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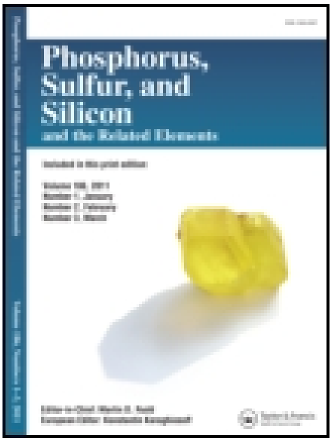

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Spiro[2,5-dibenzo-1,4-disilacyclohexa-2,5-diene-1,7′-2′,5′-dibenzo-1′,4′,7′-trisilanorbornadiene]: Unusual Dimerization of Silyl-Substituted 9,10-Disila(Dewar Anthracene)

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SPIRO[2,5-DIBENZO-1,4-DISILACYCLOHEXA-2,5-DIENE-1,7′-2′,5′- DIBENZO-1′,4′,7′-TRISILANORBORNADIENE]: UNUSUAL DIMERIZATION OF SILYL-SUBSTITUTED 9,10-DISILA(DEWAR ANTHRACENE)

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The reduction of 9,10-dibromo-9,10-dihydro-9,10-disilaanthracene (3) with 2.2 equiv. of KC_8 in THF afforded the unexpected spiro[2,5-dibenzo-1,4-disilacyclohexa-2,5-diene-1,7′-2′,5′-dibenzo-1′,4′,7′-trisilanorbornadiene] (4) through the dimerization of the transient 9,10-disila-9,10-Dewar anthracene (5). The formation of 5 was demonstrated by low-temperature NMR spectroscopy.

Keywords Dewar anthracene; disilaanthracene; silicon; spiro compound; X-ray crystallography

INTRODUCTION

Photochemical reactions of aromatic compounds are well known for forming interesting valence isomers.[1] The photolysis of anthracenes is known to result in the formation of the 9,10-Dewar anthracenes or the corresponding [4 + 4] dimers.[2] Although a number of [4 + 4] dimers of anthracene derivatives have been structurally characterized,[3] the crystal structures of 9,10-Dewar anthracenes are little known because of their thermal instability. The only known example of an X-ray crystallographic analysis of 9-*tert*-butyl-9,10-Dewar anthracene was reported by Angermund et al.[4] On the other hand, there has been much interest in the chemistry of silaaromatic compounds in recent decades.[5] Recently, Shinohara et al. succeeded in the synthesis and characterization of a stable 9-silaanthracene using a bulky substituent.[6] They also carried out the photolysis of this 9-silaanthracene to form the corresponding Dewar-type isomer, 9,10-Dewar 9-silaanthracene; however, it could not be isolated because of its thermal instability.[7]

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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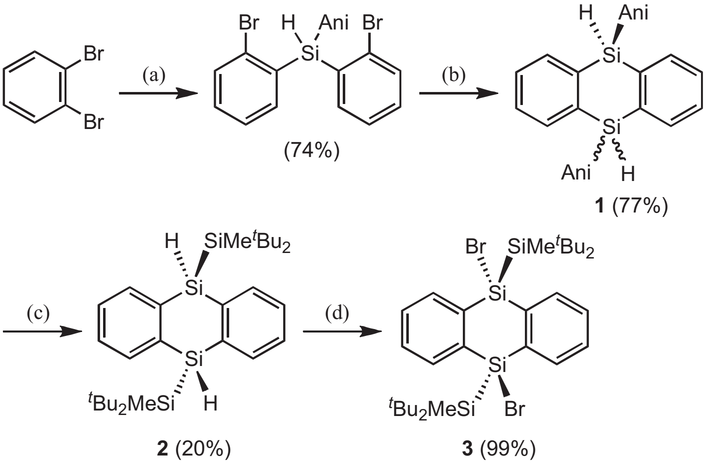
Meanwhile, we reported a simple new synthetic method for a silyl-substituted 1,4-disila(Dewar benzene) derivative together with its unique photochemical reaction[8] and reduction with lithium metal to give the 1,4-disilacyclohexa-2,5-diene-1,4-diide, representing a nonaromatic 8π-electron cyclic system.[9] We have now extended our chemistry to the 9,10-disilaanthracene system, and we have found an unexpected product resulting from 9,10-disila-9,10-Dewar anthracene. In this article, we report the spectroscopic observation of 9,10-disila-9,10-Dewar anthracene generated by the reduction of 9,10-bis(di-*tert*-butylmethylsilyl)-9,10-dibromo-9,10-dihydro-9,10-disilaanthracene (**3**) with KC_8 at low temperature and its unusual dimerization to give a spiro compound, spiro[2,5-dibenzo-1,4-disilacyclohexa-2,5-diene-1,7′-2′,5′-dibenzo-1′,4′,7′-trisilanorbornadiene] (**4**).

RESULTS AND DISCUSSION

At first, 9,10-dihydro-9,10-disilaanthracene derivative **1** bearing two anisyl groups (Ani = 4-methoxyphenyl) was prepared by modification of the literature method[10] as a 4:3 mixture of *syn* and *anti* isomers (Scheme 1). Dearylation/triflation of **1** with CF_3SO_3H at −78°C followed by reaction with ^{t}Bu$_2$MeSiNa at room temperature gave the silyl-substituted 9,10-dihydro-9,10-disilaanthracene derivative **2** in 20% yield. Finally, careful bromination of **2** with Br_2 resulted in the quantitative formation of the corresponding dibromide **3**, which is a suitable precursor for a 9,10-disila-Dewar anthracene derivative.



(a) 1) ^{n}BuLi, THF, Et_2O, -110 °C; 2) $AniSiHCl_2$, THF.

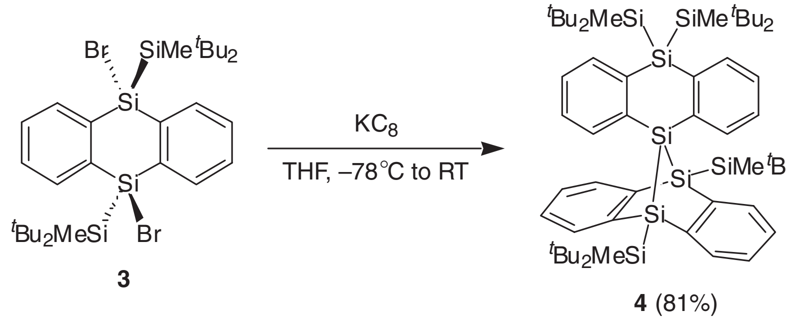
(b) 1) ^{n}BuLi, THF, -78 °C; 2) $AniSiHCl_2$, THF.

(c) 1) CF_3SO_3H, toluene, -78 °C; 2) ^{t}Bu$_2$MeSiNa, THF, RT.

(d) Br_2, CH_2Cl_2, 0 °C.

Scheme 1

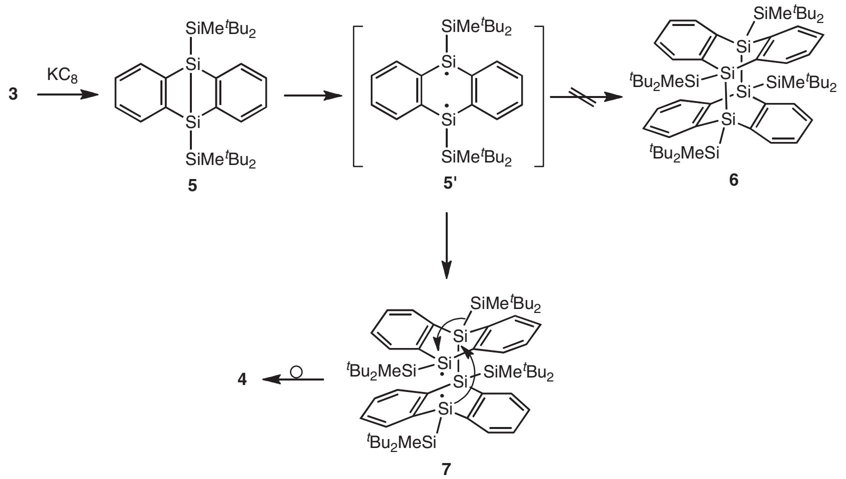
The reduction of **3** with KC_8 (2.2 equiv) in THF at −78°C gradually afforded a red-brown reaction mixture due to the formation of 9,10-disila-9,10-Dewar anthracene **5**. However, compound **5** was unstable at room temperature, and it formed an unexpected spiro compound, 1′,4,4,4′-tetrakis(di-*tert*-butylmethylsilyl)spiro[2,5-dibenzo-1,4-disilacyclohexa-2,5-diene-1,7′-2′,5′-dibenzo-1′,4′,7′-trisilanorbornadiene] (**4**), which was obtained in 81% yield as colorless crystals (Scheme 2). The structure of **4** was unambiguously determined by NMR spectral data and X-ray crystallographic analysis (Figure 1). The crystal structure of **4** showed that the 9,10-dihydro-9,10-disilaanthracene framework containing Si3 and Si4 atoms adopts a somewhat twisted structure, probably because of the steric influence of the bulky ^{t}Bu$_2$MeSi groups. This is reflected in the chemical shifts of the ^{29}Si nuclei of the ring atoms. Thus, the ^{29}Si NMR spectrum showed five signals at −44.0, −30.1, 9.6, 10.4, and 25.0 ppm, of which the signal at highest field (−44.0 ppm) can be assigned to the spiro silicon atom (Si3). The most deshielded signal at 25.0 ppm can be assigned to the Si4 atom, the geometry around which is distorted, as shown by the stretched bond lengths of Si4–Si7 (2.4597(11) Å) and Si4–Si8 (2.4733(12) Å), as well as by the increased bond angle of Si7–Si4–Si8 (124.25(4)°). The ^{29}Si signal due to the Si1 and Si2 atoms was observed at −30.1 ppm, and the signals due to the ^{t}Bu$_2$MeSi substituents were found at 9.6 and 10.4 ppm.



Scheme 2

Although the mechanism to form **4** is not clear at present, one might be able to postulate the intermediacy of an extremely reactive biradical species **5′**, which is generated by the cleavage of the strained central Si–Si bond in Dewar derivative **5** (Scheme 3), as found in the 1,4-disila-Dewar benzene derivative.[8] Thus, the formation of **4** can be explained by dimerization of **5′** through stepwise Si–Si bond formation to give a biradical intermediate **7** and the subsequent migration of a ^{t}Bu$_2$MeSi group. In contrast, no dimerization of **5′** to give **6** occurred, probably because of the steric repulsion between the bulky ^{t}Bu$_2$MeSi groups.

Next, we spectroscopically observed Dewar-type species **5** by a low-temperature NMR measurement. When the reduction of **3** with 2.2 equiv of KC_8 was performed in THF-d_8 at −30°C, the reaction was completed within 10 h, and the generation of **5** was confirmed by NMR spectra at 243 K. Thus, the ^{1}H NMR resonances of **5** were observed at 0.38, 1.21, 7.09, and 7.43 ppm. The ^{29}Si NMR spectrum of **5** showed two signals at −14.9 and 11.4 ppm, which are assignable to the ring silicon atom and ^{t}Bu$_2$MeSi groups, respectively. This assignment was reasonably supported by comparison with the observed



Scheme 3

chemical shifts of silyl-substituted 1,4-disila(Dewar benzene) (−26.3 for skeletal Si and 11.0 ppm for $^t\mathrm{Bu}_2\mathrm{MeSi}$).[8] Compound **5** is thermally unstable, similar to 9,10-Dewar-9-silaanthracene.[7] Thus, the signals of the dimeric product **4** appeared upon warming to room temperature with concomitant disappearance of the NMR signals due to **5**.

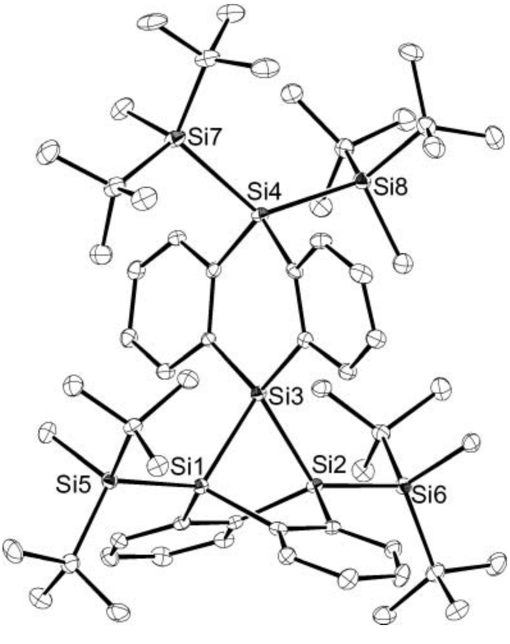


Figure 1 ORTEP drawing of **4** (30% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1–Si3 = 2.4377(12), Si1–Si5 = 2.4000(12), Si2–Si3 = 2.4178(11), Si2–Si6 = 2.3966(12), Si4–Si7 = 2.4597(11), Si4–Si8 = 2.4733(12), Si5–Si1–Si3 = 126.13(4), Si6–Si2–Si3 = 129.02(5), Si1–Si3–Si2 = 77.93(4), Si7–Si4–Si8 = 124.25(4).

EXPERIMENTAL

All experiments were performed using high-vacuum line techniques or in an argon atmosphere using an MBRAUN MB 150B-G glove box. All solvents were dried and degassed over a potassium mirror in vacuum prior to use. NMR spectra were recorded with Bruker AC-300FT NMR (^{1}H NMR at 300.1 MHz, ^{13}C NMR at 75.5 MHz, ^{29}Si NMR at 59.6 MHz) and AV-400FT NMR (^{1}H NMR at 400 MHz, ^{13}C NMR at 100.6 MHz, ^{29}Si NMR at 79.5 MHz) spectrometers. High-resolution mass spectra were measured with Bruker Daltonics micrOTOF-TU mass spectrometer with APCI (atmospheric pressure chemical ionization method). ^{t}Bu$_2$MeSiNa was prepared according to the reported method.[11]

9,10-Bis(4-methoxyphenyl)-9,10-dihydro-9,10-disilaanthracene (1)

1.57 M ^{n}BuLi solution in hexane (24.0 mL, 37.7 mmol) was added to a solution of bis(2-bromophenyl)-4′-methoxyphenylsilane (7.88 g, 17.6 mmol) in THF (120 mL) at −78°C under an argon atmosphere. After being stirred for an additional 1 h, a solution of 4-methoxyphenyldichlorosilane (7.33 g, 35.4 mmol) in THF (6 mL) was added dropwise to the mixture. Then the reaction mixture was allowed to warm to room temperature, was refluxed for 4 h and quenched with water. The mixture was diluted with Et$_2$O, and the organic layer was washed with brine and dried over Na$_2$SO$_4$. After the solvent was evaporated, the crude product was purified by column chromatography on SiO$_2$ (hexane:Et$_2$O = 1:1) to give 9,10-dihydro-9,10-disilaanthracene **1** as a mixture of *syn* and *anti* isomers (5.75 g, 77%, 3:4 mixture as estimated by ^{1}H NMR). Mp 145–146°C; ^{1}H NMR (C$_6$D$_6$): $\delta = 3.22$ (s, 3H, OMe), 3.25 (s, 3H, OMe), 5.74 (s, 1H, SiH), 5.76 (s, 1H, SiH), 6.70–6.78 (m, 4H, arom-H), 7.15 (brs, 4H, arom-H), 7.46–7.54 (m, 4H, arom-H), 7.70 (brs, 4H); ^{13}C NMR (C$_6$D$_6$): $\delta = 54.5$, 114.4, 114.5, 129.2, 136.1, 137.8, 138.0, 141.7, 161.8; ^{29}Si NMR (C$_6$D$_6$): $\delta = -29.9$, −30.7; Anal. Calcd for C$_{26}$H$_{24}$Si$_2$O$_2$: C, 73.54; H, 5.70. Found: C, 73.70; H, 6.10.

9,10-Bis(di-*tert*-butylmethylsilyl)-9,10-dihydro-9,10-disilaanthracene (2)

CF$_3$SO$_3$H (1.2 g, 8.0 mmol) was added to a solution of **1** (1.70 g, 4.0 mmol) in toluene (75 mL) at −78°C under an argon atmosphere and stirred for 5 h. Then the reaction mixture was allowed to warm to room temperature, and a solution of ^{t}Bu$_2$MeSiNa (1.6 g, 8.8 mmol) in THF (10 mL) was added dropwise to the mixture. The mixture was diluted with hexane, and the organic layer was washed with brine and dried over Na$_2$SO$_4$. After the solvent was evaporated, compound **2** was obtained as colorless crystals (0.41 g, 20%). Mp 183–184°C; ^{1}H NMR (C$_6$D$_6$): $\delta = 0.04$ (s, 6H, Me), 0.96 (s, 36H, ^{t}Bu), 5.52 (s, 2H, SiH), 7.15 (dd, $J = 3.3$, 5.5 Hz, 4H, arom-H), 7.77 (dd, $J = 3.3$, 5.5 Hz, 4H, arom-H); ^{13}C NMR (C$_6$D$_6$): $\delta = -6.1$, 21.1, 29.6, 127.8, 136.8, 141.5; ^{29}Si NMR (C$_6$D$_6$): δ −47.7, 1.7. Anal. Calcd for C$_{30}$H$_{52}$Si$_4$: C, 68.62; H, 9.98. Found: C, 68.43; H, 9.94.

9,10-Bis(di-*tert*-butylmethylsilyl)-9,10-dibromo-9,10-dihydro-9,10-disilaanthracene (3)

Br$_2$ (0.16 g, 1.0 mmol) was added to a solution of **2** (0.24 g, 0.46 mmol) in CH$_2$Cl$_2$ (5 mL) at 0°C. Then the reaction mixture was allowed to warm to room temperature and was stirred for 30 min. After the solvent was evaporated, the crude product was washed with hexane to give *anti*-9,10-dibromo-9,10-dihydro-9,10-disilaanthracene **3** as colorless crystals (0.31 g, 99%). Mp 233–234°C. ^{1}H NMR (C_6D_6): $\delta = 0.16$ (s, 6H, Me), 0.92 (s, 36H, ^{t}Bu), 7.15 (dd, $J = 3.3, 5.6$ Hz, 4H, arom-H), 8.10 (dd, $J = 3.3, 5.6$ Hz, 4H, arom-H); ^{13}C NMR (C_6D_6): $\delta = -6.5$, 22.0, 29.8, 129.3, 137.4, 142.3; ^{29}Si NMR (C_6D_6): $\delta = -8.2$, 1.8. Anal. Calcd for $C_{30}H_{50}Br_2Si_4$: C, 52.77; H, 7.38. Found: C, 52.34; H, 7.57.

Reduction of 9,10-Dibromo-9,10-dihydro-9,10-disilaanthracene 3 with KC_8

Potassium graphite (88 mg, 0.64 mmol) and **3** (200 mg, 0.29 mmol) were placed in a glove box into a glass tube with a magnetic stirring bar, then dry THF (2 mL) was vacuum transferred into the tube. After one day of stirring at room temperature, the solvent was removed in vacuo, and then hexane was added. The product was purified by column chromatography on SiO_2 (toluene) to give 1′,4,4,4′-tetrakis(di-*tert*-butylmethylsilyl)spiro[2,5-dibenzo-1,4-disilacyclohexa-2,5-diene-1,7′-2′,5′-dibenzo-1′,4′,7′-trisilanorbornadiene] (**4**) as colorless crystals (120 mg, 81%). Mp > 300°C; ^{1}H NMR (C_6D_6): $\delta = 0.21$ (s, 6H, Me), 0.44 (s, 6H, Me), 1.06 (s, 36H, ^{t}Bu), 1.16 (s, 36H, ^{t}Bu), 6.09 (d, $J = 7.7$ Hz, 2H, arom-H), 6.64 (dd, $J = 7.7, 7.7$ Hz, 2H, arom-H), 6.92 (dd, $J = 7.7, 7.7$ Hz, 2H, arom-H), 7.32 (dd, $J = 3.5, 5.4$ Hz, 4H, arom-H), 8.00 (d, $J = 7.7$ Hz, 2H, arom-H), 8.69 (dd, $J = 3.5, 5.4$ Hz, 4H, arom-H); ^{13}C NMR (C_6D_6): $\delta = -3.6, -1.2$, 21.8, 23.1, 31.5, 31.6, 127.0, 127.3, 128.3, 135.7, 135.9, 139.4, 144.0, 144.8, 150.9; ^{29}Si NMR (C_6D_6): $\delta = -44.0, -30.1$, 9.6, 10.4, 25.0. HRMS (APCI, toluene as solvent) m/z calcd for $C_{60}H_{101}Si_8$ [$(M+H)^+$] 1045.6052, found 1045.6070.

Observation of 9,10-Bis(di-*tert*-butylmethylsilyl)-9,10-disila-9,10-Dewar Anthracene (5) by Low Temperature NMR Spectroscopy

Dry THF-d_8 (0.5 mL) was vacuum transferred to a mixture of potassium graphite (13 mg, 0.097 mmol) and **3** (30 mg, 0.044 mmol) in an NMR tube, and then the NMR tube was sealed under vacuum. The reaction was complete in 11 h at −30°C, and 9,10-disila-9,10-Dewar anthracene **5** was formed (77%) together with **4** (23%), as estimated by ^{1}H NMR spectroscopy. ^{1}H NMR (243 K, THF-d_8): $\delta = 0.38$ (s, 6H, Me), 1.21 (s, 36H, ^{t}Bu), 7.09 (m, 4H, arom-H), 7.43 (m, 4H, arom-H); ^{13}C NMR (243 K, THF-d_8): $\delta = -6.4$, 21.3, 30.0, 128.4, 133.7, 157.1; ^{29}Si NMR (243 K, THF-d_8): $\delta = -14.9$, 11.4.

X-Ray Crystallographic Analysis of Compound 4

Single crystals of **4** suitable for X-ray diffraction were obtained from a toluene solution. The intensity data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized MoKα radiation ($\lambda = 0.71071$ Å). The structure was solved by direct methods (SIR97)[12] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97).[13] Crystal data for **4**: $C_{60}H_{100}Si_8$, MW = 1046.12, monoclinic, space group $P2_1$/n (no. 14), $a = 15.2150(10)$, $b = 22.4140(16)$, $c = 19.5000(8)$ Å, $\beta = 108.339(4)°$, $V = 6312.3(7)$ Å^3, $Z = 4$, $D_{calc} = 1.101$ g cm^{-3}, R_1 ($I > 2\sigma(I)$) = 0.0518, wR_2 (all data) = 0.1079 for 12406 reflections and 641 parameters, GOF = 1.040. CCDC No. 698632 for **4** contains supplementary crystallographic data. These data can be obtained free of charge via the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223–336-033; e-mail: deposit@ccdc.cam.ac.uk).

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