

Synthesis, structure, and photochemical reaction of 9,10-dihydro-9-silaanthracene derivatives carrying bulky substituents

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Received 13 December 1999; received in revised form 3 March 2000; accepted 14 March 2000

Abstract

Some of 9-aryl-9,10-dihydro-9-silaanthracenes (**1**) were prepared and the alkylation of the compounds gave *trans*-9-aryl-10-alkyl-9,10-dihydro-9-silaanthracenes exclusively. Upon photolysis of a 9-phenyl derivative, 9-phenyl-9-silaanthracene was confirmed by spectroscopic analysis. Also, structural studies of the dihydro compounds were performed by NMR and X-ray. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silaaromatics; Structure of dihydro-9-silaanthracene; Photolysis of dihydro-9-silaanthracene

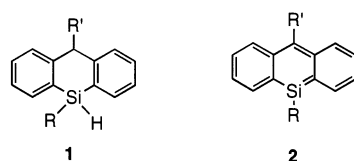
1. Introduction

Although a number of unsaturated compounds containing silicon–carbon or silicon–silicon double bonds are well-known as a silene or disilene, only a few silaaromatic compounds have been prepared apart from silabenzene, disilabenzene, and 9-silaanthracenes [1], which were confirmed by Maier et al. as matrix isolation products or Diels–Alder adducts of flash pyrolysis intermediates of the dihydro- or tetrahydro-derivatives [2,3]. Recently, isolation of 2-silaphthalene having a sterically bulky substituent on the silicon atom at room temperature has been reported via dehydrohalogenation of the precursor by Tokitoh, Okazaki, and co-workers [4]. A recent interest of our group in regard to organosilicon compounds is the chemistry of dihydro derivatives of 9-sila- and 9,10-

disilaanthracene, assumed as either a precursor of silaaromatics or a new reducing agent. In addition, the structural chemistry of these compounds is also attractive for us. We have previously reported first photochemical formation of 9-silaanthracenes from 9,10-dihydro-9-silaanthracene in rigid glass [5] and reductive reactions of organic halides using 9,10-dihydro-9,10-disilaanthracene [6]. In our preliminary communication, 9-methyl- and 9-phenyl-9,10-dihydro-9-silaanthracene (**1a** and **b**) gave 9-silaanthracene derivative (**2a** and **b**) on UV irradiation and, especially, the latter **1b** resulted in the silaanthracene derivative **2b** effectively (Scheme 1). Therefore, we attempted to establish a general synthetic route of the precursor of the silaanthracene framework and silaanthracene itself having a sterically bulky group around the silicon atom. In this paper, we would like to report a synthesis of 9-aryl-9,10-dihydro-9-silaanthracene (**1b–h**), the photolytic reaction of some of these compounds, and a structural analysis using NMR and X-ray [7] technique.

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- a: R = Me, R' = H
 b: R = Ph, R' = H
 c: R = Mes, R' = H
 d: R = Tip, R' = H
 e: R = Tip, R' = Me
 f: R = Tip, R' = *i*-Pr
 g: R = Ttp, R' = H
 h: R = Ttp, R' = *i*-Pr
 i: R = H, R' = H
- Mes = 2,4,6-trimethylphenyl
 Tip = 2,4,6-triisopropylphenyl
 Ttp = 2,4,6-tri-*t*-butylphenyl

Scheme 1.

2. Results and discussion

2.1. Synthesis

According to the synthetic route for 9-phenyl-9,10-dihydro-9-silaanthracene (**1b**) [8], a reaction of 2,4,6-trimethylphenyldichlorosilane (MesSiCl₂H) with di-Grignard reagent, which was prepared from 2,2'-dichlorodiphenylmethane (**3**) with activated magnesium [9], gave 9-(2,4,6-trimethylphenyl)-9,10-dihydro-9-silaanthracene (**1c**) in 28% yield (Scheme 2). On the other hand, treatment of 2,4,6-triisopropylphenylsilane (TipSiH₃) with 2,2'-dilithiodiphenylmethane, which was formed by dilithiation of 2,2'-dibromodiphenylmethane with butyllithium, afforded 9-(2,4,6-triisopropylphenyl)-9,10-dihydro-9-silaanthracene (**1d**) in 71% yield. With the more bulky 2,4,6-tri-*t*-butylphenylsilane (TtpSiH₃), refluxing the reaction mixture overnight was necessary to obtain the 9-(2,4,6-tri-*t*-butylphenyl)-9,10-dihydro-9-silaanthracene (**1g**) in moderate yield (48%).

We next carried out the introduction of an alkyl group into the 10-position in order to create more crowded environment around the Si atom. After treatment of the compound **1d** with butyllithium, the resultant carbanion was quenched by iodomethane or 2-iodopropane to afford the corresponding 10-alkylated compound **1e** or **1f** in 51 or 60% yield, respectively. The incorporation of the alkyl group exclusively occurred

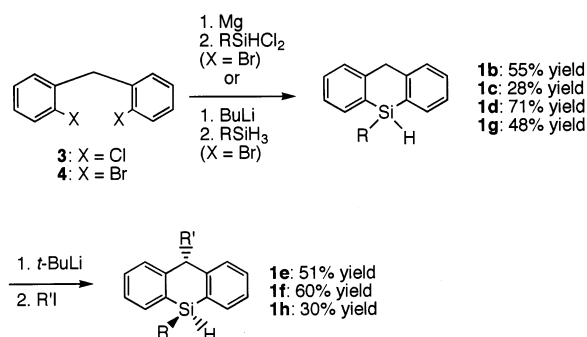
from *trans* to the 9-aryl group, which was confirmed by X-ray crystallographic analysis [7]. A similar reaction of the compound **1g** with 2-iodopropane furnished the compound **1h** in 30% yield.

These 9,10-dihydro-9-silaanthracenes, except for the compound **1b**, are unknown compounds and show satisfactory ¹H-, ¹³C-, and ²⁹Si-NMR, IR, and HRMS data.

2.2. Structure of the 9,10-dihydro-9-silaanthracenes (**1**)

In the ¹H-NMR spectra of the compounds **1c** and **1d**, two kinds of methyl or isopropyl group of 9-aryl, which correspond to *ortho* and *para* substituents on the aromatic ring, were observed as expected. For example, compound **1d** showed the sharp signals of the isopropyl groups at δ 1.02 (d, *J* = 7 Hz, 12H) and 1.31 (d, *J* = 7 Hz, 6H) at 22°C. The dihedral angle (θ) between two phenyl rings in the dihydroanthracene framework was 152°. This shows that two isopropyl groups at the 2- and 6-positions of the Tip group are considered to be equivalent. The aryl substituent exists as pseudo-equatorial on the silicon atom of the 1-silacyclohexadiene ring. For **1c**, two methyl groups at the 2- and 6-positions of the mesityl group are equivalent at δ 2.34. On the other hand, the signals of the *t*-butyl group of 9-(2,4,6-tri-*t*-butyl)phenyl derivative **1g** appeared at δ 1.07 (br, 9H), 1.39 (s, 9H), and 1.59 (br, 9H) at 22°C. The very broad signals at δ 1.07 and 1.59 were assigned to be the *t*-Bu groups at 2- and 6-positions, and these two *t*-butyl groups should be non-equivalent at 22°C, namely, the bond rotation about Si–Ar is very slow because of steric hindrance between the *t*-Bu group and the dihydroanthracene framework. From variable temperature NMR measurement, these signals coalesced at around 35°C and three kinds of very sharp singlets were observed at δ 0.99, 1.38, and 1.61 at –60°C (the bond rotation about Si–Ar was frozen at this temperature). The dihedral angle θ is 154°, similar to that of **1d**. Molecular structure of **1g** is shown in Fig. 1 and the emphasized structural feature of the Ttp group is illustrated in Fig. 2. The benzene ring of the aryl group is found bent with an angle of 17°. From these investigations, it became clear that the Si–Ar bond of **1b**, **1c**, and **1e**, rotates freely but that of **1g** is sterically restricted at room temperature and the dihedral angle θ of these compounds is almost similar, not due to the aryl substituent.

For **1e** and **1f**, the incorporation of the alkyl group exclusively occurred from *trans* to the 9-aryl group. By introducing the alkyl group into the 10-position of **1**, however, the rotation about the Si–Ar bond depended upon the alkyl substituent. The rotation of the aryl group of compound **1f**, obtained from **1d** by introduction of an isopropyl group at the 10-position, was restricted at 22°C, as checked by NMR. Also, the



Scheme 2.

dihedral angle θ of the compound **1f** (141°) is 10° smaller than that of **1d**, due to compression by the isopropyl group at the 10-position. The values of the dihedral angle θ and chemical equivalency of the *ortho* substituents on the aryl ring of **1c–h** are compiled in Table 1.

2.3. Photolysis of 9,10-dihydro-9-silaanthracenes

It is well known that anthracene is easily produced by the photolysis of 9,10-dihydroanthracene. As mentioned above, Maier et al. observed 9-silaanthracene produced by flash pyrolysis [3]. We studied the photochemical formation of 9-silaanthracene derivatives for 9,10-dihydro-9-silaanthracene (**1i**) [10] and 9-phenyl-9,10-dihydro-9-silaanthracene (**1b**). By photolysis of **1b**, 9-phenyl-9-silaanthracene (**2b**) was formed. This was confirmed by comparing absorption spectrum with that reported for 9-phenyl-9-silaanthracene produced by

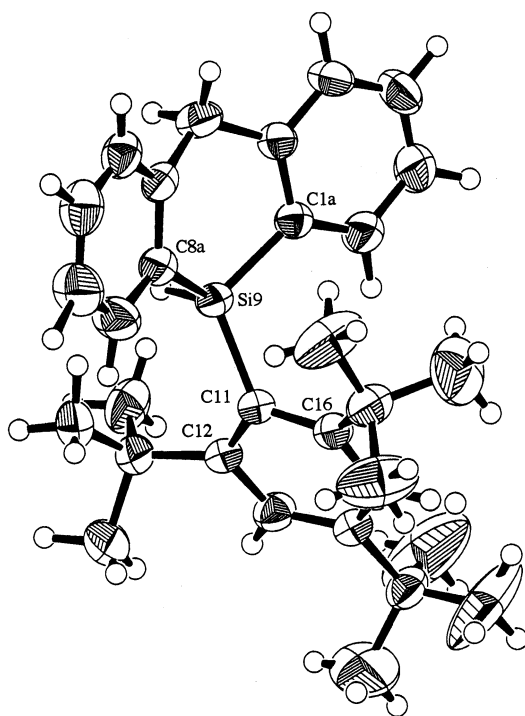


Fig. 1. Molecular structure of **1g**. Important bond lengths (Å) and angles ($^\circ$): Si(9)–C(1a) = 1.869(3), Si(9)–C(8a) = 1.871(3), Si(9)–C(11) = 1.896(3); C(1a)–Si(9)–C(8a) = $104.2(1)$, C(1a)–Si(9)–C(11) = $112.0(1)$, C(8a)–Si(9)–C(11) = $122.8(1)$, Si(9)–C(11)–C(12) = $117.4(2)$, Si(9)–C(11)–C(16) = $122.7(2)$, C(12)–C(11)–C(16) = $116.8(3)$.

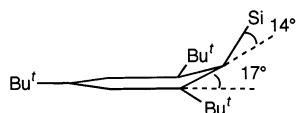


Fig. 2. Emphasized structural feature of Ttp group of compound **1g**.

Table 1

Dihedral angle θ between two phenyl rings in the dihydroanthracene framework and chemical equivalency of the *ortho* substituents of the aryl group

Compound	Dihedral angle ^a ($^\circ$)	<i>Ortho</i> substituents ^b
1c		Equivalent
1d	152	Equivalent
1e	158	Equivalent
1f	141	Nonequivalent
1g	154	Nonequivalent
1h		Nonequivalent

^a Determined by X-ray analysis [7].

^b Observed in 400 MHz $^1\text{H-NMR}$ at 22°C .

flash thermolysis technique [3]. The 407 nm band was assigned to the $^1\text{L}_b$ transition by the results of fluorescence polarization measurements and the calculated results by CNDO/S-CI method [11]. Although formation of 9-silaanthracene (**2i**) from **1i** was also confirmed by the observation of its absorption band at 400 nm, its yield was very small. From these results, it is considered that steric hindrance and electron-donating ability of a substituent group at the 9-position play an important role in the formation process of 9-silaanthracene derivatives. Here we have studied the photolysis of the 9,10-dihydro-9-silaanthracene derivatives having a 2,4,6-triisopropylphenyl or 2,4,6-tri-*t*-butylphenyl group at the 9-position, which are considered to be much more bulky and/or have electron-donating ability.

Fig. 3a–d show absorption spectra of **1i**, **1b**, 9-(2,4,6-triisopropylphenyl)-9,10-dihydro-9-silaanthracene (**1d**), and 9-(2,4,6-tri-*t*-butylphenyl)-9,10-dihydro-9-silaanthracene (**1g**) in 3MP (3-methylpentane) at 77 K before (dotted line) and after (full line) the photolysis with 253.7 nm light, respectively. Upon photolysis of **1d**, a new absorption peak appeared at 405 nm, and this absorption band is assigned to the $^1\text{L}_b$ band of the corresponding 9-silaanthracene, although its formation amount was relatively smaller. In the case of **1g**, a broad absorption band was slightly observed at 408 nm.

Formation yields of the corresponding 9-silaanthracenes are in the order of **1b** > **1i** > **1d** > **1g**. These results indicate that electron-donating power or bulkiness of the substituent is not the only important factor for the formation of a 9-silaanthracene derivative. Moreover, the reactivity of these compounds might be dependent upon the structure of the ground state, as suggested by structural analysis.

Other attempts for generation of silaanthracene, i.e., 1,4-dehydrochlorination and 1,4-dehydrogenation, were made, but the product was not the compound expected.

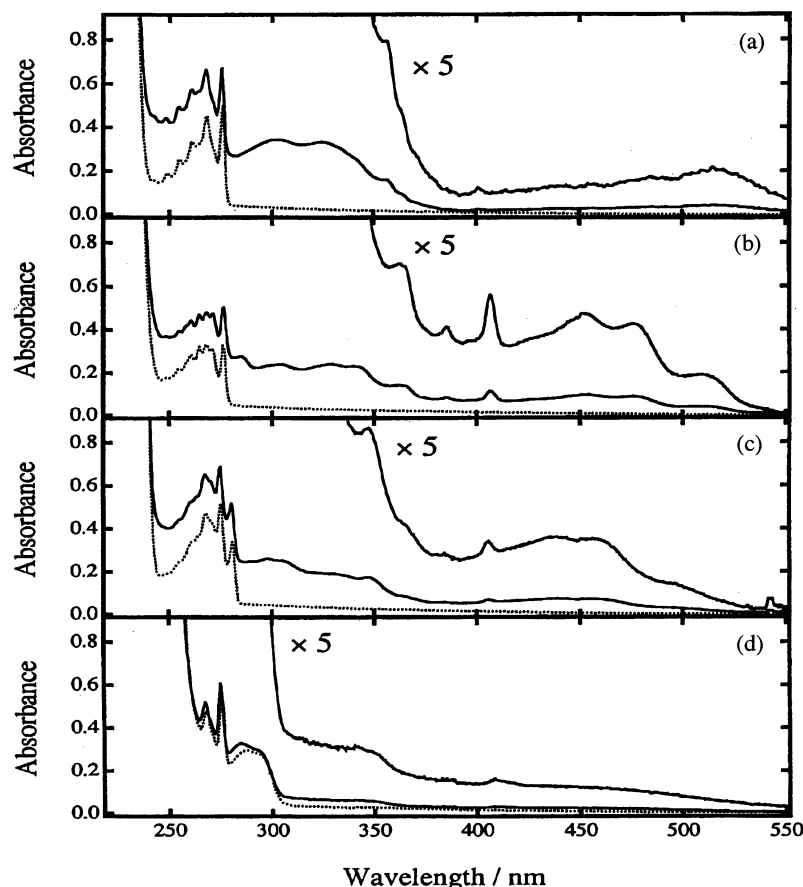


Fig. 3. Absorption spectra of **1i** (a), **1b** (b), **1d** (c), and **1g** (d) in 3MP at 77 K before (dotted line) and after (full line) photolysis with 253.7 nm light.

3. Experimental

3.1. General

GC measurements were performed on a Shimadzu GC-18A and a GL Sciences GC-380 gas chromatograph using a 50 m $\times$ 0.25 mm methyl silicone capillary column (Quadrex). TLC was carried out on Merck silica gel 60 F₂₅₄. Flash column chromatography was performed on Merck silica gel 60 (230–400 mesh). Infrared spectra were recorded on a Perkin–Elmer 1600 infrared spectrometer. ¹H-, ¹³C-, and ²⁹Si-NMR spectra were measured on a Varian UNITY-400 spectrometer. All chemical shifts are reported as δ -values (ppm) relative to residual chloroform (δ_{H} 7.26), the central peak of deuteriochloroform (δ_{C} 77.0) or tetramethylsilane (δ_{Si} 0.0). GC-MS was measured with the direct combination of GC (Hewlett–Packard GC 5890 Series II with a 25 m $\times$ 0.25 mm methyl silicone capillary column) and a JEOL JMS-AX-500 spectrometer with DA7000 data system.

3.2. Materials and solvents

Most of the starting materials and reagents were commercial products and were used as accepted. 2,2'-Dichlorodiphenylmethane (**3**) [8], 2,2'-dibromodiphenylmethane (**4**) [12], 2,4,6-trimethylphenyldichlorosilane [13], 2,4,6-triisopropylphenylsilane [14], and 2,4,6-tri-*t*-butylphenylsilane [15] were prepared according to the literature. Solvents were distilled over sodium in the presence of benzophenone.

3.3. 9-(2,4,6-Trimethylphenyl)-9,10-dihydro-9-silaanthracene (**1c**)

To Mg turnings (560 mg, 24.0 mmol) was added 1,2-dibromoethane (4.51 g, 24.0 mmol) in THF (40 ml), and the mixture was refluxed under argon atmosphere for 1 h. After the solution was cooled to room temperature (r.t), K (1.75 g, 45.0 mmol), KI (1.66 g, 10.0 mmol) was added and refluxed for 2 h. Then, 2,2'-dichlorodiphenylmethane (**3**, 1.89 g, 8.00 mmol) was

added to the resulting black suspension of activated Mg and the mixture was heated to reflux for 3 h, after which 2,4,6-trimethylphenyldichlorosilane (2.11 g, 9.60 mmol) was added at r.t. After being stirred at r.t. overnight, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The organic layer was dried over MgSO_4 and evaporated. The crude product was purified by flash chromatography on silica gel and elution with hexane gave 9-silaanthracene (**1c**) (690 mg, 28%) as colorless plates, m.p. 107–109°C. $^1\text{H-NMR}$ (CDCl_3): δ 2.24 (s, 3H), 2.34 (s, 6H), 4.13 and 4.29 (ABq, $J = 18$ Hz, 2H), 5.66 (s, 1H), 6.92 (s, 2H), 7.17 (m, 2H), 7.34 (m, 2H), 7.41 (m, 4H). $^{13}\text{C-NMR}$ (CDCl_3): δ 21.2, 24.2, 41.6, 124.9, 125.8, 128.2, 128.9, 129.4, 132.1, 134.3, 140.4, 145.6, 146.5. $^{29}\text{Si-NMR}$ (CDCl_3): δ -47.5. IR (KBr): $\nu_{\text{Si-H}}$ 2139.1 cm^{-1} . HRMS (EI): m/z 314.1526 [M^+ , Calc. for $\text{C}_{22}\text{H}_{22}\text{Si}$ 314.1491].

3.4. 9-(2,4,6-Triisopropylphenyl)-9,10-dihydro-9-silaanthracene (**1d**)

To a solution of 2,2'-dibromodiphenylmethane (**4**, 10.0 g, 30.7 mmol) in ether (150 ml) was added 1.6 M butyllithium in hexane (43 ml, 68.8 mmol) at 0°C under Ar atmosphere. After the solution was stirred at r.t. for 1 h, 2,4,6-triisopropylphenylsilane (10.78 g, 46.1 mmol) was added at r.t. After being stirred at r.t. overnight, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The organic layer was dried over MgSO_4 and evaporated. The crude product was recrystallized from ethanol to give 9-silaanthracene (**1d**) (8.61 g, 72%) as colorless plates, m.p. 160–162°C. $^1\text{H-NMR}$ (CDCl_3): δ 1.02 (d, $J = 7$ Hz, 12H), 1.31 (d, $J = 7$ Hz, 6H), 2.93 (sep, $J = 7$ Hz, 1H), 3.17 (sep, $J = 7$ Hz, 2H), 4.15 and 4.32 (ABq, $J = 18$ Hz, 2H), 5.71 (s, 1H), 7.09 (s, 2H), 7.18 (m, 2H), 7.34 (m, 2H), 7.40 (m, 2H), 7.43 (m, 2H). $^{13}\text{C-NMR}$ (CDCl_3): δ 23.8, 24.6, 33.7, 34.4, 41.6, 121.4, 123.7, 125.5, 128.1, 129.3, 133.2, 134.8, 144.7, 151.5, 157.7. $^{29}\text{Si-NMR}$ (CDCl_3): δ -49.3. IR (KBr): $\nu_{\text{Si-H}}$ 2143.4 cm^{-1} . HRMS (EI): m/z 398.2421 [M^+ , Calc. for $\text{C}_{28}\text{H}_{34}\text{Si}$ 398.2430].

3.5. 9-(2,4,6-Tri-*t*-butylphenyl)-9,10-dihydro-9-silaanthracene (**1g**)

To a solution of 2,2'-dibromodiphenylmethane (**4**, 1.30 g, 4.00 mmol) in ether (20 ml) was added 1.6 M butyllithium in hexane (6.2 ml, 9.92 mmol) at 0°C under Ar atmosphere. After the solution was stirred at r.t. for 1 h, 2,4,6-tri-*t*-butylphenylsilane (1.66 g, 6.00 mmol) was added at r.t. After refluxing overnight, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The organic layer was dried over MgSO_4 and evaporated. The crude product was

purified by flash chromatography on silica gel and elution with hexane gave 9-silaanthracene **1g** (840 mg, 48%) as colorless plates, m.p. 172–173°C. $^1\text{H-NMR}$ (CDCl_3): δ 1.07 (br, 9H), 1.39 (s, 9H), 1.59 (br, 9H), 4.08 and 4.21 (ABq, $J = 18$ Hz, 2H), 5.65 (s, 1H), 7.17 (m, 2H), 7.31 (m, 6H), 7.52 (br, 2H). $^{13}\text{C-NMR}$ (CDCl_3): δ 31.2, 34.1, 34.8, 39.6, 41.6, 121.4, 122.9, 125.4, 127.9, 128.9, 135.1, 135.6, 143.7, 151.2, 161.7. $^{29}\text{Si-NMR}$ (CDCl_3): δ -46.5. IR (KBr): $\nu_{\text{Si-H}}$ 2156.3 cm^{-1} . HRMS (EI): m/z 440.2942 [M^+ , Calc. for $\text{C}_{31}\text{H}_{40}\text{Si}$ 440.2899].

3.6. 10-Methyl-9-(2,4,6-triisopropylphenyl)-9,10-dihydro-9-silaanthracene (**1e**)

To a solution of 9-silaanthracene (**1d**) (1.45 g, 3.64 mmol) in THF (25 ml) was added 1.7 M *t*-butyllithium in pentane (3.30 ml, 5.61 mmol) at -78°C under Ar atmosphere. After the solution was stirred for 1 h, iodomethane (2.28 g, 16.1 mmol) was added. After being stirred at r.t. overnight, the reaction mixture was quenched with H_2O and extracted with ether. The organic layer was dried over MgSO_4 and evaporated. The crude product was purified by flash chromatography on silica gel and elution with hexane gave 9-silaanthracene **1e** (767 mg, 51%) as a colorless solid, m.p. 146–148°C. $^1\text{H-NMR}$ (CDCl_3): δ 0.97 (d, $J = 7$ Hz, 12H), 1.31 (d, $J = 7$ Hz, 6H), 1.50 (d, $J = 7$ Hz, 3H), 2.93 (sep, $J = 7$ Hz, 1H), 3.09 (sep, $J = 7$ Hz, 2H), 4.30 (q, $J = 7$ Hz, 1H), 5.89 (s, 1H), 7.06 (s, 2H), 7.16 (m, 2H), 7.36 (m, 2H), 7.40 (m, 4H). $^{13}\text{C-NMR}$ (CDCl_3): δ 23.8, 24.4, 29.1, 33.5, 34.4, 48.4, 121.3, 124.1, 125.4, 128.0, 129.7, 132.1, 135.2, 150.7, 151.4, 157.7. $^{29}\text{Si-NMR}$ (CDCl_3): δ -50.8. IR (KBr): $\nu_{\text{Si-H}}$ 2149.9 cm^{-1} . HRMS (EI): m/z 412.2548 [M^+ , Calc. for $\text{C}_{29}\text{H}_{36}\text{Si}$ 412.2586].

3.7. 10-Isopropyl-9-(2,4,6-triisopropylphenyl)-9,10-dihydro-9-silaanthracene (**1f**)

To a solution of 9-silaanthracene (**1d**) (1.19 g, 3.00 mmol) in THF (25 ml) was added 1.7 M *t*-butyllithium in pentane (2.25 ml, 3.83 mmol) at -78°C under Ar atmosphere. After the solution was stirred for 1 h, 2-iodopropane (601 mg, 3.60 mmol) was added. After refluxing overnight, the reaction mixture was quenched with H_2O and extracted with ether. The organic layer was dried over MgSO_4 and evaporated. The crude product was purified by flash chromatography on silica gel and elution with hexane gave 9-silaanthracene **1f** (790 mg, 60%) as a colorless solid, m.p. 171–173°C. $^1\text{H-NMR}$ (CDCl_3): δ 0.49 (d, $J = 7$ Hz, 6H), 0.79 (d, $J = 7$ Hz, 6H), 1.30 (d, $J = 7$ Hz, 6H), 1.41 (d, $J = 7$ Hz, 6H), 2.00 (m, 2H), 2.92 (sep, $J = 7$ Hz, 1H), 3.64 (d,

$J = 9$ Hz, 1H), 3.97 (sep, $J = 7$ Hz, 1H), 5.91 (s, 1H), 6.92 (s, 1H), 7.16 (m, 2H), 7.18 (s, 1H), 7.33 (m, 4H), 7.41 (m, 2H). ^{13}C -NMR (CDCl_3): δ 21.7, 23.7, 24.9, 32.8, 33.8, 34.3, 37.1, 61.4, 120.5, 121.8, 124.6, 125.2, 128.5, 129.7, 132.9, 135.3, 148.7, 151.2, 157.5. ^{29}Si -NMR (CDCl_3): δ -49.5. IR (KBr): $\nu_{\text{Si-H}}$ 2146.1 cm^{-1} . HRMS (EI): m/z 440.2861 [M^+ , Calc. for $\text{C}_{31}\text{H}_{40}\text{Si}$ 440.2899].

3.8. 10-Isopropyl-9-(2,4,6-tri-*t*-butylphenyl)-9,10-dihydro-9-silaanthracene (**1h**)

To a solution of 9-silaanthracene (**1g**) (970 mg, 2.21 mmol) in THF (20 ml) was added 1.7 M *t*-butyllithium in pentane (1.85 ml, 3.15 mmol) at -78°C under Ar atmosphere. After the solution was stirred for 1 h, 2-iodopropane (500 mg, 2.90 mmol) was added. After refluxing overnight, the reaction mixture was quenched with H_2O and extracted with ether. The organic layer was dried over MgSO_4 and evaporated. The crude product was purified by flash chromatography on silica gel and elution with hexane gave 9-silaanthracene (**1h**) (321 mg, 30%) as a colorless solid, m.p. 130 – 132°C . ^1H -NMR (CDCl_3): δ 0.68 (d, $J = 7$ Hz, 6H), 0.79 (s, 9H), 1.39 (s, 9H), 1.69 (s, 9H), 1.88 (m, 1H), 3.57 (d, $J = 9$ Hz, 1H), 5.83 (s, 1H), 7.14 (m, 2H), 7.27 (m, 6H), 7.42 (d, $J = 1.9$, 1H), 7.54 (d, $J = 1.9$, 1H). ^{13}C -NMR (CDCl_3): δ 21.9, 31.2, 33.7, 33.8, 34.2, 34.8, 36.7, 39.4, 39.6, 61.6, 122.3, 122.9, 123.3, 125.2, 128.3, 129.8, 135.8, 147.9, 151.0, 160.6, 162.7. ^{29}Si -NMR (CDCl_3): δ -47.4. IR (KBr): $\nu_{\text{Si-H}}$ 2172.1 cm^{-1} . HRMS (EI): m/z 482.3332 [M^+ , Calc. for $\text{C}_{34}\text{H}_{46}\text{Si}$ 482.3369].

3.9. Photolysis of 9,10-dihydro-9-silaanthracenes

Photolysis was carried out at low temperature using the 266 nm light; output of fourth harmonics from the Nd^{3+} : YAG laser with 8 ns-pulse width. Liquid nitrogen cryostat (Oxford DN-1704) and temperature controller (Oxford ITC-1) were used for measurements at various temperatures between 77 and 100 K.

Absorption spectra were measured by using a Hitachi U3300 spectrophotometer. Fluorescence emission and excitation spectra were measured using a Hitachi M850 fluorescence spectrometer with band pass of 3 or 5 nm for both excitation and emission.

3.10. X-ray structure determination of **1g**

Crystal data: $\text{C}_{31}\text{H}_{40}\text{OSi}$, monoclinic, $P2_1/c$, $a = 16.752(1)$, $b = 10.6925(6)$, $c = 15.179(1)$ Å, $\beta = 95.522(6)^\circ$, $U = 2706.2(3)$ Å³, wavelength = 1.5418 Å, $Z = 4$, $\mu(\text{Cu-K}\alpha) = 0.855$ mm⁻¹, $D_{\text{calc}} = 1.082$ Mg m⁻³, number of reflection collected/unique = 6035/5515. Colorless rod crystals of **1g** were grown from

ethanol solution at r.t. Diffraction data using a crystal with the dimensions of $0.5 \times 0.1 \times 0.1$ mm were collected on Nonius CAD4 Turbo four-circle diffractometer. Of a total of 6035 reflections collected up to $\theta = 74.11^\circ$ ($-20 < h < 20$, $-13 < k < 0$, $-18 < l < 0$) in ω - 2θ scan mode using graphite monochromated Cu-K α radiation, 5515 were independent ($R_{\text{int}} = 0.015$). These data were corrected empirically for absorption (with maximum 0.998 and minimum 0.968 transmission). Hydrogen atoms were fixed on calculated positions. Non-hydrogen atoms were refined anisotropically based on F by full-matrix least-squares method. The final R_1 and wR_2 for 3644 reflections with $I > 3\sigma(I)$ are 0.0632 and 0.0916, respectively. An ORTEPII drawing is shown in Fig. 1.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 140081. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

One of the authors (K.N.) gratefully acknowledges financial support of a Grant-in-Aid for Scientific Research (No. 09640646) from the Ministry of Education, Science, Sports and Culture of Japan.

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