estimate the quantum yield to be less than 10%. A (nonstatistical) branching into several dissociation channels in the first step of the photolysis has already been suggested for other metal carbonyls.[7]

To support proposed mechanism 1, we have carried out LCGTO-Xα calculations[9] for the ground state and for several excited state potential energy curves of $Ni(CO)_4$ and of $Ni(CO)_3$. A detailed discussion of the theoretical investigations will be given elsewhere.[1] The basis sets were identical with those used in a previous study on $Ni(CO)_4$[10] except for the addition of one *f*- and *g*-function (exponents 0.56) to both of the auxiliary basis sets (charge and exchange fitting). The energies of the excited singlet (open shell) states were obtained by correcting the energy of the configuration with opposite spins for its triplet admixture.[11]

First, one metal-carbon bond of $Ni(CO)_4$ was elongated, keeping the $Ni(CO)_3$ moiety frozen in the experimental geometry of the parent complex.[12] Besides the $Ni(CO)_4$ ground state ($^1A_1$ symmetry in C_{3v}), the first excited singlet state, ^1E, is pertinent to mechanism 1. The latter may be characterized as the Ni $d_{xz},d_{yz}(e) \rightarrow$ CO $2\pi(a_1)$ transition, belonging to the HOMO-LUMO excitation manifold in $Ni(CO)_4$ ($8t_2 \rightarrow 9t_2$, T_d). This lowest lying excited state ^1E is repulsive. At equilibrium geometry, it is calculated to lie 4.83 eV above the ground state. Thus one may assume a one-photon excitation into this state to be the first step of the photolysis, if one takes into account the well-known tendency of local density methods to favor high d occupations.[1,13] The next singlet state (derived from a Ni $d_{xz},d_{yz}(e) \rightarrow$ CO $2\pi(e)$ excitation) is not expected to be involved in the photolysis since it is bound with respect to removal of one CO moiety. All other singlet states lie at least 1 eV higher in energy[1] and therefore should not be relevant in the present case.

Furthermore, the bending (umbrella mode) of a $Ni(CO)_3$ fragment has been investigated. For the pyramidal configuration of the fragment these curves are connected to those discussed above in the asymptotic limit of Ni-C separation. Therefore all bond lengths were kept unchanged in our model.[1] At tetrahedral fragment angle the lowest excited singlet state ^1E lies 2.46 eV above the corresponding ground state $^1A_1$. However, the shape of the potential curves for the bending motion is quite different for these two states. The ground state curve shows a pronounced minimum at planar geometry (in agreement with matrix isolation experiments[13]) whereas the potential curve of the first excited state is predicted to exhibit a rather shallow double well, with the minima at a C-Ni-C angle of about 115°. Consequently, the excitation energy $^1A_1 \rightarrow {}^1E$ varies strongly with this bending angle (from 3.14 eV at planar geometry to 2.16 eV at an angle of 102°). This variation is considered responsible for the rather wide spectrum observed. Except for a uniform overestimation of all excitation energies by about 0.8 eV due to the local density approximation[1] this energy range is in almost quantitative agreement with that of the experimental luminiscence spectrum. These limitations of the LCGTO-Xα method certainly do not invalidate proposed mechanism 1.[9,10]

The correlation between both ground and lowest excited states of $Ni(CO)_4$ and $Ni(CO)_3$ is in remarkable contrast to the situation found in calculations on the dissociation of $Fe(CO)_5$.[14] The $Fe(CO)_4$ fragment has been found to have an open-shell ground state, the spatial symmetry of which is correlated with the excited state of the parent molecule. Therefore no luminiscence is to be expected during photolysis of $Fe(CO)_5$.

The shape of the LUMO of $Ni(CO)_3$ which becomes occupied in the ^1E state has been discussed previously.[15] At nonplanar geometries it was found to be a bonding linear combination of the CO $2\pi^*$ orbitals with a $s-p_z-d_{z^2}$ hybrid on Ni, the latter pointing away from the remaining carbonyl ligands. This low-lying Ni orbital serves as an acceptor for the 5σ lone pair of a carbonyl ligand approaching the fragment, resulting in a strong bonding interaction.[15] The antibonding partner of this interaction forms the LUMO of the dissociating $(CO)_3Ni-CO$ system. Its occupation will weaken the corresponding metal-ligand bond. As the calculations indicate, this effect is strong enough to make the potential energy curve strongly repulsive in the corresponding excited state.

The luminiscence of the excited $Ni(CO)_3$ fragment occurs in the visible since its HOMO-LUMO gap is smaller than that of $Ni(CO)_4$ for two reasons. Taking one-electron energies as an indicator, one can attribute about two-thirds of the reduction to the lowering of the LUMO as a consequence of the lesser σ repulsion and one-third to the rising metal 3d levels due to reduced back-donation.

Luminiscence from charge-transfer excited fragments seems to be a rather general phenomenon following the photolysis of transition-metal complexes in the gas phase.[8] Several other systems are currently being investigated.

After completion of this work, transient *absorption* spectra observed after photolysis of $Cr(CO)_6$ have been published and an interpretation has been given attributing them to the fragment $Cr(CO)_5$.[16]

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[9] For an explanation of the method, see: Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 3396-3402, 4993-4999.

[10] Jörg, H.; Rösch, N. *Chem. Phys. Lett.* **1985**, *120*, 359-362. Rösch, N.; Jörg, H.; Dunlap, B. I. In *Quantum Chemistry: the Challenge of Transition Metals and Coordination Compounds*: Veillard, A., Ed.; Reidel: Dordrecht, 1986, pp 179-187.

[11] Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *43*, 261-271. Barth, U. v. *Phys. Rev. A* **1979**, *20*, 1693-1703.

[12] Hedberg, L.; Iijima, T.; Hedberg, K. *J. Chem. Phys.* **1979**, *70*, 3224-3229.

[13] De Kock, R. L. *Inorg. Chem.* **1971**, *10*, 1205-1211.

[14] Daniel, C.; Benard, M.; Dedieu, A.; Wiest, R.; Veillard, A. *J. Phys. Chem.* **1984**, *88*, 4805-4811.

[15] Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058-1076. Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *7*, 1755-1759.

[16] Breckenridge, W. H.; Stewart, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 364-367.

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^{29}Si NMR Observation of an Unprecedented Rearrangement in Tetraaryldisilenes

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We report here the first observation of a facile intramolecular rearrangement of tetraaryldisilenes involving the exchange of two aryl substitutents between the silicon atoms of the silicon-silicon double bond.[1]

The disilenes were generated photochemically by irradiation of their trisilane precursors[2,3] in pentane solution at -60 °C and the crude photolysates were examined by ^{29}Si NMR in benzene. Pure disilenes **11** and **22** were produced by photolysis of trisilanes **1** or **2** and gave in each case only a single ^{29}Si signal in the disilene

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[1] For reviews of disilene, see: (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 1, 163-173. (b) West, R.; Fink, M. J.; Michalczyk, M. J.; De Young, D. J.; Michl, J. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood Ltd.: New York, 1985; Part 1, Chapter 1, pp 3-14.

[2] (a) Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1984**, *4*, 826-829. (b) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *Organometallics* **1984**, *3*, 793-800. (c) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon, Germanium, Tin and Lead Compounds*, in press. (d) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419-509.

[3] All new compounds were characterized by ^{1}H NMR, high-resolution, MS, and elemental analysis.

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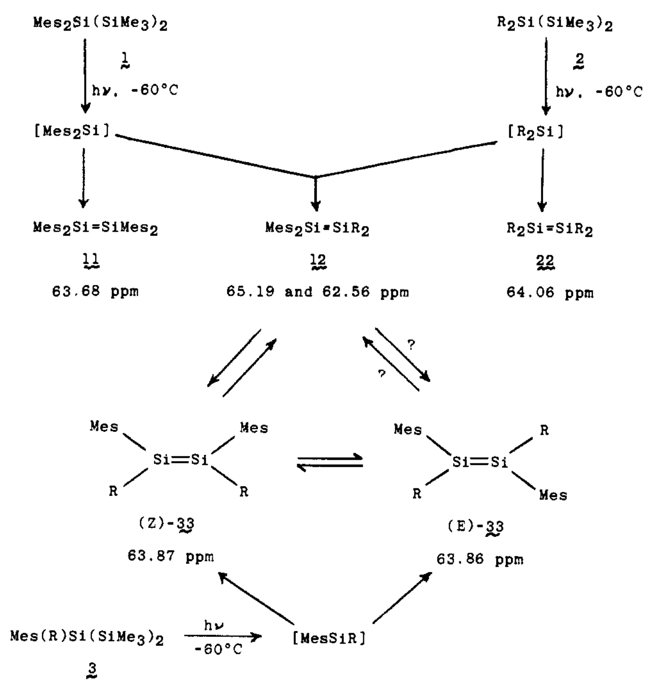
Scheme I. Results from Photolysis of Trisilanes[a]



[a] Mes = 2,4,6-trimethylphenyl, R = 2,6-dimethylphenyl.

region, at 63.68 and 64.06 ppm, respectively (Scheme I).[4,5] When an equimolar mixture of trisilanes **1** and **2** was irradiated, four signals were initially observed in the disilene region (60–65 ppm) in an approximately 1:1:1:1 intensity ratio.[6] These four resonances may be assigned to the three expected disilenes formed by dimerization of the silylenes; they are disilenes **11** (63.68 ppm) and **22** (64.06 ppm) and mixed disilene **12** (62.56 and 65.19 ppm).

These results are consistent with the now well-established dimerization of silylenes in solution to give disilenes. The disilenes are apparently formed in near-statistical 1:2:1 ratio, as expected if there is negligible steric or electronic preference for one disilene or another and if the intermediate silylenes, Mes$_2$Si and (2,6-xylyl)$_2$Si, are formed at approximately the same rate.

When a benzene solution of the photolysate from the cophotolysis of **1** and **2** was examined by ^{29}Si NMR over the course of several weeks (20–25 °C), two new signals at 63.87 and 63.86 ppm appeared in the spectrum, almost centered between the signals for **12**. The resonance at 63.87 ppm appeared first, in excess over the higher field resonance by at least 3:1 (Figure 1a). The two new signals increased in intensity relative to those signals for **11** and **22**, while at the same time the signals for the mixed disilene **12** were diminshed. After 70 days, a near steady-state condition was reached; the signals for disilene **12** were then barely discernible from the base-line noise, and the two new signals were dominant features of the spectrum (Figure 1b). We assign the two new resonances to the *Z* and *E* isomers of disilene **33**, formed from **12** by aryl group migration.[8] Irradiation of trisilane **3** generated two ^{29}Si signals at the same frequencies, 63.87 and 63.86 ppm (Scheme I), from the stereoisomers of the disilene (*Z*)-**33** and (*E*)-**33**.[9] However, in contrast with the rearranged material derived from disilene **12**, the upfield isomer appears to be produced in a slight (4:3) molar excess.

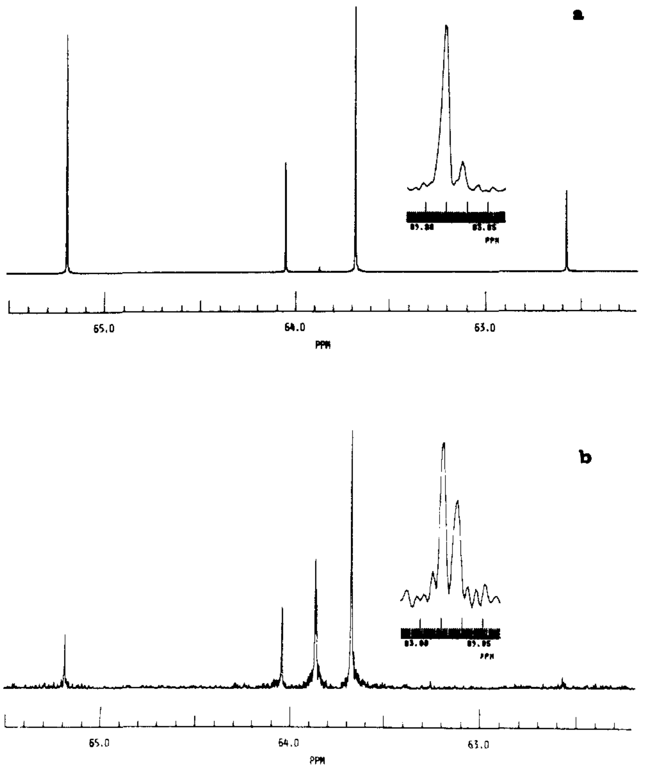
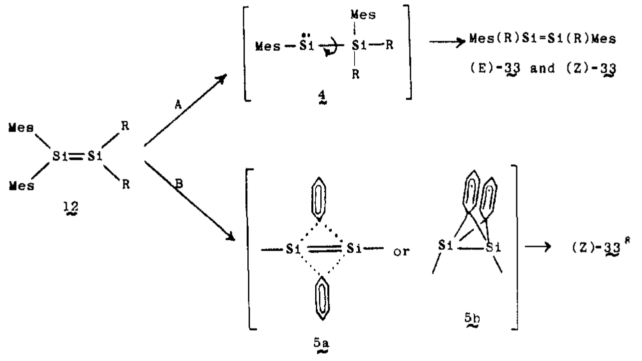


Figure 1.[5] ^{29}Si NMR spectra of disilenes obtained from photolysis of a 1:1 mixture of **1** and **2**. (a) After 7 days at 25 °C; (b) after 70 days at 25 °C. (Line intensities do not represent concentrations, see ref 6.)

Scheme II. Possible Mechanisms for Rearrangement of Disilenes[a]



[a] Methyls omitted from **5a** and **5b** for clarity.

When a benzene solution of (*Z*)-**33** and (*E*)-**33** was heated in a sealed tube at 70 °C for several days, or allowed to stand at room temperature for 6 weeks, two new signals appeared in the ^{29}Si NMR spectrum at 62.58 and 65.19 ppm. We are confident in assigning these signals to the disilene **12** observed in the cophotolysis of trisilanes **1** and **2**. This result demonstrates the reversibility of aryl migration in disilenes.

Two mechanistic pathways are under consideration to account for the observed rearrangement (Scheme II). The first mechanism (A) involves successive 1,2-aryl migrations wherein the initial shift generates a silylsilylene intermediate (**4**), followed by the shift of a second aryl group back to the incipient silylene. The second

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(4) Disilene **22** was previous observed but ^{29}Si NMR data were not reported. Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150–1153.

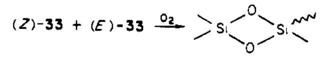
(5) ^{29}Si spectra were recorded on a Bruker AM500 (100.33 MHz) spectrometer. Chemical shifts are reported in parts per million downfield from a tetramethylsilane external reference.

(6) Product ratios were determined from line intensities obtained from standard acquisition NMR experiments. Spectra shown in Figure 1 are power spectra determined by INEPT technique,[7] optimized for mesityl substituents.

(7) For a discussion of polarization transfer NMR spectroscopy for ^{29}Si, see: Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193–218.

(8) The assignment of the more downfield signal to the *Z* isomer is tentative.

(9) Oxidation of the *E*/*Z* mixture of disilene **33** gave the expected mixture of 1,3-dioxetanes:



See: Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826–829.

(B) invokes a dyotropic[10] rearrangement of two aryl groups, that is, a concerted intramolecular migration of these two σ-bonded groups across the silicon–silicon double bond. The transition state might be linear (**5a**) or 1,3-disilabicyclobutane-like (**5b**). The stereochemical demands of these two mechanisms are quite different. The dyotropic mechanism implies stereoselectivity in the **12** to **33** rearrangement in which only a single isomer should be formed. In contrast, free rotation about the Si–Si bond in the silylsilylene should result in the loss of stereoselectivity. The fact that one isomer is formed preferentially is consistent with pathway B. Analysis is, however, complicated by the concurrent cis/trans isomerization of (*Z*)-**33** and (*E*)-**33**.[2a,11] Experiments are in progress to further elucidate the mechanism and generality of this rearrangement.

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(10) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33–65.

(11) Murakami, S.; Collings, S.; Masamune, S. *Tetrahedron Lett.* **1984**, *25*, 2131–2134.

Synthon for the Silicon–Silicon Triple Bond

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The recent surge of interest in multiply bonded silicon compounds has resulted in reports of transient species or stable compounds containing Si=C,[1] Si=Si,[2] Si=N,[3] Si=O,[4] and Si=P[5] double bonds.[6] However, no experimental evidence is yet available for species containing a silicon–silicon triple bond,[7] and theoretical calculations on the parent disilyne suggest that the linear triple bond familiar from carbon chemistry may not exist in the silicon series.[8] In this paper evidence is presented for a thermolysis reaction providing the synthetic equivalent of dimethyldisilyne (MeSi≡SiMe).

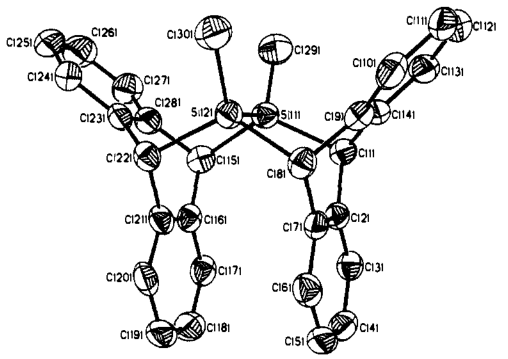
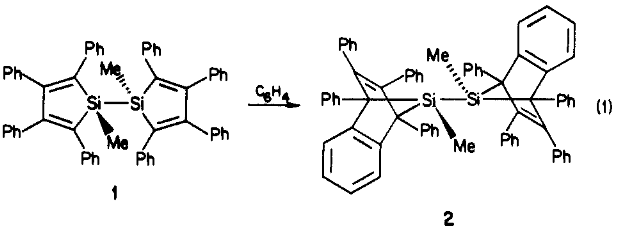


Figure 1. Crystal structure of **4**. Bond lengths (pm); 232.3 [Si(1)–Si(2)], 192.1 [Si(1)–C(1)], 192.5 [Si(1)–C(15)], 185.9 [Si(1)–C(29)], 192.1 [Si(2)–C(8)], 193.0 [Si(2)–C(22)], 186.6 [Si(2)–C(30)]. Torsion angle (deg) of Me–Si–Si–Me, 7.5°.

To synthesize the precursor molecule **2**, bisilole **1**,[9] obtained from 1,2-dimethyltetrachlorodisilane and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, was allowed to react with benzyne by using a modification of the method of Neumann[10,11] (eq 1). A mixture of **2** (1.85 mmol), anthracene (4.17 mmol), and benzene (ca. 1.5 g) was heated in a sealed tube at 350 °C for 2 h, producing 1,2,3,4-tetraphenylnaphthalene (**3**) (1139 mg, 71%), as well as 258 mg (32%) of the formal adduct of dimethyldisilyne **4**: mp >300 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ −0.03 (s, 6 H, SiMe), 3.86 (s, 4 H, Ar CH), 6.58–6.70 (m, 4 H, Ar H), 6.70–6.81 (m, 4 H, Ar H), 6.88–7.06 (m, 8 H, Ar H); ^{13}C NMR (CDCl$_3$) δ −10.5 (q), 43.8 (d), 125.1 (d), 125.8 (d), 126.2 (d), 126.5 (d), 137.4 (s), 141.1 (s); ^{29}Si NMR (CDCl$_3$) 12.5 ppm; high-resolution mass (EI, 30 eV), m/z 442.1597 (calcd for $C_{30}H_{26}Si_2$ 442.1573). Formation of **4** takes place stereospecifically to give exclusively the cis isomer. The crystal structure of **4** is shown in Figure 1.[12]



These results show that **2**, upon thermolysis, serves as a dimethyldisilyne synthon and raise the question of a mechanism for transfer of the (MeSi)$_2$ unit to the anthracene molecules. Because

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(1) (a) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191. (b) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (c) Wiberg, N.; Wagner, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1005. (d) Wiberg, N.; Wagner, G. *J. Organomet. Chem.* **1984**, *271*, 381.

(2) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C)* **1981**, *214*, 1344. (b) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (c) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (d) Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821.

(3) (a) Wiberg, N.; Schurz, K.; Fisher, G. *Angew. Chem.* **1985**, *97*, 1058. (b) Sekiguchi, A.; Ando, W.; Honda, K. *Chem. Lett.*, in press. (c) Zigler, S. S.; West, R.; Michl, J. *Chem. Lett.*, in press.

(4) Arrington, C. A.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 6176. Withnall, R.; Andrews, L. *Ibid.* **1985**, *107*, 2567.

(5) Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011.

(6) For a general review of unsaturated organosilicon compounds, see: Raabe, G.; Michl, J. *Chem. Rev.* **1985**, 85, 419.

(7) Very recently, the existence of a formal Si≡N triple bond has been reported. Bock, H.; Dammel, R. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 111.

(8) (a) Wirsam, B. *Theor. Chim. Acta* **1972**, *25*, 169. (b) Blustin, P. H. *J. Organomet. Chem.* **1976**, *105*, 161. (c) Obara, S.; Kitaura, K.; Morokuma, K. *Theor. Chim. Acta* **1981**, *60*, 227. (d) Kawai, F.; Noro, T.; Murakami, A.; Ohno, K. *Chem. Phys. Lett.* **1982**, *92*, 479. (e) Snyder, L. C.; Wasserman, Z. R.; Moskowitz, J. W. *Int. J. Quantum. Chem.* **1982**, *21*, 565. (f) Lischka, H.; Köhler, H. J. *J. Am. Chem. Soc.* **1983**, *105*, 6646. (g) Binkley, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 603.

(9) The bisilole, bi(1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadien-1-yl), was prepared as a yellow-green solid, mp >300 °C in 33% yield by the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with 1,2-dimethyl-1,1,2,2-tetrachlorodisilane in THF. ^{1}H NMR (CDCl$_3$) δ 0.18 (s, 6 H), 6.59–7.10 (m, 40 H); HRMS (EI, 30 eV), m/z 798.3157 (calcd for $C_{58}H_{46}Si_2$, 798.3138).

(10) Schriewer, M. S.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.

(11) A solution of 5.01 mmol of **1** and 30.1 mmol of *o*-bromofluorobenzene in 1 L of hot THF was added to excess activated magnesium in THF. Upon workup **2** was isolated as a white solid (4.47 g, 94%); the pure compound was obtained by recrystallization from hexane/benzene or acetone/benzene. Of the two possible isomers, only a single product was obtained, to which the anti structure is tentatively assigned. Mp 284–285 °C dec; ^{1}H NMR (CDCl$_3$) δ 0.53 (s, 6 H, SiMe), 6.19–6.34 (m, 10 H, Ar H), 6.65–6.78 (m, 10 H, Ar H), 6.78–7.19 (m, 28 H, Ar H); ^{13}C NMR (CDCl$_3$) δ 1.31, 60.3, 123.1, 124.0, 125.4, 125.8, 127.2, 127.6, 128.3, 131.1, 136.7, 138.3, 148.2, 149.8; ^{29}Si NMR (CDCl$_3$) 58.2 ppm; HRMS (FAB, M$^+$ + 1) 951.3806 (calcd for $C_{70}H_{55}Si_2$, 951.3828).

(12) A crystal of $C_{30}H_{26}Si_2$ (**4**), $M = 442$, 0.15 mm × 0.2 mm × 0.5 mm, was found to be orthorhombic with $a = 10.147$ (4) Å, $b = 17.267$ (7) Å, $c = 26.645$ (11) Å, $U = 4668$ Å^3, space group P_{bca}, $Z = 4$, μ(Mo Kα) = 1.6 cm^{-1}, $D_c = 1.26$ g cm^{-3}. Data were collected on a Nicolet $P_{3/F}$ diffractometer with Mo Kα X-radiation using θ–2θ scans. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically to $R = 0.093$ for 5269 observed reflections ($|F_o| > 3\sigma|F_o|$, $2\theta \leq 54.9°$).

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