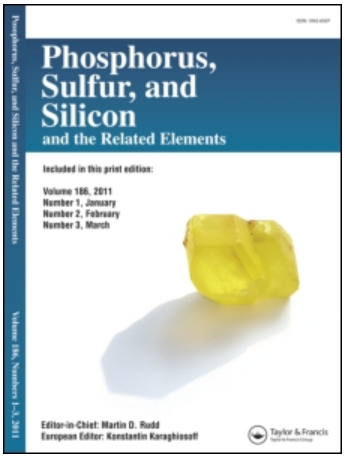

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Carbo-siloles, Part 2: Synthesis and Stereochemical Resolution of a *Carbo*-silolane Redox Equivalent

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Carbo-siloles, Part 2: Synthesis and Stereochemical Resolution of a *Carbo*-silolane Redox Equivalent

Catherine Saccavini, Christine Tedeschi, Christine Lepetit, Leila Yahi, Caroline Pistre, Valérie Maraval, and Remi Chauvin
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Carbo-*siloles could a priori be generated by eliminative aromatization of sila[5]pericyclyne precursors with adjacent C—OR and C—H vertices. The synthesis of tetraoxy-sila[5]pericyclyne representatives (“*carbo-*silolanes” **2a** and **2b**) has been tackled through several [(15–n)+n] ring formation strategies. After having first attempted a [14+1] route from dichlorodiphenylsilane and a skipped pentayne (**3**), a [5+10] route proceeded successfully from diethynyldiphenylsilane (**7**) and a triynedial (**4**), to give the sila[5]pericyclynediol (**2a**) as a mixture of six diastereomers in 20% yield. Sequential chromatographies afforded one pure diastereomer of **2a**. DFT calculations of a model dihydroxy, dimethoxy-*carbo-*silolane indicate an envelope conformation of the* carbo-*meric five-membered ring. Methylation of the two secondary carbinol vertices of **2a** afforded the corresponding tetramethoxy* carbo-*silolane (**2b**) in 68% yield. Aromatization to the targeted carbo-silole by treatment with $Et_2O{\cdot}BF_3$ of **2b** proved awkward.*

Keywords *Carbo*-mers; β-diynes; pericyclynes; silolane; silole; stereochemical resolution

INTRODUCTION

To date, efforts for the synthesis of aromatic ring *carbo*-mers have been reported in the carbocyclic series only. They were all based

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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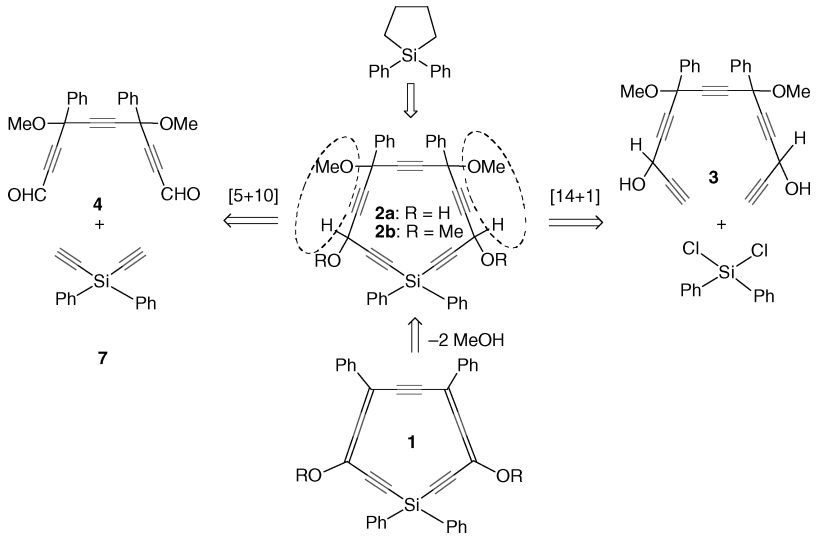
on the retrosynthetic scheme: *carbo*-[n]annulene => functional [n] pericyclyne.[1] The related heterocyclic *carbo*-silole ring has been theoretically predicted to be an intriguing structure, not only from an academic standpoint, but also for unweiling new horizons in the design of functional materials with chromophoric and/or conducting properties.[2] The tetraphenyl representative **1** could be a priori stabilized by extended conjugation, and can be targeted from functional sila-[5]pericyclynes **2**, here termed as "*carbo*-silolanes." Double elimination of methanol from **2** to **1** is indeed a priori a reasonable principle (Scheme 1).



SCHEME 1 Retrosynthetic scheme to tetraphenyl-*carbo*-silolanes **2** and *carbo*-siloles **1**.

According to Scott et al.'s definition,[3] "[n]pericyclynes" are 3n-membered homoconjugated macrocycles. These rings, first exemplified for n = 5 in the hydrocarbon series,[3,4] were then generalized in the functional series by introduction of carbinol vertices (and ether thereof).[5] The C(OR')R vertices generate stereochemical ambiguity, but several pentaoxy[5]pericyclynes were stereochemically resolved by semi-preparative HPLC.[5] In principle, the ease of resolution depends on the number of possible stereoisomers and is simplified for molecules of high topographical symmetry (e.g., when all vertices are chemically identical). An ideal way to reduce the number of stereoisomers is to remove the stereogenicity of one or more vertices: This was achieved for a *carbo*-cyclopentanone equivalent, where the keto vertex was masked as a symmetrical ketal ($C(OR')_2$). Symmetrization by two identical

non-oxy substituents is however more problematic: a general method for the preparation of quaternary 1,4-diynes R′—C≡C—C(R_2)—C≡C—R′ is indeed missing for R = alkyl, aryl.[6] Although double substitution at X_2CR_2 vertices is an awkward process, the analogous process at Cl_2SiR_2 vertices is facilitated by the polarity of the Si–Cl bonds.[7]

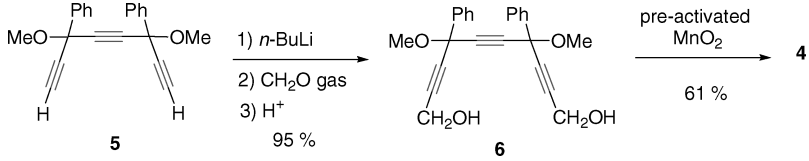
The tetraoxy-tetraphenyl-sila[5]pericyclyne structures **2**, namely the ring *carbo*-mers of the parent silolanes, are therefore reasonable targets. The results of two different [(15–n)+n] strategies for the ring formation step are hereafter reported for n = 1 and n = 10 (Scheme 1).

RESULTS AND DISCUSSION

Attempted [14+1] Ring Formation Route

A [11+4] ring formation strategy based on a double substitution process was previously explored in the C_{15} [5]pericyclyne series.[8] In the $C_{14}Si$ series, a generalization of the double substitution strategy has thus been first attempted from Ph_2SiCl_2 and the bisacetylide of pentayne **3** (Scheme 1).

Pentayne **3** was previously obtained by reaction of two equivalents of acetylene magnesium bromide with the triyndial **4**.[1b] The preparation of **4** is however tedious. In particular, double formylation of the known triyne **5** required purification by chromatography, resulting in partial decomposition and affording **4** in a poor 32% yield.[4] An alternative hydroxymethylation-oxidation route was thus explored. Hydroxymethylation of **5** was achieved in excellent yield (95%) by bubbling formaldehyde gas through a solution of the dilithium salt of **5** (Scheme 2). The diol product **6** was then submitted to various oxidizing reagents (Swern,[9] DCC/Py/TFA,[10] $BaMnO_4/CuSO_4/Al_2O_3$,[11] etc.), but most of them were not selective, affording mixtures of mono- and dialdehydes. The use of a large excess of MnO_2 (40 equivalents) in dichloromethane gave spectroscopically pure triyndial **4** in 29% yield after simple filtration: the side-products (likely resulting from over-oxidation of **6** to carboxylic acids) thus remain adsorbed on MnO_2. Finally, pretreatment of MnO_2 under vacuum at 150°C for 17 h allowed us to increase the yield of **4** to 61% (Scheme 2).

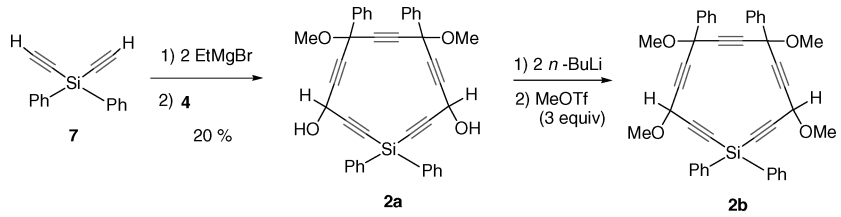


SCHEME 2 Preparation of triyndial **4** without a requirement of chromatographic purification.

The synthesis of **3** was then performed from **4** according to the described method.[1b] Deprotonation of **3** with four equivalents of EtMgBr followed by addition of Cl_2SiPh_2 was unsuccessful: After treatment, only unreacted **3** and unidentified insoluble (polymeric) products were recovered. Since the tetraanion of **3** did not precipitate, the lack of selectivity was likely not due the tetraanionic nature of the nucleophile. Protection of the OH groups of **3** was therefore not attempted, and we turned to an alternative ring formation strategy.

[5+10] Ring Formation Route

The alternative [5+10] double addition strategy was devised from the C_4Si β-diyne **7** and the C_{10} dialdehyde **4** (Scheme 1), the preparation of which has been improved (see above).



SCHEME 3 Synthesis of *carbo*-silolanes **2a** and **2b**.

Diethynylsilane **7** was obtained from two equivalents of ethynyl magnesium bromide and Cl_2SiPh_2 in 88% yield (Scheme 3).[12] The dilithium salt of **7** (soluble in THF) reacted with triyndial **4** to give a mixture of the targeted sila[5]pericyclyne **2a** along with the unexpected acyclic C_{14} pentayne **3**. Despite several chromatographic runs, **2a** could not be enriched beyond 80% of purity. The formation of **3**, which could result from a Brook [1,4]rearrangement followed by hydrolysis of the O–Si bond,[13] therefore had to be prevented. Considering that the lithium alkoxide groups of the product (before hydrolysis) are prone to cleave the vicinal ≡C–Si bonds, deprotonation of **7** was tentatively achieved with EtMgBr instead of *n*–BuLi. And indeed, the dimagnesium salt of **7** readily reacted with **4** (over a 1 min reaction time before hydrolysis) to give the sila[5]pericyclyne **2a** as a mixture of six diastereomers, in 20 % yield after chromatography over silica gel (Combiflash®). The orange oily product was resolved by further Combiflash chromatography. One of the diastereomers was thus separated. Since single signals were obtained for both the C*H*(OH) and OCH_3 types of protons (Figure 1, *top*), the structure of this diastereomer is either C_2-symmetric (**E**, **F**) or C_s–symmetric (**A**, **B**) (Scheme 4).

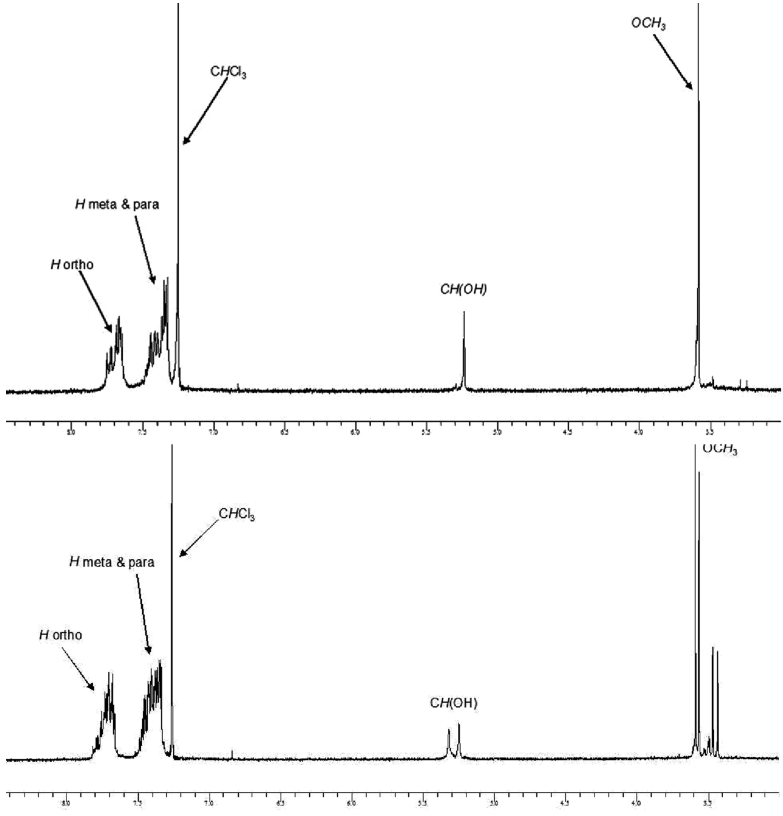
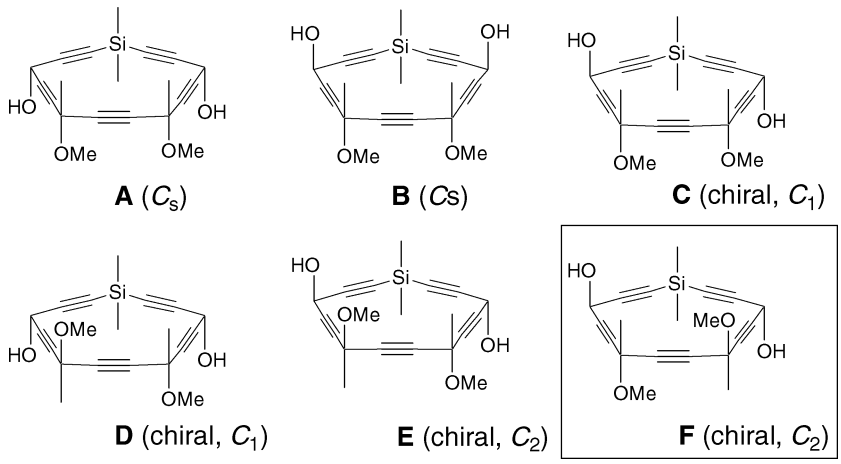


FIGURE 1 ^{1}H NMR spectra (250 MHz, $CDCl_3$) of one ideally C_2- or C_s-symmetric diastereomer of **2a** (*top,* structure **A**, **B**, **E** or **F** in Scheme 4) and a 70:30 mixture of two non-symmetric diastereomers (*bottom*, structures **C** and **D** in Scheme 4).

A second fraction contained a mixture of two other diastereomers of **2a** in a 70:30 ratio, where both the OC*H*$_3$ and C*H*(OH) groups are in distinct chemical environments (Figure 1, *bottom*): they can thus be ascribed to the non-symmetric structures **C** and **D** (Scheme 4).

Alkylation of the CH(OH) vertices was achieved with methyl triflate on a small sample of **2a**. The tetramethylether **2b** was obtained in 68% yield and characterized by MS, IR, ^{1}H, and ^{13}C NMR analyses (Scheme 3).

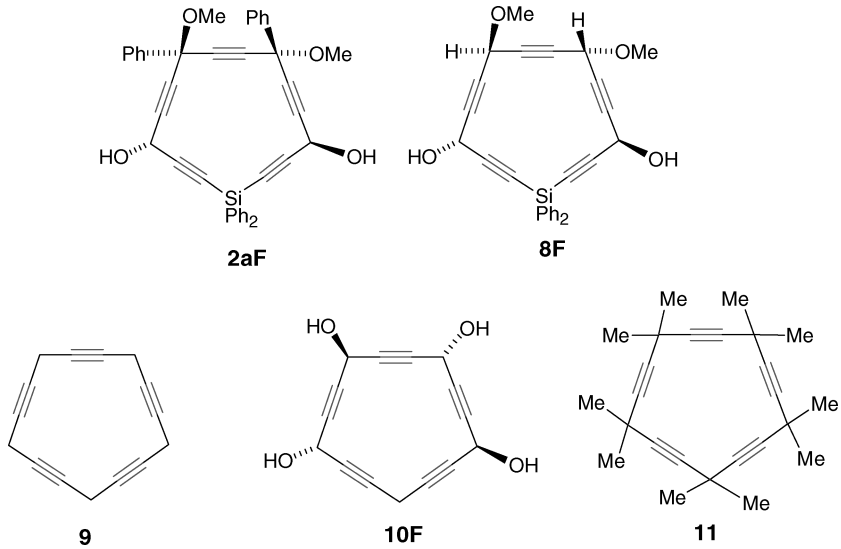
Since no X-ray crystal structure determination of **2a** or **2b** has been made possible, the geometry of a model **8F** of the *carbo*-silolane **2a** was investigated theoretically at the B3PW91/6-31G** level of calculation. The selected stereochemistry corresponds to the stereochemistry



SCHEME 4 Haworth representations of the six possible diastereomers of sila[5]pericyclyne **2a** (vertical lines feature C–Ph bonds). The chiral isomer **F** has been selected for DFT calculations.

of diastereomer **2aF** (Schemes 4 and 5). In the model **8F**, the two phenyl C-substituents of **2a** are replaced by H atoms.

Geometrical and electronic features of the calculated structure **8F** (Figure 2) were compared with those of all-carbon [5]pericyclynic analogues (Scheme 5, Table I). By contrast to the calculated planar



SCHEME 5 Set of representative [5]pericyclynes and sila analogues studied either experimentally (**2aF**, **11**), or computationally (**8F**, **9**, **10F**).

TABLE I Comparison of Selected Experimental (XRD) and Calculated (B3PW91/6-31G) Geometrical Data in the *Carbo*-Silolane and [5]Pericyclyne Series**

	Bond lengths (Å)					Envelope	HOMO	LUMO	GAP
	Si—Ph	≡C–Si	CC≡CSi	CC≡CC	C_{sp}–C_{sp3}	folding	(a.u.)	(a.u.)	(eV)
8F (calcd)	1.876	1.834	1.218	1.209	1.466 1.473	16.7°	−0.2565	−0.0362	5.996
9 (calcd)	—	—	—	1.208	1.466	0°	−0.2414	−0.0244	7.231
10F (calcd)	—	—	—	1.209	1.466, 1.473	9.7°	−0.2605	−0.0119	6.763
11 (XRD)[14]	—	—	—	1.190	1.480	40.1°	—	—	—
$Ph_2Si(C{\equiv}CR)_2$	1.855[b]	1.822[a]	1.207[a]	—	—	—	—	—	—
(XRD)		1.816[b]	1.200[b]	—	—	—	—	—	—

Distances are given in Å, angles in degrees.
[a]From reference [17].
[b]From reference [18].

structure of unsubstituted [5]pericyclyne **9**, the 15-membered ring of **8F** is folded by angle $\theta = 16.7$ degrees, where the Si atom is part of a quasi-planar C_9Si moiety. The folding is not only due to the presence of a silicon atom in the 15-membered ring of **8F**: the planarity of the [5]pericyclyne **9** also is lost in tetrahydroxy-[5]pericyclyne **10F** ($\theta = 10$ degrees), displaying the enantiomeric stereochemistry of *carbo*-silolane **8F**. More generally, substitution of [5]pericyclyne **9** induces an out-of-plane distorsion. Indeed, an envelope conformation was also observed by X-ray diffraction analysis of decamethyl [5]pericyclyne **11** ($\theta = 40$ degrees),[14] and related twisted conformations were obtained by DFT calculations of various stereoisomers of pentahydroxy[5]pericyclynes.[15]

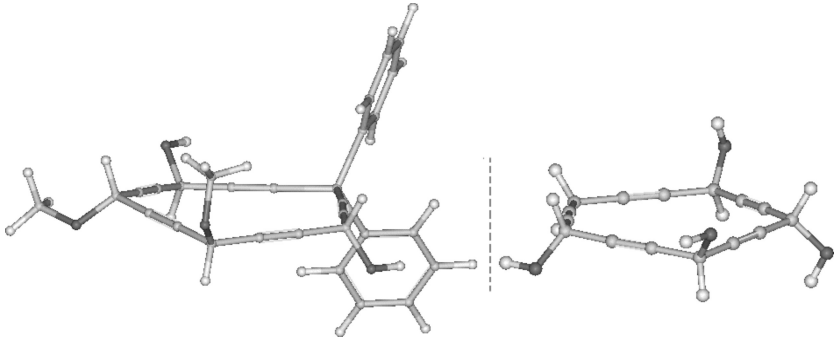


FIGURE 2 Calculated structures of the model *carbo*-silolane **8F** (*left*) and a related diastereoisomer of tetrahydroxy[5]pericyclyne **10F** (*right*).

It is however noteworthy that the global geometry of **8F** is very similar to that of **10F** at the same level of calculation (Table I, Figure 2). The angle between the Si–phenyl substituent planes of **8F** (63 degrees) falls close to the range (79–84 degrees) observed in related crystallographic structures of hexaphenylsilole[16] or oligoacetylenic silanes.[17,18] The calculated bonds lengths are also in quite good agreement with related available X-ray diffraction data (Table I), thus validating the calculation level used for **8F** and **10F**. As previously recognized,[19] the calculated bond distances are just slightly longer than those suggested by X-ray diffraction data.

CONCLUSION

The first functional sila[5]pericyclynes **2a** and **2b** have been obtained via a [5+10] cyclization route in nine and ten steps (including the previously described preparation of triyne **5**), in 4.5% and 3% overall yields, respectively. For this purpose, an improved preparation of the key triyndial **4** has been developed. One of the five vertices ($SiPh_2$) being not stereogenic, the reduced number of diastereomers (six in all) allowed us to purify one of them by silica gel chromatography (for the *carbo*-cyclopentane analogues, the use of semi-preparative HPLC techniques had been necessary).[5] In the absence of crystallographic data for **2a**, the geometry of a model stereoisomer (**10F**) has been studied at the DFT level. The optimized geometry of **10F** is envelope-shaped, as already observed for related substituted all-carbon [5]pericyclynes, but the silicon atom does not occupy the tip of the envelope. Non-reducing eliminative aromatization of **2b** was attempted with two equivalents of a Lewis acid ($Et_2O{\cdot}BF_3$) in dichloromethane, but the expected *carbo*-silole **1** could not be detected beside polymeric products. In spite of this failure, both *carbo*-silolanes **2a** and **2b** can be regarded as redox (or isohypsic) equivalents of **1** after elimination of two MeOH molecules. Further investigations will focus on the aromatization step. Keeping in mind the ultimate potential applications in material sciences,[2] the numerous physicochemical properties of the silole core[20] could indeed be tuned in its ring *carbo*-mer and justify these efforts.

EXPERIMENTAL

General

All reagents were used as their commercially available form (from Acros Organics, Avocado, Aldrich, Lancaster, Strem) without

further purification. THF and diethylether were dried and distilled on sodium/benzophenone, pentane, and dichloromethane on P_2O_5. Commercial solutions of EtMgBr are 3M in diethylether. Commercial solutions of *n*–BuLi are 1.6 or 2.5 M in hexane, and their effective concentrations were checked by titration with 2,2, 2′-trimethylpropionanilide.[21] All reactions were conducted under either a nitrogen or argon atmosphere, using Schlenk and vacuum line techniques. Thin layer chromatography plates were purchased from SDS (60F254, 0.25 mm) and revealed by treatment with an ethanolic solution of phosphomolybdic acid (20%). Column chromatographies were carried out with SDS silicagel (60 Å, 70–200 μ m). Special chromatographies were performed with a Combiflash Graduate ISCO System on Normal Phase Silice packs. The following analytical instruments were used: IR: 0.1 mm CaF_2 cell, Perkin-Elmer GX FT-IR; ^1H and ^{13}C NMR: Brucker AC 200, WM 250, DPX 300, or AMX 400; Mass spectrometry: Quadrupolar Nermag R10-10H; Elemental analyses: Perkin-Elmer 2400 CHN (flash combustion and detection by catharometry). IR absorption frequencies ν are in cm^{-1}. NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants J are in Hz. As most compounds were isolated as oily mixtures of diastereomers, characteristic assignments are given in order to trace the analytical consistency within the quite homogeneous series of compounds.

Syntheses

4,7-Dimethoxy-4,7-diphenyldeca-2,5,8-triyndial (4)

To a solution of **6** (100 mg, 0.267 mmol) in CH_2Cl_2 (10 mL) at 0°C, MnO_2 (928 mg, 10.7 mmol) was added after having been activated by drying under vacuum (10^{-2} mbar) for 17 h at 150°C. After 30 min at 0°C and 5 h 30 min at r.t., the reaction mixture was filtered over celite and concentrated under reduced pressure to give **4** as a yellow oil (60 mg, 61%). The spectroscopic data were identical to those previously reported.[1b]

4,7-Dimethoxy-4,7-diphenyldeca-2,5,8-triyn-1,10-diol (6)

A solution of *n*–BuLi (14 mL, 32 mmol) was added dropwise to a solution of **5** (4.6 g, 14.6 mmol) in THF (150 mL) at –78°C. The reaction mixture was warmed to –40°C for 10 min and at –40°C, fresh formaldehyde (dried over drierite and just formed from *p*-formaldehyde heated at 165°C) was bubbled via a needle into the solution for 2 h and another 1 h at –20°C. The bubbling was then stopped, and the solution

was stirred for 30 min at –20°C followed by 30 min at r.t. The reaction mixture was then quenched with the addition of a saturated NH_4Cl solution and washed with a solution of KOH (5%) to neutralize potential excess of formaldehyde. Further addition of saturated aqueous NH_4Cl decreased the pH to 7. The aqueous layer was extracted with Et_2O, and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographied over silica gel (heptane/AcOEt 2:8) to give **6** as an orange oil (5.21 g, 95%). $R_f \approx 0.35$ (heptane/AcOEt 4:6). MS (DCI/NH_3): m/z = 392 ($[M+NH_4]^+$), 360 ($[M+NH_4–MeOH]^+$), 343 ($[M+H–MeOH]^+$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.81 (s, 2 H, O-*H*), 3.46, 3.49 (s, 6 H, OC*H*$_3$), 4.27 (s, 4 H, C*H*$_2$OH), 7.32–7.41 (m, 6 H, *m*-, *p*-C$_6$*H*$_5$), 7.69–7.75 (m, 4 H, *o*-C$_6$*H*$_5$). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 50.71 (t, $^1J_{C-H}$ = 148 Hz, *C*H$_2$OH), 53.25 (q, $^1J_{C-H}$ = 144 Hz, O*C*H$_3$), 71.85 [s, Ph*C*(OMe)], 82.27 (s, Ph–C–C≡C–C–Ph), 84.36 (s, *C*≡C–CH$_2$OH), 85.74 (s, C≡*C*–CH$_2$OH), 125.10–130.44 (m, *o*-, *m*-, *p* – C$_6$H$_5$), 139.60 (s, *ipso*-*C*$_6$H$_5$–COMe). IR ($CDCl_3$): ν = 3423 (m, O–H), 2935 (m, C$_{sp3}$–H), 2826 (m, OC$_{sp3}$–H), 1599, 1490 and 1453 (m, C=C), 1068 (m, C–O).

Diethynyldiphenylsilane (7)

A solution of ethynylmagnesium bromide (45.7 mL, 22.8 mmol) was added dropwise to a solution of dichlorodiphenylsilane (1.2 mL, 5.7 mmol) in THF (20 mL) at 0°C. After stirring for 15 min at 0°C and 17 h at r.t., the solution was treated with saturated NH_4Cl solution. The organic layer was extracted with Et_2O, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give **7** as a red oil (1.158 g, 88%). $R_f \approx 0.37$ (heptane/AcOEt 9:1). MS (DCI/NH_3): m/z = 267 ($[M+N_2H_7]^+$), 250 ($[M+NH_4]^+$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.79 (s, 2 H, ≡C–*H*), 7.46–7.48 (m, 6 H, *m*-, *p*-C$_6$*H*$_5$), 7.81–7.84 (m, 4 H, *o*–C$_6$H$_5$). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$): δ = 83.40 (*C*≡CH), 97.55 (C≡*C*–H), 128.29 (*C*$_m$ of Ph), 130.72 (*C*$_p$ of Ph), 131.29 (*C*$_i$ of Ph), 134.83 (*C*$_o$ of Ph). IR ($CDCl_3$): ν = 3288 (C$_{sp}$–H), 3073 and 3055 (C$_{sp2}$–H), 2926 (C$_{sp3}$–H), 2042 (C≡C), 1589, 1486 and 1430 (C≡C of cycle).

7,10-Dimethoxy-1,1,7,10-tetraphenyl-1silacyclopentadeca-2,5,8,11,14-pentayn-4,13-diol (2a)

A solution of **7** (200 mg, 0.86 mmol) in THF (50 mL) was treated with EtMgBr (574 μL, 1.72 mmol) at 0°C. After stirring for 30 min at 0°C and 2 h at r.t., a solution of triyne dialdehyde **4** (319 mg, 0.86 mmol) in THF (100 mL) was added dropwise. After stirring 1 min at r.t., the

solution was treated with saturated NH_4Cl solution. The organic layer was extracted with Et_2O, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Purification through silica Combiflash column chromatography (heptane/AcOEt 8:2) gave **2a** as an orange oil (107 mg, 20%). $R_f \approx 0.08$ (heptane/AcOEt 8:2). MS (DCI/NH_3): m/z = 620 ($[M+NH_4]^+$), 588 ($[M–MeO^-+NH_3]^+$), 571 ($[M+H–MeOH]^+$). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.48 (s, br, 2 H, O–*H*), 3.42–3.58 (m, 6 H, OC*H*$_3$), 5.23–5.30 (m, 2 H, C*H*–OH), 7.32–7.46 (m, 12 H, *m*-, *p*-C_6H_5), 7.66–7.78 (m, 8 H, *o*–C_6H_5). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$): δ = 52.78 (O*C*H$_3$), 53.50 (*C*HOH), 71.92 (*C*–OMe), 80.99–83.72 (*C*≡C), 104.25 (C≡*C*–Si), 126.51–129.12 (C_m, C_o et C_p of Ph-C and C_p of Ph-Si), 130.79 (C_m of Ph-Si), 134.90 (C_o of Ph-Si), 139.12, 139.21 (C_i of Ph-Si and C_i of Ph-C). IR ($CDCl_3$): ν = 3584 (O–H), 3073 (C_{sp2}–H), 2935 (C_{sp3}–H), 2186 (CC≡CC), 2042 (SiC≡CC), 1590, 1490, 1450 and 1430 (C=C of cycle), 1068 (C–O).

4,7,10,13-Tetramethoxy-1,1,7,10-tetraphenyl-1-silacyclopentadeca-2,5,8,11,14-pentayne (2b)

A solution of pentayne **2a** (24 mg, 0.04 mmol) in Et_2O (10 mL) was treated with *n*–BuLi (32 μL, 0.08 mmol) for 3 min at –78°C. Methyl triflate (13 μL, 0.12 mmol) was then added dropwise. The temperature was allowed to warm to 0°C and the stirring was continued for 17 h at 0°C. After neutralization with $NaHCO_3$ (5%), the organic layer was hydrolized with saturated NH_4Cl solution, extracted with Et_2O, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give **2b** as an orange oil (17 mg, 68%). MS (DCI/NH_3): m/z = 648 ($[M+NH_4]^+$), 616 ($[M–MeO^-+NH_3]^+$), 599 ($[M+H–MeOH]^+$). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.40–3.62 (m, 12 H, OC*H*$_3$), 5.14–5.21 (m, 2 H, C*H*–OMe), 7.31–7.45 (m, 12 H, *m*-, *p*-C_6H_5), 7.66–7.79 (m, 8 H, *o*–C_6H_5). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 54.05 (PhC–O*C*H$_3$), 55.33 (HC–O*C*H$_3$), 60.76 (H–*C*–OMe), 69.97 (Ph–*C*–OMe), 80.96–84.89 (*C*≡C), 102.41 (C≡*C*–Si), 126.88–131.34 (C_m, C_o and C_p of Ph-C and C_p of Ph-Si), 128.64 (C_m of Ph–Si), 135.27 (C_o of Ph–Si), 139.76, 139.90 (C_i of Ph–Si and C_i of Ph–C). IR ($CDCl_3$): ν = 3073 (C_{sp2}–H), 2952 and 2933 (C_{sp3}–H), 2182 (CC≡CC), 2038 (SiC≡CC), 1589, 1490, 1450 and 1430 (C=C of cycle), 1074 (C–O).

Computational Details

Geometries were fully optimized (under symmetry constraint when possible) at the B3PW91/6-31G** level in the singlet spin state, using Gaussian98.[22] Vibrational analysis was performed at the same level in

order to check that a minimum was obtained on the potential energy surface.

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