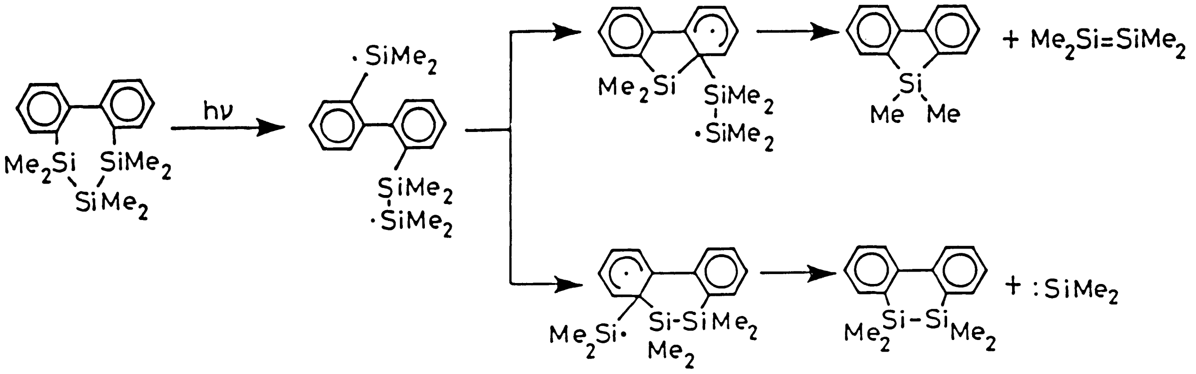
CHEMISTRY LETTERS, pp. 1075-1078, 1987.

Preparation and Photochemistry of Biphenyls Bridged by Si-X-Si Chains[1)]

Hideki SAKURAI,* Kenkichi SAKAMOTO, and Mitsuo KIRA
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

Photolysis of several biphenyls bridged by Si-X-Si chains are described where the X's are O, S, NH, and $Fe(CO)_4$. Dimethylsilathione was successfully generated by this method and the first evidence of reductive elimination from bis(silyl)iron to give disilane was demonstrated.

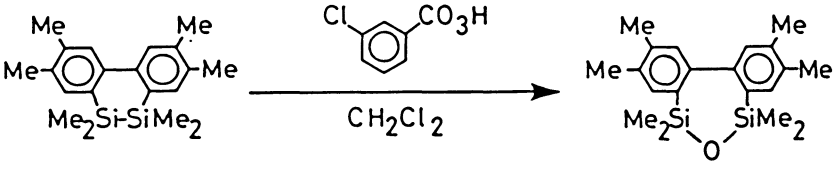
Previously we have reported the facile extrusion of tetramethyldisilene from dibenzotrisilacycloheptadiene under photochemical conditions (Scheme 1).[2)]



Scheme 1.

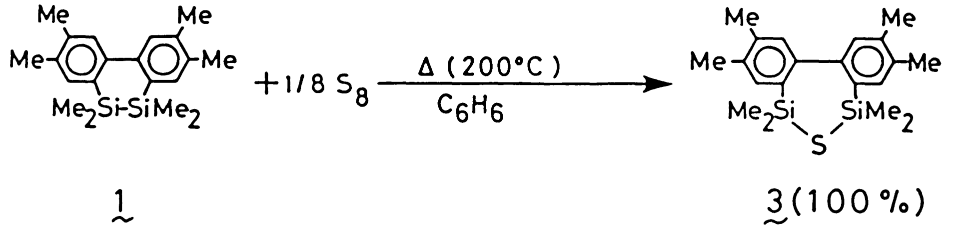
As an extension of the study, we have prepared several biphenyls bridged by Si-X-Si chains and examined the possibility of these compounds as precursors of Si=X double bonded species ($Me_2Si=X$).

Dibenzo-2-oxa-1,3-disilacycloheptadiene (2)[3)] was prepared by oxidation of dibenzodisilacyclohexadiene (1)[4)] with m-chloroperbenzoic acid in quantitative yield.[5)]

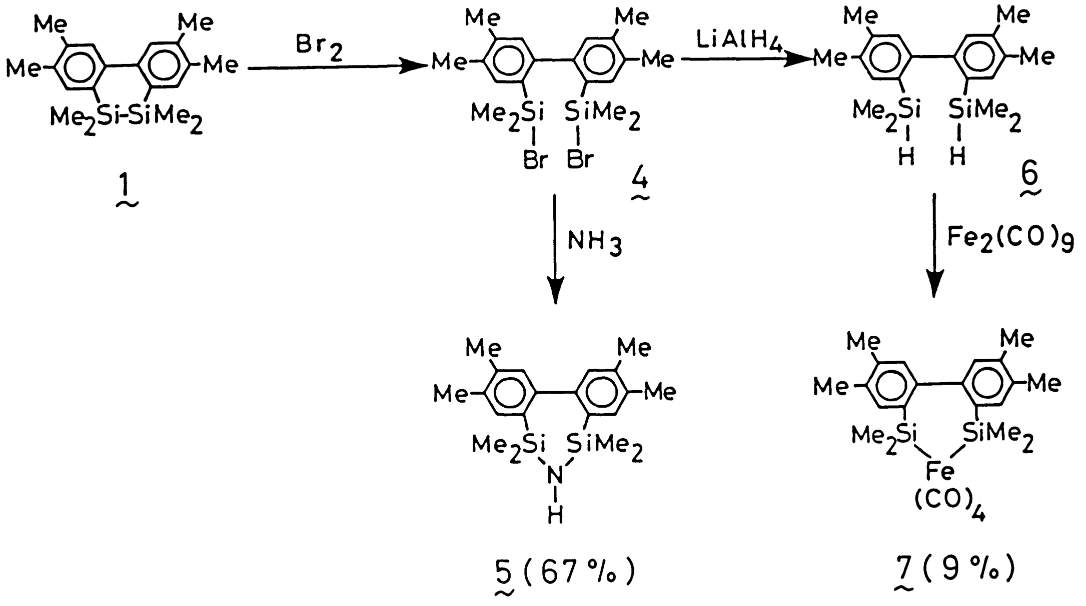


1 2(100%)

Dibenzo-1,3-disila-2-thiacycloheptadiene (3)[6)] was prepared by the reaction of 1 with elemental sulfur in benzene in an ampoule at 200 °C for 24 h in quantitative yield. Similar results of the formation of Si-S-Si species have been reported for the reaction of strained silicon-containing cyclic compounds such as silacyclopropanes,7) silacyclobutanes,8) cyclopentasilanes,9) and cyclotetrasilanes10) and elemental sulfur. 3 was rather sensitive to moisture to give 2 by hydrolysis.



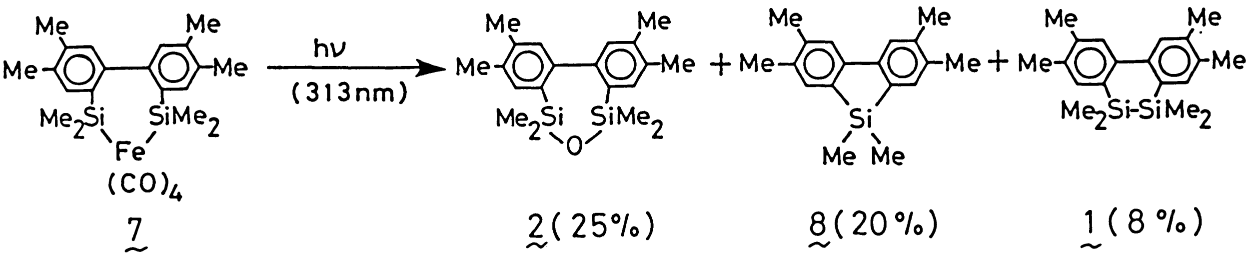
Dibenzo-2-aza-1,3-disilacycloheptadiene (5)11) and dibenzo-2-ferra-1,3-disilacycloheptadiene (7)12a) were prepared from the corresponding bromosilane (4) and hydrosilane (6), respectively as shown in Scheme 2. 5 was also sensitive to moisture to result in the formation of 2 by hydrolysis. The iron complex (7) was air-sensitive and decomposed slowly on exposure to air.12b)



Scheme 2.

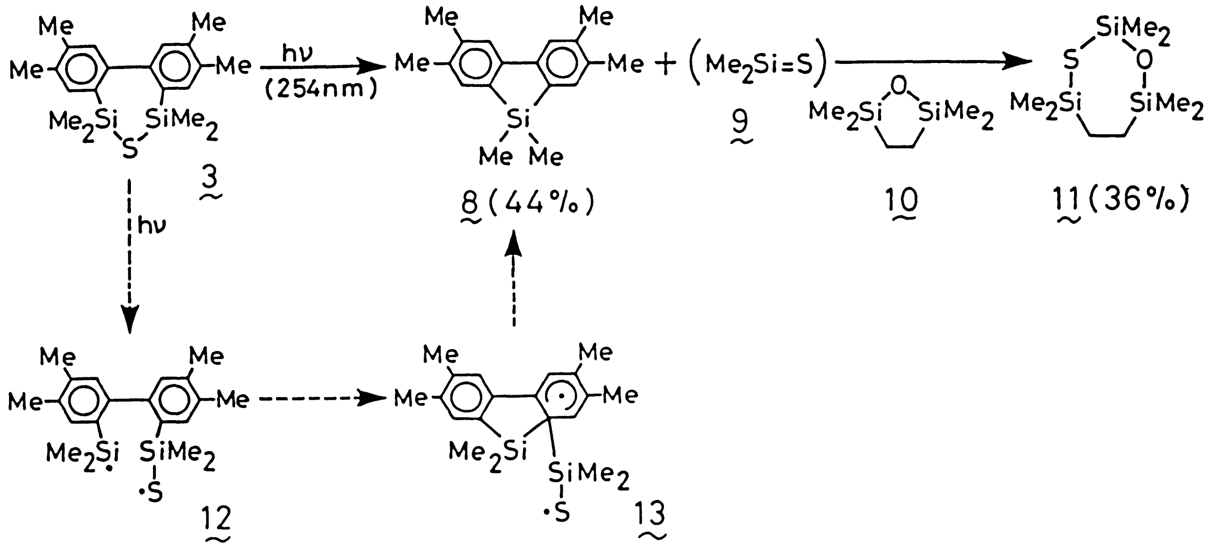
The structures of 3, 5, and 7 were determined on the basis of ^{1}H and ^{13}C NMR, MS, and IR spectra. While 2 has Si-CH$_3$ signals of broad line widths in the ^{1}H NMR spectra, 3, 5, and 7 show two sharp Si-CH$_3$ signals. This can be explained by inhibition of ring inversion in the NMR time scale for the latter biphenyl ring systems.

Irradiation of 2 and 5 with a low-pressure mercury arc lamp (125 W) gave no product at all. Thus 2 and 5 are photochemically inert. However, irradiation of a benzene solution of 7 gave a complex mixture containing 2, silafluorene (8), and 1 in 25, 20, and 8% yield, respectively. It is interesting to note the formation of 1 which suggests that a disilane can be eliminated reductively from a disilyliron complex under photochemical conditions. This is the first clear experimental demonstration of the reductive elimination to form an Si-Si bond from a transition metal complex. The reverse reaction, oxidative addition of an Si-Si bond to an iron carbonyl complex, has been reported previously.13)



On the other hand, irradiation of **3** in benzene with a low-pressure mercury arc lamp (125 W) under argon atmosphere gave **8**. The formation of **8** suggests extrusion of dimethylsilathione (**9**). Accordingly, we have examined trapping the silathione intermediate which has been reported to be trapped effectively with a cyclic siloxane, 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (**10**).14) The irradiation of **1** in the presence of large excess **10** in benzene for 5 h resulted in the formation of the expected 1,1,3,3,5,5-hexamethyl-2-oxa-1,3,5-trisila-4-thiacycloheptane (**11**) in 36% yield together with **8** in 44% yield.

As shown in Scheme 3, the photochemical extrusion of dimethylsilathione from **3** is best explained by intramolecular ipso aromatic silylation of the intermediate biradical (**12**), in an analogous way of the mechanism of disilene extrusion from the trisilane bridged biphenyl, as shown in Scheme 1. The diradical (**12**) is formed by the cleavage of a silicon-sulfur bond on irradiation.



Scheme 3.

No photochemical precursor of silathione has been known except for 1,1,2,2-tetramethyl-1,2-disila-3,6-dithiacyclohexane reported by Weber et al.15) Therefore, **3** is promising as a new photochemical precursor of dimethylsilathione.

The difference in the photochemical behaviors among **2**, **3**, **5**, and **7** may be most simply explained by the difference of respective bond energies. Related works are in progress.

We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes. The work was supported in part by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 61125004).

References

1) Chemistry of Organosilicon Compounds 233.
2) H. Sakurai, K. Sakamoto, and M. Kira, Chem. Lett., 1982, 1379.
3) **2**: white crystals, mp 166 °C; ^{1}H NMR (CCl$_4$, δ) −0.17 (bs, 6H), 0.60 (bs, 6H), 2.44 (s, 12H), 7.17 (bs, 2H), 7.30 (bs, 2H); MS m/e (%) 340 (M$^+$,30), 325 (100), 251 (14), 162 (10); High resolution MS, Found: 340.1680, Calcd for $C_{20}H_{28}Si_2O$: 340.1679.
4) H. Sakurai, K. Sakamoto, and M. Kira, Chem. Lett., submitted.
5) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, J. Am. Chem. Soc., 87, 4001 (1965).
6) **3**: white crystals, mp 173-174 °C; ^{1}H NMR (CCl$_4$, δ) −0.32 (s, 6H), 0.62 (s, 6H), 2.37 (s, 12H), 6.98 (bs, 2H), 7.27 (bs, 2H); MS m/e (%) 356 (M$^+$,25), 343 (12), 342 (23), 341 (65), 325(18), 252 (25), 251 (100); High resolution MS, Found: 356.1453, Calcd for $C_{20}H_{28}Si_2S$: 356.1450.
7) D. Seyferth, D. P. Duncan, and C. K. Haas, J. Organomet. Chem., 164, 305 (1979).
8) J. Dubac and P. C. R. Mazerolles, Acad. Sci. Paris, Ser. C, 276, 411 (1968); Chem. Abstr., 69, 106844 (1968).
9) M. Wojnowska, W. Wojnowski, and R. West, J. Organomet. Chem., 199, C1 (1980).
10) E. Hengge and H. G. Schuster, J. Organomet. Chem., 231, C17 (1982).
11) **5**: white crystals, mp 157 °C; ^{1}H NMR (CCl$_4$, δ) −0.43 (s, 6H), 0.42 (s, 6H), 2.34 (s, 12H), 7.03 (bs, 2H), 7.17 (bs, 2H); MS m/e (%) 339 (M$^+$,18), 324 (100), 256 (19), 162 (23); High resolution MS, Found: 339.1838, Calcd for $C_{20}H_{29}Si_2N$: 339.1839.
12) a) **7**: white crystals, mp 110 °C; ^{1}H NMR (C_6D_6, δ) 0.07 (s, 6H), 0.77 (s, 6H), 2.10 (s, 6H), 2.14 (s, 6H), 6.97 (bs, 2H), 7.37 (bs, 2H); ^{13}C NMR (C_6D_6, δ) 4.9, 8.5, 20.0, 20.1, 131.7, 134.8, 136.2, 137.5, 139.0, 148.7, 207.3, 209.1; ^{29}Si NMR (C_6D_6, δ) 8.8; MS m/e (%) 492 (M$^+$,0.3), 469 (0.9), 436 (1.5), 408 (3.8), 380 (10), 267 (100), 251 (50) ; High resolution MS, Found: 492.0865, Calcd for $C_{24}H_{28}Si_2O_4Fe$: 492.0876; IR (CCl$_4$) ν_{CO} / cm^{-1} 2060, 2000, 1980.
b) **7** was prepared by refluxing a hexane (10 ml) solution of **6** (191 mg, 0.586 mmol) and $Fe_2(CO)_9$ (501 mg, 1.38 mmol) under argon for 7 h. Under the conditions, a large amount of the starting materials was left unreacted. An analytically pure sample was obtained by successive treatment with silica gel TLC and medium-pressure LC. No **1** was detected by TLC, so that thermal reductive elimination of **7** did not occur at least under the conditions.
13) H. Sakurai, T. Kobayashi, and Y. Nakadaira, J. Organomet. Chem., 162, C43 (1978).
14) H. S. D. Soya and W. P. Weber, J. Organomet. Chem., 165, C1 (1979).
15) H. S. D. Soya, I. N. Jung, and W. P. Weber, J. Organomet. Chem., 171, 177 (1979).

(Received February 27, 1987)