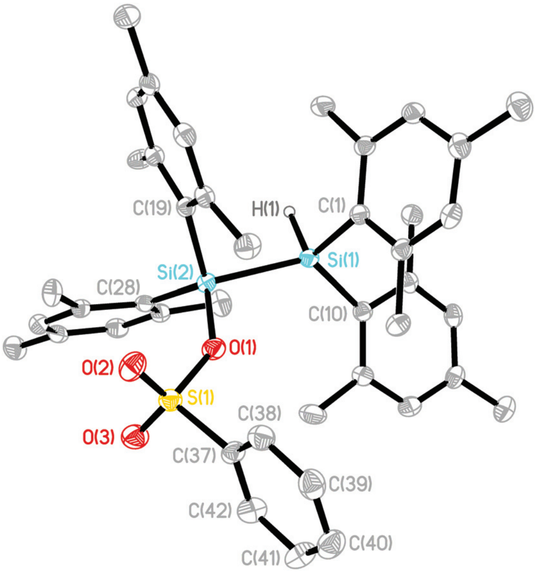
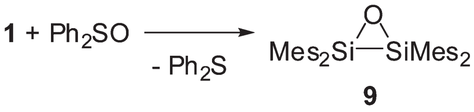


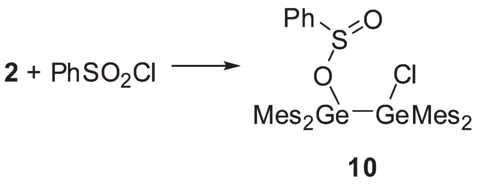
Fig. 2 Displacement ellipsoid plot of **8**. Ellipsoids are at the 50% probability level and hydrogen atoms were omitted for clarity except the hydrogen on Si1. Selected bond lengths (Å) and angles (°): Si1–Si2 = 2.3757(10), Si1–H1 = 1.46(2), Si2–O1 = 1.7127(16), S1–O3 = 1.4253(17), S1–O2 = 1.4274(16), S1–O1 = 1.5486(16); C1–Si1–Si2 = 110.96(7), C1–Si1–H1 = 106.3(8), C10–Si1–H1 = 107.2(8), Si2–Si1–H1 = 96.6(8), O1–Si2–Si1 = 106.10(6).



Scheme 5 Reaction of **1** with diphenyl sulfoxide.

In a similar fashion, the addition of benzenesulfonyl chloride to digermene **2** in THF at room temperature produced 2-chlorotetramesityldigermyl benzenesulfinate **10** (Scheme 6), as confirmed by X-ray crystallography. All bond lengths and angles of **10** are within normal ranges. The sulfur exhibits pyramidal geometry similar to **6** and **7**; in this case, the sulfur is displaced from the plane by 0.6615(20) Å (see the ESI‡ for the molecular structure of **10**).

Similar to disilene **1**, no reaction was observed upon the addition of benzenesulfonyl fluoride and diphenyl sulfone to digermene **2**.



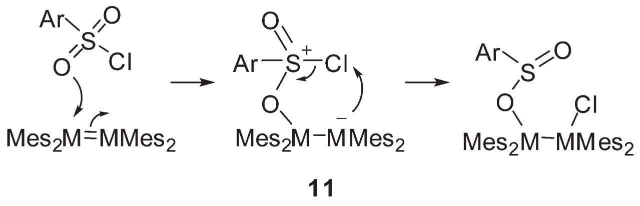
Scheme 6 Synthesis of arylsulfinate **10**.

Discussion

The lack of reaction between dimethyl and diphenyl sulfone and disilene **1** and digermene **2** is interesting. Although addition reactions are not known between sulfones and alkenes,[8] it did not seem unreasonable that sulfones may react with ditetrelenes given that ditetrelenes are more reactive than alkenes and often exhibit reactivity which is unprecedented in alkene chemistry.[1,9] For example, the addition of nitro compounds to alkenes, in general, proceeds through the nitronate isomer,[10] whereas the addition of the same functional group to ditetrelenes gives a [3 + 2] cycloadduct.[3] Furthermore, the possibility of forming a sulfurane (oxide) from the reaction with a sulfone was appealing. The lack of reactivity between the sulfones and the ditetrelenes may be attributable to the reduction potential of sulfones in comparison to nitro compounds. The standard reduction potential for diphenyl sulfone is about −2.42 V *versus* Fc/Fc$^+$,[11] whereas that for nitrobenzene is −1.49 V *versus* Fc/Fc$^+$.[12,13] The electronic structure of sulfones, with two highly polarized oxygen–sulfur bonds having important contributions from negative (reciprocal) hyperconjugation interactions,[14] in comparison to nitroalkanes is apparently not amenable to reaction, even with ditetrelenes, to give a sulfurane (oxide).

In contrast, arylsulfonyl chlorides readily react with ditetrelenes, albeit to give β-chlorosulfinates and not a cycloadduct. Notably, arylsulfonyl chlorides are more easily reduced than sulfones (−0.33 V *versus* Fc/Fc$^+$).[11b,15] We propose the following mechanism to account for the formation of the sulfinate adducts **6**, **7** and **10**. Nucleophilic attack by one of the sulfonyl oxygens on the ditetrelene would give intermediate **11**, consistent with the mechanism postulated for the addition of water (or alcohols) to disilenes.[16] The nucleophilic addition of water to disilenes is strongly exothermic with a small activation energy.[17] In a second step (if the reaction is not concerted), the silicon (or germanium) attacks the chlorine, reducing the sulfur atom and giving the final product (Scheme 7). The addition of *p*-toluenesulfonyl azide to tetramesityldisilene was also proposed to be stepwise, where nucleophilic attack of oxygen on the disilene was followed by ring closure and simultaneous loss of N$_2$ resulting in the formation of **5**.[5]

The proposed mechanism for the formation of the sulfinates **6**, **7** and **10** is consistent with the observed lack of reactivity of benzenesulfonyl fluoride towards tetramesityldisilene and -digermene. The nucleophilicity of a terminal oxygen in benzenesulfonyl fluoride is expected to be lower than that in



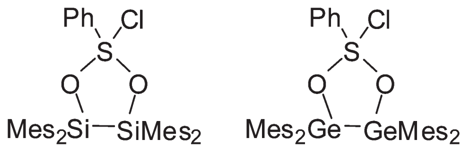
Scheme 7 Proposed mechanism for the formation of the arylsufinates.

benzenesulfonyl chloride, reducing the rate of the first step. Furthermore, the low polarizability of fluorine in comparison to chlorine would further inhibit the reaction, as the halide abstraction would not be facile for the fluoride derivative.

The reaction of the sulfonyl chlorides with the ditetrelenes gives an acyclic isomer, rather than a cyclic sulfurane. The relative energies of the two isomeric pairs (**6**/**12** and **10**/**13**; Chart 1) as calculated at the M06/6-311+G* level of theory[18] are consistent with this observation: sulfurane **12** is 92.1 kJ mol^{-1} higher in energy than the 1,2-adduct **6**, and sulfurane **13** is 119.2 kJ mol^{-1} higher in energy than the 1,2-adduct **10**. Attempts to optimize the isomeric 4-membered ring sulfurane oxide structures (nominally through a 1,2-dipolar addition) were unsuccessful; the structures eventually optimized to the 5-membered sulfuranes for both the silicon and the germanium analogs.

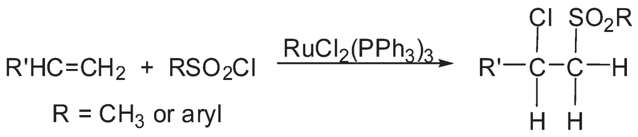
It is interesting to compare the observed reactivity of ditetrelenes towards sulfonyl chlorides with the chemistry of the analogous alkenes. Although the addition of organosulfonyl chlorides to alkenes in the presence of a peroxide to form a β-chlorosulfone has been known for some time,[19] the yields of the reactions are often low due to competing reactions.[19,20] However, in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium, the addition of alkyl- and arylsulfonyl chlorides to alkenes at high temperature (120 °C) proceeds cleanly in high yield (Scheme 8).[21] The use of the Ru(III) complex, [Cp*$RuCl_2(PPh_3)$] as a pre-catalyst in combination with AIBN improved the yield of the β-chlorosulfones at lower temperatures (60 °C) and with higher turnover numbers.[22] The reaction of sulfonyl chlorides with alkenes is believed to proceed *via* a radical redox mechanism.

In contrast, the addition of sulfonyl chlorides to ditetrelenes proceeds almost instantly without a catalyst or heat to give β-chlorosulfinates. The formation of the strong Si–O bond and a difference in reaction mechanisms (radical *versus* heterolytic) may account, at least in part, for the difference in the products formed. Notably, the sulfur in the β-chlorosulfones, resulting from the addition of sulfonyl chlorides to alkenes, has the same oxidation number (+6) as the starting sulfonyl chloride whereas, in the β-chlorosulfinate esters, resulting from the addition of sulfonyl chlorides to a ditetrelene, the sulfur is reduced from the +6 to the +4 oxidation number. The selective two electron reduction of sulfonyl chlorides mirrors the same reduction of nitroalkanes by ditetrelenes.



12 **13**

Chart 1 Sulfuranes **12** and **13**.



Scheme 8 Reaction of alkenes with sulfonyl chlorides.

The sulfur atom in diphenyl sulfoxide is also reduced by disilene **1** going from the +4 to the +2 oxidation state, albeit the reaction follows a different pathway. In this case, an oxygen is abstracted to give an oxadisilirane and the corresponding sulfide. The reduction of sulfoxides to their corresponding sulfides has been reported using both main group compounds and metal complexes.[23] The addition of benzenesulfonic acid also exhibits different reactivity in comparison to the sulfonyl chloride; however, this is completely expected. Addition across the OH bond of the sulfonic acid is observed, a common reaction mode with hydroxyl-containing compounds.[1] Not surprisingly, the sulfur in benzenesulfonate **8**, has the same oxidation number (+6) as the starting sulfonic acid.

Sulfinates are an important class of molecules which have recently been exploited in organic synthesis due to their versatility and accessibility and various procedures have been reported for their preparation.[24] Most relevant to the current discussion is the reduction of sulfonyl chlorides without an α-hydrogen using trialkoxy-[25] or triarylphosphines[26] and an amine. The generation of silylated/germylated sulfinates **6**, **7** and **10**, *via* the addition of sulfonyl chlorides to ditetrelenes, offers an alternative, facile route for the formation of sulfinates, which proceeds without the use of heat or a catalyst under very mild conditions. However, given that disilene **1** and digermene **2** are not commercially available and are quite reactive requiring manipulation under inert conditions, the use of ditetrelenes for the synthesis of sulfinates will be limited to specialty applications which also require inert conditions.

Conclusions

In conclusion, the addition of sulfonyl chlorides to tetramesityldisilene and tetramesityldigermene leads to the facile formation of the 1,2-addition products, 2-chlorotetramesityldisilyl benzene(*p*-toluene)sulfinate and 2-chlorotetramesityldigermyl benzenesulfinate, respectively. On the other hand, the addition of a sulfonyl fluoride or a sulfone to both disilene and digermene gave no reaction. The formation of sulfinates (**6**, **7** and **10**) reveals a mild two-electron reduction of the sulfur centres using ditetrelenes. In the case of a sulfoxide, oxygen abstraction by the disilene was observed and addition across an OH was observed upon the addition of a sulfonic acid to a disilene. Although oxygen abstraction and the σ-addition of a hydroxyl group are well-known reactivity motifs in ditetrelene chemistry, the reduction of sulfonyl chlorides to give β-chlorosulfinates is unprecedented and could be exploited in synthetic or materials chemistry.

Experimental

General experimental details

All air sensitive reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk techniques or a glove box. Hexanes and THF were obtained from a solvent purification system (SPS-400-5, Innovative Technology Inc.). NMR spectra were recorded on a Varian Inova 400 or an Inova 600 MHz NMR spectrometer. The NMR standards used were residual C_6D_5H (7.15 ppm) for ^1H NMR spectra and the central signal of C_6D_6 (128.00 ppm) for $^{13}C\{^1H\}$ NMR spectra. ^1H, ^{13}C and ^{29}Si NMR signals were assigned using ^1H–^1H gCOSY, ^1H–^{13}C gHSQC, ^1H–^{13}C gHMBC and/or ^{29}Si–^1H gHMBC NMR spectroscopy. IR spectra were recorded (cm^{-1}) from thin films on a Bruker Tensor 27 FT-IR spectrometer. ESI-TOF mass spectra were obtained using a Bruker micrOTOF instrument. Mass spectral data are reported in mass-to-charge units, *m*/*z*. X-ray data were obtained using a Bruker Apex II Diffractometer. Ge_3Mes_6[27] and $(Me_3Si)_2SiMes_2$[28] were synthesized according to the literature procedures. Due to small sample sizes and the air- and moisture-sensitivity of the samples, elemental analyses were not performed.

Addition of benzenesulfonyl chloride (or *p*-toluenesulfonyl chloride) to tetramesityldisilene (1)

$Mes_2Si(SiMe_3)_2$ (50 mg, 0.12 mmol) was placed in a quartz tube, dissolved in hexanes (3 mL), and then placed in a quartz Dewar. The solution was irradiated (254 nm) for ∼18 h to give a bright yellow solution. The solution was cooled to −60 °C during the irradiation by circulating cold methanol. Excess benzenesulfonyl chloride (14 mg, 0.08 mmol) (or *p*-toluenesulfonyl chloride (13 mg, 0.08 mmol)) was added to the yellow solution at room temperature and the mixture was allowed to stir. After 5 min, the solution became pale yellow. The hexanes were evaporated giving a pale yellow oil which was redissolved in a minimal amount of hexanes. ^1H NMR spectroscopy revealed the presence of only one product. The solution was placed in the freezer (−20 °C) for 24 h to give colourless crystals, which were isolated by decantation. The solid was triturated with pentane yielding colourless, clear crystals of **6** (30 mg, 53%). m.p. 174–176 °C; ^1H NMR (C_6D_6, 600 MHz, 70 °C) δ 7.59 (br s, 2H, Ph *o*-H), 7.00 (3H, Ph *m*-H + *p*-H), 6.75 (br s, 2H, Mes *m*-H), 6.69 (br, 4H, Mes *m*-H), 6.59 (s, 2H, Mes *m*-H), [2.40 (br s, Mes *o*-CH_3), 2.21 (br s, Mes *o*-CH_3), 2.11 (s, Mes *p*-CH_3), 2.08 (s, Mes *p*-CH_3), 2.07 (s, Mes *p*-CH_3), 2.01 (s, Mes *p*-CH_3) all together 36H]; ^{13}C NMR (C_6D_6, 150 MHz, 70 °C) δ 150.16 (Ph *i*-C), 144 (Mes *o*-C),[29] 140.25 (Mes *p*-C), 140.01 (Mes *p*-C), 139.72 (Mes *p*-C), 139.60 (Mes *p*-C), 131.69 (Mes *i*-C + Ph *p*-CH), 130.20 (Mes *m*-CH), 130.17 (Mes *m*-CH), 129.5 (br s, Mes *m*-CH), 128.77 (Ph *m*-CH), 124.67 (Ph *o*-CH), 25 (Mes *o*-CH_3),[30] 20.99 (Mes *p*-CH_3), 20.89 (Mes *p*-CH_3), 20.87 (Mes *p*-CH_3), 20.81 (Mes *p*-CH_3); ^{29}Si NMR (C_6D_6, 119 MHz, 70 °C)[31] δ −4.19, −4.15; FTIR (thin film, cm^{-1}) 2920 (br s), 1603 (s), 1445 (s), 1143 (m), 819 (m), 755 (m); high resolution ESI-MS *m*/*z* for $C_{42}H_{49}O_2NaSi_2S^{35}Cl$ calc. 731.2578 found 731.2568.

Colourless, clear crystals **7** (35 mg, 50%) m.p. 172–174 °C; ^1H NMR (C_6D_6, 600 MHz, 70 °C) δ 7.54 (br s, 2H, Ph *o*-CH), 6.84 (m, 2H, Ph *m*-CH), 6.76 (s, 2H, Mes *m*-CH), 7.00 (br s, 4H, Mes *m*-CH), 6.60 (s, 2H, Mes *m*-CH), [2.42 (br s, Mes *o*-CH_3), 2.24 (br s, Mes *o*-CH_3), 2.12 (s, Mes *o*-CH_3), 2.08 (s, Mes *p*-CH_3), 2.07 (s, Mes *p*-CH_3), 2.01 (s, Mes *p*-CH_3), 1.94 (s, Tol *p*-CH_3) all together 39H]; ^{13}C NMR (C_6D_6, 150 MHz, 70 °C) δ 147.50 (Ph *i*-C), 145.20 (br s, Mes *o*-C), 142.18 (Ph *p*-C), 140.20 (Mes *p*-C), 139.95 (Mes *p*-C), 139.68 (Mes *p*-C), 139.57 (Mes *p*-C), 131.96 (br s, Mes *i*-C), 130.17 (Mes *m*-CH), 129.97 (br s, Mes *m*-CH), 129.44 (Ph *m*-CH), 124.79 (Ph *o*-CH), 25.39 (br s, Mes *o*-CH_3), 21.13 (Tol. *p*-$CH_{3)}$, 21.00 (Mes *p*-CH_3), 20.90 (Mes *p*-CH_3), 20.87 (Mes *p*-CH_3), 20.81 (Mes *p*-CH_3); ^{29}Si NMR (C_6D_6, 119 MHz, 70 °C) δ −4;[32] FTIR (thin film, cm^{-1}) 3017 (s), 2958 (s), 2921 (s), 1603 (s), 1449 (s), 1139 (m), 824 (s), 757 (s); high resolution ESI-MS *m*/*z* for $C_{43}H_{51}O_2NaSi_2SCl$ calc. 745.2735 found 745.2749.

Addition of benzenesulfonic acid to tetramesityldisilene

$Mes_2Si(SiMe_3)_2$ (100 mg, 0.24 mmol) was placed in a quartz tube, dissolved in hexanes (3 mL), and then placed in a quartz Dewar. The solution was irradiated (254 nm) for ∼18 h to give a bright yellow solution. The solution was cooled to −60 °C during the irradiation by circulating cold methanol. Excess benzenesulfonic acid (23.7 mg, 0.15 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir. After 5 min, the solution became colourless. The hexanes were evaporated giving a pale yellow powder, which was redissolved in a minimal amount of hexanes. The flask was placed in the freezer (−20 °C) for 24 h. A fine precipitate formed which was isolated by centrifugation. The solid was triturated with pentane yielding colourless, clear crystals of **8** (80 mg, 77%) White powder; m.p. 188–190 °C; ^1H NMR (C_6D_6, 400 MHz) δ 7.82 (d, 2H, Ph *o*-H, *J* = 8 Hz), 6.89 (t, 1H, Ph *p*-H, *J* = 7 Hz), 6.84 (t, 2H, Ph *m*-H, *J* = 8 Hz), [6.66 (s, Mes *m*-H) 6.63 (s, Mes *m*-H) all together 8H], 5.68 (s, 1H, Si–H), 2.30 (br s, 24H, Mes *o*-CH_3), [2.06 (s, Mes *p*-CH_3), 2.04 (s, Mes *p*-CH_3) all together 12H]; ^{13}C NMR (C_6D_6, 150 MHz) δ 145.51 (Mes *o*-C), 144.58 (Mes *o*-C), 140.63 (Ph *i*-C), 140.10 (Mes *p*-C), 139.12 (Mes *p*-C), 132.48 (Ph *p*-CH), 131.69 (Mes *i*-C), 129.99 (Mes *m*-CH), 129.96 (Mes *m*-CH), 129.94 (Mes *m*-CH), 129.93 (Mes *m*-CH), 129.02 (br s, Mes *m*-CH), 128.99 (Mes *m*-CH), 128.54 (Ph *m*-CH), 127.92 (Ph *o*-CH), 24.72 (br s, Mes *o*-CH_3), 24.67 (Mes *o*-CH_3), 24.65 (Mes *o*-CH_3), 21.04 (Mes *p*-CH_3), 21.12 (Mes *p*-CH_3), 21.00 (Mes *p*-CH_3), 20.98 (Mes *p*-CH_3); FTIR (thin film, cm^{-1}) 3022 (s), 2961 (s), 2920 (s), 2200 (m), 1604 (s), 1448 (s), 1350 (s), 1185 (s), 909 (s), 757 (s), 597 (s); ^{29}Si NMR (C_6D_6, 119 MHz) δ 5 (Si–O), −55 (Si–H);[32] high resolution ESI-MS *m*/*z* for $C_{42}H_{50}O_3NaSi_2S$ calc. 713.2917 found 713.2918.

Addition of diphenyl sulfoxide to tetramesityldisilene

$Mes_2Si(SiMe_3)_2$ (50 mg, 0.12 mmol) was placed in a quartz tube, dissolved in hexanes (3 mL), placed in a quartz Dewar. The solution was irradiated (254 nm) for ∼18 h to give a bright yellow solution. The solution was cooled to −60 °C during the irradiation by circulating cold methanol. Excess diphenyl sulfoxide (16 mg, 0.08 mmol) dissolved in hexanes (1 mL) was added to the yellow solution at room temperature, the reaction mixture turned colourless immediately. Tetramesityloxadisilirane (**9**),[6] Mes_4Si_2O, and diphenylsulfide were observed as determined by ^1H NMR spectroscopy.

Addition of benzenesulfonyl chloride to tetramesityldigermene (2)

Ge_3Mes_6 (100 mg, 0.107 mmol) was placed in a quartz tube[33] and dissolved in THF (5 mL) and then irradiated (350 nm) in a quartz Dewar[33] at −60 °C for ~18 h to a give yellow solution. Excess benzenesulfonyl chloride (30 mg, 0.17 mmol) was added to the yellow solution at room temperature and the reaction was allowed to stir. After 5 min, the solution became colourless. The solvent was evaporated giving a clear, colourless oil. The oil was redissolved in a minimal amount of hexanes. The solution was placed in a freezer (−20 °C) for 24 h, yielding crystalline material, which was isolated by decantation. The crystals were triturated with hexanes yielding colourless clear, crystals of **10** (110 mg, 80%). The crystalline material was contaminated with an unidentified compound. Attempts to purify **10** by chromatography (50 : 50 hexanes : DCM) resulted in the decomposition of **10**: m.p. 160–162 °C; ^1H NMR (C_6D_6, 600 MHz, 70 °C) δ 7.65 (dd, 2H, Ph *o*-CH, *J* = 8, 2 Hz), 7.06–7.02 (m, 3H, Ph *m*-H + *p*-H), 6.71 (s, 4H, Mes *m*-H), 6.64 (s, 4H, Mes *m*-H), 2.47 (s, 12H, Mes *o*-CH_3), 2.31 (s, 12H, Mes *o*-CH_3), [2.07 (s, Mes *p*-CH_3), 2.03 (s, Mes *p*-CH_3), all together 12H];[34] ^{13}C NMR (C_6D_6, 150 MHz, 70 °C) δ 152.31 (Ph *i*-C), 143.89 (Mes *p*-C), 143.65 (Mes *p*-C), 139.97 (br s, Mes *o*-C), 139.82 (br s, Mes *o*-C), 136.78 (br s, Mes *i*-C), 136.71 (br s, Mes *i*-C), 130.97 (Ph *p*-CH), 130.09 (Mes *m*-CH), 130.06 (Mes *m*-CH), 128.69 (Ph *m*-CH), 124.45 (Ph *o*-CH), 25.11 (br s, Mes *o*-CH_3), 24.77 (br s, Mes *o*-CH_3), 20.86 (Mes *p*-CH_3), 20.81 (Mes *p*-CH_3);[35] FTIR (thin film, cm^{-1}) 3017 (s), 2964 (s), 2923 (s), 1601 (s), 1446 (s), 1405 (m), 1382 (m), 1147 (s), 849 (s), 754 (s); high resolution ESI-MS for $C_{42}H_{49}O_2S^{70}Ge_2$ $[M - Cl]^+$ (*m*/*z*) calc. 757.1938, found 757.1928; low resolution ESI-MS: 757–769 $[M - Cl]^+$, 815–828 $[M + Na^+]$.[36]

Computational details

All calculations were performed using Gaussian 09[18] on the Shared Hierarchical Academic Research Computing Network (SHARCNET, http://www.sharcnet.ca). Computations were run using two AMD Opteron 2.2 GHz 24 core CPUs with 32 GB of memory. Initial optimization was performed from either crystal structures or modified from previously obtained crystal structures. Optimization was initially performed at the Opt = Loose level until convergence was achieved, upon which the default optimization restraints were used. All optimization and frequency calculations were performed at the B3LYP level of theory,[37] using the 6-31G* basis set, and an ultra fine integration grid. Molecular orbital and single-point energy calculations were performed using the normal population method, using the M06 functional,[38] and the 6-311+G* basis set and using an ultra fine integration grid.

Conflicts of interest

There are no conflicts to declare.

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30 Chemical shift extracted from the ^{1}H–^{13}C gHSQC spectrum.

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34 Additional signals were observed in the ^{1}H NMR spectrum of **10** at 6.69, 2.42, 2.40, 2.06, 1.20, 1.99 ppm in ratio of 1 : 0.06.

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