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Silicon–carbon unsaturated compounds

XLVI*. Nickel-catalyzed reaction of 2-tolyl- and 2-phenyl-2-(phenylethynyl)hexamethyltrisilanes in the presence of 2,3-dimethylbutadiene and dicyclopentadiene

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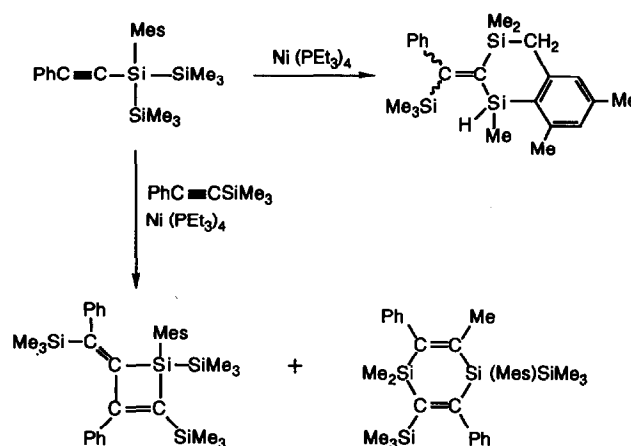
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Abstract

The reaction of 2-phenyl-2-(phenylethynyl)-hexamethyltrisilane (**1a**) with 2,3-dimethylbutadiene in the presence of Ni(cod)₂ at 200°C for 20 h gave 1-[2,3-dimethyl-4-(trimethylsilyl)-2-butenyl]-1-phenyl-1-(phenylethynyl)trimethyldisilane and bis[2,3-dimethyl-4-(trimethylsilyl)-2-butenyl]phenyl(phenylethynyl)silane, while treatment of **1a** with dicyclopentadiene in the presence of Ni(cod)₂ gave an isomerization product, 1-phenyl-1,2-bis(trimethylsilyl)-1-silaindene. Similar reactions of 2-phenylethynyl-2-*o*-tolyl-hexamethyltrisilane, 2-phenylethynyl-2-*m*-tolylhexamethyltrisilane, and 2-phenylethynyl-2-*p*-tolylhexamethyltrisilane are also described.

1. Introduction

We have found that the nickel-catalyzed reaction of phenylethynylpolysilanes affords silapropadiene–nickel complexes, nickelasilacyclobutenes, and nickeladisilacyclopentenes as reactive intermediates [1–4]. The reaction course leading to the final products from these intermediates is remarkably affected by substituents on silicon atoms of the starting phenylethynylpolysilanes, as well as the presence of trapping agents in the reaction system. For example, treatment of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane with the tetrakis(triethylphosphine)nickel(0) catalyst in the presence of phenyl(trimethylsilyl)acetylene affords 1-mesityl-3-phenyl-2-[phenyl(trimethylsilyl)methylene]-1,4-bis(trimethylsilyl)-1-silacyclobut-3-ene and 1-mesityl-4,4,6-trimethyl-2,5-diphenyl-1,3-bis(trimethylsilyl)-1,4-disilacyclohexa-2,5-diene, while the same reaction in the absence of the acetylene leads to C–H bond activation of a methyl group on the mesityl ring to give two



isomers of a 5,6-benzo-1,3-disilacyclohexane derivative [3].

In order to learn more about the chemical behaviour of Ni-containing reactive intermediates, we have investigated the bis(1,5-cyclooctadiene)nickel(0)-catalyzed reaction of 2-phenyl-2-(phenylethynyl)hexamethyltrisilane (**1a**), 2-phenylethynyl-2-*o*-tolylhexamethyltrisilane (**1b**), 2-phenylethynyl-2-*m*-tolylhexa-

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methyltrisilane (**1c**), and 2-phenylethynyl-2-*p*-tolyl-hexamethyltrisilane (**1d**) in the presence of 2,3-dimethylbutadiene, dicyclopentadiene, and norbornadiene.

2. Results and discussion

The nickel-catalyzed reaction of trisilanes **1a–d** was carried out in a degassed sealed tube. When **1a** was treated with 5 molar equiv. of 2,3-dimethylbutadiene in the presence of 8 mol% of bis(1,5-cyclooctadiene) nickel(0) at 200°C for 20 h, 1-[2,3-dimethyl-4-(trimethylsilyl)-2-butenyl]-1-phenyl-1-(phenylethynyl)trimethyl-disilane (**2a**) and bis[2,3-dimethyl-4-(trimethylsilyl)-2-butenyl]phenyl(phenylethynyl)silane (**3a**) were obtained in 18% and 20% yields, respectively, together with 23% of the starting compound **1a**, while the reaction of **1b** using 4 molar equiv. of dimethylbutadiene in the presence of 10 mol% of the catalyst at 200°C for 20 h gave 1-[2,3-dimethyl-4-(trimethylsilyl)-2-butenyl]-1-phenylethynyl-1-*o*-tolyltrimethyl-disilane (**2b**) and bis[2,3-dimethyl-4-(trimethylsilyl)-2-butenyl](phenylethynyl)-*o*-tolylsilane (**3b**) in 18% and 42% yields, respectively, in addition to 5% of the starting compound **1b** (Table 1).

In marked contrast to these experiments, the reaction of **1a–d** with dicyclopentadiene as the diene in the presence of the same catalyst led only to the respective isomerization products. Thus, when **1a** was treated with 3 molar equiv. of dicyclopentadiene and 6 mol% of Ni(cod)₂ at 250°C for 20 h, 1-phenyl-1,2-bis(trimethylsilyl)-1-silaindene (**4a**) was obtained in 19% yield as the sole volatile product, but no reaction was observed at 190°C for 20 h. Similarly, in the reaction of tolyl derivatives **1b–d**, silaindenes were obtained in much higher yields. Thus, the reaction of **1b** with a catalytic amount of Ni(cod)₂ and 2 molar equiv. of dicyclopentadiene at 180°C for 20 h afforded 1-*o*-tolyl-1,2-bis(trimethylsilyl)-1-silaindene (**4b**) in 76% yield, together with 19% of **1b**. As reported previously [4], the reaction

of **1b** with a catalytic amount of Ni(PEt₃)₄ results in C–H bond activation of a methyl group on the tolyl ring to give a 5,6-benzo-1,3-disilacyclohexane derivative. The reaction of **1b** with Ni(cod)₂, however, does not afford such a product but produces only isomerization product **4b**. The reaction of **1c** at 250°C and **1d** at 150°C produced 1-*m*-tolyl-1,2-bis(trimethylsilyl)-1-silaindene (**4c**) and 1-*p*-tolyl-1,2-bis(trimethylsilyl)-1-silaindene (**4b**) in 45% and 56% yield, respectively. In these reactions, cyclopentadiene formed thermally from dicyclopentadiene may act as the ligand for the nickel catalyst leading to silaindenes. Silaindenes **4b–d** were also obtained when norbornadiene was used as the diene, but the yields were much lower than those in the reaction with dicyclopentadiene. It is worth noting that the isomerization reaction of *o*- and *p*-tolyl derivatives **1b** and **1d** proceeds at lower temperatures than the reaction of phenyl and *m*-tolyl derivatives **1a** and **1c**. This may be ascribed to increasing electron density on the silicon atoms with electron-donating *o*- and *p*-tolyl substituents.

In order to trap the reactive intermediates leading to silaindenes, the Ni-catalyzed reaction of **1b** was carried out in the presence of 1 molar equiv. of dicyclopentadiene and 3 molar equiv. of phenyl(trimethylsilyl)acetylene at 190°C for 20 h. Interestingly, the presence of phenyl(trimethylsilyl)acetylene in the reaction system of **1b** completely suppressed the formation of the silaindene derivative, but afforded 1-[1-phenyl-2,2-bis(trimethylsilyl)ethenyl]-1-phenylethynyl-1-*o*-tolyl-trimethyl-disilane (**5b**) in 21% yield, together with 63% of the unreacted starting compound **1b**. That all products obtained here are formed from the nickel-catalyzed reaction, but not from the thermal reaction is shown by the fact that heating **1c** and dicyclopentadiene in the absence of the nickel catalyst at 250°C for 20 h affords non-volatile products. In this reaction, 33% of the starting compound **1c** was recovered unchanged.

Scheme 1 illustrates a possible mechanism leading

TABLE 1. Nickel-catalyzed reaction of trisilanes in the presence of dienes

Trisilane	Catalyst (mol%) ^a	Diene (equiv.) ^a	Temperature (°C)	Time (h)	Products (%)
1a	Ni(cod) ₂ (8.3)	DMB ^b (5.2)	200	20	1a (23), 2a (18), 3a (20)
1b	Ni(cod) ₂ (9.9)	DMB (4.3)	200	20	1b (5), 2b (18), 3b (42)
1a	Ni(cod) ₂ (2.9)	DCP ^c (0.8)	190	20	No reaction
1a	Ni(cod) ₂ (5.5)	DCP (2.8)	250	20	4a (19)
1b	Ni(cod) ₂ (8.0)	DCP (2.2)	180	20	1b (19), 4b (76)
1c	Ni(cod) ₂ (5.1)	DCP (2.7)	250	20	1c (28), 4c (45)
1d	Ni(cod) ₂ (5.1)	DCP (3.0)	150	20	4d (56)
1b	Ni(cod) ₂ (7.3)	NBD ^d (1.0)	190	20	1b (17), 4b (26)
1c	Ni(cod) ₂ (5.4)	NBD (3.5)	250	20	4c (29)
1d	Ni(cod) ₂ (5.5)	NBD (1.2)	140	20	4d (29)
1b	Ni(cod) ₂ (10.2)	DCP (1.0), PTA ^e (3.0)	190	20	1b (63), 5b (21)

^a Amounts are shown relative to trisilane. ^b 2,3-Dimethylbutadiene. ^c Dicyclopentadiene. ^d Norbornadiene. ^e Phenyl(trimethylsilyl)acetylene.

to the observed products. The formation of **2a**, **2b**, **3a**, **3b**, and **5b** is understood in terms of Si-Si bond activation with the nickel catalyst, Ni(cod)₂ to give an intermediate **A**. The intermediate **A** can be trapped with dimethylbutadiene or phenyl(trimethylsilyl)acetylene to give the doubly silylated olefinic products. The mechanism also involves the isomerization of **A** to a nickelasilacyclobutene (**C**) via a silapropadiene-nickel complex (**B**). The silaindenes **4a-d** are probably formed by activation of a C-H bond of the phenyl group in **C**, followed by reductive elimination of nickel species. The intermediate formation of **A**, **B**, and **C** has been proposed previously. Moreover, the fact that addition of phenyl(trimethylsilyl)acetylene to the reaction system of **1b** interferes with the formation of silaindene **4b** and gives an insertion product **5b** supports this mechanism.

The structures of the products were verified by spectrometric analysis, as well as by elemental analysis. For example, the ¹³C NMR spectrum of **2b** shows signals at δ -1.24, -0.56 (two SiMe₃); 20.70, 23.58, 26.38 (three Me); 21.15, 22.95 (two CH₂); 92.24, and 110.10 ppm (C≡C), together with resonances due to sp² carbons (seven HC and five C), suggesting the presence of phenyl, tolyl, and olefinic units. The ¹H NMR spectrum of **2b** reveals five singlet resonances at δ 0.00, 0.22 (two SiMe₃), 1.61, 1.68 (two Me), and 2.54 ppm (*o*-Me), four doublet resonances at δ 1.47, 1.59, 1.95, and 2.04 ppm (two isolated CH₂), and multiplet resonances at δ 7.15-7.84 ppm (ring 9H), in agreement with the structure of **2b**.

¹H NMR chemical shifts for **4b** and **5b** are shown in Fig. 1. As expected, an ¹H-¹H COSY experiment for **4b** at 400 MHz clearly revealed the interaction between adjacent protons (H_a to H_d and H_e to H_h). The structure was also confirmed by NOE-FID difference

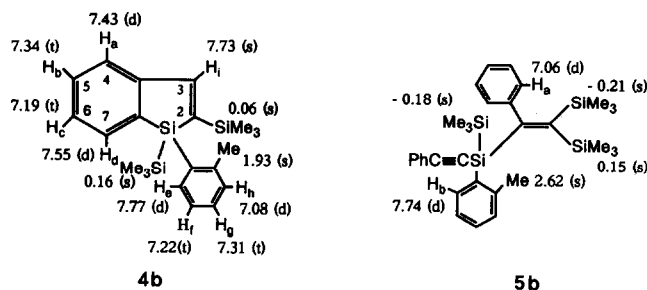


Fig. 1. ¹H NMR chemical shifts of **4b** and **5b**.

experiments at 270 MHz. Saturation of trimethylsilyl protons (CSiMe₃) at δ 0.06 ppm caused strong enhancement of protons (SiSiMe₃, *o*-Me, and H_i) at δ 0.16, 1.93, and 7.73 ppm, while irradiation of the trimethylsilyl protons (SiSiMe₃) at δ 0.16 ppm led to positive NOE of protons (CSiMe₃, *o*-Me, H_d, and H_e) at δ 0.06, 1.93, 7.55 and 7.77 ppm. Irradiation of *o*-Me protons at δ 1.93 ppm induced enhancement of the signals (CSiMe₃, SiSiMe₃, H_h, H_d, and H_i) at δ 0.06, 0.16, 7.08, 7.55, and 7.73 ppm. Saturation of the protons (H_h, H_d, and H_i) at 7.08, 7.55, and 7.73 ppm led to positive NOE of the signals (H_g, H_c, and H_a) at δ 7.31, 7.19, and 7.43 ppm, respectively.

For **5b**, irradiation of trimethylsilyl protons at δ 0.15 ppm caused positive NOE of protons (CSiMe₃, *o*-Me, and H_b) at δ -0.21, 2.62, and 7.74 ppm. Irradiation of trimethylsilyl protons at δ -0.18 ppm caused strong enhancement of signals (*o*-Me, H_a, and H_b) at δ 2.62, 7.06, and 7.74 ppm, while saturation of trimethylsilyl protons at δ -0.21 ppm led to positive NOE of signals (CSiMe₃ and H_a) at δ 0.15 and 7.06 ppm. Irradiation of *o*-methyl protons at δ 2.62 ppm caused enhancement of signals (SiSiMe₃ and CSiMe₃) at δ -0.18 and 0.15 ppm. All these results are consistent with the structure proposed for **5b**.

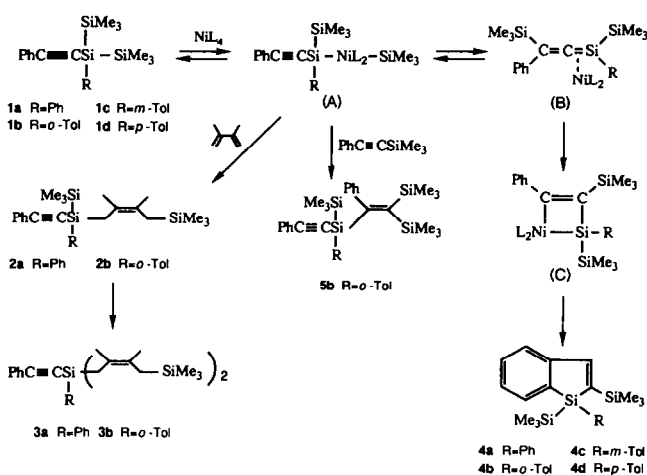
3. Experimental details

3.1. General

All reactions for the synthesis of the starting compounds **1a-d** were carried out under a nitrogen atmosphere. The synthesis of **1a** and **1b** has been reported previously [4]. ¹H NMR, ¹³C NMR, and ²⁹Si NMR spectra were determined using a JEOL Model EX-270 spectrometer. Mass spectra were recorded on a Shimadzu Model GC-MS-QP 1000. Infrared spectra were recorded on a Perkin-Elmer 1600-FT-IR spectrometer.

3.2. Preparation of 2-phenylethynyl-2-*m*-tolylhexamethyltrisilane (**1c**)

To a solution of 9.87 g (40.2 mmol) of 2,2-dichlorohexamethyltrisilane in 30 ml of ether, was added 50 ml



Scheme 1.

of an ether solution of *m*-tolyllithium prepared from *m*-bromotoluene (40.2 mmol) and lithium at room temperature, and the solution was stirred overnight. To this, a solution of phenylethynyllithium prepared from 50 ml of a THF solution of phenylacetylene (4.08 g, 40.2 mmol) and 67 ml of a butyllithium/hexane solution (40 mmol) was added slowly under ice cooling. The mixture was stirred at room temperature overnight and then hydrolyzed with water. The organic layer was separated and washed with water, and dried over anhydrous magnesium sulphate. The solvents were evaporated off and the product **1c** was isolated by distillation followed by MPLC: b.p. 121°C/1 mmHg: $^1\text{H NMR}$ (CDCl_3): δ 0.24 (s, 18H, SiMe_3); 2.36 (s, 3H, *m*-Me); 7.10–7.56 (m, 9H, aromatic ring H): $^{13}\text{C NMR}$ (CDCl_3): δ -1.11 (SiMe); 21.62 (*m*-Me); 88.90, 110.53 ($\text{C}\equiv\text{C}$); 127.71, 128.20, 129.06, 131.72, 131.91, 135.40 (aromatic ring HC); 124.03, 133.80, 137.14 (Ph and *m*-Tol *ipso* C): MS: *m/e* 366 (M^+), 351 ($\text{M}^+ - \text{Me}$), 293 ($\text{M}^+ - \text{SiMe}_3$): IR: 2146 ($\text{C}\equiv\text{C}$) cm^{-1} . Anal. Found: C, 68.71; H, 8.17. $\text{C}_{21}\text{H}_{30}\text{Si}_3$ calc.: C, 68.78; H, 8.25%.

3.3. Preparation of 2-phenylethynyl-2-*p*-tolylhexamethyltrisilane (**1d**)

To a solution of 30 g (122 mmol) of 2,2-dichlorohexamethyltrisilane in 100 ml of ether, was added 60 ml of an ether solution of the Grignard reagent prepared from *p*-bromotoluene (122 mmol) and magnesium at room temperature, and the solution was stirred overnight. To this, a solution of phenylethynyllithium prepared from 50 ml of a THF solution of phenylacetylene (122 mmol) and 122 ml of a butyllithium/hexane solution (122 mmol) was added slowly under ice cooling. The mixture was stirred at room temperature overnight and then hydrolyzed with water. The organic layer was separated and washed with water, then dried over anhydrous magnesium sulphate. The solvents were evaporated off and the product **1d** was isolated by distillation followed by MPLC; b.p. 124–126°C/1 mmHg: $^1\text{H NMR}$ (CDCl_3): δ 0.23 (s, 18H, SiMe_3); 2.35 (s, 3H, *p*-Me); 7.13–7.55 (m, 9H, aromatic ring H): $^{13}\text{C NMR}$ (CDCl_3): δ -1.13 (SiMe); 21.46 (*p*-Me); 89.00, 110.41 ($\text{C}\equiv\text{C}$); 128.14, 128.20, 128.81, 131.91, 134.74 (aromatic ring HC); 124.01, 130.05, 137.93 (Ph and *p*-Tol *ipso* C): MS: *m/e* 366 (M^+), 351 ($\text{M}^+ - \text{Me}$), 293 ($\text{M}^+ - \text{SiMe}_3$): IR: 2146 cm^{-1} . Anal. Found: C, 68.78; H, 8.20. $\text{C}_{21}\text{H}_{30}\text{Si}_3$ calc.: C, 68.78; H, 8.25%.

3.4. Nickel-catalyzed reaction of trisilanes

All nickel-catalyzed reactions of trisilanes **1a–d** were carried out in a degassed sealed tube (1.0 cm \times 20 cm). Trisilane (0.5–1 mmol) was heated together with a given amount of bis(1,5-cyclooctadiene)nickel(0) catalyst and diene under the conditions shown in Table 1.

Products were analyzed by GLC using 2% OV-17 as the column and yields were determined using pentadecane as internal standard. Products **2a**, **2b**, **3a**, **3b**, **4a–d**, and **5b** were isolated either by medium-pressure liquid chromatography on silica gel or gel-permeation chromatography using Shodex GPC H-2001 and 2002 as the columns.

For **2a**: $^1\text{H NMR}$ (CDCl_3): δ 0.01 (s, 9H, SiMe_3); 0.17 (s, 9H, SiMe_3); 1.44 (d, 1H, HCH , $J = 14$ Hz); 1.56 (d, 1H, HCH , $J = 14$ Hz); 1.60 (s, 3H, Me); 1.68 (s, 3H, Me); 1.92 (d, 1H, HCH , $J = 14$ Hz); 1.98 (d, 1H, HCH , $J = 14$ Hz); 7.31–7.66 (m, 10H, ring H): $^{13}\text{C NMR}$ (CDCl_3): δ -1.94 (SiMe_3); -0.50 (SiMe_3); 20.85, 21.13 (CH_2); 22.73, 26.38 (Me); 91.07, 109.52 ($\text{C}\equiv\text{C}$); 127.75, 128.23, 128.39, 128.73, 131.88, 134.54 (ring HC); 121.19, 123.67, 132.63, 135.81 (*ipso* and olefinic C): MS: *m/e* 434 (M^+): IR: 2150 ($\text{C}\equiv\text{C}$) cm^{-1} . Anal. Found: C, 71.75; H, 8.77. $\text{C}_{26}\text{H}_{38}\text{Si}_3$ calc.: C, 71.82; H, 8.81%.

For **2b**: $^1\text{H NMR}$ (CDCl_3): δ 0.00 (s, 9H, SiMe_3); 0.22 (s, 9H, SiMe_3); 1.47 (d, 1H, HCH , $J = 14$ Hz); 1.59 (d, 1H, HCH , $J = 14$ Hz); 1.61 (s, 3H, Me); 1.68 (s, 3H, Me); 1.95 (d, 1H, HCH , $J = 14.0$ Hz); 2.04 (d, 1H, HCH , $J = 14.0$ Hz); 2.54 (s, 3H, *o*-Me); 7.15–7.84 (m, 9H, ring H): $^{13}\text{C NMR}$ (CDCl_3): δ -1.24, -0.56 (SiMe_3); 20.70, 23.58 (Me); 21.15, 22.95 (CH_2); 26.38 (*o*-Me); 92.24, 110.10 ($\text{C}\equiv\text{C}$); 125.01, 128.21, 128.28, 129.18, 129.52, 131.70, 136.26 (ring HC); 121.55, 123.70, 134.25, 134.41, 143.36 (*ipso* and olefinic C): $^{29}\text{Si NMR}$: δ (CDCl_3) -35.32, -17.01, 0.96: MS: *m/e* 448 (M^+), 375 ($\text{M}^+ - \text{SiMe}_3$), 354: IR: 2152 ($\text{C}\equiv\text{C}$) cm^{-1} . Anal. Found: C, 72.17; H, 8.89. $\text{C}_{27}\text{H}_{40}\text{Si}_3$ calc.: C, 72.25; H, 8.98%.

For **3a**: $^1\text{H NMR}$ (CDCl_3): δ -0.09 (s, 18H, SiMe_3); 1.31 (d, 2H, HCH , $J = 14.0$ Hz); 1.46 (d, 2H, HCH , $J = 14.0$ Hz); 1.51 (s, 6H, Me); 1.54 (s, 6H, Me); 1.69 (d, 2H, HCH , $J = 14.0$ Hz); 1.85 (d, 2H, HCH , $J = 14.0$ Hz); 7.17–7.63 (m, 10H, ring H): $^{13}\text{C NMR}$ (CDCl_3): δ -0.50 (SiMe); 20.85, 21.21 (Me); 23.79, 26.11 (CH_2); 91.97, 107.76 ($\text{C}\equiv\text{C}$); 127.57, 128.23, 128.52, 129.18, 131.90, 134.38 (ring HC); 120.70, 123.47, 123.94, 136.48 (*ipso* and olefinic C): MS: *m/e* 516 (M^+), 501 ($\text{M}^+ - \text{Me}$), 443 ($\text{M}^+ - \text{SiMe}_3$): IR: 2160 cm^{-1} . Anal. Found: C, 74.54; H, 9.32. $\text{C}_{32}\text{H}_{48}\text{Si}_3$ calc.: C, 74.34; H, 9.36%.

For **3b**: $^1\text{H NMR}$ (CDCl_3): δ -0.01 (s, 18H, SiMe_3); 1.42 (d, 2H, HCH , $J = 14$ Hz); 1.57 (d, 2H, HCH , $J = 14$ Hz); 1.61 (s, 6H, Me); 1.64 (s, 6H, Me); 1.84 (d, 2H, HCH , $J = 14$ Hz); 2.02 (d, 2H, HCH , $J = 14$ Hz); 2.59 (s, 3H, *o*-Me); 7.13–7.89 (m, 9H, ring H): $^{13}\text{C NMR}$ (CDCl_3): δ -0.52 (SiMe_3); 20.70, 26.15 (Me); 21.26, 23.90 (CH_2); 29.69 (*o*-Me); 92.89, 108.14 ($\text{C}\equiv\text{C}$); 123.97, 124.98, 128.21, 128.39, 129.51, 129.79, 131.73 (ring HC); 121.11, 123.68, 134.84, 136.08, 143.40 (*ipso* and olefinic C): MS: *m/e* 530 (M^+): IR: 2160 ($\text{C}\equiv\text{C}$)

cm⁻¹. Anal. Found: C, 74.50; H, 9.47. C₃₃H₅₀Si₃ calc.: C, 74.64; H, 7.49%.

For **4a**: ¹H NMR (CDCl₃): δ 0.12 (s, 9H, SiMe₃); 0.20 (s, 9H, SiMe₃); 7.18–7.63 (m, 9H, aromatic ring H); 7.72 (s, 1H, C(3)H): ¹³C NMR (CDCl₃): δ -1.24, 0.13 (SiMe); 124.31, 126.70, 127.98, 129.15, 129.25, 132.70, 135.31, 156.78 (ring HC); 133.85, 140.70, 145.79, 151.05 (*ipso*, C(2), and fused C): MS: *m/e* 352 (M⁺), 337 (M⁺ - Me), 297 (M⁺ - SiMe₃). Anal. Found: C, 68.22; H, 8.04. C₂₀H₂₈Si₃ calc.: C, 68.11; H, 8.00%.

For **4b**: ¹H NMR (CDCl₃): δ 0.06 (s, 9H, SiMe₃); 0.16 (s, 9H, SiMe₃); 1.93 (s, 3H, *o*-Me); 7.02–7.81 (m, 8H, aromatic ring C); 7.73 (s, 1H, C(3)H): ¹³C NMR (CDCl₃): δ -1.24, -0.12 (SiMe₃); 21.48 (*o*-Me), 124.49, 125.03, 126.60, 128.86, 129.67, 129.90, 132.27, 137.54, 155.87 (ring HC); 132.74, 141.60, 145.82, 146.16, 150.44 (*ipso*, C(2), and fused C): MS: *m/e* 366 (M⁺), 351 (M⁺ - Me), 293 (M⁺ - SiMe₃). Anal. Found: C, 68.68; H, 8.17. C₂₁H₃₀Si₃ calc.: C, 68.78; H, 8.25%.

For **4c**: ¹H NMR (CDCl₃): δ 0.13 (s, 9H, SiMe₃); 0.18 (s, 9H, SiMe₃); 2.30 (s, 3H, *m*-Me); 7.09–7.62 (m, 8H, aromatic ring C); 7.69 (s, 1H, C(3)H): ¹³C NMR (CDCl₃): δ -1.22, 0.15 (SiMe₃); 21.46 (*m*-Me); 124.30, 126.67, 127.84, 129.08, 130.08, 132.40, 132.70, 135.90, 156.73 (ring HC); 133.51, 137.23, 140.79, 145.82, 151.00 (*ipso*, C(2), and fused C): MS: *m/e* 366 (M⁺), 351 (M⁺ - Me), 293 (M⁺ - SiMe₃). Anal. Found: C, 68.81; H, 8.31. C₂₁H₃₀Si₃ calc.: C, 68.78; H, 8.25%.

For **4d**: ¹H NMR (CDCl₃): δ 0.12 (s, 9H, SiMe₃); 0.18 (s, 9H, SiMe₃); 2.34 (s, 3H, *p*-Me); 7.09–7.63 (m, 8H, aromatic ring C); 7.68 (s, 1H, C(3)H): ¹³C NMR (CDCl₃): δ -1.24, 0.13 (SiMe); 21.51 (*p*-Me), 124.26, 126.65, 128.84, 129.06, 132.65, 135.36, 156.62 (ring HC); 129.90, 139.17, 140.93, 145.98, 151.00 (*ipso*, C(2), and

fused C): MS: *m/e* 366 (M⁺), 351 (M⁺ - Me), 293 (M⁺ - SiMe₃). Anal. Found: C, 68.75; H, 8.25. C₂₁H₃₀Si₃ calc.: C, 68.78; H, 8.25%.

For **5b**: m.p. 98–100.5°C: ¹H NMR (CDCl₃): δ -0.21 (s, 9H, SiMe₃); -0.18 (s, 9H, SiMe₃); 0.15 (SiMe₃); 2.62 (s, 3H, *o*-Me); 7.04–7.77 (m, 14H, aromatic ring C): ¹³C NMR (CDCl₃): δ -1.44, 3.45, 3.78 (SiMe); 24.21 (*o*-Me); 92.20, 111.14 (C≡C); 124.82, 126.43, 127.89, 128.23, 128.37, 128.66, 129.22, 129.92, 131.64, 136.60 (ring HC); 123.88, 134.88, 143.65, 150.42, 166.16, 169.94 (*ipso* and olefinic C): MS: *m/e* 540 (M⁺), 525 (M⁺ - Me), 467 (M⁺ - SiMe₃): IR: 2149 (C≡C) cm⁻¹. Anal. Found: C, 70.88; H, 8.20. C₃₂H₄₄Si₄ calc.: C, 71.03; H, 8.20%.

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References

- 1 M. Ishikawa, S. Matsuzawa, K. Hirotsu, S. Kamitori and T. Higuchi, *Organometallics*, **3** (1984) 1930.
- 2 M. Ishikawa, S. Matsuzawa, T. Higuchi, S. Kamitori and K. Hirotsu, *Organometallics*, **4** (1985) 2040.
- 3 M. Ishikawa, J. Ohshita and Y. Ito, *Organometallics*, **5** (1986) 1518.
- 4 M. Ishikawa, Y. Nomura, E. Tozaki, A. Kunai and J. Ohshita, *J. Organomet. Chem.*, **399** (1990) 205.
- 5 J. Ohshita, Y. Masaoka, M. Ishikawa and T. Takeuchi, *Organometallics*, **12** (1993) 876.