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Stereoselective polycyclisations of allyl and enyne silanes: evidence for a bicyclo[3.2.0]hept-1(7)ene structure

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Dedicated to Professor F. Mathey on occasion of his 60th birthday

Abstract

The intramolecular copper(I)-catalyzed [2 + 2]-photocycloaddition of diphenyldiallylsilane (**1**) (or tetraallylsilane (**4**)) led to sila-3-bicyclo[3.2.0]heptane (**3**) (or to spiro analogous **6**) in the *cis* (or *cis–cis*) configuration whereas the α,ω-diiodide (**2**) obtained by cyclozirconation of **1** (or from the homologous tetraiodide **5**) followed by addition of *n*-BuLi, produced the sila-3-bicyclo[3.2.0]heptane (**3**) (or to the spiro analogous **6**) in the *trans* (or *trans–trans* configuration). The same cyclozirconation reaction, starting from the hetero enyne **7**, selectively led to the highly strained silacyclobutene moiety **15** which represents the first stable hetero bicyclo[3.2.0]hept-1(7)ene skeleton, hypothetical intermediate in metathesis reactions. © 2002 Published by Elsevier Science B.V.

Keywords: Photocycloaddition; Cyclo and spirozirconation; Allyl silanes; Enyne silanes; Sila-3-bicyclo[3.2.0]heptanes; Bicyclo[3.2.0]hept-1(7) ene; Metathesis reactions

1. Introduction

Intramolecular carbometalations offer an exciting opportunity to form rings under mild conditions. In particular, metal-promoted bicyclisations of 1,6-dienes and 1,6-enynes are synthetically attractive and fruitfully methodologies [1].

In the literature, zirconocene promoted stereoselective cyclisation of 1,6-dienes led to *cis–trans* disubstituted cyclopentanes with a predominant *trans* isomer [2].

Our previous results, starting from heterodienes, confirmed that the selectivity depends on several parameters [3] as the relative size of the substituents or/and the nature of the heteroelement. In the case of the corresponding diallyl phosphine boranes [4], we noted the absence of selectivity of the zirconocyclization. All symmetrical (C_{2v}) diallyl silanes and germanes led to *trans* heterocyclopentanes only. By a similar process, the formation of a *trans–trans* isomer was induced by the spirozirconation of tetrallyl silane and germane (T_d) [5].

We applied such reactions to prepare silabicyclo[3.2.0]heptanes **3** and **6** in *trans* and *trans–trans* configurations (A) (Fig. 1). The synthesis of the corresponding *cis* isomer (B) was selectively obtained by photocycloaddition.

On the other hand, the catalytic reaction on 1,6-enynes has already provided a valuable approach to cyclic 1,3- and 1,4-dienes. In particular, the mechanism of a palladium-catalyzed intramolecular carbometallation proposed by Trost et al. [6], for the production of the unexpected skeletally rearranged product, invokes the intermediacy of a bicyclo[3.2.0]hept-1(7)-ene (E). Such cyclobutene moiety was postulated as an intermediate

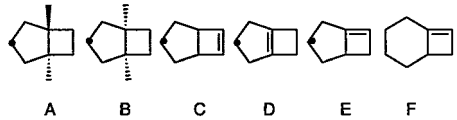

Fig. 1. Bicyclo[3.2.0]heptane and heptane isomers.

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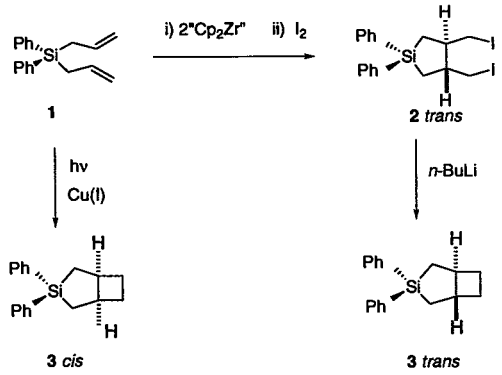
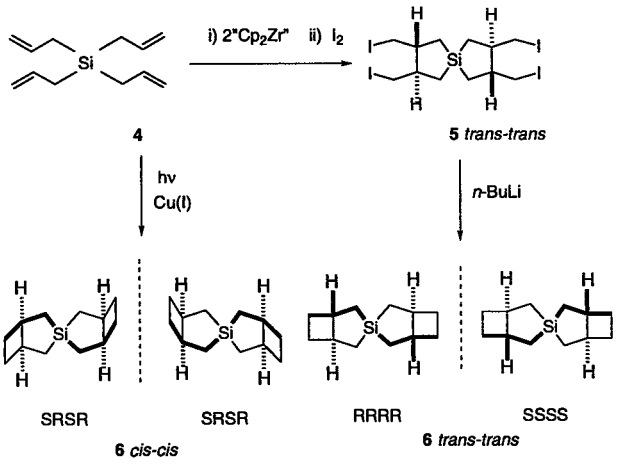


Scheme 1.



Scheme 2.

in transition metal-catalyzed [2 + 2]-cycloaddition. However, unlike cyclobutenes (C) [7], (D) [8] and (F) [9], this intermediate (E), structurally equivalent to the *trans* cycloheptene [10], was not yet isolated.

2. Results and discussion

2.1. Allyl silanes cyclisation

We investigated two different stereoselective cyclisations, in order to prepare sila bicyclic compounds in *cis* and *trans* configurations.

We carried out the intramolecular copper(I)-catalyzed [2 + 2]-photocycloaddition of the di- and tetraallyl silanes **1** and **4**, using the method first described by Evers [11] and extensively investigated by Salomon [12]. The irradiation at 254 nm for 37 h of a THF solution of diphenyldiallylsilane (**1**) in presence of one equivalent of CuOTf, leads selectively to the sila-3-bicyclo[3.2.0]heptane (**3**) in *cis* configuration [13] (Scheme 1). The same stereoselectivity was observed in the formation of the four stereogenic centers of the spiro derivative **6** (Scheme 2). The photocyclometalation produces the racemic (SRSR/SRSR) spirocyclic silane **6** *cis–cis*.

Nakanishi et al. [14] have shown that the irradiation of **1** and **4**, in presence of 1,4-dicyanonaphtalene in benzene, afforded the intramolecular [2π + 2π] photocycloadducts in good yields via (1,4-DCN–C_6H_6–Si compound) triplexes. However, no information about the streochemistry was given.

On the other hand, the cyclozirconation of **1** was also stereoselective and the successive addition of I_2 and *n*-BuLi [15,16] on the metal complex leads to the corresponding bicyclic silane **3** in the *trans* configuration (Scheme 1). By the same process, the spirozirconation of **4** produces the racemic **6** *trans–trans* (RRRR/SSSS) (Scheme 2). In this case, the possible **6** meso (RRSS/SSRR) was not observed. The **6** *trans–trans* configuration was recently confirmed by an X-ray structural determination of the corresponding spirocyclic tetrabromide analogous to **5** [5].

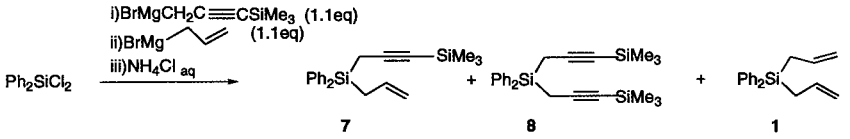
The *cis–trans* isomerism was easily characterized by ^{13}C-NMR. The high symmetry (C_2 axis) of the *trans–trans* isomers involves an equivalence of the C_2/C_5, C_3/C_4 and C_2/C_6 carbons while these carbons in the *cis–cis* isomerism are diastereotopic [17]. Furthermore, the chemical shifts of the C_3 and C_4 stereogenic carbons are quite different: $38.2 < \delta^{13}C < 39.1$ in the *cis* configuration and $47.0 < \delta^{13}C < 47.3$ in the *trans* configuration.

2.2. Enyne silane cyclisation

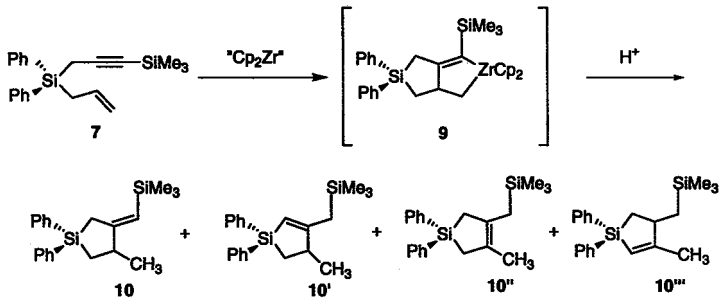
The metal-promoted bicyclisation reaction of enynes is also of particular interest, since desired products would readily allow further regioselective transformations. This reaction was extensively studied by several authors [18,19]. Negishi et al., by cyclozirconation of 1,6-enynes, followed by treatment with I_2 and addition of *n*-BuLi, synthesized cleanly the 8-(trimethylsilyl)bicyclo[4.2.0]oct-1(8)-ene (F) in 70% yield [9]. The same method failed to prepare the corresponding bicyclo[3.2.0] (E).

The enyne **7** was prepared by the successive addition of 3-bromo-1-trimethylsilyl-1-propyne and allyl magnesium bromide on diphenyldichlorosilane (Scheme 3). The desired product, after purification with Chromatotron, was isolated in moderate yield (38%) because of the unavoidable formation of two symmetrical silanes: the diyne **8** and the corresponding diallylsilane **1**. An excess of zirconocene precursor was added at low temperature to the enyne **7**. The bicyclic intermediate **9**, characterized by NMR, was quenched by various electrophiles.

The protonation at 0 °C by a solution of HCl (0.1 M) led to a mixture of silacyclopentenes **10** – **10‴**,



Scheme 3.



Scheme 4.

obtained in form of colorless oil after purification with Chromatotron. The presence of four different isomers **10**, **10′**, **10″** and **10‴**, detected by NMR, is a consequence of the lability of the double bond in acidic media (Scheme 4).

The addition of a slight excess of bromine in CCl_4 solution, at -78 °C, after hydrolysis by H_2SO_4 (10%) led to Z/E isomers **11** and **11′** (Scheme 5).

When the same intermediate **9** was treated by I_2 and hydrolyzed by aqueous NH_4Cl, the diiodo derivative **12** was selectively isolated in form of Z isomer (Scheme 5). This assigned structure was confirmed by a subsequent cyclisation.

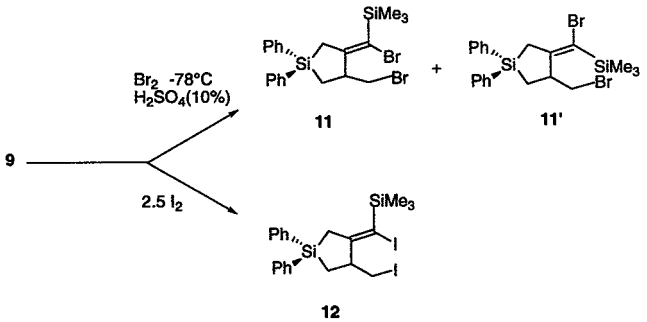
In order to extend cyclometallation reactions to the dienynes, we synthesized the dienyne **13** by addition of the Grignard reagent $BrMgCH_2C{\equiv}CSiMe_3$ on dichlorodiallylsilane (Scheme 6).

The cyclozirconation of **13**, carried out by the usual method and followed by addition of bromine, was effective. The spiranic tetrabromides **14**–**14′** decomposed on silica but were characterized by mass spectra and ^{13}C-NMR.

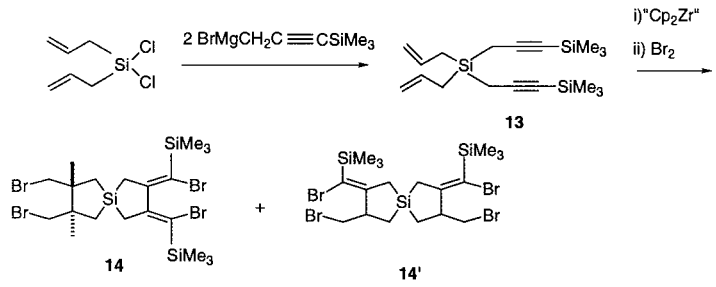
Using the Negishi method, by treatment of **12** in the Z form with one equivalent of *n*-BuLi in ether at -78 °C, we prepared **15** in 82% yield (Scheme 7). This strained cyclobutene represents the first stable bicyclo[3.2.0]hept-1(7)ene skeleton (E). The bicyclisation was confirmed by ^{13}C-NMR. The important deshielding of quaternary C_3 and C_6 ($\delta = 168.2$ and 138.8, respectively) is in good agreement with the bicyclo[3.2.0]hept-1(7)ene skeleton (E). The stable cyclobutene (F) presents similar values for the corresponding sp_2 carbons [9].

This molecule **15** represents the first example of the hypothetical intermediate of the intramolecular enyne metathesis reaction. The suggestion that the transition-metal catalyzed olefin metathesis might proceed by a [2 + 2]-cycloaddition followed by cycloreversion was proved incorrect. Nevertheless, the intriguing prospect for transition metal-catalyzed [2 + 2] cycloaddition remains [6]. Various attempts to stabilize the corresponding cylobutene (E) by substitution [9] or complexation [6] failed. Yet, few examples of (E) structures exist in some polycyclic derivatives [20–23]. Recently, Blum et al. [24] described a novel $PtCl_4$ catalyzed cycloarrangement of 1,6-enyne and suggested that the primary cyclisation product was the bicyclo[3.2.0]heptene (E). But, in the absence of oxygen, the authors observed a polymerisation of this intermediate. To underline the steric strain, Trost [25] performed molecular mechanics calculations. Three cyclobutenes (E) were studied indicating that the high steric strain was dependent on the substitution pattern. The calculated energies (between 58 and 64 kcal mol^{-1}) confirmed the high steric strain of these models.

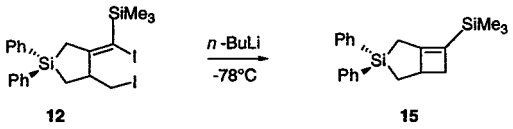
The possible reasons of the relative stability of **15** would be due to the presence of diphenylsilane and trimethylsilyl groups in α and β positions relative to the intracyclic double bond [26].



Scheme 5.



Scheme 6.



Scheme 7.

In conclusion, it appears that the photocycloaddition and the cyclozirconation are two complementary methods to obtain pure *cis* or pure *trans* bicyclic (or spiranic) compounds starting from the same allylic derivative. In the case of enyne, the cyclozirconation, carried out with moderate yield, allow us to obtain the high strained cyclobutene **15**. This structure (E) was often postulated as an intermediate in metathesis reactions.

3. Experimental

3.1. General procedure

All manipulations, except chromatography on silica gel with Chromatotron® apparatus, were carried under an argon atmosphere. Tetrahydrofuran, Et_2O and C_6H_{14} were distilled from sodium–benzophenone solution and stored under Ar. All NMR spectra were recorded at 25 °C on Bruker AC 80 and 250 MHz in $CDCl_3$. The ^1H and ^{13}C chemical shifts are referenced relative to Me_4Si. Coupling constants are given in Hertz. Mass spectra were obtained on a Ribermag R1010 under electron impact (EI) or chemical ionization (DCI conditions) with CH_4 or NH_3. Low-resolution mass spectra were determined by GC–MS using Hewlett–Packard 5890 series II gas chromatograph equipped with a HP/MS 5989A mass selective detector. M.p. were determined in evacuated capillaries with a Buchi–Tottoli apparatus. IR spectra were recorded on Perkin–Elmer 1600 Series FTIR. Elemental analyses were performed by the Microanalytical Laboratory of the Ecole Nationale Supérieure de Chimie de Toulouse. Irradiations were carried out using as light source a Rayonet photochemical reactor.

3.2. Compound **2** trans

To a solution of dichlorozirconocene (Cp_2ZrCl_2) (0.87 g, 3 mmol) in 10 ml of THF at −78 °C was added *n*-BuLi 1.6 M (3.8 ml, 6 mmol). After stirring (1 h), the diphenyldiallylsilane (**1**) (0.60 g, 3.0 mmol) in 5 ml THF was added at −78 °C. The solution was stirred for 12 h at room temperature (r.t.). Then 1.9 g (2.5 equivalents, 7.5 mmol) of I_2 were added at −78 °C.The reaction was quenched with H_2SO_4 (10%). After extraction with ether, the reaction mixture was washed with aq. $NaHCO_3$, dried over $MgSO_4$ and filtered. Removal of the solvents followed by purification with Chromatotron (C_6H_{14}) gave **2** *trans* (69% yield) as white powder (m.p.: 116–118 °C).

^1H-NMR (250 MHz, $CDCl_3$): $\delta = 1.2$–1.6 (m, 6H, CH_2Si, CH), 3.3–3.6 (m, 4H, CH_2I); 7.2–7.6 (m, 10H, arom.). ^{13}C-NMR (62.89 MHz, $CDCl_3$) (J.mod): $\delta =$ 17.2 (s, CH_2I), 19.3 (s, CH_2Si), 44.9 (s, CH), 135.4 (s, C_{ipso}) MS (EI): $m/z = 391$ $[M - I]^+$ (100%). Anal. Calc. for $C_{18}H_{20}I_2Si$: C, 41.69, H, 3.96. Found: C, 42.27; H, 4.01%.

3.3. Compound **3** trans

n-BuLi (one equivalent, 1.7 ml, 2.7 mmol) was slowly added at −78 °C to **2** *trans* (one equivalent 1.4 g, 2.7 mmol) in 15 ml of ether. The mixture was then allowed to warm to r.t. After hydrolysis with 50 ml of NH_4Cl_{aq}, the product extracted by ether, dried by $MgSO_4$ and filtrated, was purified with Chromatotron (C_6H_{14}) and obtained as colorless oil in 45% yield.

^1H-NMR (250 MHz, $CDCl_3$): $\delta = 0.9$–1.8 (m, 8H, CH_2Si, CH_2), 2.0–2.1 (m, 2H, CH), 7.4–7.7 (m, 10H, arom.). ^{13}C-NMR (62.89 MHz, $CDCl_3$) (J.mod): $\delta =$ 19.0 (s, CH_2Si), 29.9 (s, CH_2), 47.3 (s, CH), 137.1 (s, C_{ipso}). MS (DCI–NH_3): $m/z = 282$ $[M, NH_4]^+$ (100%). Anal. Calc. for $C_{18}H_{20}Si$: C, 81.8, H, 7.6. Found: C, 80.7; H, 7.8%.

3.4. Compound **3** cis

In a quartz vessel, 0.05 equivalent (0.024 g, 0.05 mmol) of CuOTf was added to one equivalent (0.30 g,

1.14 mmol) of **1** in 3 ml of ether. The mixture was irradiated at 254 nm for 37 h. After removal of the solvent, the product was purified with Chromatotron (hexane) and obtained as colorless oil in 44% yield.

^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 1.0–2.7$ (m, 8H, CH_2Si, CH_2), 2.7–3.2 (m, 2H,CH), 7.2–7.8 (m, 10H, arom.). ^{13}C-NMR (62.89 MHz, $CDCl_3$) (J.mod): $\delta =$ 18.6 (s, CH_2Si), 27.7 (s, CH_2), 39.1 (s, CH), 136.9 (s, C_{ipso}), 137.1 (s, C_{ipso}) MS (DCI–NH_3): $m/z = 282$ [M, NH_4]$^+$ (100%). Anal. Calc. for $C_{18}H_{20}Si$: C, 81.8, H, 7.6. Found: C, 80.7; H, 7.7%.

3.5. Compound **5** *trans–trans*

To a solution of Cp_2ZrCl_2 (2.68 g, 9.4 mmol) in 10 ml of THF at −78 °C was added *n*-BuLi 1.6 M (5.95 ml, 9.4 mmol). After 1 h stirring, the tetraallylsilane (**4**) (0.9 g, 4.7 mmol) in 5 ml THF was added at −78 °C. The solution was stirred for 12 h at r.t. Then 5.9 g (five equivalents, 23.4 mmol) of I_2 in 24 ml of THF were added at −78 °C. The reaction was quenched with H_2SO_4 (10%). After extraction with ether, the reaction mixture, neutralized with NH_4Cl_{aq} was dried over $MgSO_4$ and filtered. After crystallisation in C_6H_{14}–CH_2Cl_2 (98/2) **5** *trans–trans* was obtained as white powder in 64% yield (m.p.: 144–145 °C).

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 0.5–1.5$ (m, 12H, CH_2Si, CH), 3.1–3.5 (m, 8H, CH_2I). ^{13}C-NMR (62.89 MHz, $CDCl_3$) (J.mod): $\delta = 16.9$ (s, CH_2I), 19.1 (s, CH_2Si), 44.6 (s, CH) MS (EI): $m/z = 573$ [M − I]$^+$ (100%). Anal. Calc. for $C_{12}H_{20}I_4Si$: C, 20.58, H, 2.86. Found: C, 20.65; H, 2.94%.

3.6. Compound **6** *trans–trans*

n-BuLi (two equivalents, 3.4 ml, 5.4 mmol) was slowly added at −78 °C to **5** *trans–trans* (one equivalent, 1.9 g, 2.7 mmol) in 15 ml of ether. The mixture was then allowed to warm to r.t. After hydrolysis with NH_4Cl_{aq}, the product, extracted by ether, dried by $MgSO_4$ and filtrated, was purified with Chromatotron (C_6H_{14}) and obtained as colorless oil in 40% yield.

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 1.4–1.7$ (m, 16H, CH_2), 1.8 (m, 4H, CH). ^{13}C-NMR (62.89 MHz, $CDCl_3$) (J.mod): $\delta = 19.7$ (s, CH_2Si), 30.0 (s, CH_2), 47.0 (s, CH).

3.7. Compound **6** *cis–cis*

In the same experimental conditions as **3** *cis*, 0.05 equivalent (0.024 g, 0.05 mmol) of CuOTf was added to one equivalent (0.218 g, 1.14 mmol) of **4** in 3 ml of ether. The mixture was irradiated at 254 nm for 08:30 h. After removal of the solvent, the product was purified with Chromatotron (C_6H_{14}) and obtained as colorless oil in 40% yield.

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 0.3–2.1$ (m, 20H, CH_2Si, CH_2, CH). ^{13}C-NMR (62.89 MHz, $CDCl_3$) (J.mod): $\delta = 18.7$ (s, CH_2Si), 19.7 (s, CH_2Si), 27.1 (s, CH_2), 28.3 (s, CH_2), 38.2 (s, CH), 38.9 (s, CH).

3.8. Compound **7**

3-Bromo-1-trimethylsilyl-1-propyne (10 g, 1.1 equivalents, 5.3×10^{-2} mol) in 10 ml of ether are added to 4.9 g of Mg (4.5 equivalents, 1.07×10^{-1} mol) in 10 ml of ether. After addition of 80 ml of ether and 4 h stirring at r.t., the supernatant was introduced, at 0 °C, to a solution of Ph_2SiCl_2 (one equivalent, 4.76×10^{-2} mol) in 10 ml of ether. The solution was stirred 12 h at r.t. (solution I). Separately, a solution of allyl MgBr (solution II) was prepared by addition of 6.3 ml of allyl bromide (1.1 equivalents, 5.2×10^{-2} mol) on 2.7 g of Mg (two equivalents, 0.12 mol) in ether. After 1 h refluxing, the supernatant was added to solution I. After 12 h refluxing, the solution was hydrolyzed (NH_4Cl). The product, extracted with ether, dried with $MgSO_4$, and concentrated, was purified with Chromatotron (C_6H_{14}–$CH_2Cl_2 = 90/10$) and obtained as colorless oil in 38% yield.

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 0.1$ (s, 9H, $SiMe_3$), 2.2–2.3 (m, 4H, CH_2Si, 4.8–5.1 (m, 2H, H_2C=), 5.7–6.1 (m, 1H, CH), 7.4–7.8 (m, 10H, H arom.). ^{13}C-NMR (62.89 MHz, $CDCl_3$): $\delta = 0.1$ (s, $SiMe_3$), 5.2 (s, $SiCH_2$–CH=), 20.1 (s, $SiCH_2$–C≡C–), 85.2 (s, Si–C≡C–), 104.4 (s, Si–C≡C–), 115.1 (s, H_2C=), 133.8 (s, C_{ipso}), 127.8–135.1 (CH arom.).

3.9. Compound **10**

To a solution of Cp_2ZrCl_2 (0.84 g, 2.9×10^{-3} mol) in 10 ml of THF at −78 °C was added *n*-BuLi 1.6 M (3.6 ml, 6.5×10^{-3} mol). After 1 h stirring, the enyne **7** (1.8×10^{-3} mol) in 10 ml of THF was added. The reaction was stirred 12 h at r.t., leading to the bicyclo intermediate **9**. The solution of **9** was quenched by HCl (0.1 M) at 0 °C. After stirring 30 min at r.t., the product **10**, extracted, dried and purified with Chromatotron (C_6H_{14}) was isolated in form of colorless oil (28% yield).

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = -0.07$, 0.11, 0.12, 0.21, (s, 9H, $SiMe_3$), 0.9–2.4 (m, 8H, CH_2SiMe_3, CH_2Si, CH, CH_3), 5.4–5.9 (m, 1H, Ph_2SiCH= or =$CHSiMe_3$), 7.4–7.6 (m, 10H, H arom.).

^{13}C-NMR (62.9 MHz, $CDCl_3$): $\delta = -1.7$, −1.0, −0.7, −0.3 (s, $SiMe_3$), 19.9, 20.7, 21.1, 21.6, 21.7, 22.1 (s, Ph_2SiCH_2), 21.5, 21.6, 22.8, 23.6 (CH_3), 26.3, 26.9 (CH_2SiMe_3), 42.6, 42.8, 43.1 (s, CH), 114.4, 114.9 (s, Cq), 120.1 (s, =$CHSiMe_3$), 128, (s, Ph_2SiCH=), 128.5 (s, Ph_2SiCH=), 127, 135 (CH arom.), 165 (s, Cq). MS (DCI–NH_3): $m/z = 354$ [M, NH_4]$^+$ (100%), 337 [MH]$^+$ (18%). IR: ν (cm^{-1}) = 3069, 2059, 1593, 1564, 1248, 854, 734.

3.10. Compound **11**

Br_2 (0.22 ml, 2.35 equivalents, 4.2 mmol) in CCl_4 (8 ml) were added at −78 °C on the intermediate **9** (1.8 mmol). The solution was allowed to warm to r.t. (12 h). After hydrolysis by H_2SO_4 (10%) and stirring (30 min), the organic phase was extracted with ether, washed with K_2CO_{3aq} and dried with $MgSO_4$. The solution was concentrated under reduced pressure and the residue, purified with Chromatotron (C_6H_{14}–CH_2Cl_2 = 98/2), was obtained as a yellow oil in 41% yield.

^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.23$ (s, 9H, $SiMe_3$) (isomer I); 0.25 (s, 9H, $SiMe_3$) (isomer II); 1.55–1.57 (Part AB of ABX, $^2J_{AB} = 15$ Hz, $^3J_{AX} = 4$ Hz, $^3J_{BX} = 7$ Hz, 2H, CH_2Si), 2.00–2.44 (Part A′B′ of A′B′X, $^2J_{AB} = 15$ Hz, $^4J_{BX} = 1.5$ Hz, $^4J_{AX} = 0$ (2H, CH_2Si) (isomer I), 2.00–2.45 (A″B″ system), $^2J_{AB} = 16.5$ Hz, 2H, CH_2Si) (isomer II), 3.38 (ft, $^2J_{HH} = {}^3J_{HH} = 9.5$ Hz, 1H, C*H*HBr), 3.61 (dd, $^2J_{HH} = 9.5$Hz, $^3J_{HH} = 4.5$ Hz, 1H, CH*H*Br), 3.9–4.1 (m, 1H, CH), 7.3–7.7 (10H, H arom.). ^{13}C-NMR (62.9 MHz, $CDCl_3$): $\delta = 0.6$ (s, $SiMe_3$) (isomer I), 0.8 (s, $SiMe_3$). (isomer II); 15.5 (s, C_5), 21.8 (s, C_2) (isomer I or II); 22.1 (s, C_2) (isomer I or II); 38.5 (s, C_7); 49.1 (s, C_4), 124.1 (s, C_6), 133.6 (s, C_{ipso}), 128–134 (CH arom.), 153.9 (s, C_3) (isomer I or II), 154.7 (s, C_3) (isomer I or II). MS (DCI–NH_3): $m/z = 512$ [M, NH_4]$^+$, 432 [M − Br, NH_4]$^+$. Anal. Calc. for $C_{21}H_{26}Br_2Si_2$: C, 51.01, H, 5.26. Found: C, 51.34; H, 5.84%.

3.11. Compound **12**

In the same conditions as before, 1.1 g of I_2 (2.5 equivalents, 4.5 mmol) in 6 ml of THF were added to **9** (1.8. mmol) at −78 °C. The solution was allowed to warm to r.t. for 12 h and stirred for 96 h. The reaction mixture was hydrolyzed with NH_4Cl solution, extracted with ether, dried, concentrated and purified with Chromatotron (C_6H_{14}–CH_2Cl_2 = 90/10). Compound **12** was obtained as a yellow oil in low yield (14%).

^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.3$ (s, 9H, $SiMe_3$), 1.59, 1.61 (Part AB of ABX, $^2J_{AB} = 10.1$ Hz, $^3J_{AX} = 5.8$ Hz, $^3J_{BX} = 2.9$ Hz, 2H, CH_2Si), 2.1–2.5 (AB system, $^2J_{AB} = 11.5$ Hz, CH_2Si), 3.1 (ft, $^2J_{HH} = {}^3J_{HH} = 9.5$ Hz, 1H, C*H*HI), 3.46 (dd, $^2J_{HH} = 9.5$ Hz, $^3J_{HH} = 4.0$ Hz, 1H, CH*H*I), 3.8–3.9 (m, 1H, CH), 7.4–7.7 (10 H, H arom.). ^{13}C-NMR (62.9 MHz, $CDCl_3$): $\delta = 1.9$ (s, $SiMe_3$), 13.1 (s, C_7), 17.6 (s, C_5), 22.0 (s, C_2), 56.5 (s, C_4), 109.5 (s, C_6), 127–134 (CH arom.), 160.1 (s, C_3). MS (DCI–NH_3): $m/z = 606$ [M, NH_4]$^+$ (100%); 589 [MH]$^+$.

3.12. Compound **13**

3-Bromo-1-trimethylsilyl-1-propyne (7.1 g, 2.2 equivalents, 3.7×10^{-2} mol) in ether (10 ml) are added to Mg (2.5 g) (six equivalents, 1.02×10^{-1} mol) in ether (10 ml). After adition of 80 ml of ether and stirring (4 h) at r.t., the supernatant was added, at 0 °C, to a solution of dichlorodiallylsilane (one equivalent, 1.7×10^{-2} mol) in 10 ml of ether. After addition, the solution was allowed to warm to r.t., stirred for 12 h and hydrolyzed with 100 ml of distilled water. The product extracted with ether, dried with $MgSO_4$ and concentrated, was obtained as an orange oil in 95% yield without purification.

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 0.1$ (s, 18H, $SiMe_3$), 1.7–1.8 (m, 8H, CH_2Si), 4.8–5.1 (m, 4H, H_2C=), 5.7–6.1 (m, 2H, CH).

3.13. Compound **14**

After the cyclozirconation reaction (carried out by the usual method as for compound **9**) 0.65 ml of Br_2 (4.2 equivalents, 12.6×10^{-3} mol) in 15 ml of CCl_4 were added at −78 °C on 1.8 mmol of the intermediate. The solution was allowed to warm to r.t. for 12 h. After hydrolysis by H_2SO_4 (10%) and stirring (30 min), the organic phase was extracted with ether, washed with K_2CO_{3aq} and dried with $MgSO_4$. The product decomposes on silica but the solution of the crude product indicates the presence of tetrabromide spirosilane **14**.

^{13}C-NMR (62.9 MHz, $CDCl_3$): $\delta = 0.7$ (s, $SiMe_3$), 17.1 (s, C_5), 22.0 (s, C_2), 40.4 (s, C_7), 47.7 (s, C_4), 120.0 (s, C_6), 154.1 (s, C_3). MS (DCI–NH_3): $m/z = 670$ [M, NH_4]$^+$, 653 [MH]$^+$.

3.14. Compound **15**

n-BuLi (0.16 ml, one equivalent, 2.55×10^{-4} mol) were added at −78 °C, to (0.15 g, one equivalent, 2.55×10^{-4} mol) **12** in ether (3 ml). The solution was allowed to warm to r.t. (1 h). After hydrolysis, the organic phase was extracted with ether, dried with $MgSO_4$ and concentrated. The product, obtained as colorless oil (82% yield), is stable, with or without solvent, at r.t. But during purification with Chromatotron apparatus, a slight decomposition was observed.

^{1}H-NMR (80 MHz, $CDCl_3$): $\delta = 0.2$ (s, 9H, $SiMe_3$), 0.8–3.2 (m, 7H, CH_2Si, CH_2, CH), 7.1–7.8 (m, 10H, H arom.). ^{13}C-NMR (50.3 MHz, C_6D_6): $\delta = -1.2$ (s, $SiMe_3$), 17.9 (s, C_5), 20.2 (s, C_2), 38.6 (s, C_7), 44.5 (s, C_4), 128–135 (*C*H arom), 138.8 (s, C_6), 168.3 (s, C_3). MS (EI): $m/z = 334$ [M$^+$].

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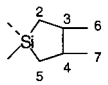

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