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Linear 2,2-diaryl-substituted trisilanes: structure and photolysis to disilenes *

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Abstract

Synthesis of the new disilene, *E/Z*-IsMesSi=SiIsMes (1) is reported; the isomer Is_2Si=$SiMes_2$ (2) was obtained by photolysis of a mixture of $Mes_2Si(SiMe_3)_2$ (3) and $Is_2Si(SiMe_3)_2$ (5). Isomerization of $1 \rightleftharpoons 2$ does not take place up to 80°C. X-Ray crystal structures are reported for trisilanes 3, $IsMesSi(SiMe_3)_2$ (4), and 5.

1. Introduction

Photolysis of linear trisilanes containing an aryl group in the 2-position provides a general method for the preparation of arylsilylenes; when the substituents on silicon are sufficiently large, dimerization of the silylenes takes place leading to stable disilenes [1]. This method was used in the synthesis of the first isolable disilene, Mes_2Si=$SiMes_2$, by photolysis of $Mes_2Si(SiMe_3)_2$ (3) [2], and more recently for the synthesis of Is_2Si=$SiIs_2$ from $Is_2Si(SiMe_3)_2$ (5) [3]. In this paper we report the synthesis of the mixed disilene IsMesSi=SiIsMes (1) by photolysis of $IsMesSi(SiMe_3)_2$ (4), as well as preparation of a solution containing the isomeric disilene Is_2Si=$SiMes_2$ (2) by the cophotolysis of 3 and 5. Crystal structures for 3–5 are also described, along with studies of their rates of photolysis at 254 nm in solution.

2. Results and discussion

2.1. *Synthesis of 4*

Compounds 3 and 5 were prepared as described earlier [2,4]; trisilane 4 was obtained by reductive coupling of $IsMesSiCl_2$ [5] with Me_3SiCl under standard conditions, using lithium metal in THF [6].

2.2. *Solid state structures of 3–5*

Structural analysis of 3–5 was undertaken to investigate the effects of hindering groups on both the bond lengths and angles of linear diaryl substituted trisilanes. The molecular geometries of 3–5 are shown in Figs. 1–3. Experimental crystallographic data are summarized in Table 1, while selected bond angles and distances along with data for some related compounds are listed in Table 2. In all three compounds, the bonds around the central silicon atom are longer than normal [7]. The Si–C bond lengths to the more hinder-

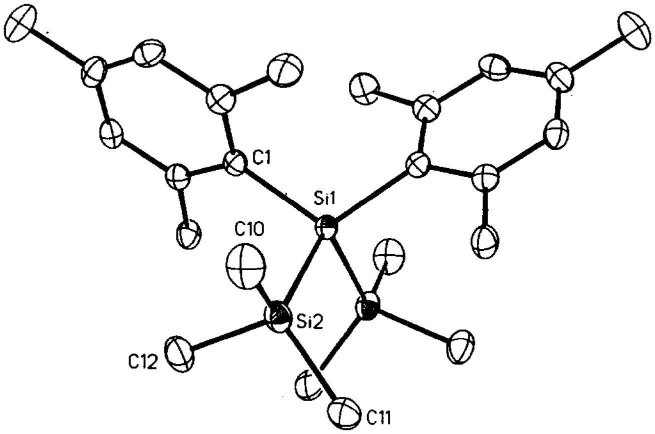

Fig. 1. Thermal ellipsoid drawing of 3.

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* Dedicated to Professor M.G. Voronkov in recognition of his many contributions to organometallic chemistry.

Nomenclature: Is = isityl = 2,4,6-triisopropylphenyl; Mes = mesityl = 2,4,6-trimethylphenyl; Xyl = xylyl = 2,6-dimethylphenyl; Dmt = 2,6-dimethyl-4-(t-butyl)phenyl; 2/3Is = 2,6-diisopropylphenyl; Cyp = 1,2,3-tri-tert-butylcyclopropenyl.

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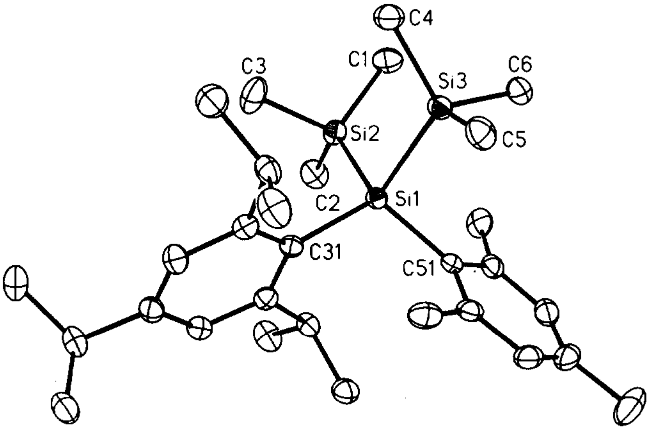


Fig. 2. Thermal ellipsoid drawing of **4**.

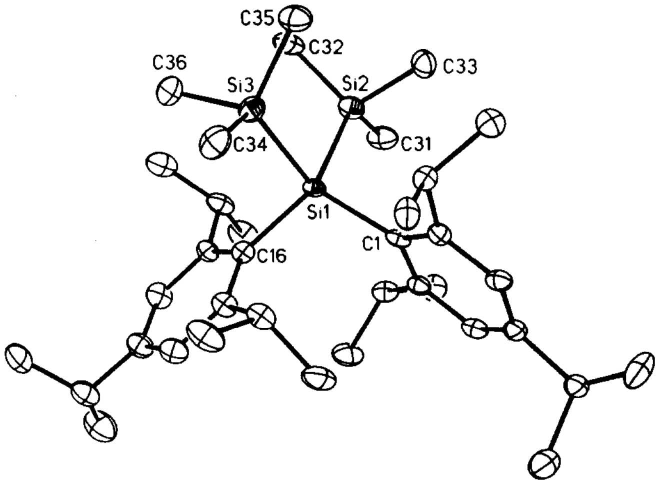


Fig. 3. Thermal ellipsoid drawing of **5**.

ing isityl groups are greater than to the mesityl groups. The silicon–silicon distances in **3**–**5** are also long compared to the normal bond length of 234–235 pm, but are similar to those in other sterically hindered compounds (see Table 2). The distortion in these compounds is also reflected in the bond angles around the central silicon. Large substituents cause a compression of the Si–Si–Si bond angle, most noticeable in **4**, **5**, and CypMesSi(SiMe$_3$)$_2$ (see Table 2). For the other compounds listed in Table 2 the distortion from tetra-

TABLE 1. Experimental crystallographic data for **3**, **4**, and **5**

	3	**4**	**5**
Empirical formula	$C_{24}H_{40}Si_3$	$C_{30}H_{52}Si_3$	$C_{36}H_{64}Si_3$
Formula weight	412.8	497.0	581.1
Cryst. size (mm)	0.1 × 0.4 × 0.4	0.25 × 0.45 × 0.55	0.2 × 0.2 × 0.3
Temp (K)	113(2)	113(2)	113(2)
Cryst. system	Orthorhombic	Triclinic	Orthorhombic
Space group	*Pccn*	*P*1	*Pna*2$_1$
Unit cell dimensions			
a (Å)	9.091(3)	9.530(2)	20.156(4)
b (Å)	15.535(7)	10.424(2)	10.393(2)
c (Å)	17.667(7)	16.046(3)	17.571(4)
α (°)	–	81.74(2)	–
β (°)	–	80.81(2)	–
γ (°)	–	82.42(2)	–
V (Å^3)	2495(2)	1547.5(6)	920.3(4)
Z	4	1	4
Density (calc., g cm^{-3})	1.099	1.067	1.049
Absorption coeff. (mm^{-1})	0.192	1.512	1.327
2θ range (deg)	3.5 to 50	4.0 to 114.0	4.0 to 114.0
Scan type	Wyckoff	Wyckoff	Wyckoff
Scan speed (deg min^{-1} in ω)	Variable (2–20)	Variable (2–20)	Variable (2–20)
Scan range (ω)	0.80	0.60	0.50
Observed reflections ($F > 4.0\sigma(F)$)	1613	3860	2431
Data to parameter ratio	12.9:1	12.9:1	6.9:1
Largest diff. peak (e Å^{-3})	0.39	0.59	0.47
Largest diff. hole (e Å^{-3})	−0.33	−0.45	−0.48
R (%)	5.06	4.67	5.27
R_w (%)	5.67	7.08	6.52
Goodness of fit	1.38	3.38	1.75

TABLE 2. Selected bond angles and distances for 2,2-disubstituted linear trisilanes

	θ(Si–Si–Si) (°)	θ(R–Si–R) (°)	r(Si–Si) (pm)	r(Si–C) (pm)	Ref.
3	105.2(1)	109.9(2)	238.0(2)	191.6(3)	–
4	101.0(1)	110.4(2)	238.8(1)	192.8(2) [a]	–
			239.3(1)	191.3(2) [b]	–
5	97.5(1)	107.7(2)	239.1(2)	192.7(6)	–
			238.6(2)	194.7(6)	–
CypMesSi(SiMe$_3$)$_2$ [c]	93.97(6)	109.2(2)	245.5(2)	193.2(4) [d]	8
			242.6(2)	195.9(4) [e]	–
CypPhSi(SiMe$_3$)$_2$ [c]	102.1(7)	105.7(2)	239.6(2)	189.3(5) [d]	8
			239.8(2)	194.0(4) [e]	–
$\frac{2}{3}$IsO(Mes)Si(SiMe$_3$)$_2$ [c]	105.9(1)	104.6(1)	237.1(1)	191.1(3)	9
			239.3(1)	–	–
PhO(Mes)Si(SiMe$_3$)$_2$	109.7(1)	110.1(2)	235.5(2)	189.4(5)	9
			237.8(2)	–	–

[a] r(Si–C$_{\text{isityl}}$). [b] r(Si–C$_{\text{mesityl}}$). [c] See ref. 1. [d] r(Si–C$_{\text{aryl}}$). [e] r(Si–C$_{\text{Cyp}}$).

hedral geometry is smaller, and in the least hindered trisilane, PhO(Mes)Si(SiMe$_3$)$_2$, distortion is insignificant.

2.3. Photolysis rate of 3–5

From Table 2 it can be seen that there is a steady decrease in Si–Si–Si angle with increase of steric bulk. We were interested to see if compounds showing a smaller bond angle around the central silicon might photolyse faster than those with larger bond angles. In trisilanes in which the Me$_3$Si groups are close together, they might be cleaved more rapidly, since the new silicon–silicon bond would be more easily formed. Therefore, the rates of photolysis of **3**–**5**, using a 254 nm light source, were determined in cyclohexane and chloroform and are listed in Table 3. After correcting for the difference in absorption at 254 nm, the predicted trend in rates of photolysis was found, but the differences are small. The rate ratio between **5** and **3** was only 1.5 in chloroform, and slightly less in cyclohexane. It appears that photolysis rates for trisilanes are only slightly affected by structural changes around the central silicon atom.

2.4. Synthesis of 1 and 2

Low temperature photolysis of **4** in a pentane solution produced a mixture of the *cis* and *trans* isomers of disilene **1** (eqn. (1)). An equilibrium mixture of the isomeric disilenes can be recrystallized from the crude photolysate yielding a yellow–orange solid. Although crystallization purified the *E/Z* disilene mixture, it was not possible to crystallize either isomers selectively. Therefore, the assignment of the ^{29}Si NMR signals to the respective isomers is arbitrary. For most

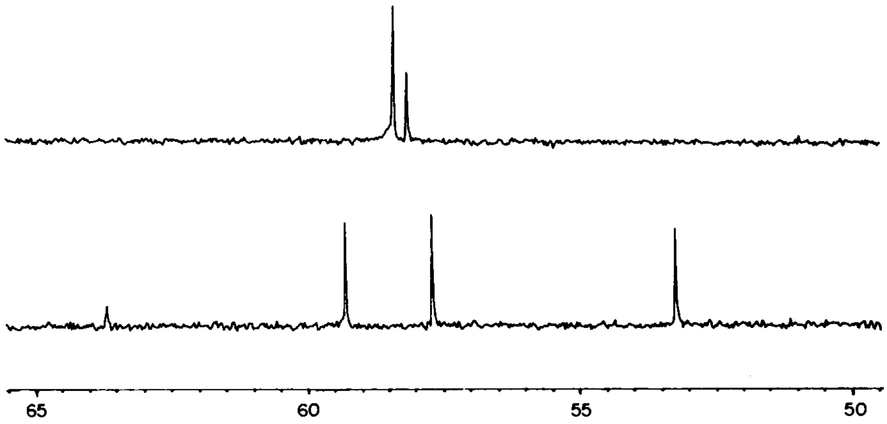


Fig. 4. (top) ^{29}Si NMR spectrum of the *E/Z* mixture of disilene **1** (+59.44 and +58.18). (bottom) ^{29}Si NMR spectrum of disilenes obtained from cophotolysis of a 1 : 1 mixture of **3** and **5**; Mes$_2$Si=SiMes$_2$ (+63.7 ppm), Is$_2$Si=SiIs$_2$ (+53.4 ppm), **2** (+59.38 ppm and +57.78 ppm).

TABLE 3. Rates of photolysis of **3**, **4**, and **5**

	ϵ (254 nm) (10^4 M^{-1} cm^{-1})	Cyclohexane		Chloroform	
		k [a] (10^{-9} mol^{-1})	k * [b]	k [a] (10^{-9} mol^{-1})	k * [b]
3 [c]	1.77	5.3	3.9	5.0	3.7
4 [c]	1.51	4.5	3.9	5.1	4.5
5 [c]	1.32	5.6	5.6	5.6	5.6

[a] Experimental error is ±7.5%, to 95% confidence. [b] Rate corrected for the difference in absorption at 254 nm. [c] The $\epsilon(\lambda_{max})$ (10^4 M^{-1} cm^{-1}) values are: for **3**, 1.92 (248 nm); for **4**, 1.65 (246 nm); for **5**, 1.77 (246 nm).

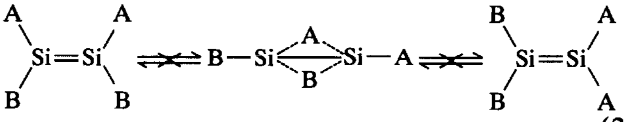
disilenes the ^{29}Si chemical shift for the *trans* isomer is upfield from that for the *cis* isomer [2], and following this pattern we tentatively assign the resonance at +58.44 ppm to the *cis* isomer and that at +58.19 ppm to the *trans*. If these assignments are correct, the *cis*/*trans* ratio is 55:45 (Fig. 4 (top)).

$$\underset{(\mathbf{4})}{2IsMesSi(SiMe_3)_2} \xrightarrow[-Me_3SiSiMe_3]{h\nu} \underset{(\mathbf{1})}{IsMesSi{=}SiIsMes} \quad E/Z \text{ mixture} \qquad (1)$$

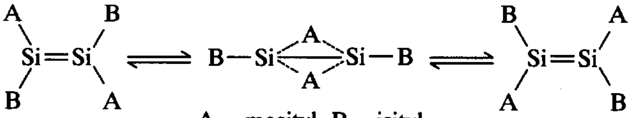
Earlier it was shown that tetraaryl disilenes of the type $A_2Si{=}SiB_2$ (A = Mes, B = Xyl, Dmt) undergo exchange of aryl groups between the silicon atoms to give the dyotropic 1,2-aryl rearrangement, $A_2Si{=}SiB_2 \rightleftharpoons ABSi{=}SiBA$ [10]. For these two rearrangements the steric hindrance in the transition state is probably about the same, since methyl groups are present in the positions *ortho* to silicon on all of the aromatic rings. Since the rates of photolysis of **3** and **5** are similar, as shown above, we reasoned that cophotolysis of these two trisilanes might produce $Is_2Si{=}SiMes_2$ (**2**), a more hindered tetraaryl disilene. In fact photolysis of a 1:1 mixture of **3** and **5** gave a mixture of $Mes_2Si{=}SiMes_2$, $Is_2Si{=}SiIs_2$ and **2**, containing almost the statistical amount of **2** (50%) (see Fig. 4 (bottom)). Thus not only the photolyses but also the rates of combination of silylenes Mes_2Si: and Is_2Si: to give different disilenes must take place at rather similar rates.

In attempts to bring about the 1,2 aryl rearrangement of **2** to **1** the reaction mixture containing **2** was heated at 80°C. Surprisingly, no change was observed even after one month at this temperature. Likewise, heating of the equilibrium mixture of *E*/*Z*-**1** produced no **2**.

The mechanism proposed for the 1,2 aryl disilene rearrangement is a concerted, intramolecular dyotropic migration of two σ-bonded aryl groups across the silicon–silicon double bond. Conversion of **2** to *Z*-**1** would require simultaneous migration of an isityl and a mesityl group. The results for **1** and **2** are therefore consistent with this proposal, if isityl groups are too large to migrate (eqn. (2)). Degenerate 1,2 aryl rearrangement of *E*-**1** may take place, but would not be observed (eqn. (3)) without additional tagging.



(2)



A = mesityl, B = isityl

(3)

2.5. *Silylenes*

As mentioned above, photolysis of 2,2-diaryl trisilanes leads to the formation of silylenes. These highly reactive species may be isolated in cold matrices. Using standard matrix isolation techniques [11], trisilane **4** was photolyzed in 3-methylpentane at 77 K to yield an intensely blue silylene, IsMesSi:, with λ_{max} at 582 nm. This wavelength is intermediate between those for dimesityl silylene (577 nm) [11] and diisityl silylene (584 nm) [12].

3. Experimental section

3.1. *General procedures*

All reactions and manipulations with air sensitive compounds were conducted under a nitrogen or argon atmosphere by using standard Schlenk techniques. Routine ^1H NMR (200 MHz) spectra were collected on a Bruker WP-200 spectrometer. ^{29}Si NMR were collected on either a Bruker WP-270 (53.67 MHz) or a Bruker AM-360 (71.55 MHz) spectrometer using INEPT pulse sequences and complete proton decoupling [13]. Chemical shifts are reported in ppm from a tetramethylsilane external standard. High resolution mass spectra were recorded on a Kratos MS-80 mass spectrometer. Gas chromatographic analysis were performed on a Hewlett-Packard (HP) 5890A gas chromatograph with an AP series 30 m fused silica column and HP 3390A integrating recorder. Reported melting points are uncorrected.

Hydrocarbon solvents were dried and distilled over either sodium or potassium. Solvents for photolysis or UV spectroscopy were deolefinated by washing twice each with a 50% H_2SO_4–50% HNO_3 mixture, H_2SO_4, H_2O, KOH (aq), and H_2O, 200 ml per 600 ml of hydrocarbon. The solvents were then dried over $MgSO_4$ and distilled over CaH_2 under nitrogen.

Photolyses were carried out in a Rayonet Model RPR-208 photoreactor equipped with 254 nm lamps. Low temperatures for photolysis were maintained by the use of a quartz Dewar vessel equipped with a liquid nitrogen blowoff system and temperature controller.

3.2. IsMesSi(SiMe$_3$)$_2$ (4)

To a solution containing IsMesSiCl$_2$ [5] (5.0 g, 0.012 mol) and chlorotrimethylsilane (13 g, 0.12 mol) in THF (150 ml) were added small chunks of lithium metal (0.36 g, 0.052 mol). The solution was stirred at room temperature for 12 h and then refluxed for an additional 6 h at which time GC analysis indicated the reaction to be complete. The reaction mixture was filtered to remove unreacted lithium and insoluble salts. The filtrate was evaporated to dryness and 200 ml of hexane was added. The remaining salts were removed by filtration and the filtrate was evaporated to a crude solid. The solid was recrystallized from hexane yielding 2.1 g of **4**. The mother liquor was recrystallized from ethanol yielding an additional 2.6 g of **4**: total yield 4.7 g (79%) of **4** as a white solid, m.p. 128–129°C. ^{1}H NMR (C$_6$D$_6$) δ: 7.13 (s, 1 H, Mes*H*), 7.02 (s, 1 H, Mes*H*), 6.71 (s, 2 H, Is*H*), 3.49 (sept, 1 H, *ortho*-C*H*(CH$_3$)$_2$), 3.15 (sept, 1 H, *ortho*-C*H*(CH$_3$)$_3$), 2.80 (sept, 1 H, *para*-C*H*(CH$_3$)$_2$), 2.27* (s, 6 H, *ortho*-C*H*$_3$), 2.08 (s, 3 H, *para*-C*H*$_3$), 1.41 (d, 6 H, *ortho*-CH(C*H*$_3$)$_2$), 1.21 (d, 6 H, *para*-CH(C*H*$_3$)$_2$), 0.90* (d, 6 H, *ortho*-CH(C*H*$_3$)$_2$), 0.28 (s, 18 H, Si(C*H*$_3$)$_3$) (signals marked with an asterisk could only be observed at 70°C and even at that temperature they were very broad due to hindered rotation). ^{29}Si NMR (C$_6$D$_6$) δ: -11.21 (SiMe$_3$), -82.59 (SiAr$_2$). HRMS [14*] exact mass for $C_{29}H_{48}{}^{28}Si_2{}^{29}Si_1$ [M–CH$_3$] calculated *m/e* 481.3059, found *m/e* 481.3073 (2.5%); exact mass for $C_{27}H_{43}Si_2$ [M–C$_3$H$_9$Si] calculated *m/e* 423.2903, found *m/e* 423.2936 (45.4%). Anal. Found: C, 72.67; H, 10.73. Calc. for $C_{30}H_{52}Si_2$: C, 72.49, H, 10.55%.

3.3. X-Ray data collection

Single crystals of **3–5** were grown by slow cooling of a saturated solution in ethanol to -20°C. Suitably sized crystals were taken from the solution and mounted on a thin glass thread with cyanoacrylate cement. A thin coat of this cement was used to seal the surface of all the crystals. All studies were carried out on a Siemens P3F diffractometer equipped with Cu Kα radiation (except Mo Kα for **3**) and a graphite crystal monochromator. Unit cell parameters were obtained from least-squares refinements based on the setting angles of 25 reflections. Data collection and refinement parameters used for the structure determinations are summarized in Table 1. Throughout data collection standard reflections were measured every 100 reflections to monitor stability. The structures were solved by direct methods using Siemens SHELXTL PLUS (VMS). E maps revealed the positions of the silicon and carbon atoms. Further electron density difference maps revealed the hydrogen atoms. In the final cycles of refinement all non-hydrogen atoms were assumed to vibrate anisotropically and all hydrogen atoms were assumed to vibrate isotropically.

3.4. Determination of the photolysis rate of 3–5

To quartz NMR tubes containing 2.4×10^{-5} mol of **3**, **4**, or **5** was added 0.75 ml of deuterated solvent (cyclohexane-*d*$_{12}$ or CDCl$_3$) with tetramethylsilane (TMS) as internal standard. The samples were photolyzed at 254 nm and the ^{1}H NMR was determined every 10 min over a period of 80 min, after which time the reaction was more than 75% complete. The rates of photolysis were determined by comparing the relative intensities of 3–5 with the TMS standard (a relaxation delay of 2 s was used to ensure total relaxation of the silyl protons). The rates were then calculated using standard regression analysis; results are summarized in Table 3. The correlation coefficients are, for **3**, 0.990; **4**, 0.978; **5**, 0.987 (chloroform); **3**, 0.985; **4**, 0.988; **5**, 0.993 (cyclohexane).

3.5. IsMesSi=SiIsMes (1)

A solution of **4** (1 g, 2.0 mmol) in dry deolefinated pentane (0.40 ml) was placed in a quartz photolysis tube equipped with a fritted filter for recrystallization. The solution was degassed (3 ×) and photolyzed at -60°C using a 254 nm light source. After 48 h of photolysis an orange-red solution was obtained. Two-thirds of the volume of the solution was removed *in vacuo* and the product was precipitated at -78°C. The disilene was filtered yielding 0.44 g (64%) as a yellow solid. The product contains a mixture of the *E/Z* isomers of the disilene **1**. ^{29}Si NMR δ: +58.44 (presumed *Z*), δ +58.19 (presumed *E*) (ratio 55:45) (see also Fig. 4a); HRMS exact mass for $C_{48}H_{68}Si_2$: calculated *m/e* 700.4859, found *m/e* 700.4860 (5.7%). UV: λ_{max} (3-methylpentane) 431 nm [15*].

3.6. Cophotolysis of 3 and 5

A solution containing a 1:1 ratio of **3** (300 mg, 5.2×10^{-4} mol) and **5** (213 mg, 5.2×10^{-4} mol) in dry deolefinated pentane (40 ml) was degassed (3 ×) and photolyzed at -60°C using a 254 nm light source. After 48 h of photolysis, the solvent was removed *in*

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* Reference number with asterisk indicates a note in the list of references.

vacuo and C_6D_6 (0.5 ml) was added to dissolve the product mixture. ^{29}Si NMR is shown in Fig. 4b, the signals at +59.38 and +57.78 ppm are assigned to disilene **2**.

4. Supplementary material available

Tables of crystal data, bond lengths, bond angles, atomic coordinates, equivalent isotropic displacement coefficients and occupancies, anisotropic displacement coefficients, and hydrogen atom coordinates (24 pages) and listings of observed and calculated factor amplitudes (33 pages) for compounds **3**–**5** are available from the authors.

Acknowledgments

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15 A disilene with similar structure, ($^{2/3}$Is)MesSi=Si($^{2/3}$Is)Mes [1], showing an identical λ_{max} was recently reported by S. A. Batcheller, R. Tsumuraya, O. Tempkin, W. M. Davis and S. Masamune, *J. Am. Chem. Soc., 112* (1990) 9394.