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Z-1,2-Bis(t-butyldimethylsilyl)-1,2-bis(trimethylsilyl)ethylene. The Most Crowded Known cis-Olefin[1)]

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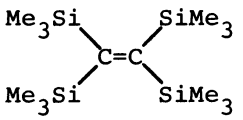
Z-1,2-Bis(t-butyldimethylsilyl)-1,2-bis(trimethylsilyl)ethylene was prepared, the structure being determined by X-ray crystallography. Remarkably, the compound is fixed to cis configuration and a considerable pyramidarization occurs at olefinic carbons with large twisting of the double bond.

Synthesis of crowded olefins has been an intriguing target chemistry because one can anticipate unusual physical and chemical properties due to the molecular distortion for those olefins.[2)] We have reported tetrakis(trimethylsilyl)ethylene (1),[3)] 1,1-bis(t-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (2)[4)] and other tetrasilylethylenes as an interesting new class of overcrowded olefins.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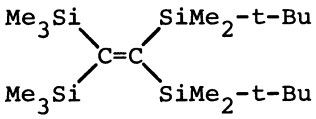
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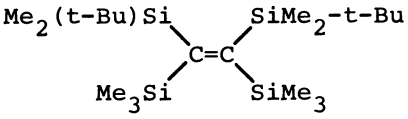
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The molecular structures of those olefins are of interest to see how the molecules relieve their inherent repulsive nonbonded interactions. Widening bond angles, nonplanar distortions of double bond, and/or carbon pyramidarization can be the factors determining the most stable conformations of the molecules. In this context, it is interesting to note that olefinic carbon atoms of both 1 and 2 keep perfect trigonal geometry; namely no pyramidarization occurs. However, the dihedral angles between the two C(sp^2) planes for both 1 and 2 are very large, 29.5° (-70 °C)[3b)] and 49.6° (15 °C),[4)] respectively.

We now report herein preparation and properties of Z-1,2-bis(t-butyldimethylsilyl)-1,2-bis(trimethylsilyl)ethylene (3), an isomer of 2. As we have reported previously, the reaction of Z-1,2-bis(bromodimethylsilyl)-1,2-bis(trimethylsilyl)-ethylene (4) with t-butyllithium resulted in the formation of 2 rather than the expected 3 due to rearrangement during the preparation.

Inspection of molecular models clearly indicates that 3 is much more crowded than 2 so that the preparation of 3 seemed to be a challenging problem. Apparently, introduction of bulky t-butyl groups at the last stage of the preparation is not feasible. Methyl groups should be introduced later. Only one methyl group

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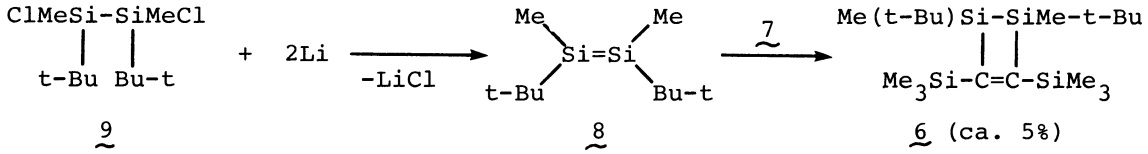
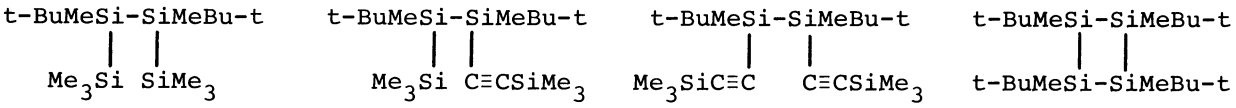
could be introduced, however, when methyllithium was added to Z-1,2-bis(fluoro-t-butylmethylsilyl)-1,2-bis(trimethylsilyl)ethylene (5a). The fluoro groups may be covered by other groups preventing from access of methyllithium. Other methods, especially trimethylsilylmanganization[5] of 1,2-bis(t-butyldimethylsilyl)acetylene also did not work, only a small amount of 1 being obtained.

We planed then to start with Z-1,2-bis(bromo-t-butylmethylsilyl)-1,2-bis(trimethylsilyl)ethylene (5b). We thought that bulky bromo groups could be exposed outside of the molecule and the attack of methyllithium could be possible. The requisite precursor, 1,2-di-t-butyl-1,2-dimethyl-3,4 -bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (6) was prepared by the reaction of bis(trimethylsilyl)acetylene (7) and 1,2-di-t-butyl-1,2-dimethyldisilene (8), generated by reductive dechlorination[6] from 1,2-di-t-butyl-1,2-dichloro-1,2-dimethyldisilane (9).



9 8 6 (ca. 5%)

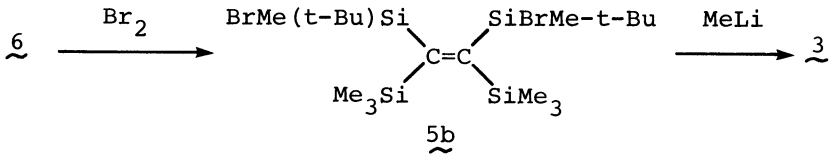
Nagai et al. have reported that 8 can be trapped rather efficiently with 1,2-diphenylacetylene, dimerization of 8 to the corresponding cyclic tetrasilane being negligible.[6] Trapping of 8 with 7 is unprecedented but indeed occurs to give 6 in low yield with many side products as listed below.



10 11 12 13

The optimization of the reaction was then attempted to give the maximum yield of the disilacyclobutene 6 and we found that the ratio of 9:Li:7 = 1:3:20 gave the best result so far. The ratio of the products (6:10:11:12:13) was approximately 1:1:2:1:1. Distillation combined with GLC and HPLC (MeOH, inverse phase) gave analytically pure 6. ^{1}H NMR reveals that 6 is a 3:1 isomeric mixture.[7]

The reaction of 6 with bromine (1.5 mmol) in THF (10 ml) was conducted with a sample of 6 (0.98 g) contaminated by approximately the same amount of 10 which did not interfere the reaction. After 5 min, 2.1 ml of methyllithium in ether (4.5 mmol) was added to the solution. The work-up gave 3 as a mixture with 10. Purification with HPLC followed by recrystallization gave pure 3 (153 mg, estimated yield of 50%). 3 is red crystals of mp 173 °C (in sealed tube) and sublimes at 140 °C. ^{1}H NMR ($CDCl_3$) δ 0.30 (18H, s, $SiMe_3$), 0.38 (12H, s, $SiMe_2$), 0.85 (18H, s, CMe_3); ^{13}C NMR ($CDCl_3$) δ 0.91 ($SiMe_2$), 5.42 ($SiMe_3$), 19.8 ($\underline{C}Me_3$), 27.9 ($C\underline{Me}_3$), 207.9



5b

(C=C); ^{29}Si NMR ($CDCl_3$) δ -9.50, -4.46; UV (hexane) λ_{max} nm (ε) 245 (8600), 425 (558); MS m/e (%) 343 (M^+-57, 0.3), 327 (M^+-73, 0.4), 285 (M^+-115, 4.0), 197 (18), 155 (22), 115 (12), 73 (100); Exact MS Found; 400.2834. Calcd for $C_{20}H_{48}Si_4$; 400.2833.

The molecular structure of 3 was determined by X-ray crystallography.[8] The ORTEP drawing is shown in Fig. 1a with pertinent bond angles and bond lengths. To our surprise, 3 is a cis olefin! Trigonal carbons deviate from planarity. Namely, pyramidarization occurs for both olefinic carbons. Therefore, we can define two twisting angles, 50.2° (C(1)-Si(2), C(1')-Si(2')) and 47.1° (C(1)-Si(1), C(1')-Si(1')). The larger value is exactly the same with that found for 2.

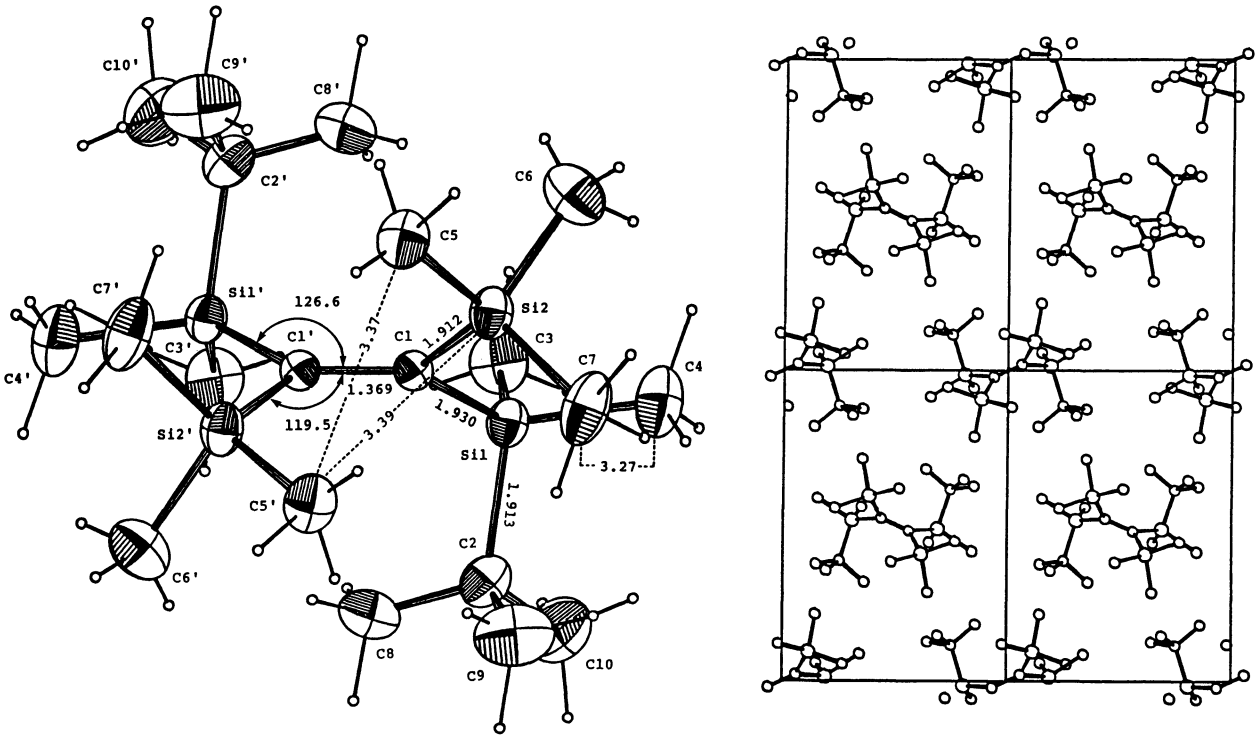


Fig. 1. (a) ORTEP and (b) stereo packing diagrams of 3.

One can find several interesting structural features for 3 besides the large twisting. Similarly to other congested tetrasilylethylenes,[3,4] considerable bond elongation is observed, especially for the C(1)=C(1') (1.369 Å), C(1)-Si(1) (1.930 Å), C(1)-Si(2) (1.912 Å) and C(2)-Si(1) (1.913 Å) bonds. On the other hand, separation between non-bonded C(4) and C(7) is unusually small (3.27 Å). Large widening of the C(1)-C(1')-Si(1') angle (126.6°), presumably due to the overcrowding two t-BuMe_2Si groups, is also noteworthy. Consequently, rather short contacts appear between the vicinal Me_3Si groups; 3.39 Å for between Si(2) and C(5') and 3.37 Å for C(5) and C(5').

Unit cells contain two enantiomers as shown in Fig. 1b. We have tried to isomerize 3 to the trans isomer both thermally and photochemically. Previously, we have described rapid thermal E/Z isomerization for 1,2-bis(dimethylphenylsilyl)-

1,2-bis(trimethylsilyl)ethylene with a very low activation energy (30 kcal/mol),[9] so that we have expected rather rapid E/Z isomerization for 3. However, no E/Z isomerization took place at all! Under forced conditions, only decomposition occurred. Apparently, 3 is too overcrowded to undergo E/Z isomerization. Similar to other tetrasilylethylenes, 3 shows temperature-dependent electronic spectra.

Observations described in this paper raised several interesting questions. For example, how much can olefin tolerate twisting of double bond simply by steric congestion? The loss of overlap between two p orbitals increase very sharply from around 50° according to the $\cos^2\theta$ rule. We have observed the same maximum twisting angle for both 2 and 3 but olefinic carbons of 2 remained perfect trigonal geometry. Apparently, steric crowdness of 3 is larger than that of 2 and other factors than twisting start to play a role to relieve the steric congestion.

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7) 6a: ^{1}H NMR (C_6D_6) δ 0.38 (18H, s, $SiMe_3$), 0.44 (6H, s, SiMe), 1.26 (18H, s, t-Bu); ^{13}C NMR (C_6D_6) δ -2.74 (SiMe), 2.42 ($SiMe_3$), 19.3 ($\underline{C}Me_3$), 29.2 ($C\underline{Me}_3$), 200.8 (C=C). 6b: ^{1}H NMR (C_6D_6) δ 0.37 (18H, s, $SiMe_3$), 0.54 (6H, s, SiMe), 1.18 (18H, s, t-Bu); ^{13}C NMR (C_6D_6) δ -2.28 (SiMe), 2.02 ($SiMe_3$), 18.8 ($\underline{C}Me_3$), 28.9 ($C\underline{Me}_3$), 202.0 (C=C).

8) Crystal Data: $C_{20}H_{48}Si_4$, Fw = 400.94, orthorhombic, space group Fdd2, a = 28.350 (2), b = 20.154 (2), c = 9.393 (1) Å, V = 5366.8 (6) Å^3, Z = 8, ρ_{calcd} = 0.99 g/cm^3. Intensities were measured on a Rigaku automated diffractometer using MoK_α radiation within 2θ = 55° and independent 1400 reflections within $|Fo| \geq 3\sigma|Fo|$ were used in the structure refinement. Some of hydrogen atoms were located and the others calculated. The final R factor was 0.065. The molecular structure has a crystallographic two-fold symmetry around the normal axis of the midpoint of the C(1)=C(1') bond. The atomic coordinates and the other structural data are available from the authors as a supplementary material.

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