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The positions of λ_{max} for some trimethylsilyl-substituted silylenes ☆

S.G. Bott *, Paul Marshall *, P.E. Wagenseller, Y. Wang, R.T. Conlin *

Center for Organometallic Research and Education, Department of Chemistry, University of North Texas, Denton, TX 76205-5068, USA

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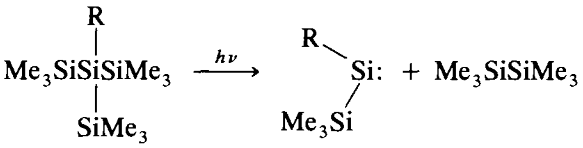
Abstract

Low-temperature photolysis of tris(trimethylsilyl)silane derivatives in a 3-methylpentane glass at 77 K yields hexamethyldisilane and trimethylsilyl-substituted silylenes. These silylenes exhibit broad n → p absorptions at wavelengths typically > 600 nm in the UV and have been captured by 2,3-dimethylbutadiene in cyclohexane at room temperature. Exceptions to the usual position of λ_{max} have been observed and are discussed.

Keywords: Silicon; Silylenes; Electronic spectra; Matrix isolation

1. Introduction

Attention to the polysilanyl group as a conveniently accessible chromophore for silylene production was noted as early as 1970 [1] and has since been utilized synthetically for many previously unknown structures [2–4]. The initial photophysical events of these excited polysilanes include a range of possibilities such as dual fluorescence, phosphorescence, and formation of intramolecular charge-transfer states [5]. Although the primary photochemical events of polysilane photolysis have typically provided silylenes, a variety of other pathways have been observed. For example, photolysis of molecules containing the tris(trimethylsilyl)silyl group in conjunction with unsaturated chromophores such as a vinyl [6], acyl [7], and phosphirenyl [8] functionalities yields silenes and rearrangement products [9]. Spectral observation of the n → p transition for a wide variety of silylenes frozen in low-temperature organic glasses, supported by chemical trapping studies, has allowed identification of divalent silicon intermediates from the photolysis of polysilanes [10].



1a–1g **2a–2g**

R: **a** = Mes, **b** = Is, **c** = *o*-Tol, **d** = *p*-Tol, **e** = Ph, **f** = *o*-Me_2NCH_2Ph, **g** = $CH_2{=}CH$

Nonetheless, in some instances the assignment of these absorptions to silylenes has not been obvious and theoretical support of the original experimental observations has proved to be helpful [11]. A particularly interesting prediction of theory is that silyl-substituted silylenes should display an absorption that is significantly shifted to longer wavelength. Experimental support of this computational result is sparse and herein, we report λ_{max} values of the long wavelength absorption for a variety of (aryl)(trimethylsilyl)silylenes [12]. (We do not suggest that elimination of a silylene is the exclusive and primary pathway for all of the substituted tris(trimethylsilyl)silanes described in this work. In fact, recent laser flash photolysis experiments on analogous di- and polysilane indicate that other pathways yielding silene products may proceed by both radical and concerted pathways.)

A link between the microscopic spectroscopy and macroscopic product isolation requires that photolysis

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☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University and for his many keystone contributions to organosilicon chemistry.

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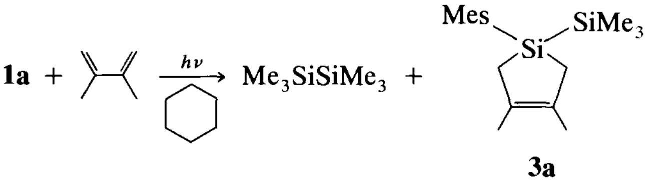
of the polysilanes at low temperature provide UV spectra that show a λ_{max} in the range predicted for (trimethylsilyl)substituted-silylenes and also afford products typical of silylene reactions. Products that indicate the formation of divalent silicon intermediates are hexamethyldisilane (HMDS), the co-product from photolysis of $RSi(Me_3Si)_3$ and adducts such as silacyclopent-3-enes and triethyltrisilanes.

2. Results and discussion

Photolysis of mesityltris(trimethylsilyl)silane **1a** (10^{-3} M in a 3-methylpentane glass) at 77 K afforded a broad and relatively weak UV signal at 776 nm that immediately disappeared upon warming (Fig. 1). When the photolysis was carried out in the presence of 2,3-dimethylbutadiene, either at low or ambient temperature in hydrocarbon solvents, two products, hexamethyldisilane and mesityl(trimethylsilyl)silacyclopent-3-ene **3a** were formed in approximately the same yield ($\approx 90\%$) at low percentage conversion ($< 30\%$) of the starting material **1a** (unlike dimesitylsilylene, reactions of mesityl(trimethylsilyl)silylene do not provide evidence for stable 2-vinylsiliranes) [13].



3a

When triethylsilane served as the trapping agent at room temperature, the products, HMDS and trisilane **4a** (from insertion of **2a** into the silicon hydrogen bond) were isolated in good yield. With longer irradiation times, 12 h, photolysis of the primary insertion product 1,1,1-triethyl-2,2-dimesityl-3,3,3-trimethyltrisilane **4a** produced secondary products, 1,1,1-triethyl-2-mesityldisilane **5** and triethyltrimethyldisilane (when triethylsilane is the trapping agent for photogenerated silylenes, similar observations of secondary photolysis have been reported) [14]. Although hydridosilanes are well known as effective scavengers of silylenes, the resulting trisilanes are as, if not more, photolabile as the starting polysilane and therefore silyl hydrides were not used in trapping studies for other (trimethylsilyl)silylenes. Another complication is that the primary insertion products of silylsilylenes, hydrotrisilanes, are expected to be more reactive toward silylenes than the original trapping agent, triethylsilane, a silyl hydride [15].

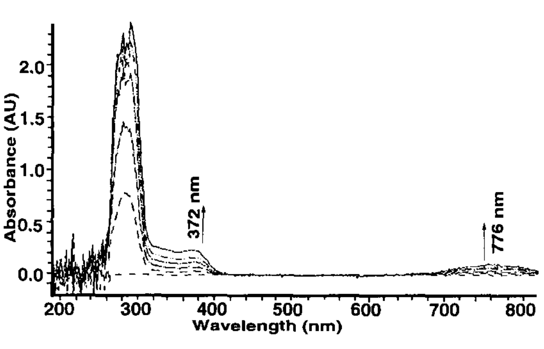


Fig. 1. Low-temperature UV spectrum for the photolysis of mesityltris(trimethylsilyl)silane **1a** (10^{-3} M in 3-methylpentane) at 0, 2, 5, 10, 20, and 40 min. The highest trace for the broad signal at 776 nm (after 40 min) is assigned to mesityl(trimethylsilyl)silylene. The rise for absorbance at 372 nm is probably due to dimerization of silylene **1a**, present in high concentration in order to observe the weak n → p transition. Arrows above the absorption maxima point up for those bands that increase with photolysis time.

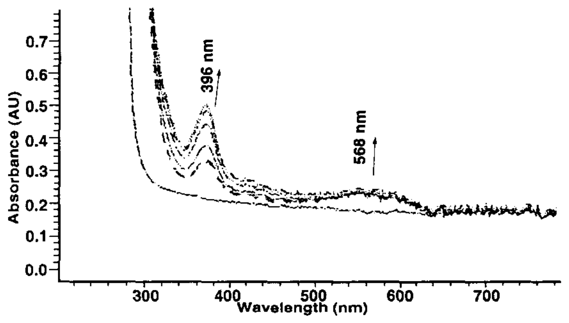
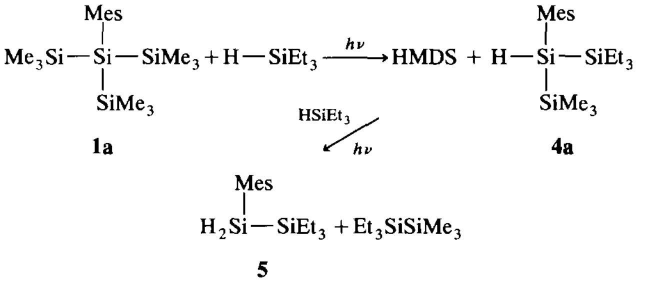


Fig. 2. Low-temperature UV spectra for the photolysis of isetyltris(trimethylsilyl)silane **2b** and **2b** (10^{-3} M in a soft matrix, see text) at 0, 5, 10, 20, 30 and 40 min. The highest trace for the broad signal at 568 nm (after 40 min) is assigned to isetyl(trimethylsilyl)silylene. The rise for absorbance at 396 nm is probably due to dimerization of silylene **1b**. Arrows above the absoption maxima point up for those bands that increase with photolysis time.



$$Me_3Si-\overset{Mes}{\underset{SiMe_3}{Si}}-SiMe_3 + H-SiEt_3 \xrightarrow{h\nu} HMDS + H-\overset{Mes}{\underset{SiMe_3}{Si}}-SiEt_3$$

$$\mathbf{1a} \qquad \xleftarrow[h\nu]{HSiEt_3} \qquad \mathbf{4a}$$

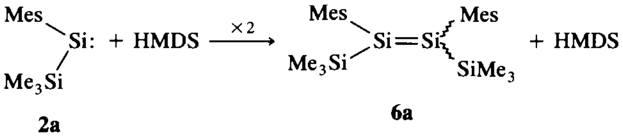
$$H_2\overset{Mes}{Si}-SiEt_3 + Et_3SiSiMe_3$$

$$\mathbf{5}$$

Photolysis of other aryltris(trimethylsilyl)silanes, $Ar(Me_3Si)_3Si$, **1c** = *o*-Tol, **1d** = *p*-Tol, **1e** = Ph, and vinyltris(trimethylsilyl)silane **1g** = $CH{=}CH_2$ afforded low-temperature UV spectra consistent with predictions of long wavelengths for **2c**, **2d**, **2e** and **2g**: λ_{max} = 662 nm, 676 nm, 672 nm and 619 nm, respectively. Typical examples, for **2b** in this case are given in Fig. 2. The simple aryl(trimethylsilyl) silylenes also show more intense absorbances at shorter wavelengths that might be attributed to σ, π^* transitions of a silyl-substituted benzene. Furthermore, the silylenes provided the expected silacyclopent-3-enes: **3b–3d** as determined by GC/MS and ^1H NMR.

3. Annealing experiments

The rate of dimesitylsilylene dimerization to tetramesityldisilene has been reported to proceed at nearly the diffusion-controlled limit in cyclohexane at room temperature [17]. We assume that other, less bulky, silylenes will dimerize at about the same rate, if not faster. Of course, possible exceptions to this generalization might occur if other reactive intermediates are present in concentrations greater than the silylene. In a soft glass such as one consisting of a 4:1 ratio of isopentane to n-pentane [18], dimesitylsilylene is known to dimerize [19]. Consequently, we expect that silylene dimerization is the main reaction channel for decay of the silylene signal in an increasingly fluid medium and in the absence of other reactive intermediates (recently, synthesis of several stable silyl-substituted disilenes has been reported) [20]. When a liquid N_2 cooled solution of **1a** (10^{-3} M in 4:1 isopentane/3-MP) was irradiated for several min in a soft matrix as above, a weak and broad 776 nm absorption was observed at the start of the photolysis but also accompanied by an initially weaker absorption at ≈ 372 nm (Table 1). At lower concentrations of the silylene precursor, the absorbances at ≈ 372–396 nm were not observed and we tentatively attribute them to disilenes. The new species, presumably the 1,2-diaryl-1,2-di(trimethylsilyl)disilene, persisted for hours after the glass was warmed to room temperature in the absence of O_2 and moisture. Since none were not isolated, we do not know the stereochemistry of the possible disilene products. (In the new disilenes reported by West and coworkers, the initial dimerization product mixture, disilenes, contains both cis and trans isomers, with the presumably less-stable cis predominating).



In a similar manner, low-temperature photolysis of *o*-tris(trimethylsilyl)silyltoluene yields HMDS and *o*-tolyl(trimethylsilyl)silylene **1c** (λ_{max} = 662 nm). As the glass softened, the silylene absorption disappeared and a new structure with a λ_{max} = 388 nm appeared. The position of the absorption and the lifetime of the intermediate, less than that of **6a** but much longer than the silylene, suggest that it is the disilene **6c** from dimerization of **2c**.

Curiously, the intensity of the absorptions from annealing silylenes **2c**, **2d**, and **2e** was not as intense as observed for **6a** and **6b**, the expected disilenes from dimerization of **2a** and **2b**. Without information about the extinction coefficients for these other disilenes, we do not know if the relatively reduced intensity of these unstable disilenes is due to an intrinsically lower intensity of the 1,2-disilyl-1,2-(diaryl)-substituted chromophore or if other pathways compete with oligomerization (although the possibility of unimolecular isomerization of the silyl-substituted disilenes upon warm-up appears unlikely in view of the 30 + kcal mol^{-1} barrier for calculated for a 1,2 silyl shift in a silyl substituted disilene the possibility of isomerization of intermediates that are formed on the pathway to oligomerization remains) [21].

4. R(trimethylsilyl)silylenes with λ_{max} < 600 nm

Although the usual position of the typical absorbance for trimethylsilyl-substituted silylenes is now established to occur at λ_{max} > 600 nm, the electron donor or acceptor properties of the other substituent on the divalent silicon atom are also significant. These influences are relatively easy to detect because the usual position of the n → p transition for the silylene occurs in a relatively low energy (long wavelength) region free of other signals. The exceptions reported here in **2b** and **2f** represent different steric and electronic influences on

Table 1
Position of λ_{max} for silylenes **2a–2g** and of products from annealing

Silylene	n → p	Annealing product [a]
a Mes(trimethylsilyl)Si:	= 776 nm	372
b 2,4,6-Triisopropylphenyl(trimethylsilyl)Si:	= 568	396 [b]
c *o*-Tol(trimethylsilyl)Si:	= 662	388
d *p*-Tol(trimethylsilyl)Si:	= 676	386, 420
e Ph(trimethylsilyl)Si:	= 672	384
f *o*-Me_2N-$CH_2C_6H_4$(trimethylsilyl)Si:	= 480 [16]	*
g Vi(trimethylsilyl)Si:	= 619	378

[a] The position of the bands from annealing were obtained by allowing the matrix to melt gradually or by conducting the photolysis in a soft matrix, see text. It is probable that the bands from annealing are due to disilenes and/or rearrangement products. The asterisk * indicates that an annealing band could not be assigned unambiguously.

[b] Reported by R. West et al. [19]. In that paper, the abbreviation, Is = isetyl, is used for 2,4,6-triisopropylphenyl.

silylene absorbance. The remarkably long wavelength position of **2a** is also rationalized.

Pertinent to **2f**, the hypercoordinated silylene, it has been reported previously that dimesitylsilylene displays an intense λ_{max} at 577 nm and the position is displaced to 404 nm when one of the mesityl groups is replaced by the nitrogen atom of a bis(trimethylsilyl)amino substituent [10]. Similarly, replacement of a mesityl group with an oxygen atom of a t-butoxy group displaces λ_{max} to 396 nm for mesityl(t-butoxy)silylene. Such effects may be viewed as intramolecular blue shifts for the silylene $n \rightarrow p$ transition in the UV spectrum. Blue shifts have also been observed intermolecularly by the addition of Lewis bases (R_2O, R_3N, R_3P and R_2S) as dopants to the organic solvent prior to formation of the glassy matrix and photolysis [22,23]. These spectral shifts are thought to indicate the partial occupation of the silylene p-type orbital by a lone pair of electrons from the Lewis base. The UV data reported in this paper for silylene **2f** resemble more closely those obtained when the silylene is complexed to an external base via a σ coordination such as that reported for amines [24].

Unexpected changes for the position of λ_{max} were observed for silylenes **1a**, **1b** and **1f**. As a reference for bis(triisopropylphenyl)silylene **1b** whose absorbance occurs at 568 nm, we compare phenyl(trimethylsilyl)silylene ($\lambda_{max} = 672$ nm) and the anomalously lower energy (longer wavelength) UV transition of mesityl(trimethylsilyl)silylene **1a**, $\lambda_{max} = 776$ nm. It is important to realize, however, that the large shift in wavenumbers occurs at a relatively low energy region of the spectrum. For example, the difference in energy between a mole of photons at 600 nm and 700 nm is ≈ 6.9 kcal mole^{-1}. The discussion begins with the electronic effects due to both the trimethylsilyl group and the p-orbital of the ipso-carbon of the phenyl substituent. At the heart of the issue is the large red shift of silyl-substituted silylenes predicted by Apeloig and Karni [11]. Our general understanding of this matter draws from the work of Liebman and coworkers who explicitly address electronic effects for the substituents on the divalent atom. That is "as the ligands become more electropositive and electrons are transferred from the ligands to the central atom, the σ orbital loses s character and the RCR [1] bond angle opens" [25].

The implications of that statement are far reaching. Firstly, it predicts that a trimethylsilyl group, an electropositive substituent, will increase the Ar–Si–SiMe$_3$ bond angle α, between the two substituents on the divalent atom. Secondly, as the substituents become larger, α is predicted to increase and the $S_0 \rightarrow S_1$ absorbance occurs at lower energy (longer wavelength) transition. The combination of these two factors account for the remarkably long wavelength position of λ_{max} of **1a**, (trimethylsilyl)(Mes)Si:, at 776 nm. An apparent exception to this trend in the UV spectra of silylenes is the position of λ_{max} for **1b**, triisopropylphenyl(trimethylsilyl)Si:, at 568 nm. We had expected that the larger Ar group, triisopropylphenyl, would increase the angle α even further relative to trimethylsilyl(Mes) thus producing a $S_0 \rightarrow S_1$ transition at even longer wavelength. Since the red shift was not observed, the theoretical basis for this expectation needed to be reconsidered [26].

A model for the conformation of phenyl(trimethylsilyl)silylene **1e** may be approximated by assuming that the p-orbital on the ipso-carbon atom of the phenyl ring and the p-type orbital of the divalent silicon are coplanar. The base value for the $S_0 \rightarrow S_1$ absorbance, 672 nm, shows only a minor variation upon *o*- and *p*-substitution of hydrogen by a methyl group (**1c** = 662 nm and **1d** = 676 nm, respectively). The influence an additional *o*-methyl group on the phenyl ring requires that the bond angle α expands while still maintaining the co-planarity between the p-orbitals of the ipso-phenyl carbon and the divalent silicon atom. When the *o*-methyls of the mesityl substituent are replaced by the larger *o*-isopropyl groups, the co-planarity of the aromatic π system and the silylene p-orbital can no longer be maintained due to the steric congestion between the isopropyl and trimethylsilyl groups. Consequently the triisopropylphenyl ring is forced out of conjugation with the vacant p-type orbital of the divalent silicon atom and the energy of the $S_0 \rightarrow S_1$ transition increases [25].

Finally we consider the vinyl(trimethylsilyl)silylene **2g**, $\lambda_{max} = 619$ nm. We might not have detected the very weak transition for the $CH_2{=}CH$(trimethylsilyl)Si: signal for the $n \rightarrow p$ transition without the theoretical prompting of Apeloig and Karni. Even so, an assignment of such a diminutive absorbance may seem speculative [27,28].

5. Experimental

5.1. General

All reactions were carried out in a nitrogen atmosphere and with dried and distilled solvents. Photolyses at room temperature were performed in a Rayonet photochemical reactor equipped with 16 medium pressure Hg lamps. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200, Varian VXR 300 or JEOL FX90Q spectrometer with C_6D_6, $CDCl_3$ or external D_2O as lock solvents. ^{29}Si NMR spectra were determined using the INEPT pulse sequence [29]. Ultraviolet spectra were recorded on HP 8451A diode array spectrometer and typically recorded in the subtraction mode. Concentrations of the starting of tetrasilanes **1a–1g** were higher than usual, optical density > 1.0, in order to observe the relatively weak and broad $n \rightarrow p$ silylene absorption.

Mass spectra were determined on a HP 5970 mass selective analyzer coupled to a HP 5790A gas chromatograph. High-resolution mass measurements were obtained at Rice University or at UCLA. Mesityltris(trimethylsilyl)silane was synthesized by the method of Fink and co-workers [30]. Aryl and vinyltris(trimethylsilyl)silanes **1c**–**1g** and vinyltris(trimethylsilyl)silane were synthesized by modifications of known methods [5].

5.2. General procedure for solution photolyses of substituted tris(trimethylsilyl)silanes 1a–1g with trapping agents

The same method was used in all experiments and is described in detail for the photochemical reaction of **1a** with **2**, 3-dimethylbutadiene. Mesityltris(trimethylsilyl)silane, 100 mg (0.27 mmol), was added to a quartz vessel containing 2.2 g (27 mmol) of 2,3-dimethylbutadiene in 10 ml hexane. The diene/hexane solution had previously been passed through an alumina column to remove impurities. The solution was purged with Ar for 30 min or subjected to three freeze/thaw cycles on a vacuum line and photolyzed for 24 h. Analysis of aliquots of the reaction mixture by ^{29}Si NMR during the first 3 h of photolysis did not reveal any 2-vinylsilirane intermediates. Analytical VPC (HP 5890A, SP-2100 column, 1.5 ft × 0.25 in; flow rate, 55 ml min^{-1}) indicated the ratio of product to starting material was 9:1. The solution was concentrated under vacuum and chromatographed on an OV-17 column (15 ft × 0.25 in; flow rate, 75 ml min^{-1}) for isolation of **3a**.

5.3. 1-trimethylsilyl-1-mesitylsilacyclopent-3-ene **3a** *$(Me_3Si)_3Si(Mes)SiCH_aH_bCHCH_3CHCH_3CH_aH_b$*

^{1}H NMR (CDCl$_3$): δ 0.01 (9H, s, Me$_3$Si); 1.63 (2H, d, $J = 15.6$ Hz, CH$_a$Si); 1.70 (6H, d, 1.5 Hz, CH$_3$C=); 2.05 (2H, d, $J = 15.6$ Hz, CH$_b$Si); 2.29 (6H, s, *o*-MeAr); 2.25 (s, 3H, *p*-MeAr); 6.80 (s, 2H, HAr).

^{13}C NMR (neat): δ 1.58, (s); 18.85 (t); 20.93 (q); 24.29 (q); 26.28 (q); 128.55 (d); 130.73 (s); 137.81 (s), 143.39 (s).

^{29}Si (neat): δ −13.57, −18.53.

GC/MS, *m/e* (relative abundance): 302 (31), 229 (100), 185 (66), 173 (17), 159 (24), 109 (35), 73 (30).

High-resolution mass: Calc. for $Si_2C_{18}H_{30}$ 302.1886; Found 302.1862.

Tris(trimethylsilyl)mesitylsilane **1a**, 100 mg (0.27 mmol), was photolyzed with 1.1 ml of (6.8 mmol) triethylsilane in 10 ml of hexane that had been passed through an alumina column. The solution was then purged with Ar for ≈ 15 min and then photolyzed with seven medium pressure Hg lamps. After photolysis for 2 h, a product peak was observed with a retention time of 15.5 min. After an additional 10 h of photolysis, a second product peak was observed at 13 min. The photolysis was stopped at 12 h, solvent removed and the residue was chromatographed on a OV-17 column (15 ft × 0.25 in; flow rate, 55 ml min^{-1}). The ratio of the major products **4a**, **5**, and hexamethyldisilane was 3:1:4.

5.4. Triethyl-2-mesityldisilane, $Et_3SiSiMesH_2$ 5

^{1}H NMR (neat): δ 0.70 (6H, q, $J = 7.2$ Hz, CCH$_2$Si); 0.94 (9H, t, $J = 7.2$ Hz, CH$_3$CSi); 2.37 (6H, s, *o*-CH$_3$Ar); 2.56 (3H, s, *p*-CH$_3$Ar); 4.10 (2H, s, H$_2$Si).

^{13}C NMR (neat): δ 4.7 (q); 7.9 (t); 21.1 (q); 24.3 (q); 126.1 (s); 128.6 (d); 138.5 (s); 144.2 (s).

^{29}Si NMR (neat): δ −6.44, −83.06.

GC/MS, *m/e* (relative abundance): 264 (12), 179.1 (14), 148 (29), 115 (83), 87 (100), 59 (49).

High-resolution mass: Calc. for $Si_2C_{15}H_{28}$ 264.1730; Found 264.1746.

5.5. Triethyl-2-mesityl-3,3,3-trimethyltrisilane, $Et_3SiSiHMesSiMe_3$ **4a**

^{1}H NMR (neat): δ 0.21 (9H, s, Me$_3$SiSi); 0.79 (6H, q, $J = 6.8$ Hz, (CH$_3$C)$_3$Si); 0.98 (9H, t, $J = 6.8$ Hz, CH$_3$CSi); 2.12 (3H, s, *p*-CH$_3$Ar); 2.40 (6H, s, *o*-CH$_3$Ar); 4.16 (H, s, HSi); 6.73 (2H, s, HAr).

^{13}C NMR: (neat) δ 3.11 (q); 7.75 (q); 10.49 (t); 23.28 (q); 27.95 (q); 130.90 (d); 130.98 (s); 139.70 (d); 146.22 (d).

^{29}Si (solvent): δ −2.09, −13.18, −81.46.

GC/MS, *m/e* (relative abundance): 336 (13), 262 (52), 205 (100), 177 (33), 147 (25), 73 (30).

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