Photochemistry of Dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene and the Germanium Analogue. Exclusive Extrusion of the Divalent Species[1]

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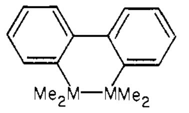
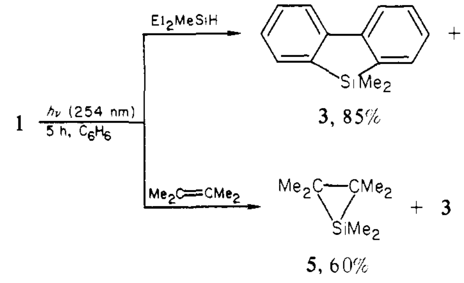
We report herein the photoreaction[2,3] of dibenzo[*c*,*e*]-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene (**1**) as well as the germanium analogue (**2**),[4] which exclusively afford dimethylsilylene and dimethylgermylene, respectively, after the primary metal–metal bond homolysis as proposed earlier.[5]

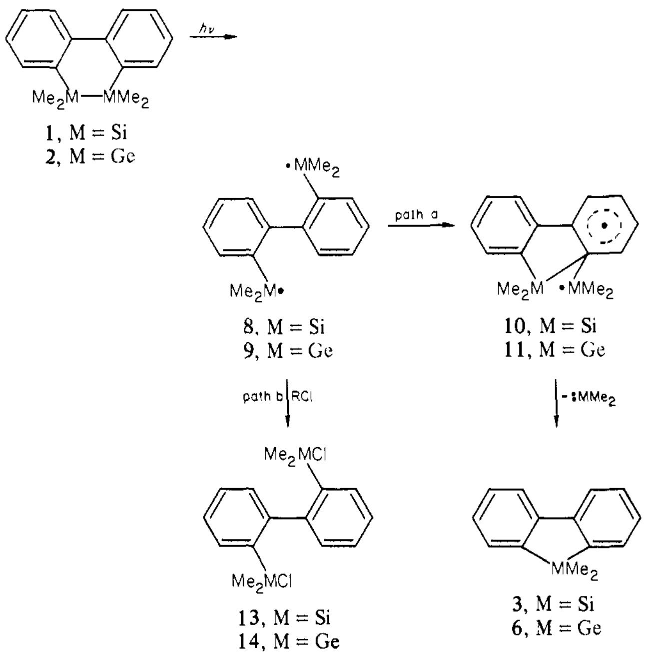


1, M = Si
2, M = Ge

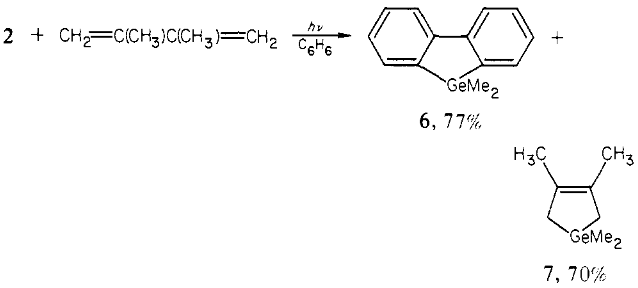
Irradiation of **1** in benzene[6] with a 10-W low-pressure Hg arc lamp under Ar atmosphere gave 9,9-dimethyl-9-silafluorene (**3**) in 85% yield after complete disappearance of **1**. Irradiation of **1** and 10 M excess diethylmethylsilane in benzene for 5 h gave 1,1-diethyl-1,2,2-trimethyldisilane (**4**)[7] in 83% yield together with **3** (85%). On irradiation of a benzene-d_6 solution of **1** and excess 2,3-dimethyl-2-butene, hexamethylsilirane (**5**)[8] was obtained as a major product in 60% yield (determined by ^{1}H NMR). ^{1}H, ^{13}C, and ^{29}Si NMR data of **5** agreed well with those reported.[8]



Scheme I

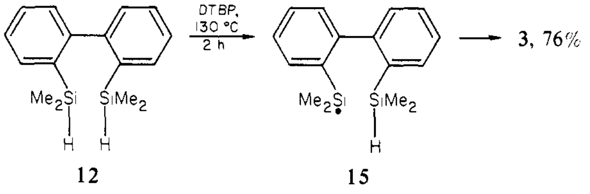


Similarly, irradiation of **2** with a 10-W low-pressure Hg arc lamp in the presence of excess, 2,3-dimethylbuta-1,3-diene in benzene afforded a germafluorene (**6**, 77%)[9] and 1,1,3,4-tetramethyl-1-germacyclopent-3-ene (**7**, 70%)[10] after 50 h. Competitive experiments show that **2** decomposed about 13 times slower than **1**.



The dimethylsilylene extrusion from **1** is best explained by the path a in Scheme I involving intramolecular ipso aromatic silylation.[11,12]

We also found that the intramolecular aromatic ipso substitution occurred preferably in the reaction of 2,2′-bis(dimethylsilyl)biphenyl (**12**) with di-*tert*-butyl peroxide at 130 °C for 2 h to produce **3** in 76% yield.



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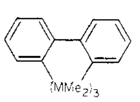

16, M = Si
17, M = Ge

(4) **1** was prepared by the reaction of 2,2′-dilithiobiphenyl with 1,2-difluoro-1,1,2,2-tetramethyldisilane in ether in 55% yield. The main byproducts were **3** (33%) and a dibenzotrisilacycloheptadiene (**16**) (0.3%) Similarly, **2** was obtained in 56% yield together with **6** (31%) and a dibenzotrigermacycloheptatriene (**17**) (1.7%) when 1,2-dichloro-1,1,2,2-tetramethyldigermane is used as a metal dichloride. The photoreaction of **16** and **17** will be reported in a forthcoming paper. **1**: white crystals; mp 61 °C; MS, *m*/*e* 268 (M$^+$, 36), 253 (20), 195 (100); ^{1}H NMR (CCl$_4$) δ 0.23 (s, 12 H), 7.1–7.5 (m, 8 H); ^{13}C NMR (CDCl$_3$) δ –5.40, 126.4, 129.7, 129.8, 133.2, 135.4, 147.3; ^{29}Si NMR (CDCl$_3$) δ –28.17; UV λ_{max} (nm) (ϵ) 239 (28 000), 280 (3100). Anal. Calcd for $C_{16}H_{20}Si_2$: C, 71.64; H, 7.46. Found: C, 71.37; H, 7.61. 2: white crystals; mp 58–60 °C; ^{1}H NMR (CCl$_4$) δ 0.48 (s, 12H), 7.10–7.60 (m, 8 H); ^{13}C NMR (CDCl$_3$) δ –4.96, 126.4, 129.2, 130.4, 132.6, 138.3, 146.9; MS, *m*/*e* 358 (M$^+$, 14), 342 (11), 241 (100); UV λ_{max} (nm) (ϵ) 237 (25 000), 270 (sh, 3800). Anal. Calcd for $C_{16}H_{20}Ge_2$: C, 53.75; H, 5.64. Found: C, 53, 69; H, 5.89.

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(6) The reaction occurs in *n*-hexane equally well.

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(9) **6**: mp 85–87 °C; ^{1}H NMR (CCl$_4$) δ 0.63 (6 H, s), 7.10–7.90 (8 H, m). Anal. Calcd for $C_{14}H_{14}Ge$: C, 65.98; H. 5.54. Found: C, 65.68; H, 5.53.

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

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Table I. Products and Yields of the Photoreaction of **1** and **2** in Various Polychloromethanes[a]

	products from **1**			products from **2**		
solvent	conv, %	**3**, %	**13**, %	conv, %	**6**, %	**14**, %
CCl_4[b]	85	0	86	85	0	80
$CDCl_3$	67	49	32	78	0	66
CH_2Cl_2	57	63	0	27[c]	37	41

[a] Unless otherwise noted, irradiation was carried out for 1 h with a 450-W high-pressure Hg arc lamp filtered by Pyrex glass. The yields were determined by ^{1}H NMR. [b] Hexachloroethane was produced in 60% and 53% yields for the reactions of **1** and **2**, respectively. [c] After irradiation for 8 h.

A similar mechanism may be applied to the photoreaction of **2**. Relatively slow disappearance of **2** is in good accord with the known low reactivity of germyl radicals toward aromatic substitution.[12,13]

Intermediacy of diradicals **8** and **9** in the reaction was supported by the photoreaction in various polychloromethanes in which dichlorination took place competitively with the extrusion of the divalent species to afford 2,2′-bis(chlorodimethylsilyl)biphenyl (**13**) and the germanium analogue (**14**)[14] from **1** and **2**, respectively (path b in Scheme I). The results are summarized in Table I. In carbon tetrachloride, extrusion of the divalent species from **8** and **9** was completely suppressed and the dichlorinated compounds were obtained in high yields. The relative importance of the latter products decreased in the order $CCl_4 > CDCl_3 > CH_2Cl_2$, in accord with the reported relative rates of chlorine abstraction of silyl radicals.[15]

Contrary to the photolysis of dodecamethylsilacyclohexane at 77 K,[16] **1** was not photolyzed at temperatures lower than 200 K. Instead, irradiation of **1** at 77 K in a 3-methylpentane glass matrix with a 500-W xenon lamp afforded a triplet species which was detected by ESR and emission spectra ($D = 0.0988$ and $E = 0.0040$ cm^{-1}, $E_T \simeq 64$ kcal mol^{-1}, $\tau_T < 1$ s). These facts suggest that the intramolecular ipso substitution requires a small but significant activation energy. Since the photoreaction of **1** was neither sensitized by benzophenone triplet ($E_T = 68.6$ kcal mol^{-1})[17] nor quenched by piperylene ($E_T \simeq 59$ kcal mol^{-1}), the excited state responsible for the photoreaction of **1** should be the lowest excited singlet state.

Registry No. 1, 85590-07-4; **2**, 87842-16-8; **3**, 13688-68-1; **4**, 38041-07-5; **5**, 55644-09-2; **6**, 64526-49-4; **7**, 5764-66-9; **12**, 87842-17-9; **13**, 87842-18-0; **14**, 87842-19-1; dimethylmethylsilane, 760-32-7; 2,3-dimethyl-2-butene, 563-79-1; 2,3-dimethylbuta-1,3-diene, 513-81-5; dimethylsilylene, 6376-86-9; dimethylgermylene, 74963-95-4; di-*tert*-butyl peroxide, 110-05-4; 2,2′-dilithiobiphenyl, 16291-32-0; 1,2-difluoro-1,1,2,2-tetramethyldisilane, 661-68-7.

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(12) (a) Sakurai, H.; Nozue, I.; Hosomi, A. *J. Am. Chem. Soc.* **1976**, *98*, 8279; (b) *Chem. Lett.* **1976**, 129. (c) Griller, D.; Dimroth, K.; Fyles, T. M.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 5526.

(13) A referee suggested a possibility that diradicals **10** and **11** might act as silylene and germylene transfer agents. At least in the case of the reaction with olefin, this interesting possibility cannot be excluded at this moment.

(14) **13**: ^{1}H NMR (CCl_4) δ 0.26 (s, 6H), 0.35 (s, 6 H), 7.15–7.95 (m, 8 H); MS, *m/e* 338 (M^+, 1.3), 195 (100), 93 (26); high-resolution mass spectrum, *m/e* 338.0461 (calcd for $C_{16}H_{20}Si_2{}^{35}Cl_2$, 338.0481). **14**: ^{1}H NMR (CCl_4) δ 0.37 (s, 6 H), 0.67 (s, 6 H), 7.15–8.00 (m, 8 H); MS, *m/e* (%) 413 ($M^+ - 15$, 22), 243 (100), 152 (84), 139 (88). Hydrolysis of **13** and **14** afforded the corresponding siloxane and germoxane, respectively, in quantitative yield.

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A Novel Molybdenum–Iron Thiolato Complex: $MoFe_2(\mu\text{-}t\text{-}BuS)_4(CO)_8$

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As part of our continuing interest in developing a novel molybdenum thiolato chemistry based on the versatile Mo(IV) complex $Mo(t\text{-}BuS)_4$,[2] we have studied possible formation of Mo–Fe mixed-metal compounds therefrom. In this communication we wish to report preparation, spectroscopic properties, and molecular structure of the title compound, which possesses a quite unusual coordination environment arund the Mo atom.

A mixture of $Mo(t\text{-}BuS)_4$ (0.4 mmol) and $Fe_2(CO)_9$ (1.2 mmol) dissolved in toluene was heated under a nitrogen atmosphere (65 °C, 24 h) to give a dark brown reaction mixture. Volatile materials being removed in vacuo, the resulting residue was washed with a small amount of hexane. The residue was then redissolved in toluene and the solution was chromatographed on alumina column (toluene eluent) to isolate a solid which after recrystallization from toluene gave dark brown crystals of composition $MoFe_2(t\text{-}BuS)_4(CO)_8$ (**1**), mp 175 °C dec. The yield amounts to 45% based on $Mo(t\text{-}BuS)_4$, the other product identified being only a small amount of the red diiron compound $Fe_2(\mu\text{-}t\text{-}BuS)_2(CO)_6$,[3] mp 75 °C (IR ν(CO) 2065, 2030, 1995, 1987; mass spectrum, *m/e* 458). The reaction employing a lower $Fe_2(CO)_9$:$Mo(t\text{-}BuS)_4$ ratio, e.g., 1:1, gave a similar result but with a lower yield of **1** (<15%).

Formulation of **1** was established by elemental analysis[4] and mass and other spectroscopic data. Thus, the mass spectrum[5] showed the parent ion (*m/e* 790) of fairly strong intensity accompanied by six isotopic bands (*m/e* 784, 786, 787, 788, 789, and 792) reflecting the isotopic distributions of Mo and Fe atoms. The fragmentation occurs loosing successively the eight carbonyl ligands and four *t*-Bu groups resulting in the strongest bands centered at *m/e* 338 and accompanied by 13 weaker peaks, which are readily assigned to a fragment ion $MoFe_2S_4^+$. The IR CO stretching bands occur at 2058, 2040, 1997, 1989, 1980, 1908, and 1864 cm^{-1}. The two low-frequency bands, 1908 and 1864 cm^{-1}, may be ascribed to the two carbonyl ligands attached to the Mo atom on the basis of the bent geometry (vide infra). The ^{1}H NMR spectrum (in toluene-d_8) measured at 27 °C shows two *t*-Bu proton signals at δ 1.31 and 1.38. The two singlet signals coalesce at ~70 °C and become a sharp single signal at higher

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(2) (a) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011–3014. (b) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T. *Ibid.* **1981**, *103*, 3572–3574. (c) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *Ibid.* **1981**, *103*, 5772–5778. (d) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Hoffmann, R. *Organometallics* **1982**, *1*, 227–230. (e) Payne, N. C.; Okura, N.; Otsuka, S. *J. Am. Chem. Soc.* **1983**, *105*, 245–251.

(3) De Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757–767.

(4) Anal. Calcd for $C_{24}H_{36}O_8S_4Fe_2Mo$: C, 36.56; H, 4.60. Found: C, 36.53; H, 4.54.

(5) Recorded on the JEOL OISG-2 mass spectrometer (ionizing potential and current are 75 eV and 200 μA, respectively; sample temperature, 150 °C).