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1,1,3,3-TETRAMETHYL-4,5-BIS(TRIMETHYLSILYL)-1,3-DISILACYCLOPENT-4-ENE. PREPARATION BY THE FIRST METHYLENE INSERTION REACTION INTO A SILICON-SILICON BOND AND ANION RADICALS[1)]

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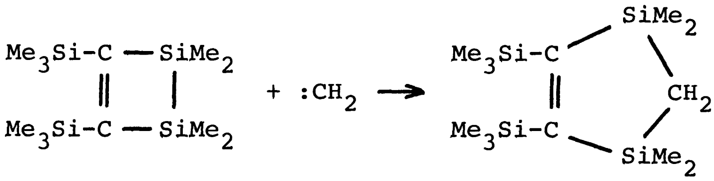
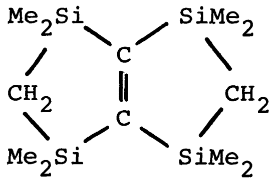
The title compound was prepared by the reaction of 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobutene with photochemically generated methylene. Anion radicals of the title compound showed temperature dependence due to ring flipping.

The silicon-silicon bond of organodisilanes is quite reactive, being subjected to a variety of insertion reactions.$^{2)}$ Divalent units such as -O- (peracid oxidation),$^{3)}$ -$SiMe_2$-,$^{4)}$ and -$Fe(CO)_4$-$^{4)}$ are known to be inserted into a silicon-silicon bond. However, no methylene (carbene) insertion reaction has been reported. For example, reactions of hexamethyldisilane with methylene$^{5)}$ and 1,2,2-trifluoroethylydene$^{6)}$ resulted in the formation of only respective products of CH bond insertion. In this paper, we report the first clear example of the methylene insertion reaction into a silicon-silicon bond.

1,1,2,2-Tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobutene$^{4)}$ was added slowly to an ether solution of diazomethane in a Pyrex tube. Then the mixture was irradiated by means of a 450-W high pressure mercury arc lamp at 0°C for 2 h under argon atmosphere. Fine bubbles of nitrogen evolved vigorously and eventually the solution became colorless. Removal of the solvent followed by column chromatography on silica gel gave 1,1,3,3-tetramethyl-4,5-bis(trimethylsilyl)-1,3-disilacyclobut-4-ene (I) in 30% yield as a colorless crystal.$^{7)}$ The structure of (I) was unequivocally established by both elemental analyses and spectroscopic studies.



(I)

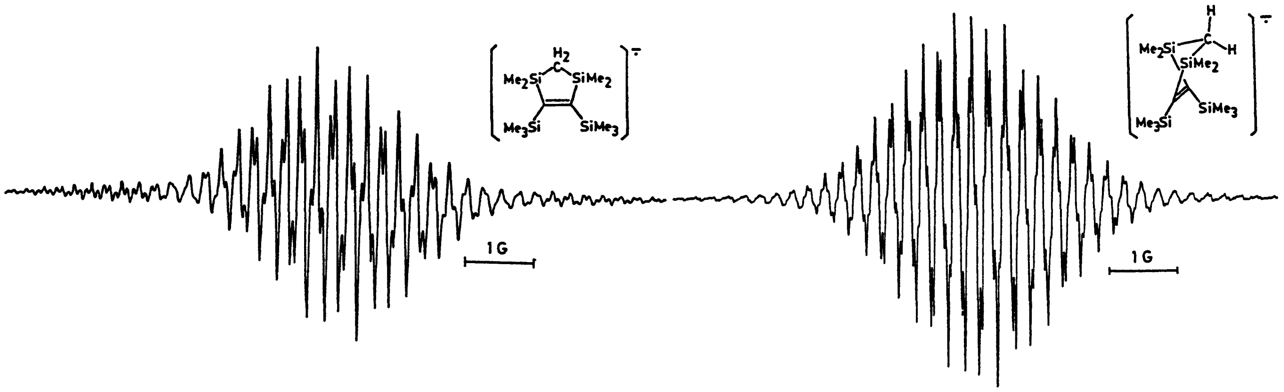


(III)

Recently, we have reported ESR spectra of anion radicals of tetrakis(trimethylsilyl)ethylene (II)$^{8)}$ which show a remarkable temperature dependence due to the nonplanarity of the olefinic bond$^{9)}$ contrary to anion radicals of (III),$^{10)}$ a rigid bicyclic analogue of (II). Therefore, it seemed very interesting to study on anion radicals of (I).

Upon reduction with potassium in dimethoxyethane at 0°C, (I) gave anion radicals which afforded well-resolved ESR spectra shown in Figure 1a. The experimental spectrum is satisfactorily reproduced by computer simulation by using a set of the following hyperfine coupling constants (hfcc in Gauss); 0.255 (18H), 0.444 (12H), and 0.440 (2H). However, the ESR spectra of $(\mathrm{I})^{\overline{\cdot}}$ gave two different hfcc at -80°C for two methylene hydrogens, giving no central line as shown in Figure 1b. The spectrum is also reproduced satisfactorily by computer simulation by a set of the following hfcc; 0.255 (18H), 0.459 (12H), 0.459 (1H), and 0.497 (1H). These results suggest the nonplanarity of the five-membered ring of $(\mathrm{I})^{\overline{\cdot}}$ and existence of the dynamic process; flipping of the methylene bridge. The frequency of this process must be lower than the ESR time scale of 10^{-7}-10^{-8} sec at -80°C.

Figure 1. ESR Spectra.of $(\mathrm{I})^{\overline{\cdot}}$: (a), at 0°C; (b), at -80°C.


(a) at 0°C

(b) at -80°C

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7) (I): mp.67-69°C; ^{1}HNMR ($CDCl_3$) δ -0.46 (2H, s), 0.22 (30H, s) ppm ; ^{13}CNMR ($CDCl_3$) δ -0.9, 2.2, 2.9, 188.9 ppm ; IR (KBr, cm^{-1}) 2945, 2890, 1405, 1245, 980, 840; MS m/e M^+ 300; Anal. Found: C, 51.95; H, 10.62. Calcd. for $C_{13}H_{32}Si_4$: C, 51.92; H, 10.72.

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