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Note

Synthesis and characterisation of two new binaphthyl trisilanes

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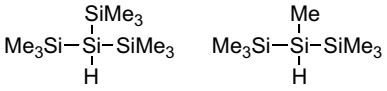
ABSTRACT

The synthesis and characterisation of two binaphthyl trisilanes is described. Reaction between 2,2′-dilithio-1,1′-binaphthyl and 1,3-dichlorohexamethyltrisilane gave 3,3,4,4,5,5-hexamethyl-4,5-dihydro-3*H*-3,4,5-trisilacyclohepta[2,1-a;4,3-a′]binaphthalene (**3**). Compound **3** was characterised by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy and a crystal structure analysis. Reaction between 2,2′-dilithio-1,1′-binaphthyl and 1,3-bis(trifluoromethanesulfonyloxy)-1,1,2,3,3-pentamethyltrisilane, generated *in situ* by treatment of 1,3-diphenyl-1,1,2,3,3-pentamethyltrisilane with trifluormethanesulfonic acid, gave 3,3,4,5,5-pentamethyl-4,5-dihydro-3*H*-3,4,5-trisilacyclohepta[2,1-a;4,3-a′]binaphthalene (**7**). Analysis by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy revealed that **7** had a very similar structure to **3**.

1. Introduction

Chiral silanes are of considerable interest as asymmetric reducing agents, and a number of approaches to these systems have been described [1]. The use of silanes as alternatives to tributyltin hydride in radical chemistry is also growing in popularity, driven by their lower toxicity, ease of separation from products and often greater selectivity [2]. Particularly of note are tris(trimethylsilyl)silane **1** and related trisilanes such as **2**, developed by Chatgilialoglu and coworkers [3,4].



1 **2**

For a silane to be an efficient hydrogen atom donor, the silicon bearing the hydrogen must be attached to two or three other silicon atoms. Whilst there have been reports of chiral stannanes [5] and germanes [6] as potential asymmetric radical reducing agents, chiral versions of **1** and **2** are unknown in the literature.

A potential solution is to incorporate the silane within a 1,1′-binaphthyl framework. 2,2′-Disubstituted-1,1′-binaphthyls are axially-chiral, and are viewed as privileged ligand scaffolds in asymmetric synthesis. When the substituents at the 2 and 2′ positions are oxygen, *e.g.* BINOL [7], or phosphorus, *e.g.* BINAP [8], the resulting binaphthyls have found wide application, and are capable of achieving very high levels of enantiomeric excess, in asymmetric transformations. A small number of chiral silanes are known, in which a single silicon is connected to the binaphthyl framework through carbon [1a,9], nitrogen [10] or oxygen [1a] substituents in the 2 and 2′ positions, although the presence of only one silicon atom in these molecules precludes their use in radical chemistry. The corresponding systems with silicon in the 2 and 2′ positions are virtually unknown [11], with the few examples published similarly incapable of functioning as radical reducing agents.

Herein, we report the first synthesis and structural characterisation of a chiral trisilane based upon the 1,1′-binaphthyl framework.

2. Results and discussion

Since the Si–H bond is relatively reactive and prone to oxidation, we chose to carry out initial studies on a model system **3** that did not contain this functionality. Our retrosynthetic strategy is outlined in Scheme 1, in which the key step is the reaction between 2,2′-dilithio-1,1′-binaphthyl and dichlorotrisilane **4**, itself prepared from 1,3-diphenylhexamethyltrisilane **5** using known chemistry.

1,3-Diphenylhexamethyltrisilane **5** was synthesised from chlorodimethylphenylsilane: reaction with lithium metal gave dimethylphenylsilyllithium which was then added slowly to dichlorodimethylsilane at 0 °C, Scheme 2 [12]. After vacuum distillation, **5** was isolated as a colourless oil containing a small amount of $(PhMe_2Si)_2$ as a contaminant. A second distillation gave pure **5** in 67% yield. In our hands, the published procedure using HCl gas and $AlCl_3$ for cleavage of the silicon-phenyl bonds gave very low yields of the desired compound, which was inseparable from many other products confirmed by GC–MS to be formed by over chlorination

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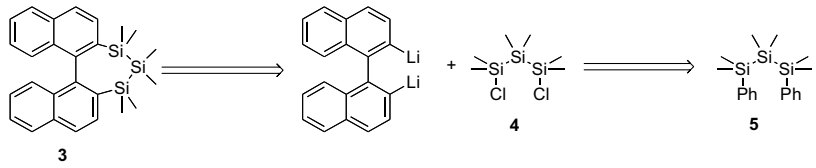
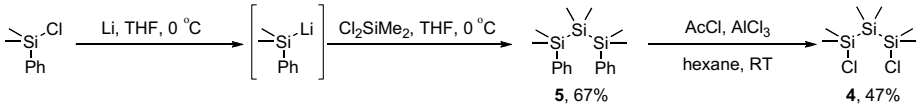


Scheme 1. Retrosynthetic analysis of **3**.



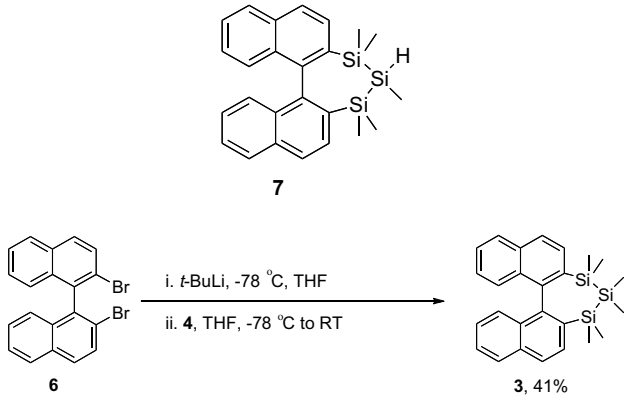
Scheme 2. Preparation of dichlorosilane **4**.

[12]. The transformation could be much more reliably accomplished using acetyl chloride/$AlCl_3$ [13]; after vacuum distillation, **4** was isolated as a colourless oil in 47% yield.

Lithiation of 2,2′-dibromo-1,1′-binaphthyl **6** in THF at −78 °C and addition of 1,3-dichlorohexamethyltrisilane **4** at the same temperature, before allowing the mixture to warm to room temperature, gave trisilane **3** in 41% yield as a white solid after column chromatography, Scheme 3.

Comprehensive NMR experiments were carried out to confirm the identity and structure of **3**. ^{1}H NMR showed three methyl environments (at −0.94, +0.06 and +0.43 ppm) corresponding to two equivalent methyl groups on the central silicon atom and the two distinct methyl environments on each of the flanking silicon atoms. The ^{29}Si NMR displayed two signals (at −20.15 and −40.64 ppm) for the central silicon atom and the two identical flanking silicon atoms. The non-coplanar nature of the two naphthyl rings means that whilst one methyl group lies in the plane of the naphthyl unit to which it is closest, the other methyl group lies out of plane, and face-on to the other naphthyl ring system. The face-on methyl group is shielded by the ring current of the aromatic ring, so resonance is observed at low chemical shift. On the other hand, the edge-on methyl groups are deshielded by the aromatic ring, leading to resonance at higher chemical shift. The face-on/edge-on arrangement of methyl groups was confirmed by nOe experiments. Excitation at the frequency of the peak at +0.43 ppm showed a nOe through to the proton in position 3 (systematic numbering; C6 and C16 crystallographic numbering) of the naphthyl ring, confirming the edge-on arrangement of this methyl group. Excitation at the frequency corresponding to the −0.94 ppm signal showed a small nOe to all aromatic protons, so confirming the face-on nature of this methyl group.

Single crystals of **3** were obtained by slow evaporation of diethyl ether and X-ray crystallography provided a crystal structure in agreement with that suggested by the NMR experiments (see Fig. 1).



Scheme 3. Synthesis of binaphthyl trisilane **3**.

Our second target was **7**, in which the central silicon atom bears a hydrogen substituent. Synthesis of this required trisilane **8**, which was prepared by reaction of $PhMe_2SiLi$, prepared as described previously, with Cl_2MeSiH, affording the product in 64% yield after vacuum distillation, Scheme 4.

The trisilane **8** was accompanied by other unidentified silicon species which were difficult to separate by column chromatography. The yield and purity of **8** was, therefore maximised by following the course of the reaction by analytical HPLC and stopping it before the side-products had formed to a significant extent.

Having obtained a clean sample of **8**, the phenyl groups had to be replaced by leaving groups to generate a species which could be coupled to dilithiobinaphthyl. We expected that the previously employed method using $AlCl_3$ and acetyl chloride to generate silyl chlorides would be problematic since Si–H bonds are known to be cleaved in the presence of $AlCl_3$/HCl [15]. However, there is literature precedent for the replacement of phenyl groups by triflate groups, in the presence of Si–H bonds, using triflic acid [16], and so bis-triflate **9** became our target. Silyl triflates are more prone to hydrolysis than silyl chlorides, so rather than attempting to isolate and purify bis-triflate **9**, we decided to form this reactive species *in situ* and use it immediately (see Scheme 5).

As the lithiation of **6** was carried out in THF, we first attempted the conversion of **8** into triflate **9** in this solvent. However, the reaction failed and starting material was quantitatively recovered. Monitoring the formation of the silyl triflate by ^{1}H NMR in deuterated toluene indicated that conversion to the highly moisture sensitive triflate was very clean and complete within 10 min in this solvent at 0 °C, and so in subsequent experiments **9**, was generated as a solution in toluene and added to a solution of 2,2′-dilithio-1,1′-binaphthyl in THF. The reaction was maintained at −50 °C overnight to afford, after chromatography, trisilane **7** as a colourless oil in 30% yield. Attempts to optimise the yield by variation of the reaction temperature, ratio of reactants and the inclusion of TMEDA were unsuccessful (see Scheme 6).

Crystals of **7** could not be obtained, but ^{1}H, ^{13}C and ^{29}Si NMR spectra confirmed that the structure was similar to **3**. Like **3**, **7** exhibited the same face-on and edge-on arrangement of the methyl groups on the flanking silicon atoms, but since the central silicon atom was now asymmetrically substituted, these methyl groups were diastereotopic, resulting in all five methyl groups being magnetically different and five separate signals being observed. The two face-on methyl groups, shielded by the naphthalene ring current, were observed close together at low chemical shift (at −0.74 and −0.65 ppm), whereas the two edge-on methyl groups, deshielded by the naphthalene ring, were observed close together at higher chemical shift (at 0.41 and 0.53 ppm); the methyl group on the central silicon (at 0.11 ppm) was split into a doublet as a result of coupling to the Si–H. In the same way, the

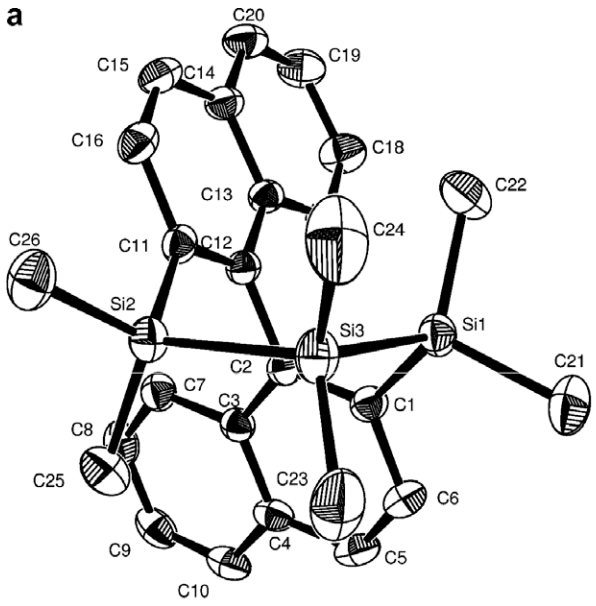
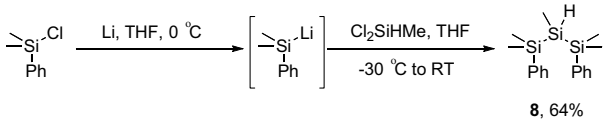
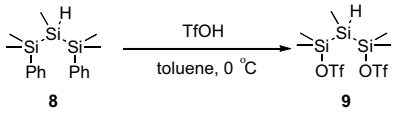


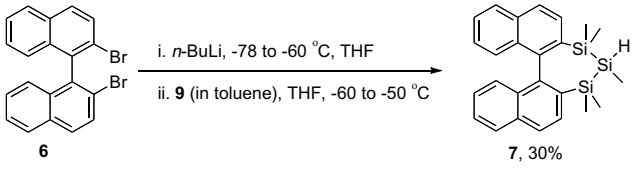
Fig. 1. (a) ORTEP [14] representation of **3**, ellipsoids at 30%. Selected geometry: C(1)–Si(1) = 1.893(2) Å, C(11)–Si(2) = 1.902(2) Å, Si(1)–Si(3) = 2.3365(9) Å, Si(2)–Si(3) = 2.3474(8) Å, C(1)–Si(1)–Si(3) = 103.71(6) °, C(11)–Si(2)–Si(3) = 104.52(6) °, Si(1)–Si(3)–Si(2) = 103.13(3) °, C(11)–Si(2)–Si(3)–Si(1) = 33.48(7) °, C(1)–Si(1)–Si(3)–Si(2) = 38.03(7) °. (b) The nOes observed between the edge-on methyl groups and the naphthyl ring.



Scheme 4. Preparation of trisilane **8**.



Scheme 5.



Scheme 6. Synthesis of binaphthyl trisilane 7.

diastereotopicity of the two flanking silicon atoms resulted in three signals in the ^{1}H-decoupled ^{29}Si spectrum.

In conclusion, we have achieved the synthesis of the first axially-chiral trisilane, based upon the 1,1′-binaphthyl framework. The methyl groups on the flanking silicon atoms adopt edge-on and face-on orientations with respect to the naphthalene rings, reinforcing the chiral environment around the Si–H bond. The synthesis should be amenable to the production of single enantiomers. Murdoch and co-workers have shown that 2,2′-dilithio-1,1′-binaphthyl, prepared from a single enantiomer of 2,2′-dibromo-1,1′-binaphthyl, is configurationally stable at temperatures below −44 °C [17]. As **7** was prepared at −50 °C, access to single enantiomers should be possible starting from enantiomerically pure 2,2′-dibromo-1,1′-binaphthyl. Future work in our laboratory will focus on the synthesis of single enantiomers of **7** and related silanes, and their evaluation as asymmetric reducing agents in radical chemistry.

3. Experimental

3.1. General

3.1.1. Chemicals and reagents

All chemicals and reagents were obtained from commercial sources and were used as supplied, except for THF and toluene which were distilled from sodium-benzophenone ketyl and acetyl chloride which was distilled under argon from PCl_5. Solutions of *n*-BuLi and *t*-BuLi were titrated against *N*-pivaloyl-*o*-toluidine prior to use according to a method developed by Suffert [18]. The term "petrol" refers to the 40–60 °C boiling fraction of petroleum ether.

Thin layer chromatography was carried out on precoated, glass-backed, silica gel plates (silica gel 60, F_{254}, thickness 0.25 mm, supplied by Merck®) and visualisation was achieved using UV light (254/365 nm) or basic $KMnO_4$ solution. Column chromatography was performed using laboratory grade solvents on silica gel 60A (43–63 μm mesh, supplied by Fluorochem®) under pressure applied using hand bellows. Unless noted, all R_f were measured using the column solvent.

All reactions were carried out using oven-dried (150 °C) or flame-dried glassware and were performed under a positive pressure of argon.

3.1.2. Instrumentation

^{1}H- and ^{13}C NMR spectra were recorded on a Bruker AC300 (at 300.13 MHz and 75.47 MHz, respectively), a Bruker AV300 (at 300.13 MHz and 75.48 MHz, respectively), a Bruker AV400 (at 400.08 MHz and 100.60 MHz) or a Bruker DRX500 (at 500.13 MHz and 125.77 MHz). All 75 MHz ^{13}C spectra were recorded using the PENDANT pulse sequence. Where necessary, COSY90, HMBC, HSQC and nOe experiments were carried out to allow unequivocal assignment of signals. ^{29}Si NMR spectra were recorded on a Bruker DRX500 at 99.35 MHz or a Bruker AV400 at 79.48 MHz.

Chemical shifts (δ) are expressed in parts per million (ppm) downfield from tetramethylsilane. Individual spectra were refer-

enced relative to residual solvent. The multiplicity of signals in ^{1}H NMR is expressed as follows: s = singlet, d = doublet, q = quartet, m = multiplet. Coupling constants *J* are reported in Hz. The term "multiplet" or "m" has been used to describe a signal arising from a single nucleus (or more than one magnetically equivalent nuclei) where coupling constants cannot be assigned. The term "envelope" describes a region of the spectrum when signals from non-equivalent nuclei overlap in such a way that coupling constants cannot be assigned. In ^{1}H NMR assignments, the signals are described in the following manner: Chemical shift (relative integration, multiplicity, coupling constant [if applicable], assignment).

Melting points were determined in open glass capillaries using a Stuart Scientific SMP1 apparatus and are uncorrected.

Infra-red spectra were recorded neat or as a film on NaCl using a Perkin–Elmer Paragon 1600 FTIR spectrometer, or as solids on a Shimadzu 8300 FTIR spectrometer.

Elemental analyses were performed on a Carlo Erba EA1110 simultaneous CHNS analyser.

EI mass spectra were recorded on either a VG ProSpec or VG Zabspec instrument at 70 eV. High resolution EI spectra were measured using perfluorokerosene (PFK) as an internal calibrant.

Single crystal diffraction data were recorded at 296(2) K on a Rigaku R-axis II diffractometer equipped with a molybdenum rotating anode source (λ = 0.71069 Å) and an image plate detector system. Structure solution was by direct methods (Molecular Structure Corporation, TEXSAN, Single Crystal Structure Analysis Software, Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1993) and refinement by SHELXL92 (G.M .Sheldrick, SHELXL92, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1993). A riding model was used for the hydrogens with atomic displacement parameters 1.2 times (1.5 times for methyl groups) those of the carbon atoms they are bonded to.

3.2. 1,3-Diphenylhexamethyltrisilane, **5**

To a suspension of hexane-washed lithium shot (5.0 g, 714 mmol) in THF (100 mL) at 0 °C was added chlorodimethylphenylsilane (15 mL, 89 mmol) over 5 min and the mixture was stirred overnight at 0 °C. Dichlorodimethylsilane (5.4 mL, 44.5 mmol) was dissolved in THF (150 mL) in a flask fitted with a dropping funnel and cooled to 0 °C. The deep red phenyldimethylsilyllithium solution was syringed off from the excess lithium and transferred to the dropping funnel. The silyllithium solution was added dropwise to the dichlorodimethylsilane solution over 4 h at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. THF was removed *in vacuo* and diethyl ether (100 mL) was added. The precipitated lithium chloride was filtered off and the diethyl ether solution concentrated *in vacuo* to give a pale brown oil. Distillation under vacuum yielded **5** as a colourless oil (9.80 g, 67%).

B.p. 145–150 °C/0.05 mmHg) (lit.[7] b.p. 117–120 °C/0.05 mmHg); δ_H (300 MHz, $CDCl_3$) 0.20 (6H, s, $SiSi(CH_3)_2Si$), 0.40 (12H, s, 2 × $Si(CH_3)_2Ph$), 7.38–7.44 (6H, envelope, 6 × H_{Ar}), 7.46–7.51 (4H, envelope, 4 × H_{Ar}); δ_C (75 MHz, $CDCl_3$) −6.2 ($SiSi(CH_3)_2Si$), −3.0 ($Si(CH_3)_2Ph$), 128.0 (*C3*), 128.7 (*C4*), 134.0 (*C2*), 139.9 (*C1*); δ_{Si} (100 MHz, $CDCl_3$) −47.7, −18.1; ν_{max} (film, cm^{-1}) 3047 (C–H aromatic), 2955 (C–H), 1427, 1242, 1103, 826, 779, 725, 694, 640; *m*/*z* (EI^+) 328 (13%, $[M]^+$), 193 (51%), 178 (18%), 163 (11%), 135 (100%), 116 (46%), 105 (7%).

3.3. 1,3-Dichlorohexamethyltrisilane, **4**

To a solution of 1,3-diphenylhexamethyltrisilane, **5** (1.75 g, 5.3 mmol) in hexane (40 mL) at −10 °C was added acetyl chloride (0.95 mL, 13.3 mmol) and anhydrous $AlCl_3$ (1.78 g, 13.3 mmol). The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction was monitored by GC to ensure complete consumption of starting silane. Once reaction was complete, the pale yellow hexane layer was removed by syringe from the orange lower layer, which was further extracted with hexane (2 × 5 mL). The combined hexane layers were concentrated *in vacuo* to give a pale brown oil. Two vacuum distillations yielded **4** as a colourless oil (0.61 g, 47%).

B.p. 42–43 °C/0.5 mmHg (lit.[7] b.p. 108 °C/30 mmHg); δ_H (300 MHz, $CDCl_3$) 0.28 (6H, s, $SiSi(CH_3)_2Si$), 0.55 (12H, s, 2 × $Si(CH_3)_2Cl$); δ_C (75 MHz, $CDCl_3$) −7.7 ($SiSi(CH_3)_2Si$), 3.0 ($Si(CH_3)_2Cl$); *m*/*z* (EI^+) 246 (10% $[M]^+$), 244 (12%), 231 (11%), 229 (51%), 211 (6%), 209 (51%), 186 (3%), 165 (12%), 153 (75%), 151 (83%), 131 (61%), 116 (82%), 101 (32%), 93 (84%), 85 (20%), 73 (100%).

3.4. 3,3,4,4,5,5-Hexamethyl-4,5-dihydro-3H-3,4,5-trisilacyclohepta[2,1-a;4,3-a′]binaphthalene, **3**

To a solution of 2,2′-dibromobinaphthyl (470 mg, 1.14 mmol) in THF at −78 °C was added *via* syringe a 1.7 M solution of *t*-BuLi in pentane (1.40 mL, 2.38 mmol). The resulting bright yellow solution was stirred at −78 °C for 90 min after which a solution of 1,3-dichlorohexamethyltrisilane **4** (278 mg, 1.13 mmol) in THF (10 mL) was added. The reaction was maintained at −78 °C for a further 60 min before being allowed to warm to room temperature and stirring overnight. The reaction mixture was poured into NH_4Cl solution (50 mL), extracted with diethyl ether (4 × 50 mL) and the combined diethyl ether layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography yielded **3** (petrol, R_f = 0.55) as colourless, crystalline plates (202 mg, 41%).

M.p. 186–190 °C; δ_H (500 MHz, $CDCl_3$) −0.94 (6H, s, $Si(CH_3)CH_3$-$Si(CH_3)_2Si(CH_3)CH_3$), 0.06 (6H, s, $SiSi(CH_3)_2Si$), 0.43 (6H, s, $Si(CH_3)CH_3Si(CH_3)_2Si(CH_3)CH_3$), 7.03 (2H, d, *J* 8.6, 2 × *H9*), 7.13–7.17 (2H, m, 2 × *H8*), 7.38–7.42 (2H, m, 2 × *H7*), 7.72 (2H, d, *J* 8.3, 2 × *H3*), 7.87 (2H, d, *J* 8.3, 2 × *H6*), 7.92 (2H, d, *J* 8.3, 2 × *H4*); δ_C (75 MHz, $CDCl_3$) −7.3 ($SiSi(CH_3)_2Si$), −4.7 ($Si(CH_3)CH_3Si(CH_3)_2$-$Si(CH_3)CH_3$), −4.0 ($Si(CH_3)CH_3Si(CH_3)_2Si(CH_3)CH_3$), 125.8 (*C7*), 125.9 (*C6*), 126.7 (*C8*), 126.9 (*C4*), 127.7 (*C5*), 130.1 (*C3*), 133.4 (*C4a*), 134.3 (*C8a*), 136.9 (*C2*), 145.5 (*C1*); δ_{Si} (100 MHz, $CDCl_3$) −40.8, −20.4; ν_{max} (solid, cm^{-1}) 3047 (C–H aromatic), 2947 (C–H), 2893 (C–H), 1913 (aromatic overtone), 1551 (C=C aromatic), 1497 (C=C aromatic), 1450, 1404, 1304, 1242, 1142, 1111, 1026, 949, 802, 756, 671, 594, 548; *m*/*z* (EI^+) 426 (50%, $[M]^+$), 411 (5%), 367 (6%), 353 (15%), 337 (6%), 310 (27%), 295 (57%), 278 (21%), 252 (81%), 226 (8%), 200 (3%), 146 (6%), 116 (100%), 101 (23%); HRMS (EI^+). Found: 426.1659. Calc. for $C_{26}H_{30}Si_3$: 426.1655; found: C 73.4, H 7.1, required for $C_{26}H_{30}Si_3$: C 73.2, H 7.1.

Crystal data: $C_{26}H_{30}Si_3$, *F* = 426.77, *T* = 296(2) K, λ = 0.71069 Å, Orthorhombic, *Pbca*, a = 17.5436(11) Å, *b* = 12.8098(8) Å, *c* = 22.0697(15) Å, volume = 4959.7(6) $Å^3$, *Z* = 8, σ_{calc} = 1.143 Mg/m^3, μ = 0.201 mm^{-1}, crystal size = 0.50 × 0.40 × 0.30 mm^3, reflections collected = 27 049, independent reflections = 4480, R_{int} = 0.089, parameters = 269, R_1 = 0.0519, wR_2 = 0.1295 for $I > 2\sigma(I)$, R_1 = 0.0545, wR_2 = 0.1307 for all data.

3.5. 1,3-Diphenyl-1,1,2,3,3-pentamethyltrisilane, **8**

To a solution of dichloromethylsilane (2.70 mL, 26.0 mmol) in THF at −78 °C was added *via* syringe a 1.1 M solution of $PhMe_2SiLi$ (48 mL, 52.8 mmol). The mixture was slowly allowed to warm to room temperature and stirred overnight. THF was removed *in vacuo* and diethyl ether (100 mL) and water (100 mL) were added. The organic phase was further washed with water (2 × 100 mL) and brine (100 mL) before being dried over $MgSO_4$ and concentrated *in vacuo* to yield a pale yellow oil. Kugelrohr distillation (oven temperature 180 °C/1 mmHg) yielded **8** as a colourless oil (5.20 g, 64%).

δ_H (300 MHz, C_6D_6) 0.09 (3H, d, *J* 5.1, Si(H)CH_3), 0.30 (12H, s, 2 × Si(CH_3)$_2$), 3.30 (1H, q, *J* 5.1, Si–*H*), 7.28–7.31 (6H, envelope, 6 × H_{Ar}), 7.38–7.42 (4H, envelope, 4 × H_{Ar}); δ_C (75 MHz, C_6D_6) −12.1 (Si(H)*C*H$_3$), −2.1 (Si(*C*H$_3$)CH$_3$), −2.0 (Si(CH$_3$)*C*H$_3$), 127.9 (*C*H$_{Ar}$), 128.7 (*C*H$_{Ar}$), 133.9 (*C*H$_{Ar}$), 135.6 (C_{Ar}); ν_{max} (neat, cm^{-1}) 3063 (C–H aromatic), 2955 (C–H), 2068 (Si–H), 1427, 1250, 1103, 1057, 872, 833, 772, 733, 694, 633; *m*/*z* (EI$^+$) 313 (5%, [M−H]$^+$), 298 (4%), 255 (11%), 197 (6%), 178 (81%), 163 (38%), 135 (100%), 121 (9%), 105 (15%); HRMS (EI$^+$). Found: 314.1329, required for $C_{17}H_{26}Si_3$: 314.1342.

3.6. 3,3,4,5,5-Pentamethyl-4,5-dihydro-3H-3,4,5-trisilacyclohepta[2,1-a;4,3-a′]binaphthalene, **7**

To a solution of 2,2′-dibromobinaphthyl (254 mg, 0.62 mmol) in THF (6 mL) at −78 °C under argon, was added a 2.2 M solution of *n*-BuLi in hexanes (616 μL, 1.36 mmol). The solution was stirred at this temperature for an hour and then the temperature was raised to −60 °C and stirring continued for another 30 min.

To a solution of trisilane **8** (202 mg, 0.62 mmol) in toluene (3 mL) at 0 °C was added triflic acid (114 μL, 1.29 mmol). The solution was stirred for 20 min before being cooled to −60 °C. The silyl triflate solution was transferred *via* cannula into the dilithiobinaphthyl solution. The reaction temperature was maintained at −60 °C for a further hour before the solution was warmed to −50 °C and stirred overnight. Saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with diethyl ether (3 × 10 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by column chromatography (hexane: diethyl ether, 9:1, R_f = 0.55) gave **7** as a colourless oil (76 mg, 30%):

δ_H (400 MHz, C_6D_6) −0.74 (3H, s, SiCH_3), −0.65 (3H, s, SiCH_3), 0.11 (3H, d, *J* 5.0, Si(H)CH_3), 0.41 (3H, s, SiCH_3), 0.53 (3H, s, SiCH_3), 3.66 (1H, q, *J* 5.0, Si–*H*), 6.87–6.94 (2H, m, 2 × H_{Ar}), 7.14–7.20 (2H, m, 2 × H_{Ar}), 7.24 (2H, d, *J* 8.6, 2 × H_{Ar}), 7.69 (2H, d, *J* 8.1, 2 × H_{Ar}), 7.70–7.82 (4H, envelope, 4 × H_{Ar}); δ_C (75 MHz, C_6D_6) −12.5 (Si(H)*C*H$_3$), −4.2 (Si*C*H$_3$), −3.2 (Si*C*H$_3$), −2.8 (Si*C*H$_3$), −1.5 (Si*C*H$_3$), 126.4 (*C*H$_{Ar}$), 126.5 (*C*H$_{Ar}$), 126.5 (*C*H$_{Ar}$), 127.1 (*C*H$_{Ar}$), 127.2 (*C*H$_{Ar}$), 127.5 (*C*H$_{Ar}$), 127.6 (*C*H$_{Ar}$), 128.2 (*C*H$_{Ar}$), 128.3 (*C*H$_{Ar}$), 130.4 (*C*H$_{Ar}$), 130.6 (*C*H$_{Ar}$), 134.2 (C_{Ar}), 134.2 (C_{Ar}), 135.0 (C_{Ar}), 135.0 (C_{Ar}), 136.7 (C_{Ar}), 136.8 (C_{Ar}), 146.1 (C_{Ar}), 146.1 (C_{Ar}) (Note: One CH_{Ar} is obscured by benzene solvent); δ_{Si} (80 MHz, C_6D_6) −65.9, −19.6, −19.5; ν_{max} (film, cm^{-1}) 3049 (C–H aromatic), 3009 (C–H aromatic), 2951 (C–H), 2893 (C–H), 2076 (Si–H), 1924 (aromatic overtone), 1584, 1548 (C=C aromatic), 1499 (C=C aromatic), 1454, 1405, 1331, 1306, 1246, 1216, 1150, 1115, 1109, 1024, 948, 871, 835, 809, 792, 760, 684, 668, 636, 626, 608; *m*/*z* (EI$^+$) 412 (92%, [M]$^+$), 397 (12%), 353 (43%), 338 (46%), 309 (13%), 295 (100%), 279 (25%), 265 (15%), 252 (14%), 116 (42%), 102 (47%); HRMS (EI$^+$). Found: 412.1487. Calc. for $C_{25}H_{28}Si_3$: 412.1499.

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Appendix A. Supplementary material

CCDC 698595 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.054.

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