Notes

Generation and Reactions of Transient 9-Silaphenanthrene Derivative

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Summary: Generation and reaction of a 9-silaphenanthrene derivative, a novel class of silaaromatic intermediates, by a thermal retro-ene elimination of propene from the corresponding allylsilane is described. The formation of the transient 9-silaphenanthrene was deduced by the isolation of trapping products from the copyrolysate of the 9-allyl-9,10-dihydro-9-silaphenanthrene derivative with MeOD.

Introduction

Much attention has been focused on the chemistry of aromatic rings containing sp^2-hybridized silicon atoms. In the past few decades, there have been many reports on the generation and reactions of transient silaaromatics[1] such as sila- and disilabenzenes, silanaphthalene, and silaanthracene. Recently, isolation of stable 2-silanaphthalene and silabenzene carrying a bulky substituent was achieved.[2] We previously reported an observation of the UV−vis absorption and fluorescence spectra of 9-silaanthracene derivatives produced by UV photolysis of the corresponding 9,10-dihydro-9-silaanthracenes.[3] In this paper, we would like to describe the first generation of a 9-silaphenanthrene derivative, a novel class of silaaromatic intermediates, by thermal retro-ene elimination of propene from the corresponding allylsilane.

Results and Discussion

9,10-Dihydro-9-silaphenanthrene derivatives **6a**−**f**, suitable precursors of 9-silaphenanthrene, are new compounds and were prepared according to Scheme 1. 2,2′-Dibromobiphenyl (**2**), prepared by a reported procedure,[4] was subjected to a formylation reaction followed by reduction with sodium borohydride to give alcohol **4**, which was subsequently transformed into dibromide **5** using phosphorus tribromide in 96% overall yield. Ring closure of the dibromide **5** with an appropriate dichlorosilane in the presence of magnesium afforded 9,10-dihydro-9-silaphenanthrenes **6a**−**f** in moderate to good yields (55−81%).

First of all, we attempted to generate the 9-silaphenanthrene **7** via thermal extrusion of a molecular hydrogen from the corresponding 9,10-dihydro-9-silaphenanthrene derivatives **6d** and **6e**. However, we could not detect the products which would indicate the intermediacy of the expected silaaromatics.

The retro-ene fragmentation of the allylsilane was also used to generate silaaromatics such as silabenzene, silatoluene, and silanaphthalene.[5] We next examined the thermolysis of 9-allyl-9,10-dihydro-9-silaphenanthrene derivatives **6a**−**c**, and the results are outlined in Scheme 2. When a copyrolysis of **6b** and methanol was carried out in a vertical quartz tube packed with quartz glass wool heated to 600 °C in a tube furnace with a 30 mL/min flow of nitrogen gas, GC analysis of the pyrolysate revealed the formation of adduct **8b** in 48% yield based on the reacted **6b**. This product can be explained as arising from an addition of methanol to the carbon−silicon double bond in the 9-methyl-9-silaphenanthrene (**7b**) generated by thermal retro-ene elimination of propene from the allylsilane **6b**. Further confirmation of the intermediacy of **7b** was obtained through the use of MeOD as a trapping agent. Thus, copyrolysis of **6b** and MeOD afforded the expected deuterated adduct **8b′** in 30% yield. The deuterium content (83%) and the ratio of the diastereoisomers (trans:cis = 50:50) were determined by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum of the deuterated product **8b′**, the methyl or methoxy group trans to the deuterium atom would suffer larger high-field shift owing to the rigid conformation of the 9,10-dihydro-9-silaphenanthrene framework. Similarly, treatment of **6c** with methanol or MeOD gave the adduct **8c** or its deuterated derivative **8c′** in 41 or 45% (89% D-content, trans:cis = 50:50) yields, respectively.

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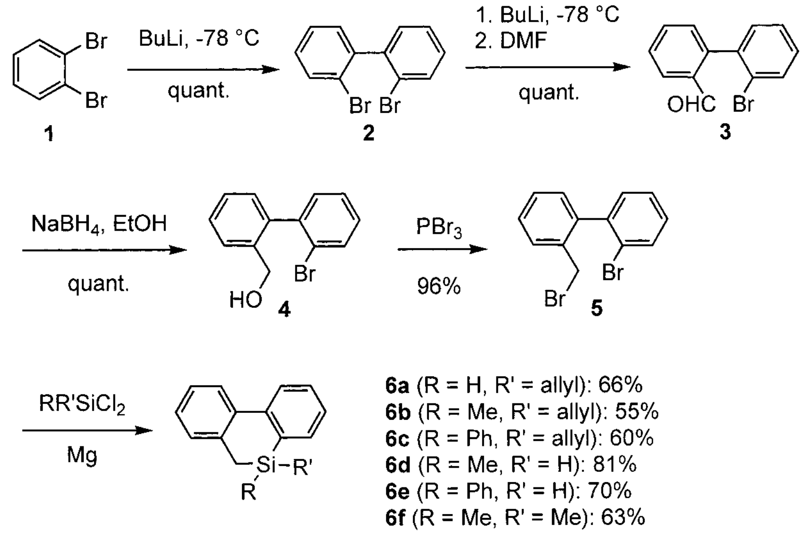
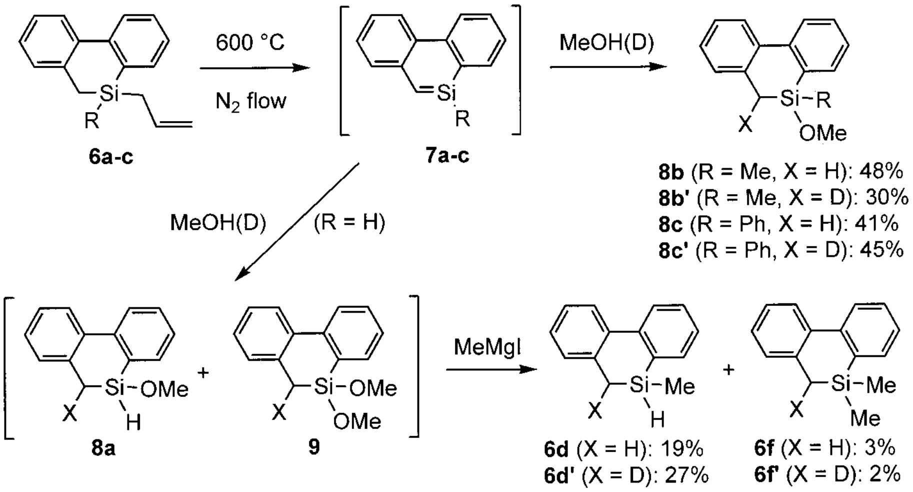
Scheme 1



Scheme 2



The evidence for the generation of the parent 9-silaphenanthrene (**7a**) in the thermolysis of **6a** also came from its copyrolysis with methanol. A direct GC–MS analysis of the copyrolysate showed the formation of adduct **8a** along with dimethoxysilane **9** produced probably by methanolysis of the adduct **8a**. Since the adduct **8a** could not be isolated from the complex reaction mixture, the copyrolysate was treated with methylmagnesium iodide to convert the methoxy function into a methyl group, and the obtained reaction mixture was analyzed by GC. It was found that the 9-methyl-9,10-dihydro-9-silaphenanthrene (**6d**) was obtained in 19% yield along with the 9,9-dimethyl derivative **6f** (3%). In this case, however, the possibility of 1,1-addition of methanol to a silylene generated by a 1,2-hydride shift of the silene intermediate can be considered. To identify the reaction pathway for the methanol addition, a labeling experiment employing MeOD was carried out. Consequently, the adduct **6d′** labeled with deuterium at the 10-position was isolated in 27% yield (86% D-content, trans:cis = 50:50) and no incorporation of the deuterium atom into the Si–H moiety was observed, supporting the intermediacy of the parent 9-silaphenanthrene (**7a**).

Experimental Section

General Procedures. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured at 400.0, 100.6, and 79.5 MHz, respectively. All chemical shifts are reported as δ values (ppm) relative to tetramethylsilane (δ_H 0.00 and δ_{Si} 0.00) and the central peak of deuteriochloroform (δ_C 77.0). High-resolution mass spectra (EI) were obtained at an ionization potential of 70 eV.

2,2′-Dibromobiphenyl (**2**) was prepared from 1,2-dibromobenzene (**1**) according to the literature.[4] All other reagents were of commercial grade and were used as supplied.

2-Bromo-2′-formylbiphenyl (3). To a solution of 2,2′-dibromobiphenyl (**2**, 20.3 g, 65.0 mmol) in THF (70 mL) was added successively 1.6 M BuLi (40.6 mL, 65 mmol) in hexane over a period of 40 min and a solution of DMF (4.75 g, 65.0 mmol) in THF (50 mL) over a period of 25 min at −78 °C under an argon atmosphere. After stirring at room temperature overnight, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, and the separated organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with a mixture of hexane and ethyl acetate (95:5) afforded the compound **3**[6] (17.3 g, 65.0 mmol) as a colorless oil in quantitative yield. ^{1}H NMR ($CDCl_3$): δ 7.26–7.34 (m, 3 H), 7.41 (m, 1 H), 7.55 (m, 1 H), 7.64–7.70 (m, 2 H), 8.04 (m, 1 H), 9.79 (s, 1 H).

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2-Bromo-2′-hydroxymethylbiphenyl (4). To a solution of the aldehyde **3** (15.7 g, 60.2 mmol) in ethanol (100 mL) was added $NaBH_4$ (3.41 g, 90.3 mmol). Completion of the reaction was checked by TLC analysis, and the mixture was extracted with ether. The organic layer was washed with water and dried over $MgSO_4$. Evaporation of the solvent gave almost pure **4** (15.8 g, 60.1 mmol) as a colorless solid in quantitative yield, mp 83−84 °C (lit.[7] 83−83.5 °C). ^1H NMR ($CDCl_3$): δ 4.41 (d, J = 13 Hz, 1 H), 4.50 (d, J = 13 Hz, 1 H), 7.15 (m, 1 H), 7.22−7.27 (m, 2 H), 7.34−7.39 (m, 2 H), 7.45 (m, 1 H), 7.58 (m, 1 H), 7.66 (m, 1 H). MS m/z 262 (M^+), 264 ($M^+ + 2$).

2-Bromo-2′-bromomethylbiphenyl (5). To the alcohol **4** (15.8 g, 60.1 mmol) was added PBr_3 (8.05 g, 30.1 mmol) at −10 °C, and the mixture was stirred at room temperature overnight. The reaction mixture was extracted with ether, and the organic layer was dried over $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel. Elution with hexane afforded the compound **5** (18.7 g, 96%) as a pale yellow solid, mp 50−51 °C (lit.[8] 55−57 °C). ^1H NMR ($CDCl_3$): δ 4.20 (d, J = 10 Hz, 1 H), 4.42 (d, J = 10 Hz, 1 H), 7.16 (m, 1 H), 7.27 (m, 1 H), 7.35−7.44 (m, 4 H), 7.54 (m, 1 H), 7.68 (m, 1 H). MS: m/z 324 (M^+), 326 ($M^+ + 2$), 328 ($M^+ + 4$).

9,10-Dihydro-9-silaphenanthrene Derivatives 6a−e. The preparation of 9-allyl-9-methyl-9,10-dihydro-9-silaphenanthrene (**6b**) is representative. To a suspension of Mg (729 mg, 30.0 mmol) in THF (30 mL) was added a solution of the dibromide **5** (3.26 g, 10.0 mmol) and allyldichloromethylsilane (1.86 g, 12.0 mmol) over a period of 40 min. After stirring overnight, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, and the separated organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with hexane afforded the compound **6b** (875 mg, 55%) as a colorless oil. ^1H NMR ($CDCl_3$): δ 0.27 (s, 3 H), 1.65 (m, 1 H), 1.67 (m, 1 H), 2.16 (d, J = 15 Hz, 1 H), 2.21 (d, J = 15 Hz, 1 H), 4.81 (m, 1 H), 4.84 (m, 1 H), 5.72 (m, 1 H), 7.16−7.20 (m, 2 H), 7.25 (m, 1 H), 7.30 (m, 1 H), 7.48 (m, 1 H), 7.53 (m, 1 H), 7.60 (m, 1 H), 7.70 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −6.63, 19.4, 20.0, 113.8, 126.20, 126.24, 126.5, 127.5, 128.0, 130.4, 131.3, 132.9, 133.8, 134.0, 135.7, 137.6, 144.7. ^{29}Si NMR ($CDCl_3$): δ −11.6. HRMS: m/z 250.1209 (M^+, calcd for $C_{17}H_{18}Si$ 250.1178). Anal. Calcd for $C_{17}H_{18}Si$: C, 81.54; H, 7.25. Found: C, 81.53; H, 7.31.

Other 9,10-dihydro-9-silaphenanthrene derivatives **6a**, **6c**, **6d**, **6e**, and **6f** were similarly prepared from the dibromide **5** and the appropriate dichlorosilane.

6a: colorless oil. ^1H NMR ($CDCl_3$): δ 1.73 (m, 1 H), 1.81 (m, 1 H), 2.22 (dd, J = 3, 15 Hz, 1 H), 2.30 (d, J = 15 Hz, 1 H), 4.36 (m, 1 H), 4.85−4.93 (m, 2 H), 5.76 (m, 1 H), 7.13−7.30 (m, 4 H), 7.47 (m, 1 H), 7.56−7.61 (m, 2 H), 7.68 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 16.7, 17.6, 114.5, 126.3, 126.5, 127.7, 128.1, 130.7, 130.9, 131.4, 133.29, 133.31, 134.2, 134.9, 137.6, 145.0. ^{29}Si NMR ($CDCl_3$): δ −24.6. IR (neat): ν_{Si-H} 2132 cm^{-1}. HRMS: m/z 236.0988 (M^+, calcd for $C_{16}H_{16}Si$ 236.1021). Anal. Calcd for $C_{16}H_{16}Si$: C, 81.30; H, 6.82. Found: C, 81.15; H, 6.87.

6c: colorless oil. ^1H NMR ($CDCl_3$): δ 1.99 (m, 1 H), 2.07 (m, 1 H), 2.39 (d, J = 15 Hz, 1 H), 2.51 (d, J = 15 Hz, 1 H), 4.78−4.90 (m, 2 H), 5.74 (m, 1 H), 7.11−7.35 (m, 7 H), 7.43−7.52 (m, 4 H), 7.59 (m, 1 H), 7.72 (m. 1 H). ^{13}C NMR ($CDCl_3$): δ 18.3, 18.8, 114.6, 126.3, 126.4, 126.6, 127.7, 127.9, 128.0, 129.7, 130.7, 131.6, 132.3, 133.4, 133.7, 134.0, 134.7, 135.1, 137.6, 145.1. ^{29}Si NMR ($CDCl_3$): δ −17.5. HRMS: m/z 312.1339 (M^+, calcd for $C_{22}H_{20}Si$ 312.1334).

6d: colorless oil. ^1H NMR ($CDCl_3$): δ 0.33 (d, J = 4 Hz, 3 H), 2.18 (dd, J = 5 and 15 Hz, 1 H), 2.31 (d, J = 15 Hz, 1 H), 4.42 (m, 1 H), 7.17−7.31 (m, 4 H), 7.48 (m, 1 H), 7.59 (m, 2 H), 7.69 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −7.04, 18.6, 126.2, 126.4, 126.6, 127.6, 128.0, 130.7, 131.2, 132.4, 133.6, 135.4, 137.6, 144.8. ^{29}Si NMR ($CDCl_3$): δ −25.8. IR (neat): ν_{Si-H} 2120 cm^{-1}. HRMS: m/z 210.0897 (M^+, calcd for $C_{14}H_{14}Si$ 210.0865).

6e: colorless solid, mp 75−76 °C. ^1H NMR ($CDCl_3$): δ 2.48 (dd, J = 15 and 2 Hz, 1 H), 2.53 (dd, J = 15 and 4 Hz, 1 H), 4.91(dd, J = 2 and 4 Hz, 1 H), 7.16−7.33 (m, 6 H), 7.38 (m, 1 H), 7.47−7.52 (m, 4 H), 7.64 (m, 1 H), 7.74 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 18.2, 126.3, 126.7, 127.8, 128.0, 128.1, 130.1, 130.8, 131.0, 131.5, 132.7, 134.6, 134.9, 135.2, 137.8, 145.1, and one carbon is overlapped elsewhere. ^{29}Si NMR ($CDCl_3$): δ −26.0. IR (neat): ν_{Si-H} 2131 cm^{-1}. HRMS: m/z 272.1012 (M^+, calcd for $C_{19}H_{16}Si$ 272.1021).

6f: colorless oil. ^1H NMR ($CDCl_3$): δ 0.28 (s, 6 H), 2.23 (s, 2 H), 7.21−7.27 (m, 2 H), 7.30 (m, 1 H), 7.36 (m, 1 H), 7.53 (m, 1 H), 7.60 (m, 1 H), 7.66 (m, 1 H), 7.75 (d, J = 8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ −4.37 (2 C), 21.3, 126.11, 126.13, 126.6, 127.5, 127.9, 130.2, 131.2, 132.5, 135.5, 136.2, 137.6, 144.5. ^{29}Si NMR ($CDCl_3$): δ −10.6. HRMS: m/z 224.1010 (M^+, calcd for $C_{15}H_{16}Si$ 224.1021). Anal. Calcd for $C_{15}H_{16}Si$: C, 80.30; H, 7.19. Found: C, 80.82; H, 7.28.

9-Methoxy-9,10-dihydro-9-silaphenanthrene Derivatives 8b and 8c. An authentic sample of the methoxysilane **8b** was prepared as follows. A mixture of the compound **6d** (1.05 g, 5.00 mmol) and $PdCl_2$ (44.3 mg, 0.250 mmol) in CCl_4 (5 mL) was refluxed for 1 h. The insoluble materials were filtered, and to the filtrate was added a solution of Et_3N (758 mg, 7.50 mmol) in methanol (12.5 mL) over a period of 140 min. The reaction mixture was washed with water and dried over $MgSO_4$. After removal of the solvent, bulb-to-bulb distillation (150 °C/0.4 mmHg) of the residue gave the oily **8b** in 76% yield. ^1H NMR ($CDCl_3$): δ 0.37 (s, 3 H), 2.11 (d, J = 15 Hz, 1 H), 2.47 (d, J = 15 Hz, 1 H), 3.29 (s, 3 H), 7.19 (m, 1 H), 7.22−7.28 (m, 2 H), 7.34 (m, 1 H), 7.53 (m, 1 H), 7.62 (m, 1 H), 7.64 (m, 1 H), 7.74 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −5.07, 21.1, 51.5, 126.3, 126.4, 126.7, 127.7, 128.0, 131.1, 131.6, 132.3, 132.7, 135.0, 137.3, 145.2. ^{29}Si NMR ($CDCl_3$): δ −0.24. HRMS: m/z 240.0945 (M^+, calcd for $C_{15}H_{16}OSi$ 240.0970).

9-Methoxy-9-phenyl-9,10-dihydro-9-silaphenanthrene (**8c**) was similarly prepared from the compound **6e** in 96% yield as a colorless oil, bp 200 °C/0.2 mmHg. ^1H NMR ($CDCl_3$): δ 2.46 (d, J = 15 Hz, 1 H), 2.61 (d, J = 15 Hz, 1 H), 3.43 (s, 3 H), 7.19 (m, 1 H), 7.23−7.36 (m, 5 H), 7.40 (m, 1 H), 7.51−7.55 (m, 2 H), 7.56−7.59 (m, 2 H), 7.66 (m, 1 H), 7.77 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 20.3, 51.9, 126.3, 126.6, 126.7, 127.8, 127.9, 128.0, 130.2, 131.2, 131.3, 131.8, 132.9, 133.8, 134.5, 134.6, 137.4, 145.8. ^{29}Si NMR ($CDCl_3$): δ −11.2. HRMS: m/z 302.1082 (M^+, calcd for $C_{20}H_{18}OSi$ 302.1127).

Copyrolysis of Allylsilane 6b and MeOH(D). A solution of the allylsilane **6b** (105 mg, 0.420 mmol) in methanol (2.04 g, 63.8 mmol) was pyrolyzed by dropwise addition over a period of 55 min through a nitrogen flow (30 mL/min) vertical quartz tube (30 × 600 mm) packed with quartz glass wool (30 mm) and heated to 600 °C in a tube furnace. The GC analysis of the pyrolysate trapped at 77 K using tetradecane as an internal standard showed the formation of 9-methoxy-9-methyl-9,10-dihydro-9-silaphenanthrene (**8b**) in 48% yield based on the recovered **6b** (12%).

A similar treatment of the allylsilane **6b** (105 mg, 0.420 mmol) in MeOD (2.01 g, 62.8 mmol) gave 9-methoxy-9-methyl-9,10-dihydro-9-silaphenanthrene-10-*d* (**8b′**) in 30% yield based on the recovered **6b** (12%). The analytical sample was obtained by bulb-to-bulb distillation (150 °C/0.4 mmHg) followed by repeated chromatography on ODS using methanol as an eluent. ^1H NMR ($CDCl_3$): δ 0.37 and 0.38 (2 s, 3 H), 2.09 (s, 0.5 H), 2.45 (s, 0.5 H), 3.29 and 3.31 (2 s, 3 H), 7.19 (m, 1 H), 7.23−7.30 (m, 2 H), 7.34 (m, 1 H), 7.53 (m, 1 H), 7.62 (m, 1 H), 7.64 (m, 1 H), 7.74 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −5.09 and −5.07 (2 s, 1 C), 20.6 and 20.7 (2 t, J = 19 Hz, 1 C), 51.5, 126.3, 126.41 and 126.43 (2 s, 1 C), 126.7, 127.7, 128.0, 131.1, 131.57 and 131.61 (2 s, 1 C), 132.27 and 132.31 (2 s, 1 C), 132.7

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and 132.8 (2 s, 1 C), 135.00 and 135.04 (2 s, 1 C), 137.3, 145.3. HRMS: *m*/*z* 241.1013 (M^+, calcd for $C_{15}H_{15}DOSi$ 241.1033).

Copyrolysis of Allylsilane 6c and MeOH(D). A solution of the allylsilane **6c** (144 mg, 0.462 mmol) in methanol (2.04 g, 63.8 mmol) and cyclohexane (2 mL) was pyrolyzed at 600 °C. The GC analysis of the pyrolysate showed the formation of 9-methoxy-9-phenyl-9,10-dihydro-9-silaphenanthrene (**8c**) in 41% yield based on the recovered **6c** (12%).

A similar treatment of the allylsilane **6c** (101 mg, 0.324 mmol) in MeOD (2.02 g, 61.2 mmol) gave 9-methoxy-9-phenyl-9,10-dihydro-9-silaphenanthrene-10-*d* (**8c′**) in 45% yield based on the recovered **6c** (6%). The analytical sample was obtained by bulb-to-bulb distillation (200 °C/0.2 mmHg) followed by repeated chromatography on ODS using methanol as an eluent. ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 0.5 H), 2.59 (s, 0.5 H), 3.43 and 3.45 (2 s, 3 H), 7.20 (m, 1 H), 7.24−7.37 (m, 5 H), 7.41 (m,1 H), 7.51−7.60 (m, 4 H), 7.67 (m, 1 H), 7.78 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 19.9 and 20.0 (2 t, $J = 19$ Hz, 1 C), 51.9 and 52.0 (2 s, 1 C), 126.3, 126.6, 126.7, 127.86, 127.92 (2 C), 128.0, 130.2, 131.14 and 131.17 (2 s, 1 C), 131.3, 131.79 and 131.83 (2 s, 1 C), 132.93 and 132.97 (2 s, 1 C), 133.8 and 133.9 (2 s, 1 C), 134.44 and 134.48 (2 s, 1 C), 134.54, 134.59, 137.37 and 137.39 (2 s, 1 C), 145.8. HRMS: *m*/*z* 303.1171 (M^+, calcd for $C_{20}H_{17}DOSi$ 303.1190).

Copyrolysis of Allylsilane 6a and MeOH(D). A solution of the allylsilane **6a** (106 mg, 0.449 mmol) in methanol (2.02 g, 63.1 mmol) was pyrolyzed at 600 °C. The pyrolysate was treated with 0.82 M MeMgI in ether (6.10 mL, 5.00 mmol) at room temperature overnight. After usual workup, the GC analysis of the reaction mixture showed the formation of **6d** (19%) and **6f** (3%) based on the recovered **6a** (3%).

A similar treatment of the allylsilane **6a** (103 mg, 0.436 mmol) in MeOD (2.05 g, 62.1 mmol) gave 9-methyl-9,10-dihydro-9-silaphenanthrene-10-*d* (**6d′**) in 27% yield based on the recovered **6a** (6%). The analytical sample was obtained by repeated chromatography on silica gel (hexane) followed by ODS using methanol as an eluent. ^{1}H NMR ($CDCl_3$): δ 0.34 and 0.35 (2 d, $J = 4$ and 3 Hz, 3 H), 2.18 (d, $J = 5$ Hz, 0.5 H), 2.31 (s, 0.5 H), 4.42 (m, 1 H), 7.18−7.34 (m, 4 H), 7.50 (m, 1 H), 7.58−7.63 (m, 2 H), 7.70 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ −7.05 and −7.04 (2 s, 1 C), 18.27 and 18.30 (2 t, $J = 19$ Hz, 1 C), 126.2, 126.5, 126.6, 127.6, 128.0, 130.7, 131.21 and 131.24 (2 s, 1 C), 132.3 and 132.4 (2 s, 1 C), 133.6 and 133.7 (2 s, 1 C), 135.32 and 135.35 (2 s, 1 C), 137.7, 144.8. HRMS: *m*/*z* 211.0937 (M^+, calcd for $C_{14}H_{13}DSi$ 211.0928).

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