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-X α calculations⁹ 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), moiety frozen in the experimental geometry of the parent complex.¹² Besides the Ni(CO)₄ ground state (${}^{1}A_{1}$ symmetry in $C_{3\nu}$), 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 energy¹ 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 ${}^{1}A_{1}$. 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 experiments¹³) 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 ${}^{1}A_{1} \rightarrow {}^{1}E$ 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 approximation¹ this energy range is in almost quantitative agreement with that of the experimental luminiscence spectrum. These limitations of the LCGTO-X α 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_{z²} 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),.16

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²⁹Si 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 ²⁹Si 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 ²⁹Si signal in the disilene

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⁽³⁾ All new compounds were characterized by ¹H NMR, high-resolution, MS, and elemental analysis.

Communications to the Editor



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, Mes₂Si and (2,6xylyl)₂Si, are formed at approximately the same rate.

When a benzene solution of the photolysate from the cophotolysis of 1 and 2 was examined by ²⁹Si 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 ²⁹Si signals at the same frequencies, 63.87 and 63.86 ppm (Scheme I), from the stereoisomers of the disilene (Z)-33 and (E)-33.9However, in contrast with the rearranged material

(5) ²⁹Si 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.

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



Figure 1.⁵ ²⁹Si 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.

derived from disilene 12, the upfield isomer appears to be produced in a slight (4:3) molar excess.

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 ²⁹Si 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

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



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(B) invokes a dyotropic¹⁰ 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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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 com-pounds containing Si=C,¹ Si=Si,² Si=N,³ Si=O,⁴ and Si=P⁵ 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

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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°.

reaction providing the synthetic equivalent of dimethyldisilyne (MeSi≡SiMe).

To synthesize the precursor molecule 2, bisilole 1,9 obtained from 1,2-dimethyltetrachlorodisilane and 1,4-dilithio-1,2,3,4tetraphenylbutadiene, 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; ¹H NMR (200 MHz, CDCl₃) 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 (CDCl₃) 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); ²⁹Si NMR (CDCl₃) 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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⁽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-tetra-chlorodisilane in THF. ¹H NMR (CDCl₃) δ 0.18 (s, 6 H), 6.59–7.10 (m, 40 H); HRMS (EI, 30 eV), m/z 798.3157 (calcd for C₅₈H₄₆Si₂, 798.3138). (10) Schriewer, M. S.; Neumann, W. P. J. Am. Chem. Soc. **1983**, 105, 807 897

⁽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 obtained by recrystallization from hexane/benzene or acctone/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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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; ²⁹Si NMR (CDCl₃) 58.2 ppm; HRMS (FAB, M⁺ + 1) 951.3806 (calcd for C₇₀H₅₅Si₂, 951.3828).

⁽¹²⁾ A crystal of $C_{30}H_{26}Si_2$ (4), $M = 442, 0.15 \text{ mm} \times 0.2 \text{ mm} \times 0.5 \text{ mm}$, was found to be orthorhombic with a = 10.147 (4) Å, b = 17.267 (7) Å, c = 26.645 (11) Å, U = 4668 Å³, space group P_{bca} , Z = 4, μ (Mo K α) = 1.6 cm⁻¹, $D_c = 1.26$ g cm⁻³. Data were collected on a Nicolet P_{3/F} diffractometer of the direct former and the dir with Mo K α X-radiation using θ -2 θ scans. The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically to R = 0.093for 5269 observed reflections $(|F_0| > 3\sigma|F_0|, 2\theta \le 54.9^\circ)$.