Disilene and Silylene Additions to the Double Bonds of Alkenes and 1,3-Dienes: Molecular Structure of a [2 + 2] Cycloaddition Product

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Tetra-*tert*-butyldisilene **3** and di-*tert*-butylsilylene **2**, formed by photolysis of the cyclotrisilane **1**, react with the CC double bonds of alkenes and 1,3-dienes to provide the silirane **4** together with the 1,2-disilacyclobutane **5** and the 2-vinylsiliranes **6** and **7**; the molecular structure of the [2 + 2] cycloaddition product **5**, formed by the reaction of **3** with *ortho*-methylstyrene, was determined by X-ray crystallography.

In spite of the presence of spatially-demanding substituents, which are necessary to shield the Si=Si double bond, the stable or relatively stable disilenes have frequently proved to be more reactive than simple alkenes.[1] For example, they undergo smooth [2 + 2] cycloaddition reactions with the CO and CS double bonds of ketones[2–4] and thioketones[5] as well as with the triple bonds of acetylenes[2,3] and nitriles.[6] Surprisingly, however, the corresponding cycloaddition reactions of disilenes to alkenes have not yet been demonstrated convincingly. Tetramesityldisilene, for instance, does not react with either alkenes or conjugated dienes.[7]

Upon photolysis (Scheme 1), hexa-*tert*-butylcyclotrisilane **1**[8] furnished both di-*tert*-butylsilylene **2** and tetra-*tert*-butyldisilene **3**.[9] In the reaction of **1** with *ortho*-methylstyrene both 1,1-di-*tert*-butyl-2-(2-methylphenyl)silirane (**4**; colourless oil, bp 62–64 °C/0.02 mbar, yield: 44%) and 1,1,2,2-tetra-*tert*-butyl-3-(2-methylphenyl)-1,2-disilacyclobutane (**5**; colourless crystals, mp 119–120 °C, yield: 70%) are formed by [2 + 1] and [2 + 2] cycloadditions of **2** and **3**, respectively, to the olefinic double bond. The constitutions of both products were substantiated by ^{1}H, ^{13}C and ^{29}Si NMR data† and confirmed, in case of **5**, by an X-ray structure analysis.‡

Compound **5** (Fig. 1) contains a non-planar four-membered ring with a folding angle of approximately 39° between the planes formed by the atoms C(1)–Si(1)–Si(2) and Si(2)–C(2)–C(1). The endocyclic Si–Si and Si–C as well as the exocyclic Si–C bond lengths are, in part, markedly longer than the normal values. They thus differ from those of the 1,2-disilacyclobutane[10] formed by a head-to-head linkage of two silene molecules and where the steric overloading is rather reflected in a considerable lengthening of the endocyclic C–C bond.

The photolysis of **1** in the presence of 1,3-dienes (Scheme 2) proceeds differently since the disilene **3** now reacts preferentially to furnish Diels–Alder products and ene adducts[11] together with only small amounts of the [2 + 2] cycloaddition products. In contrast, the silylene **2** does not react to yield the [4 + 1] cycloaddition products but rather gives rise to 2-vinylsiliranes. Thus, it behaves similarly to dimesitylsilylene which also reacts with 1,3-dienes to give 2-vinylsiliranes in addition to other products.[12] The larger spatial requirements of the *tert*-butyl groups in comparison to the mesityl groups, however, do lead to some peculiarities in the products.

Thus, the ^{1}H and ^{13}C NMR spectra of 2-methyl-2-isopropenyl-1,1-di-*tert*-butyl-1-silirane (**6**, colourless oil, bp 42–45 °C/2.5 mbar, yield: 40%) obtained from **2** and 2,3-dimethylbutadiene exhibits pronounced line broadening which is indicative of a restriction of the free rotation about the central C(2)–C(3) bond.§ Various H,H and H,C correlated spectra, in particular the COLOC (correlation spectroscopy for long-range couplings) and the NOESY NMR spectra, clearly demonstrate that **6** possesses a preferred conformation in solution in which the =CH$_2$ group and the di-*tert*-butylsilylene groups are directly adjacent so that **6** can be considered as a precursor for a possible [4 + 1] cycloaddition. On the other hand, 1,1-di-*tert*-butyl-2-isopropenyl-1-silirane (**7**; colourless oil, bp 52 °C/1.5 mbar, yield: 36%), obtained from **2** and 2-methylbutadiene, exhibits fully unrestricted free rotation on the NMR timescale, *i.e.* all ^{13}C NMR and ^{29}Si NMR resonances appear as sharp singlets. In this case, and in contrast to the corresponding addition product from dimesitylsilylene,[12] the addition occurs exclusively at the sterically less hindered –CH=CH$_2$ bond. This is corroborated by the ^{1}H NMR spectra, in which the hydrogen atoms of the three-membered ring appear as an AMX system, and by the DEPT ^{13}C NMR measurements.

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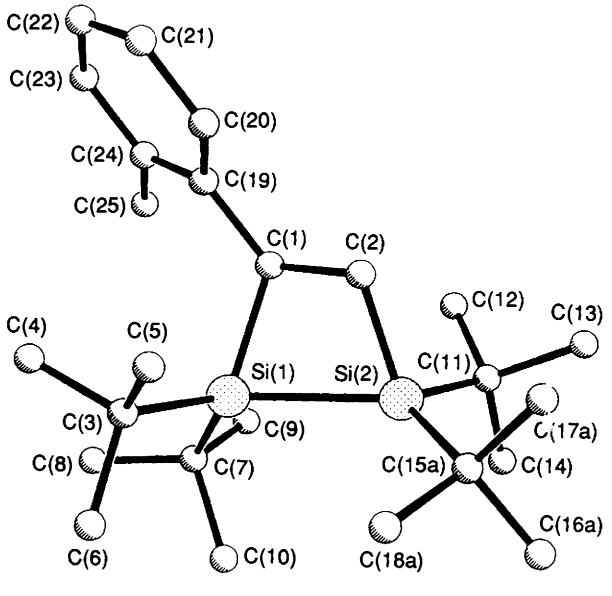
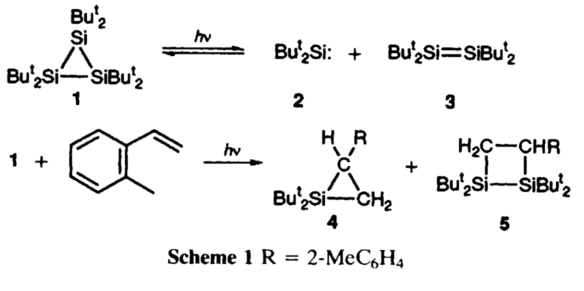
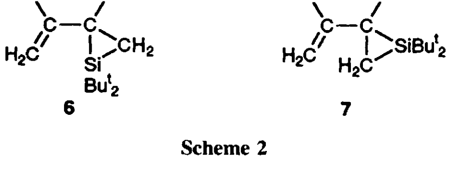


Fig. 1 Molecular structure of **5** (hydrogen atoms omitted). Only one of the two independent molecules is shown. Selected bond distances (pm) and angles (°) as follows: Si(1)–Si(2) 240.2(1), Si(1)–C(1) 196.3(3), Si(2)–C(2) 189.3(3), C(1)–C(2) 156.1(4), C(1)–Si(1)–Si(2) 74.7(1), Si(1)–Si(2)–C(2) 74.8(1), Si(2)–C(2)–C(1) 100.8(2), C(2)–C(1)–Si(2) 96.4(2).



Scheme 1 R = 2-MeC$_6$H$_4$



Scheme 2

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Footnotes

† NMR data were recorded at room temp. in C_6D_6 solution at 300 MHz (^{1}H), 75.4 MHz (^{13}C) and 59.9 MHz (^{29}Si). *Selected spectroscopic data* for **4**: ^{1}H NMR δ 0.80 (s, 9H, Bu^t), 1.06 (s, 9H, Bu^t), 0.85–1.30 (m, 2H, CH_2), 1.89–2.00 (m, 1H, CH), 2.25 (s, 3H, Me), 6.97–7.21 and 7.30–7.39 (m, 4H). ^{29}Si NMR δ −49.97 (s). **5**: ^{1}H NMR δ 1.01, 1.23, 1.24, 1.28 (each s, 9H, Bu^t), 1.38 (dd, 1H, CH_2, $^2J_{H,H}$ 14 Hz, $^3J_{H,H}$ 8 Hz), 1.80 (dd, 1H, CH_2, $^3J_{H,H}$ 14 Hz), 2.22 (s, 3H, Me), 3.03 (dd, br, 1H, CH), 7.00–7.10, 7.19–7.27 and 7.50–7.55 (m, 4H). ^{29}Si NMR δ 20.59 (s), 38.92 (s).

‡ *Crystal data* for **5**: $C_{25}H_{46}Si_2$, $M = 402.8$, crystal size = 0.75 × 0.75 × 0.85 mm, triclinic, space group $P\bar{1}$, $a = 1079.90(10)$, $b = 1584.0(2)$, $c = 1663.5(2)$ pm, $\alpha = 78.75(1)$, $\beta = 77.26(1)$, $\gamma = 72.98(1)°$. $V = 2.6278(5)$ nm^3, $Z = 4$, $D_c = 1.018$ g cm^{-3}, λ (Mo-Kα) 71.073 pm, $T = 296(2)$ K, $2\theta_{max}$ 50°, unique reflections 9223, observed $[I > 2\sigma(I)]$ 9219, variables 475. The structure was solved by direct phase determination using the SHELXL 93 program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically, $R = 0.063$, $wR2 = 0.1576$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Selected spectroscopic data* for **6**: ^{1}H NMR δ 0.55 (d, 1H, ring-CH_2, $^2J_{H,H}$ 12 Hz), 1.09 (s, 9H, Bu^t), *ca.* 1.1 (d, 1H, ring-CH_2), 1.13 (s, 9H, Bu^t), 1.47 (s, 3H, ring Me), 1.85 (dd, 3H, Me, $^4J_{H,H}$ 1.4 Hz, $^4J_{H,H}$ 0.7 Hz), 4.80 (dq, 1H, $=CH_2$, $^2J_{H,H}$ 2.2 Hz, $^4J_{H,H}$ 1.4 Hz), 4.98 (dq, 1H, $=CH_2$, $^2J_{H,H}$ 2.2 Hz). ^{13}C NMR δ 11.44 (CH_2) 19.51 (C_q), 20.41 (C_q), 24.43 (CH_3), 26.64 (ring-CH_3), 30.93 (C_p), 31.75 (C_p), 107.77 ($=CH_2$), 151.77 (C_q). ^{29}Si NMR δ −44.21 (s). **7**: ^{1}H NMR δ 0.83 (t, 1H, ring-CH_2, $^2J_{H,H}$ *ca.* $^3J_{H,H}$ 11 Hz), 0.96 (t, 1H, ring-CH_2), 0.99 (s, 9H, Bu^t), 1.08 (s, 9H Bu^t), 1.55 (t, br, 1H, CH), 1.88 (s, 3H, CH_3), 4.80–4.90 (2 × s, 2H, $=CH_2$). ^{13}C NMR δ 0.85 (CH_2), 18.68 (C_q), 20.46 (C_q), 23.09 (CH), 26.34 (CH_3) 29.89 (C_p), 30.79 (C_p) 105.25 ($C=CH_2$), 145.57 ($C=CH_2$). ^{29}Si NMR δ −48.59 (s). C_p and C_q refer to primary and quaternary carbon atoms respectively.

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