A Bis(alkylidene)silirane (Sila[3]radialene) by the Reaction of Dimesitylsilylene with Tetramethylbutatriene

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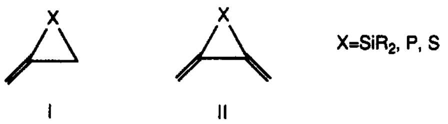
*Summary: The photolysis of 2,2-dimesitylhexamethyltrisilane (**1**) and tetramethylbutatriene (**2**) gave the first bis(alkylidene)silirane (**3**). X-ray analysis showed an almost planar and terminally-closed cisoid diene structure. This allowed cycloaddition of **3** with 4-methyl-1,2,4-triazoline-3,5-dione (**9**) to afford a ring-fused silirane (**10**). Crystal data for **3**: space group $P2/c$, $Z = 2$, $a = 8.511(1)$ Å, $b = 9.966(1)$ Å, $c = 16.429(2)$ Å, $\beta = 123.05(1)°$, $V = 1168.1$ Å^3, $R = 0.044$, $R_w = 0.045$ based on 1564 reflections with $|F_o^2| > 3\sigma|F_o^2|$.*

Three-membered heterocyclic compounds containing an exocyclic π-bond of types I and II are of interest because of the high reactivity which is a result of their strained structure.[1] Such ring systems of phosphorus and sulfur are well studied, but a silicon analogue of type II has not been reported.[2] Previously, we have described the reactions of dimesitylsilylene with allene derivatives to give isolable alkylidenesiliranes (I; X = SiR_2).[1a] As a logical consequence, we have carried out the reaction of dimesitylsilylene with tetramethylbutatriene. The product which was isolated was the first bis(alkylidene)silirane (II; X = SiR_2, sila[3]radialene).

Chart I



A ca. 100-mL cyclohexane solution of 2,2-dimesitylhexamethyltrisilane (**1**) (0.75 mmol) and tetramethylbutatriene (**2**) (ca. 6 molar equiv of 0.5 M solution in cyclohexane), freshly prepared by Zn-promoted dehalogenation of 2,5-dichloro-2,5-dimethyl-3-hexyne, was irradiated with a low pressure mercury lamp (60 W) for 36 h. After complete consumption of **1**, the solution was treated with ca. 5 mL of anhydrous MeOH and stirred for 12 h. The solvent was removed in vacuo, and the residue was separated by preparative HPLC (gel permeation chromatography, $CHCl_3$) and/or TLC (silica gel, hexane) to afford 75 mg of **6** (26% yield) together with trace amounts of **7** and **8**.[3] Without methanolysis, preparative HPLC (gel permeation chromatography, toluene) and subsequent recrystallization from hexane gave **3** in 19% yield, which was fairly stable toward air and moisture. However, the low yield and its hygroscopic instability precluded isolation of **4**. A prolonged photolysis of **3** might produce **8**, probably via the silatrimethylenemethane intermediate (**5**) which then underwent a 1,4-hydrogen shift.[1a] The structure of **3**, a new bis(alkylidene)silirane (sila[3]radialene) system, was confirmed by X-ray structure analysis, as shown in Figure 1.[4] The molecule lies on a crystallographic 2-fold axis bisecting the silirane rings. The 2-fold axis relates the two mesityl rings and two halves of the silirane ring, which are in roughly helical arrangement. The C–Si–C

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[1] Alkylidenesilirane (I, X = Si): (a) Ando, W.; Saso, H. *Tetrahedron Lett.* **1986**, *27*, 5625. (b) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567. (c) Saso, H.; Yoshida, H.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 4747. (d) Saso, H.; Ando, W.; Ueno, K. *Tetrahedron* **1989**, *45*, 1929. (e) Ando, W.; Yamamoto, T.; Saso, H.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2791. Alkylidene- and bis(alkylidene)phosphinidenes (I, II, X = PR): (f) Maerker, A.; Brieden, W. *Chem. Ber.* **1991**, *124*, 933. (g) Toyoda, K.; Yoshimura, H.; Uesugi, T.; Yoshifuji, M. *Tetrahedron Lett.* **1991**, *32*, 6879. Alkylidene- and bis(alkylidene)thiirane (I, II, X = S) (reviews): (h) Ando, W. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MYU: Tokyo, 1988; Vol. 1, p 235. (i) Ando, W.; Tokitoh, N. In *Strain and Its Implication in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series; Kluwer Academic Publishers: London, 1989; p 59 (see also references cited therein).

[2] In the early stage of silirane chemistry, Seyferth proposed that a bis(alkylidene)silirane might form a stable quasiaromatic system by cyclic interaction with a silicon d orbital: Seyferth, D. *J. Organomet. Chem.* **1975**, *100*, 237.

[3] As methanolysis products, $Mes(Me_3Si)Si(Me_2C{=}C{-}CH{=}CMe_2)$ (**6b**) and $Mes(MeO)_2Si(Me_2C{=}C{-}CH{=}CMe_2)$ (**6c**) were also obtained in 11 and 5% yields. Although their spectra were consistent with the proposed structures, the mechanism by which they were formed is not understood. In the allylic coupling of **6**, **6b**, and **6c**, their NOESY spectra showed the cross peaks between olefin protons and one allylic methyl proton, which verified a cis relationship of the trisubstituted olefin. Three other allylic methyl protons showed geminal and cis relationships with the silyl substituents of the tetrasubstituted olefin. The elucidated assignments were described with a cis or trans relationship to an olefin proton (H) or silyl substituents (Si). The NOESY spectra are available in the supplemental material. **3**: colorless crystals, mp 102–103 °C; ^1H NMR (500 MHz, C_6D_6) δ 2.02 (s, 6H), 2.05 (2, 6H), 2.07 (s, 6H), 2.61 (s, 12H), 6.70 (s, 4H); ^{13}C NMR (125 MHz, C_6D_6) δ 21.11 (q), 23.84 (q), 25.38 (q), 27.60 (q), 128.99 (d), 130.49 (s), 130.69 (s), 133.83 (s), 139.25 (s), 144.68 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ −89.74; LR mass m/z 374 (M^+), 359 ($M^+ - Me$). HR mass calcd for $C_{26}H_{34}Si$ 374.2430, found 374.2424. Anal. Calcd for $C_{26}H_{34}Si$: C, 83.37; H, 9.09. Found: C, 83.75; H, 9.16. **6**: colorless oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.32 (d, J = 1.2 Hz, 3H, trans-H), 1.55 (d, J = 1.3 Hz, 3H, cis-H), 1.66 (d, J = 1.1 Hz, 3H, trans-Si), 1.83 (d, J = 1.5 Hz, 3H, cis-Si), 2.23 (s, 6H), 2.27 (s, 12H), 3.35 (s, 3 H), 5.58 (m, 1H), 6.73 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.34 (q), 20.99 (q), 23.52 (q), 23.74 (q), 24.45 (q), 25.28 (q), 50.92 (q), 126.75 (d), 128.98 (d), 132.29 (s), 133.16 (s), 134.24 (s), 138.28 (s), 144.46 (s), 145.55 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ −15.98; IR (NaCl) 1100 cm^{-1} (Si—O—C); LR mass m/z 406 (M^+), 375 ($M^+ - OMe$). HR mass calcd for $C_{27}H_{38}OSi$ 406.2692, found 406.2669. **6b**: colorless oil; ^1H NMR (90 MHz, $CDCl_3$) δ 0.06 (s, 9H), 1.52 (d, J = 1.1 Hz, 3H, trans- or cis-Si), 1.64 (d, J = 1.5 Hz, 3H, trans-H), 1.66 (d, J = 2.3 Hz, 3H, cis-H), 1.77 (d, J = 1.2 Hz, 3H, cis- or trans-Si), 2.23 (s, 3 H), 2.36 (s, 6H), 3.43 (s, 3H), 5.79 (m, 1H), 6.74 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.62 (q), 19.49 (q), 21.00 (q), 22.72 (q), 23.69 (q), 24.08 (q), 25.46 (q), 51.27 (q), 127.50 (d), 128.83 (d), 131.47 (s), 131.63 (s), 132.77 (s), 137.98 (s), 143.78 (s), 145.10 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ −2.47, −19.34; IR (NaCl) ν 1087 cm^{-1} (Si—O—C); LR mass m/z 360 (M^+), 345 ($M^+ - Me$), 287 ($M^+ - SiMe_3$). HR mass calcd for $C_{21}H_{36}Si_2$ 360.2305, found 360.2302. **6c**: colorless oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.42 (d, J = 1.2 Hz, 3H, trans-Si), 1.63 (d, J = 1.3 Hz, 3H, cis-Si) 1.73 (d, J = 1.4 Hz, 3H, cis-H), 1.77 (d, J = 1.8 Hz, 3H, trans-H), 2.24 (s, 3H), 2.44 (s, 6H), 3.46 (s, 6H), 5.70 (m, 1H), 6.78 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.36 (q), 21.08 (q), 23.14 (q), 23.37 (q), 23.76 (q), 25.43 (q), 49.75 (q), 125.94 (d), 128.80 (d), 130.10 (s), 131.91 (s), 139.05 (s), 145.22(s), 147.35 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ −27.50; IR (NaCl) ν 1077 cm^{-1} (Si—O—C); LR mass 318 (M^+). HR mass calcd for $C_{19}H_{30}O_2Si$ 318.2015, found 318.2014. **7**: colorless oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.21 (s, 6H), 1.67 (d, J = 2.8 Hz, 6H), 2.23 (s, 6H), 2.30 (s, 12H), 3.37 (s, 3H), 5.24 (m, J = 2.8 Hz, 1H), 6.74 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.79 (q), 20.92 (q), 24.17 (q), 25.95 (q), 30.72 (s), 51.46 (q), 96.94 (s), 99.41 (d), 129.09 (d), 132.56 (s), 138.33 (s), 144.11 (s), 200.34 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ 1.43; IR (NaCl) ν 2172 (C=C=C), 1094 cm^{-1} (Si—O—C); LR mass m/z 406 (M^+), 375 ($M^+ - OMe$), 298 ($M^+ - Me_2CH{=}C{=}CMe_2$). **8**: colorless oil; ^1H NMR (90 MHz, $CDCl_3$) δ 1.28 (s, 6H), 1.88 (br, 3H), 2.24 (s, 6H), 2.36 (s, 12H), 4.88 (m, 1H), 4.97 (m, 1H), 5.62 (s, 1H), 6.67 (4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.56 (q), 21.10 (q), 22.69 (q), 23.02 (s), 92.43 (s), 98.29 (s), 112.94 (t), 128.56 (d), 130.10 (s), 138.69 (s), 142.73 (s), 144.65 (s), 210.16 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ −41.30; IR (NaCl) ν 2150 (SiH), 1939 cm^{-1} (C=C=C); LR mass m/z 374 (M^+), 359 ($M^+ - Me$). HR mass calcd for $C_{26}H_{34}Si$ 374.2430, found 374.2399.

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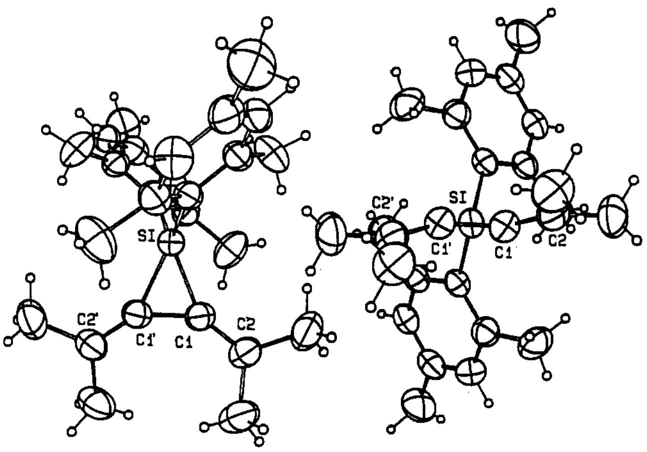
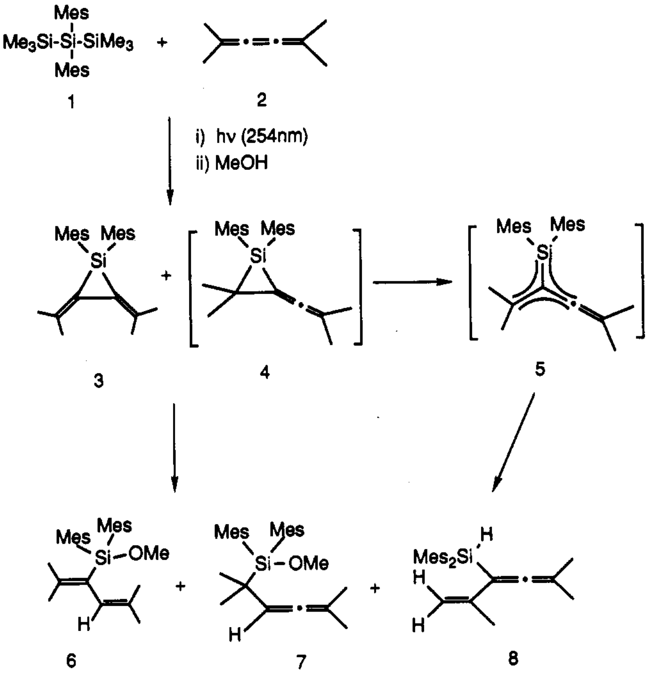


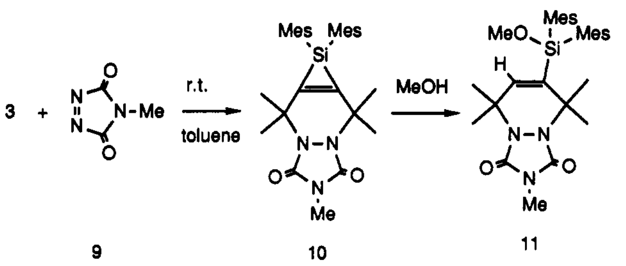
Figure 1. ORTEP drawing of **3**. The projections are parallel (left) and perpendicular (right) to the 2-fold axis. Selected bond lengths (Å) and angles (deg) are as follows: Si–C(1) 1.843(3), C(1)–C(2) 1.333(4), C(1)–C(1′) 1.446(2); C(1)–Si–C(1′) 46.9(2), Si–C(1)–C(1′) 66.6(3), Si–C(1)–C(2) 146.7(3), C(1′)–C(1)–C(2) 140.4(2).

Scheme I



bond angle (46.9(2)°) and C–C bond length (1.466(2) Å) of the C_2Si triangle are in the range reported for siliranes (1.52–1.643 Å, 49.2–52.1°),[5a,c–e] alkylidenesiliranes (1.516 Å, 48.4°),[1d] and silirene (1.34 Å, 43.5°).[5b] Furthermore the C(1′)–C(1)–C(2) angles (140.4(2)°) are smaller than that of a bis(alkylidene)thiirane (II, X = S) (149.7–159.6°)[6b] and bis(alkylidene)cyclopropane (II, X = CH_2) (150°). These indicate that the termini of the bis(alkylidene) moiety are close enough to act as a diene functionality, as in bis(alkylidene)thiirane *S*-oxide (II, X = SO).[6d,e] The [2 + 4] cycloaddition chemistry of **3** has been investigated in a preliminary manner. Addition of reddish 4-methyl-1,2,4-triazoline-3,5-dione (TAD, **9**) (0.15 mmol) to a 3-mL solution of **3** (0.15 mmol) in toluene resulted in rapid decolorization of the solution. Crystallization from benzene/hexane (1:1) provided the cycloadduct **10** in 39% yield as a moderately air and moisture sensitive compound. Evidence for the structure of **10** was provided by methanolysis which gave products **11**.[7] X-ray crystallography has confirmed the atom connectivity shown in **11**. However, a final good-quality structure is not yet in hand. Thus, the cycloaddition chemistry of **3** might lead to a variety of novel ring-fused siliranes.

Scheme II



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Supplementary Material Available: Text describing crystallographic procedures, tables of crystallographic data, atomic coordinates and thermal parameters, and bond lengths and angles for **3**, a figure showing the ORTEP structure, and figures showing NOESY spectra of **6**, **6b**, and **6c** (18 pages). Ordering information is given on any current masthead page.

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(4) Crystal data for **3**: $C_{26}H_{34}Si$, M = 374.65, monoclinic with a = 8.511(1) Å, b = 9.966(1) Å, c = 16.429(2) Å, β = 123.05(1)°, V = 1168.1 Å^3, space group $P2/c$, Z = 2, μ = 1.0 cm^{-1}, ρ = 1.07 g/cm^3. The 1564 independent reflections [$2\theta < 50°$, $|F_o^2| > 3\sigma|F_o^2|$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and the ω–2θ scan. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined with fixed thermal parameters to R = 0.044 (R_w = 0.045).

(5) Siliranes and silirenes characterized by X-ray crystal analysis: (a) Delker, G. L.; Wang, Yu.; Stucky, G. D.; Lambert, R. L., Jr.; Haas, C. K.; Seyferth, D. *J. Am. Chem. Soc.* **1976**, *98*, 1779. (b) Hirotsu, K.; Higuchi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726. (c) Ishikawa, M.; Matsuzawa, S.; Sugiyama, H.; Yano, F.; Kamitori, S.; Higuchi, T. *J. Am. Chem. Soc.* **1985**, *107*, 7706. (d) Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310. (e) Pae, D.-H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

(6) Bis(alkylidene)cyclopropane (II, X = CH_2) and -thiirane (II, X = S) do not react with dienophiles, while bis(alkylidene)thiirane *S*-oxide (II, X = SO) does: (a) Pasto, D. J.; Smorada, R. L.; Turimi, B. L.; Wamphler, D. J. *J. Org. Chem.* **1976**, *41*, 432. (b) Köbrich, G.; Heinemann, H.; Zundorf, W. *Tetrahedron* **1967**, *23*, 565. (c) Ando, W.; Hanyu, Y.; Kumamoto, Y.; Takata, T. *Tetrahedron* **1986**, *42*, 1989. (d) Ando, W.; Hanyu, Y.; Takata, T.; Ueno, K. *J. Am. Chem. Soc.* **1982**, *104*, 4981. (e) Ando, W.; Hanyu, Y.; Takata, T.; Sakurai, T.; Kobayashi, K. *Tetrahedron Lett.* **1984**, *25*, 1483. (f) Ando, W.; Hanyu, Y.; Takata, T.; Ueno, K. *J. Am. Chem. Soc.* **1984**, *106*, 2216.

(7) **10**: colorless crystals; mp 202–204 °C; ^1H NMR (90 MHz, C_6D_6) δ 1.72 (s, 12H), 2.06 (s, 6H), 2.46 (s, 12H), 2.75 (s, 3H), 6.66 (s, 4H); ^{13}C NMR (22.5 MHz, C_6D_6) δ 21.09 (q), 24.04 (q), 24.41 (q), 24.97 (q), 63.00 (s), 129.89 (d), 129.11 (s), 139.75 (s), 143.34 (s), 154.42 (s), 158.47 (s); ^{29}Si NMR (18 MHz, C_6D_6) δ -98.80; IR ν 1756, 1698 cm^{-1} (C=O); LR mass m/z 487 (M^+), 472 (M^+ - Me); HR mass calcd for $C_{29}H_{37}N_3Si$ 487.2655, found 487.2643. **11**: colorless crystals; mp 145–147 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 1.45 (s, 6H), 1.59 (s, 6H), 2.26 (s, 6H), 2.29 (s, 12H), 3.00 (s, 3H), 3.42 (s, 3H), 5.56 (s, 1H), 6.81 (s, 4H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 20.99 (q), 24.12 (q), 24.68 (q), 24.75 (q), 25.27 (q), 51.19 (q), 58.02 (s), 63.15 (s), 129.77 (d), 131.06 (s), 139.24 (s), 139.48 (s), 143.12 (d), 144.66 (s), 153.96 (s), 154.10 (s); ^{29}Si NMR (18 MHz, $CDCl_3$) δ -10.43; IR (NaCl) ν 1767, 1711 cm^{-1} (C=O); LR mass m/z 519 (M^+), 504 (M^+ - Me); HR mass calcd for $C_{30}H_{41}O_3N_3Si$ 519.2917, found 519.2882.