mmol), 61%. It was recrystalized as follows: A 5% solution of the compound in acetone was mixed with a 6-fold volume of toluene and the solvent reduced under vacuum until a white precipitate formed. The precipitate was filtered off, washed with ether, and dried. Anal. Calcd for $C_{19}H_{18}BK$: C, 84.39; H, 6.82. Found: C, 84.08; H, 6.49.

(b) Platinum Complexes. The platinum complexes *cis*-$[PtCl_2(PMe_3)_2]$ (**1a**), *cis*-$[PtCl_2(PEt_3)_2]$ (**1b**), and *cis*-$[PtCl_2(PPh_3)_2]$ (**1c**) were prepared by standard procedures.[14] $AgCF_3SO_3$ (FLUKA, purum), methanol (FLUKA, puriss), acetonitrile (FLUKA, puriss), and methylene chloride (FLUKA, puriss) were used without further purification. In all cases the AgCl precipitate was filtered off over Celite.

A solution of the monocation *cis*-$[PtCl(S)(PEt_3)_2][CF_3SO_3]$ (**3b**) was obtained by reacting 100 mg (0.2 mmol) of *cis*-$[PtCl_2(PEt_3)_2]$ (**1b**) with 51.2 mg (0.2 mmol) of $AgCF_3SO_3$ in 3 mL of methanol, the mixture was stirred for 30 min and the AgCl filtered off.

Synthesis of *cis*-$[Pt(H_2O)_2(PEt_3)_2][CF_3SO_3]_2$ (4b). A methanol (30 mL) solution of *cis*-$[PtCl_2(PEt_3)_2]$ (**1b**) (1 g, 2 mmol) and $AgCF_3SO_3$ (1.03 g, 4 mmol) was stirred at room temperature for 30 min. The precipitated AgCl was filtered off and washed with methanol. From the combined methanol phases the solvent was removed by heating under vacuum to not more than 50 °C. The resulting black slurry was dissolved in 50 mL of CH_2Cl_2 and the solution filtered through Celite. Dry ether (50 mL) was added to the CH_2Cl_2 solution and the mixture cooled to 4 °C. After some colorless crystals had formed, more ether (total 200 mL) was added and crystallization completed at 4 °C. Yield: 1.38 g (1.9 mmol), 91%. Anal. Calcd for $C_{14}H_{34}F_6O_8P_2PtS_2$: C, 21.96; H, 4.48. Found: C, 22.19; H, 4.38.

Synthesis of *cis*-$[Pt(H_2O)_2(PPh_3)_2][CF_3SO_3]_2$ (4c). To a slurry of *cis*-$[PtCl_2(PPh_3)_2]$ (**1c**) (1 g, 1.26 mmol) in CH_2Cl_2 (20 mL) was added a methanol solution (20 mL) of $AgCF_3SO_3$ (650 mg, 2.53 mmol) at 0 °C. The mixture was stirred at 0 °C for 10 min. The precipitated AgCl was filtered off, and the filtrate was evaporated to dryness at 0 °C under vacuum. The colorless solid was recrystallized from CH_2Cl_2/Et_2O as above. Yield: 591 mg (0.561 mmol), 44%. Anal. Calcd for $C_{38}H_{34}O_8F_6P_2S_2Pt$: C, 43.31; H, 3.25. Found: C, 43.60; H, 3.41.

Synthesis of *cis*-$[Pt(CH_3CN)_2(PEt_3)_2][BPh_4]_2$ (6b). To a methanol (10 mL) solution of *cis*-$[Pt(H_2O)_2(PEt_3)_2][CF_3SO_3]_2$ (**4b**) (500 mg, 0.653 mmol) was added acetonitrile (1 mL), and the mixture was stirred for 5 min. A solution of $Na[BPh_4]$ (516 mg, 1.51 mmol) in methanol (3 mL) was added. The white precipitate formed was filtered off, washed with methanol, and dried. Yield: 725 mg (0.629 mmol), 96%. Anal. Calcd for $C_{64}H_{76}N_2B_2P_2Pt_2$: C, 66.73; H, 6.65; N, 2.43. Found: C, 66.63; H, 6.85; N, 2.47.

Preparation of Solutions of the Solvento Complexes 2a and 2b. One equivalent of *cis*-$[PtCl_2L_2]$ (L = PMe_3, **1a**; L = PEt_3, **1b**) and 2 equiv of $AgCF_3SO_3$ were dissolved in methanol (20 mL of solvent/mmol of *cis*-$[PtCl_2L_2]$), and the mixture was stirred for 30 min. The precipitated AgCl was filtered off, and an equal volume of CH_2Cl_2 was added.

The Phenylation Reaction. To the above solutions was added tetraarylborate (1 equiv), and the white suspension was stirred for 30 min at room temperature. In the case of *cis*-$[Pt(S)_2(PPh_3)_2]^{2+}$ (**2c**), the complex *cis*-$[Pt(H_2O)_2(PPh_3)_2][CF_3SO_3]_2$ (**4c**) was dissolved in CH_2Cl_2 (20 mL of solvent/mmol of **4c**), a solution of tetraarylborate (1 equiv) in methanol (20 mL/mmol) added, and the solution stirred for 30 min at room temperature. Then either LiCl, LiBr, or NaI (2 equiv) was added and the mixture stirred for another 5 min. The solution was filtered through Celite and the solvent removed. The residue was suspended in water (50 mL/mmol) and extracted twice with CH_2Cl_2 (2 × 50 mL/mmol of complex). The combined organic phases were evaporated, and the solid was recrystallized from methanol/water or acetone/water. Yields ranged from 80 to 86%.

Acknowledgment. Financial support for this work by the Swiss National Science Foundation is gratefully acknowledged.

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Synthesis, Geometrical Isomerism, and Crystal Structure of a Highly Hindered Disilene

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A disilene very resistant to air oxidation, 1,2-di(1-adamantyl)dimesityldisilene, was synthesized by solution photolysis of 2-(1-adamantyl)-2-mesitylhexamethyltrisilane. The X-ray crystal structure of the *E* isomer was determined; it crystallized in the triclinic space group $P\bar{1}$, $Z = 1$, with cell dimensions $a = 8.292$ (2) Å, $b = 10.069$ (2) Å, $c = 10.772$ (2) Å, $\alpha = 105.67$ (2)°, $\beta = 93.02$ (2)°, and $\gamma = 105.68$ (2)°. Irradiation of the *E* isomer in solution gave a mixture enriched in the *Z* isomer that thermally reverted to the *E* form. The activation energy of the thermal *Z*-to-*E* isomerization was 28.8 kcal mol^{-1}.

The key to synthesis of stable disilenes[1] has been protection of the Si–Si double bond by sterically hindering substituents. In general, reactivity of disilenes decreases as the size of substituents increases; for example 1,2-di-*tert*-butyldimesityldisilene (**2**) undergoes addition reactions more slowly than tetramesityldisilene (**1**).[2] Since the 1-adamantyl group is more sterically demanding than *tert*-butyl,[3] 1,2-di(1-adamantyl)dimesityldisilene (**4**) should be especially unreactive. In this paper we report the synthesis of **4**, obtained from photolysis of the trisilane $Mes(Ad)Si(SiMe_3)_2$ (**6**, Ad = 1-adamantyl).

Synthesis

An exchange reaction between 1-iodoadamantane and *tert*-butyllithium in pentane/ether at −70 °C was used to

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(1) For reviews on disilenes see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201-1211. Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Ssons: New York, 1989; Chapter 17, pp 1015-1043.

(2) De Young, D. J.; Fink, M. J.; Michl, J.; West, R. *Main Group Met. Chem.* **1987**, *1*, 19-43.

(3) Anderson, J. E.; Pearson, H.; Rawson, D. I. *J. Am. Chem. Soc.* **1985**, *107*, 1446-1447. The 1-adamantyl group also appears to be more sterically demanding than *tert*-butyl in silenes; see: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1-44.

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$$\mathrm{Mes(R)Si{=}Si(R)Mes}$$

1, R = Mes
2, R = t-Bu
3, R = $N(SiMe_3)_2$
4, R = 1-adamantyl
5, R = 2,6-diethylphenyl

prepare 1-adamantyllithium (eq 1),[4] which was isolated in

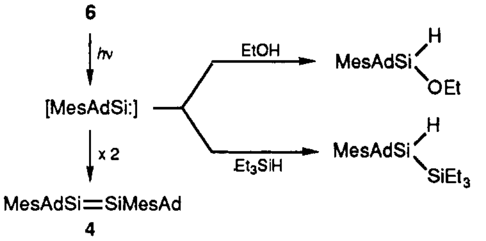
$$\mathrm{AdI} \xrightarrow[C_5H_{12}/Et_2O]{t\text{-BuLi, -70 °C}} \mathrm{AdLi} \qquad (1)$$

Ad = 1-adamantyl

fairly pure form (see Experimental Section). Reaction of adamantyllithium with mesityltrichlorosilane afforded 1-adamantylmesityldichlorosilane, which was coupled with trimethylchlorosilane to yield trisilane 6.

$$\mathrm{MesSiCl_3} \xrightarrow{AdLi} \mathrm{MesAdSiCl_2} \xrightarrow[Li,\ THF]{Me_3SiCl} \underset{6}{\mathrm{MesAdSi(SiMe_3)_2}} \qquad (2)$$

Photolysis of the trisilane in hydrocarbon solution produced 1,2-di(1-adamantyl)dimesityldisilene (4) by silylene dimerization. Intermediacy of the silylene was proven by photolyzing the trisilane in the presence of ethanol or triethylsilane and isolating the product from reaction of the silylene with the trapping reagent (eq 3). The silylene was observed directly by photolysis of the trisilane in a 3-methylpentane matrix at 77 K; λ_{max} was 526 nm.



(3)

Properties of 4. (E)-1,2-Di(1-adamantyl)dimesityldisilene (4) crystallized from toluene as a pale yellow solid. Compound 4 is unusually robust, surviving unchanged up to its melting temperature of 270–274 °C and for several minutes in the molten state at 280 °C. In comparison, decomposition temperatures are 175 °C for 1 and 225 °C for 2.[5] Like 2, 4 is not thermochromic and does not exhibit aryl group migration, both of which are properties of some tetraaryldisilenes.[6,7] Variable-temperature (+75 to −40 °C) ^{1}H NMR spectroscopy did not reveal slow rotation about the Mes–Si or Ad–Si bonds or the presence of more than one conformer. Disilene 2 likewise did not show any change in its NMR spectra (^{1}H, ^{29}Si) between +50 and −80 °C, in contrast to tetramesityldisilene (1) and the amino derivative 3 which both show effects attributed to slow aromatic ring rotation.[5,8] These results indicate that the mesityl rings in 2 and 4 are locked in position by the sterically demanding *tert*-butyl or 1-adamantyl groups.

Table I. Thermodynamic Parameters for Cis-to-Trans Isomerization in Disilenes

	2	3	4	5
E_a, kcal mol^{-1}	31.3	25.4	28.8 ± 0.6	27.7
log A	15.7	13.2	14.2	nr[a]
T_m, K	334.6	323.4	337.2	348.2[b]
ΔG^*, kcal mol^{-1}	26.9	24.8	26.3 ± 0.6	26.4
ΔH^*, kcal mol^{-1}	30.6	24.7	28.1 ± 0.6	27.0
ΔS^*, cal mol^{-1} K^{-1}	11.0	−0.3	5.4 ± 1.8	1.8
ref	13	13	this work	12

[a] Not reported. [b] Masamune, S., private communication.

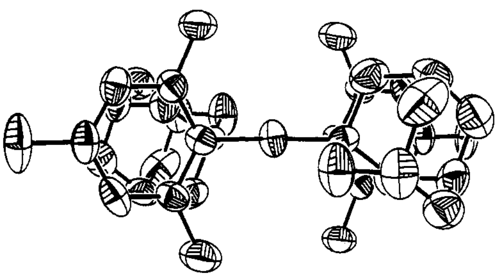
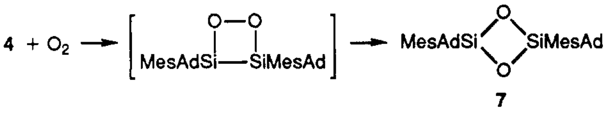


Figure 1. A 30% thermal ellipsoid drawing of a Newman projection down the Si=Si axis in (E)-4. Hydrogen atoms have been omitted for clarity.

Disilene 4, as a solid, is relatively unreactive toward oxygen. A finely powdered sample of 4 exposed to the air underwent oxidation with a half-time of ~2 days. The corresponding half-times for 1 and 2 are a few minutes and a few hours, respectively.[9,10] The product of oxidation of 4 was the expected 1,3-cyclodisiloxane 7 (eq 4).



(4)

On the other hand, in benzene solution 4 reacted slowly (over 16 h at 25 °C) with methanol or ethanol to give a complex mixture of products. Toward these reagents it therefore seems to be more reactive than tetrakis[bis(trimethylsilyl)methyl]disilene, which is reported to be unreactive toward methanol.[11]

Geometrical Isomerism. The mixed-substituent disilenes (2, 3, and 4) and a tetraaryl derivative, 1,2-bis(2,6-diethylphenyl)dimesityldisilene (5),[12] can be interconverted between cis and trans forms. Irradiation of a sample containing mostly the thermodynamically favored E isomer enriches the mixture in the Z isomer. The kinetics of the thermal Z-to-E isomerization can then be studied by using variable-temperature NMR spectroscopy. Disilene 4 was studied in much the same manner as 2 and 3.[13] Various parameters for the isomerization of the di-

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(4) Lansbury, P. T.; Pattison, V. A.; Sidler, J. D.; Bieber, J. B. *J. Am. Chem. Soc.* **1986**, *88*, 78–84. Wieringa, J. H.; Strating, J.; Wynberg, H. *Synth. Commun.* **1972**, *2*, 191–195.

(5) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070–1071. Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821–822.

(6) (a) Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, 1341–1344. (b) Fink, M. J.; De Young, D. J.; West, R. *J. Am. Chem. Soc.* **1983**, *105*, 1070–1071. (c) We have observed that tetra(2,6-xylyl)disilene is mildly thermochromic upon heating (bright yellow to light orange).

(7) Yokelson, H. B.; Maxka, J.; Siegel, D. A.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4239–4241.

(8) Michalczyk, M. J. Ph.D. Thesis, University of Wisconsin—Madison, 1984.

(9) Tetrakis(2,4,6-triisopropylphenyl)disilene is also reported to be stable for 1–2 days in air, but in our hands a finely divided sample of this compound oxidized within minutes of exposure to air. Perhaps the workers used a crystalline sample that would oxidize more slowly. See: (a) Watanabe, H.; Takeuchi, K.; Fukawa, N.; Kato, M.; Goto, M.; Nagai, Y. *Chem. Lett.* **1987**, 1341–1344. (b) Watanabe, H.; Takeuchi, K.; Nakajima, K.; Nagai, Y.; Goto, M. *Chem. Lett.* **1988**, 1343–1346.

(10) West, R.; Yokelson, H. B.; Gillette, G. R.; Millevolte, A. J. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; Chapter 26.

(11) Masamune, S.; Eriyama, Y.; Kawase, T. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 584.

(12) Masamune, S. In *Silicon Chemistry*; Corey, J. Y., Corey, E. R., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; pp 257–268.

(13) It has been shown previously that the Z–E isomerization of disilenes proceeds without breaking of the Si–Si σ bond. See: Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826–829.

silenes are listed in Table I.

The activation energies for thermal cis to trans isomerization in the disilenes range from 25.4 to 31.3 kcal mol^{-1}. These values for the barriers to rotation about the Si=Si double bond are a measure of the Si=Si π-bond strength, assuming that the transition state has no π-bond character (i.e., that there is a 90° rotation about the Si-Si bond in the transition state).[13] Recent ab initio calculations predict the silicon-silicon π bond strength in $H_2Si{=}SiH_2$ to be 22-28 kcal mol^{-1}.[14] The agreement between these calculated values and those obtained experimentally for heavily substituted derivatives is remarkably good.[15]

It is of interest to compare these values with the corresponding barriers for carbon-carbon double bonds. The π-bonding component in disilenes is somewhat weaker than the C=C π-bond in rather similar olefins such as stilbene, in which E_a (*Z* to *E*) is 43 kcal mol^{-1}.[16] However, the rotational barriers in olefins depend greatly upon substitution, ranging from 65 to less than 20 kcal mol^{-1}, usually decreasing with increasing steric bulk of the substituents.[17] It appears that the same trend is emerging in disilenes; compare the values for the adamantyl and *tert*-butyl derivatives (28.8 and 31.3 kcal mol^{-1}, respectively). For the amino derivative **3**, E_a = 25.4 kcal mol^{-1}, it is likely that electronic as well as steric effects are important; interaction of the nitrogen lone pair of electrons with the Si=Si π-system could weaken the double bond. Similarly, the E_a value for **5** (27.7 kcal mol^{-1}) may reflect interaction of the Si=Si π system with that of the aromatic substituents.

Crystal Structure. The structure of (*E*)-**4** was obtained from a crystallographic data set collected at room temperature.[18] The arrangement around the silicon atoms is almost planar, as illustrated in the Newman projection of Figure 1. Distortion from planarity is manifested by slight anti-pyramidalization (2.8°) of the silicon atoms (the degree of pyramidalization is the angle between the C-Si-C plane and the Si-Si vector). The mesityl rings are nearly orthogonal to the disilene framework with an 87° angle between the aromatic ring plane and C_{aryl}-Si-Si plane. The Si=Si bond length is 213.8 (2) pm, and the Si—C bond distances to the 1-adamantyl and mesityl groups are 190.3 (5) and 189.0 (4) pm, respectively, similar to values observed for other disilenes.[1,19]

The adamantyl groups exhibited a minor (5.8%) disorder as shown by peaks found in a difference map. These peaks approximately fit a rotation of the adamantyl group by 60° around the Si-C(1) bond.[20] Significant residual electron density (1.1 e/$Å^3$) was also observed in the CC-Si=SiCC plane, modeled as silicon atoms. Since the adamantyl and mesityl groups have similar space-filling requirements, the residual peaks may be due to Si atoms of the same molecule rotated by about 86° from the original Si=Si axis, as shown in Figure 2.

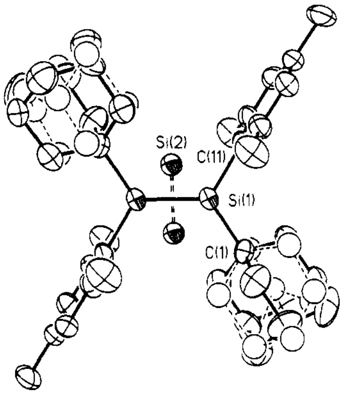

Figure 2. A 30% thermal ellipsoid drawing of (*E*)-**4** including the misaligned residual fragment (dotted lines). Also note the orthogonal orientation of the aromatic rings to the Si=Si double bond. Hydrogen atoms have been omitted for clarity.

Experimental Section

General Procedures. All reactions were done under an atmosphere of nitrogen or argon. Solvents were distilled from appropriate drying agents; CaH_2 was used routinely, but some nonhalogenated solvents were distilled from sodium benzophenone ketyl. 1-Adamantanol was prepared from adamantane[21] or purchased from Aldrich Chemical Co. Hexamethyldisilane was purchased from Petrarch Division of Hüls America Corp. (E)-1,2-Di-*tert*-butyldimesityldisilene (**2**) (for variable-temperature NMR studies) was prepared as described elsewhere.[22]

Proton spectra were recorded on a Bruker WP-200, WP-270, or AM-500 spectrometer; ^{29}Si and ^{13}C spectra were acquired on the Bruker AM-500 instrument at 100 and 125 MHz, respectively. Unless otherwise noted, the solvent was benzene-d_6. The ^{29}Si spectra were acquired by using INEPT (for ^1H-coupled spectra) and INEPTRD (INEPT with refocusing for ^1H-decoupled spectra) pulse sequences (delay times were optimized empirically).[23] High-resolution mass spectral data were obtained on a Kratos MS80 or A.E.I. MS9; GC/MS analyses were done by using a Carlos Erba GC (with a capillary column coated with a nonpolar stationary phase) interfaced to a Kratos MS25 operated at an ionizing voltage of 30 eV.

Analytical GC was done on a Hewlett-Packard 5890 instrument equipped with a 0.53 mm × 15 m open tubular column coated with methylsilicone containing 5% phenyl groups (DB-5). Preparatory GC was done on a Gow-Mac Series 550P instrument (thermal conductivity detector) typically equipped with 3 ft or 6 ft aluminum columns ($^1/_4$ in. i.d.) packed with 5% OV-101 or Dexsil-400 or 10% SE-30 on Chromasorb W or AW/DMCS. UV-visible spectra were recorded on a Perkin-Elmer Lambda Array 3840 spectrophotometer.

Melting points are uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

1-Iodoadamantane (AdI).[24] A solution of hexamethyldisilane (50 g, 0.34 mol) in $CHCl_3$ (75 mL) and a solution of 1-adamantanol (50 g, 0.33 mol) in $CHCl_3$ (250 mL) were simultaneously dripped in over 1-2 h to a mechanically stirred mixture of I_2 (165 g, 0.65 mol) in $CHCl_3$ (250 mL) at room temperature. After being stirred for 2-3 h, the reaction was complete by GC. Antimony powder (74 g, 0.61 mol) was added to remove unreacted iodine by for-

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(14) (a) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217-5227. (b) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272-295. (c) Olbrich, G.; Potzinger, P.; Reimann, B.; Walsh, R. *Organometallics* **1984**, *3*, 1267-1272.

(15) The estimated π-bond energy in 1,2-dimethyldiphenyldisilene of 26 ± 5 kcal mol^{-1} (from a thermochemical analysis of literature data) is also consistent with the experimental values; see ref 14c.

(16) Kistiakowski, G. B.; Smith, W. R. *J. Am. Chem. Soc.* **1934**, *56*, 638-642.

(17) (a) Sandstrom, J. *Top. Stereochem.* **1983**, *14*, 83-181. (b) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 25-89 (Vol. 42 of *Organic Chemistry, A Series of Monographs*, Wasserman, H. H., Ed.). (c) Gano, J. E.; Lenoir, D.; Park, B.-S.; Roesner, R. A. *J. Org. Chem.* **1987**, *52*, 5636-5638. (d) Sakurai, H.; Ebata, K.; Kabuto, C.; Nakadaira, Y. *Chem. Lett.* **1987**, 301-304. (e) Shvo, Y. *Tetrahedron Lett.* **1968**, 5923-5926.

(18) A data set collected at -105 °C resisted solution.

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(20) Rotational disorder of adamantyl groups has been observed in other molecules. See: (a) Cody, V.; Sutton, P. A.; Welsh, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 4053-4057. (b) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876-5878.

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(22) Gillette, G. R.; Yokelson, H. B.; West, R. *Organomet. Synth.* **1988**, *4*, 518.

(23) Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193-218.

(24) (a) Olah, G. A.; Narang, S. C.; Balaram Bupta, B. G.; Malhotra, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 612-614. (b) Cox, B. G.; Maskill, H. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1901-1905.

mation of insoluble SbI_3. This reaction was complete after several hours when the characteristic purple iodine color was replaced by greenish yellow solution and orange-red solid. The reaction mixture was filtered through a 2-in. bed of Celite on a coarse glass frit, and the retained solid was washed with $CHCl_3$ (200 mL). Solvent was stripped, and the resulting crude product was crystallized from methanol to give white 1-AdI in 90% yield (77 g, 0.29 mol): mp 75–76 °C (lit.[24b] 75–76 °C); ^{1}H NMR δ 1.45 (br, 6 H), 1.55 (br, 3 H), 2.48 (br, 6 H); HRMS M^+ not seen even at 28 eV, 135.1170 (100; 135.1174 calcd for $C_{10}H_{15}$), 107 (10.2), 93 (20.0), 79 (19.9). Even though the product was thoroughly dried and stored in the dark under argon, it developed a yellow discoloration. For the best results in the subsequent exchange reaction, freshly recrystallized material was used.

1-Adamantyllithium (AdLi).[4] A solution of *t*-BuLi in pentane (180 mL, 1.7 M, 0.31 mol) was cooled to −60 °C. A mixture of pentane and Et_2O (25 mL each) was cooled to −78 °C in a jacketed addition funnel. Iodoadamantane (35 g, 0.13 mol) was dissolved in pentane (50 mL) and put in another addition funnel. The contents of both addition funnels were simultaneously dripped into the magnetically stirred *t*-BuLi solution. Addition time was 15 min. The reaction flask was kept at −60 to −70 °C for 2 h. The reaction was monitored by GC using (1) a hydrolyzed aliquot to observe unreacted AdI and (2) a sample that had been reacted first with *p*-tolualdehyde and then water to see the AdLi–aldehyde adduct [(*p*-methylphenyl)(1-adamantyl)carbinol]. After the AdI was consumed, the solvent was removed by bulb-to-bulb distillation under vacuum as the flask slowly warmed to room temperature over about 8 h (almost all of the solvent was removed while the pot was at less than −30 °C to minimize product decomposition). Hexane (300 mL) was added, and the mixture was heated at reflux overnight to solubilize unreacted *t*-BuLi and byproducts such as adamantane and 1,1-biadamantane. The mixture was then cooled and filtered through an enclosed coarse glass frit, and the solid AdLi was washed with three 50-mL portions of hexane. After the mixture was dried under vacuum, an off-white solid was obtained (31 g, 0.14 mol of AdLi·Et_2O (etherate assumed); this is greater than 100% yield—the extra weight could be from additional solvent trapped in the solid or from hexane-insoluble byproducts that could include LiI and LiOEt.

Mesityltrichlorosilane. A solution of 0.25 mol of mesityllithium in 200 mL of benzene (prepared from bromomesitylene and *n*-butyllithium as previously described[6a]) was added dropwise to a refluxing solution of 60 mL of $SiCl_4$ (0.52 mol) in 1 L of dry benzene over 2 h. The mixture was refluxed for 24 h, cooled, and filtered to remove lithium salts. Concentration of the filtrate under vacuum gave a white crystalline solid; recrystallization from THF yielded 29.6 g (48%) of mesityltrichlorosilane: mp 38–40 °C; ^{1}H NMR (C_6D_6) δ 1.94 (s, 3 H), 2.54 (s, 6 H), 6.52 (s, 2 H); MS (30 eV) *m/e* 252 (M^+), 217 (M^+ − Cl), 182 (M^+ − C_9H_{11}); calcd for $C_9H_{11}SiCl_3$ *m/e* 251.9694, Cl, 41.9, found *m/e* 251.9695, Cl, 41.6.

Mesityl(1-adamantyl)dichlorosilane (MesAdSiCl$_2$). A slurry of AdLi·Et_2O (20.6 g, 0.095 mol) in benzene (150 mL) was prepared. Mesityltrichlorosilane (24.1 g, 0.095 mol) was added, and the mixture was stirred at room temperature for 24 h and then at reflux until the AdLi was consumed (about 18 h). The reaction mixture was filtered and the solvent stripped. The resulting residue was extracted with hexane (200 mL) and filtered. Removal of solvent from the filtrate left a golden brown oil. Crystallization from hexane gave white solid MesAdSiCl$_2$ in 25% yield (8.4 g, 0.024 mol): mp 87–89 °C; ^{1}H NMR (C_6D_6) δ 1.55 (br, 6 H), 1.73 (br, 3 H), 1.96 (br, 6 H), 2.00 (s, 3 H), 2.59 (s, 6 H), 6.67 (s, 2 H); ^{13}C NMR δ 20.9, 26.9, 27.6, 29.9, 36.1, 37.0, 123.7, 130.8, 141.1, 145.8; ^{29}Si NMR δ 15.0; HRMS 352.1183 (2.8; 352.1181 calcd for $C_{19}H_{26}{}^{35}Cl_2Si$), 217 (1.0), 135 (52.7), 120 (81.8), 105 (100).

2-Mesityl-2-(1-adamantyl)hexamethyltrisilane (MesAdSi(SiMe$_3$)$_2$, 6). Shiny lithium wire containing 1% Na (0.24 g, 0.035 mol) was cut in small pieces into THF (20 mL). Trimethylchlorosilane (1.85 g, 0.017 mol), freshly distilled from K_2CO_3, was added; then a solution of MesAdSiCl$_2$ (3.0 g, 0.0085 mol) in THF (20 mL) was dripped in at room temperature. The reaction mixture was stirred until the MesAdSiCl$_2$ was consumed as indicated by GC (20–40 h). Unreacted pieces of lithium were removed, and the solvent was stripped. The resulting residue was extracted with hexane and filtered. Crystallization in hexane afforded MesAdSi(SiMe$_3$)$_2$ as a white solid in 88% yield (3.2 g, 0.0075 mol): mp 191–192 °C; ^{1}H NMR δ 0.39 (s, 18 H), 1.69 (br, 6 H), 1.82 (br, 3 H), 2.03 (br, 6 H), 2.11 (s, 3 H), 2.60 (s, 6 H), 6.81 (s, 2 H); ^{13}C NMR δ 5.1, 20.8, 28.9, 29.1, 29.8, 37.6, 42.3, 129.1, 131.5, 137.9, 145.6; ^{29}Si NMR δ −32.2, −20.1; HRMS 428.2750 (0.1; 428.2751 calcd for $C_{25}H_{44}Si_3$), 355.2217 (89.9; loss of Me$_3$Si; 355.2268 calcd for $C_{22}H_{35}Si_2$), 221 (100), 219 (25.4), 177 (23.0), 147 (14.7), 73 (16.1); Anal. Calcd for $C_{25}H_{44}Si_3$: C, 70.01; H, 10.34. Found: C, 69.66; H, 10.26.

(*E*)-1,2-Di(1-adamantyl)dimesityldisilene (MesAdSi=SiMesAd, 4). A solution of MesAdSi(SiMe$_3$)$_2$ (0.50 g, 1.2 mmol) in pentane (80 mL) in a quartz tube was degassed by five cycles of freeze–evacuate–thaw. It was then cooled to −50 °C in a quartz Dewar vessel equipped with a liquid-nitrogen blow-off system and temperature controller. Upon irradiation at 254 nm the solution turned yellow and solid gradually appeared. Photolysis was continued for 24–28 h; then volatiles were removed (crude product yield was 80–90%). The crude photolysate contained both *cis*- and *trans*-disilene. Crystallization from toluene gave the *E* isomer of 4 as light yellow crystals in 41% yield (0.14 g, 0.25 mmol): mp 270–274 °C; ^{1}H NMR (trans) δ 1.53 (br, 12 H), 1.63 (br, 6 H), 1.97 (br, 12 H), 2.13 (s, 6 H), 2.95 (s, 12 H), 6.94 (s, 4 H); ^{1}H NMR (cis) δ 1.74 (br, 12 H), 1.89 (br, 6 H), 1.99 (br, 12 H), 2.19 (s, 6 H), 2.76 (s, 12 H), 6.67 (s, 4 H); ^{13}C (trans) δ 21.3, 27.9, 28.7, 30.9, 37.3, 42.6, 132.7, 138.3, 139.1, 144.6; ^{29}Si (trans) δ 87.1; ^{29}Si (cis) δ 92.6; HRMS 564.3593 (34.6; 564.3608 calcd for $C_{38}H_{52}Si_2$), 429 (100), 355 (86.7), 299 (49.7), 221 (96.7), 163 (54.7), 135 (13.5); UV-vis (nm) 338, 394 (sh).

Oxidation of 4. A solution of 4 in toluene-d_8 was cooled to −78 °C. Oxygen was bubbled in, and the solution became decolorized within several minutes. The sample was warmed to room temperature and a ^{29}Si NMR spectrum taken immediately. New signals in the spectrum were observed at +49.1 and +8.1 ppm, assigned to the 1,2- and 1,3-dioxetanes, respectively, by analogy with the more thoroughly studied *t*-Bu system.[25] Synthesis of the 1,3-dioxetane on a preparative scale involved bubbling oxygen into a room temperature solution of (*E*)-4 in benzene. Crystallization from benzene gave 1,3-cyclodisiloxane (7) as a white solid: mp 320–330 °C; ^{1}H NMR δ 1.54 (br, 12 H), 1.65 (br, 6 H), 1.92 (d, 12 H), 2.09 (s, 6 H), 2.81 (s, 12 H), 6.80 (s, 4 H); ^{29}Si NMR (C_6D_6) δ 12.5; ^{29}Si (C_7D_8) δ 8.1; HRMS 596.3488 (11.9; 596.3492 calcd for $C_{38}H_{52}O_2Si_2$), 477 (11.8), 461 (100), 327 (77.2), 299 (17.2), 235 (53.5). Anal. Calcd for $C_{38}H_{52}O_2Si_2$: C, 76.45; H, 8.78; Si, 9.41. Found: C, 76.28; H, 8.56; Si, 9.08.

Trapping of Mesityl(1-adamantyl)silylene (MesAdSi:). These reactions were done as described for preparation of the disilene except for the amount of trisilane used (0.1 g, 0.24 mmol in 15 mL of pentane), the inclusion of EtOH (1.3 mL, 5 mmol) or Et$_3$SiH (1.8 mL, 5 mmol), and an irradiation time of 11 h. After removal of volatiles, the crude product was analyzed. EtOH-trapped product MesAdSi(H)OEt: ^{1}H NMR δ 1.13 (t, *J* = 7 Hz, 3 H), 1.72 (br, 6 H), 1.83 (br, 3 H), 1.97 (br, 6 H), 2.13 (s, 6 H), 2.54 (s, 3 H), 3.64 (q, *J* = 7 Hz, 2 H), 5.12 (s, 1 H), 6.78 (s, 2 H); ^{13}C NMR δ 18.2, 21.2, 23.1, 23.9, 24.9, 28.2, 38.0, 61.1, 129.0, 129.3, 139.5, 145.4; ^{29}Si NMR δ −2.0 [^{1}J(Si–H) = 198 Hz]; HRMS 328.2216 (16.7; 328.2222 calcd for $C_{21}H_{32}OSi$), 193 (100), 177 (12.2), 147 (47.7), 73 (51.8). Et$_3$SiH-trapped product MesAdSi(H)SiEt$_3$: ^{1}H NMR δ 0.82 (q, *J* = 8 Hz, 6 H), 0.02 (t, *J* = 8 Hz, 9 H), 1.70 (s, 6 H), 1.82 (br, 3 H), 1.96 (br, 6 H), 2.12 (s, 3 H), 2.46 (s, 3 H), 2.58 (s, 3 H), 4.44 (s, 1 H), 6.78 (s, 1 H), 6.83 (s, 1 H); ^{13}C NMR δ 2.8, 5.9, 8.5, 8.8, 21.2, 26.2, 26.3, 26.6, 28.8, 37.6, 41.7, 128.3, 129.3, 129.5, 138.4, 144.2, 145.2; ^{29}Si NMR δ −29.8 [^{1}J(SiH) = 171 Hz], −6.88 (complex multiplet due to two- and three-bond Si–H coupling); HRMS 398.2805 (2.3; 398.2825 calcd for $C_{25}H_{42}Si_2$), 282 (50.2), 163 (31.7), 147 (17.8), 84 (100). The proton NMR spectrum of this compound shows a locked mesityl ring; the resonances at 2.46 and 2.58 ppm are the two ortho-methyl groups and those at 6.78 and 6.83 ppm are the two aryl protons. No coalescence was observed between 25 and 70 °C.

Observation of Mesityl(1-adamantyl)silylene (MesAdSi:). A solution of MesAdSi(SiMe$_3$)$_2$ (about 3 mg) in 3-methylpentane (1.5 mL) in a spectroscopic cell with Suprasil windows was de-

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[25] Michalczyk, M. J.; West, R.; Michl, J. *J. Chem. Soc., Chem. Commun.* 1984, 1525–1526. (b) Gillette, G. R.; McKillop, K., unpublished results.

Table II. Rate Constants for Cis–Trans Interconversion in Disilene 4

$$\textit{cis-}\mathbf{4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans-}\mathbf{4}$$

T, °C	k_1, s^{-1}	k_{-1}, s^{-1}
52.6	1.6×10^{-5}	5.1×10^{-7}
62.1	4.2×10^{-5}	1.3×10^{-6}
67.3	1.2×10^{-4}	3.8×10^{-6}
74.9	2.5×10^{-4}	8.0×10^{-6}

Table III. Crystal and Refinement Data

formula	$C_{38}H_{52}Si_2$
color, habit	yellow, prisms
cryst size, mm	0.2 × 0.5 × 0.6
cryst system	triclinic
space group	$P\bar{1}$
cell dimens	
a, Å	8.292 (2)
b, Å	10.069 (2)
c, Å	10.772 (2)
α, deg	105.67 (2)
β, deg	93.03 (2)
γ, deg	105.68 (2)
V, Å^3	826.0 (3)
Z	1
fw	565.0
D(calcd), g/cm^3	1.136
abs coeff, cm^{-1}	1.27
radiatn	Mo Kα (λ = 0.71073 Å)
temp, K	295
monochromator	graphite, incident beam
2θ range, deg	3–50
scan type, range, deg	ω, 2.00
scan speed, deg/min	2.0–29.34
bkgd	2 measurements for 25% of total scan time
index ranges	$+h,\pm k,\pm l$
data measd	3063
independent data	2850 (R_{int} = 1.38%)
obsd data	2053 [$F > 2.0\sigma(F)$]
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0110F^2$
R, R_w (obsd data)	R = 8.46%, R_w = 13.80%
R, R_w (all data)	R = 10.76%, R_w = 15.29%
goodness-of-fit	1.21
largest and mean Δ/σ	0.024 and 0.001
data-to-parameter ratio	10.9:1
largest difference peak and hole, e/Å^3	0.55 and –0.23

Table IV. Atomic Coordinates (×10^4) Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) and Occupancies

	x	y	z	U(eq)[a]	occ
Si(1)	9189 (2)	3962 (1)	4966 (1)	51 (1)	0.950 (2)
Si(2)	10295 (17)	4609 (16)	4103 (15)	40 (2)	0.050 (2)
C(1)	7908 (5)	3618 (4)	6322 (4)	43 (1)	0.950 (2)
C(2A)	8942 (7)	3332 (8)	7373 (7)	76 (1)	0.889 (2)
C(3A)	7890 (8)	3039 (8)	8494 (6)	80 (1)	0.889 (2)
C(4A)	6392 (9)	1764 (7)	7887 (9)	97 (1)	0.889 (2)
C(5A)	5204 (7)	2014 (6)	6883 (6)	73 (1)	0.889 (2)
C(6A)	4767 (7)	3358 (7)	7491 (7)	78 (1)	0.889 (2)
C(7A)	6239 (8)	4632 (6)	8103 (6)	70 (1)	0.889 (2)
C(8A)	7318 (8)	4942 (6)	7009 (6)	67 (1)	0.889 (2)
C(9A)	6287 (9)	2308 (7)	5812 (7)	85 (1)	0.889 (2)
C(10A)	7314 (8)	4365 (8)	9075 (7)	86 (1)	0.889 (2)
C(2B)	8811	4724	7612	50 (1)	0.058
C(3B)	7711	4313	8979	50 (1)	0.058
C(4B)	7888	2941	8873	50 (1)	0.058
C(5B)	7205	1874	7539	50 (1)	0.058
C(6B)	5570	2350	7554	50 (1)	0.058
C(7B)	5153	3559	7000	50 (1)	0.058
C(8B)	6142	3764	5922	50 (1)	0.058
C(9B)	7830	2078	6300	50 (1)	0.058
C(10B)	6070	4671	8308	50 (1)	0.058
C(11)	8861 (5)	2348 (4)	3487 (4)	42 (1)	0.950 (2)
C(12)	7582 (6)	2054 (5)	2440 (4)	49 (1)	0.950 (2)
C(13)	7373 (6)	836 (5)	1363 (4)	57 (1)	0.950 (2)
C(14)	8321 (6)	–101 (5)	1307 (4)	54 (1)	0.950 (2)
C(15)	9554 (6)	201 (5)	2333 (5)	56 (1)	0.950 (2)
C(16)	9844 (6)	1411 (5)	3410 (4)	50 (1)	0.950 (2)
C(17)	6434 (7)	2999 (7)	2439 (6)	82 (1)	0.950 (2)
C(18)	8033 (8)	–1414 (7)	144 (6)	87 (1)	0.950 (2)
C(19)	11290 (7)	1684 (6)	4455 (6)	72 (1)	0.950 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Bond Lengths (pm)

Si(1)–Si(1A)	213.8 (2)	Si(1)–Si(2)	149.1 (16)
Si(1)–Si(2A)	145.0 (13)	Si(1)–C(1)	190.3 (5)
Si(1)–C(11)	189.0 (4)	C(1)–C(2A)	151.9 (9)
C(1)–C(8A)	155.6 (8)	C(1)–C(9A)	155.6 (7)
C(2A)–C(3A)	157.2 (10)	C(3A)–C(4A)	148.9 (8)
C(3A)–C(10A)	152.6 (11)	C(4A)–C(5A)	153.9 (11)
C(5A)–C(6A)	148.4 (9)	C(5A)–C(9A)	154.2 (10)
C(6A)–C(7A)	147.7 (7)	C(7A)–C(8A)	156.4 (9)
C(7A)–C(10A)	146.5 (11)	C(11)–C(12)	141.7 (6)
C(11)–C(16)	139.3 (7)	C(12)–C(13)	140.5 (6)
C(12)–C(17)	151.7 (9)	C(13)–C(14)	137.4 (8)
C(14)–C(15)	137.5 (7)	C(14)–C(18)	150.9 (7)
C(15)–C(16)	139.2 (6)	C(16)–C(19)	151.4 (7)

Table VI. Bond Angles (deg)

C(1)–Si(1)–C(11)	115.4 (2)	C(1)–Si(1)–Si(1A)	123.4 (1)
C(11)–Si(1)–Si(1A)	121.2 (2)	Si(1)–C(1)–C(2A)	111.4 (3)
Si(1)–C(1)–C(8A)	111.8 (4)	Si(1)–C(1)–C(9A)	112.2 (3)
C(2A)–C(1)–C(8A)	106.4 (4)	C(2A)–C(1)–C(9A)	107.9 (5)
C(8A)–C(1)–C(9A)	106.7 (4)	C(1)–C(2A)–C(3A)	111.8 (5)
C(2A)–C(3A)–C(4A)	107.0 (5)	C(2A)–C(3A)–C(10A)	107.7 (6)
C(4A)–C(3A)–C(10A)	109.8 (6)	C(3A)–C(4A)–C(5A)	113.6 (7)
C(4A)–C(5A)–C(6A)	108.8 (5)	C(4A)–C(5A)–C(9A)	105.0 (6)
C(6A)–C(5A)–C(9A)	106.8 (6)	C(5A)–C(6A)–C(7A)	114.4 (5)
C(6A)–C(7A)–C(8A)	107.6 (5)	C(6A)–C(7A)–C(10A)	111.7 (6)
C(8A)–C(7A)–C(10A)	107.8 (5)	C(1)–C(8A)–C(7A)	111.1 (5)
C(1)–C(9A)–C(5A)	113.5 (4)	C(3A)–C(10A)–C(7A)	111.5 (5)
Si(1)–C(11)–C(12)	120.3 (3)	Si(1)–C(11)–C(16)	121.0 (3)
C(12)–C(11)–C(16)	118.7 (4)	C(11)–C(12)–C(13)	118.4 (5)
C(11)–C(12)–C(17)	122.6 (4)	C(13)–C(12)–C(17)	118.9 (4)
C(12)–C(13)–C(14)	122.6 (4)	C(13)–C(14)–C(15)	118.1 (4)
C(13)–C(14)–C(18)	120.9 (5)	C(15)–C(14)–C(18)	120.9 (5)
C(14)–C(15)–C(16)	121.7 (5)	C(11)–C(16)–C(15)	120.4 (4)
C(11)–C(16)–C(19)	122.1 (4)	C(15)–C(16)–C(19)	117.5 (5)

gassed by five cycles of freeze–evacuate–thaw. The cell was immersed in filtered liquid nitrogen in a quartz Dewar vessel constructed with Suprasil windows. After photolysis at 254 nm for 10 min, the 3-MP glass was rose colored. Analysis by UV–visible spectroscopy showed bands due to the silylene at 277 and 526 nm. The liquid nitrogen was poured out, and the changes accompanying annealing and melting of the glass were followed by UV–visible spectroscopy. The silylene bands steadily diminished in intensity as absorbances at 338 and 394 nm due to the disilene grew in.

Heating Experiments on 4. In a drybox, capillaries were loaded with the same amount of 4 and heated at 280 °C for 0–30 min in a preheated melting point block. After heating, the sample was dissolved in toluene in a spectroscopic cell and analyzed by UV–visible spectroscopy. The band at 338 nm, characteristic of the disilene, was present in samples heated for 0 and 1 min but was absent in those heated for 10 min or more.

Geometrical Isomerization. NMR samples of (E)-4 in benzene-d_6 were prepared and sealed. The *E*:*Z* ratio at thermal equilibrium at 22 °C was 97:3, corresponding to a free energy difference between the isomers of 2.0 kcal mol^{-1}. Irradiation at 350 nm at 10–25 °C for 3 h resulted in a photostationary 54/46 trans/cis mixture. No decomposition noticeable by ^{1}H or ^{29}Si NMR occurred, even after several cycles of photolysis and thermal equilibration. Samples were frozen in liquid nitrogen to preserve the isomer imbalance or were used immediately. The Bruker AM-500 NMR spectrometer probe temperature, measured with a type T thermocouple (±0.1 °C) in an NMR tube, was stabilized before a room-temperature NMR sample was introduced and allowed to equilibrate with the probe temperature for 15 min. Probe temperature was measured at the end of the experiment, also. Readings were taken every minute until three consecutive

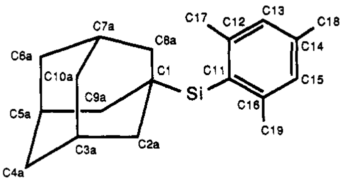

Figure 3. Numbering scheme for the independent portion of 4. See Figure 2 for structural details.

measurements were ±0.1 °C. An automated program was used to acquire proton spectra at set intervals with longer times between spectra acquisition as the experiment proceeded (8–33 spectra taken over 1–6 h). Spectra were acquired through the decoupler with an 8-s delay between pulses to allow for complete relaxation of the protons to result ion more accurate integration values. The *E*:*Z* ratios at various times were measured by integration of the ortho-methyl proton signals for the two isomers. A 5% error in NMR integration is assumed. Rate constants were calculated by a least-squares analysis of a kinetics expression applicable to a first-order process with a reversible reaction (eq 5). The data

$$\ln\left[\frac{K_{eq}[\text{cis}]_t - [\text{trans}]_t}{K_{eq}[\text{cis}]_0 - [\text{trans}]_0}\right] = -(k_1 + k_{-1})t \qquad (5)$$

for disilene 4 are listed in Table II. The Arrhenius equation ($\ln k = \ln A - E_a/RT$) was used to determine E_a from the slope of a plot of ln *k* vs $1/T$: the Eyring equation ($k = kRT \exp[-\Delta G^{*}/RT]/hN$) was used to determine ΔG^{*}; the average value is given in Table I. The enthalpy of activation was obtained from $\Delta H^{*} = E_a - RT_m$ where T_m is the mean absolute temperature for the range over which rate measurements were made; ΔS^{*} was calculated from $\Delta S^{*} = (\Delta H^{*} - \Delta G^{*})/T_m$.

Structure Determination. Crystals of (*E*)-1,2-di(1-adamantyl)dimesityldisilene (4) were grown by allowing an almost saturated, hot toluene solution to cool to room temperature. Data were collected on a single crystal mounted in a glass capillary. All measurements were made at room temperature on a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation. Three check reflections were remeasured after every 50 intensity measurements and showed no significant variation. Cell parameters were determined from 25 intensity maxima measured with $30 \le 2\theta \le 37°$. Intensity data exhibited only triclinic Laue symmetry. The space group $P\bar{1}$ was chosen because the mean $|E^2 - 1|$ was 0.938 because the structure was solvable and would refine in $P\bar{1}$ and because refinement in *P*1 was highly unstable (extreme correlations and overshifting). The structure was solved by direct methods and refined by full-matrix least squares. All calculations were performed on a DEC Micro VAX II using the *SHELXTL PLUS* software package.[26] Neutral atom scattering factors and anomalous dispersion terms were taken from ref 27. Crystal and refinement data are summarized in Table III. Atomic coordinates and selected bond distances and angles are presented in Tables IV–VI. The numbering is as shown in Figure 3.

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Registry No. 4, 114391-93-4; 6, 111060-24-3; 7, 122899-16-5; AdI, 768-93-4; AdLi, 3732-30-7; $SiCl_4$, 10026-04-7; $MesAdSiCl_2$, 122899-15-4; MesAdSi:, 111060-26-5; MesAdSi(H)OEt, 111060-33-4; $MesAdSi(SiMe_3)_2$, 122899-17-6; (*Z*)-MesAdSi=SiMesAd, 122899-18-7; 1-adamantanol, 768-95-6; [(*p*-methylphenyl)(1-adamantyl)carbinol], 102933-67-5; *p*-tolualdehyde, 104-87-0; mesityltrichlorosilane, 17902-75-9; 1,2-di(1-adamantyl)-1,2-dimesityl-1,2-cyclodisiloxane, 122923-85-7; tetra(2,6-xylyl)disilene, 80593-68-6; tetrakis(2,4,6-triisopropylphenyl)disilene, 114057-47-5.

Supplementary Material Available: Tables of H-atom coordinates and anisotropic displacement coefficients for (*E*)-4 (2 pages); a listing of calculated and observed structure factors for (*E*)-4 (11 pages). Ordering information is given on any current masthead page.

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[26] *SHELXTL PLUS*; Nicolet Instruments Corp.: Madison, WI, 1988.

[27] *International Tables for Crystallography*; Kynoch: Birmingham, England 1974; Vol. IV, Table 2.2B, pp 99–101, Table 2.3.1, pp 149–150.