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Rigid rod molecules containing two $Si(OMe)_3$ or $SiMe(OMe)_2$ groups for hybrid materials synthesis

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Abstract

The synthesis of new bis(trimethoxysilyl) and bis(dimethoxymethylsilyl)arene compounds containing rigid organic groups such as stilbenyl, diphenylacetylene or diphenylbut-1,3-diyne is reported. The Heck type reaction constituted a convenient route to these compounds, since this coupling reaction appeared compatible with the presence of $Si(OR)_3$ groups. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Trimethoxysilanes; Methyldimethoxysilanes; Synthesis; Heck reaction

1. Introduction

Over the past few years, we have focused our interest on the study of monophasic organic–inorganic hybrid materials obtained by sol–gel hydrolysis–polycondensation of organically polysubstituted alkoxysilanes [1]. Our interest in the control of the morphology of a material from the molecular level led us to study solids with various structural features, obtained from trialkoxysilylated precursors bearing two $Si(OR)_3$ groups [1]. We were particularly interested by rigid precursors with organic groups of different size. Whereas a variety of synthetic methods can be used for the trimethylsilylation of organic molecules [2], only a few ways for the preparation of trihalogenosilyl or trialkoxysilylderivatives $RSiX_3$ (X = Cl, OR…) have been developed. The trihalogenosilyl or trialkoxysilylderivatives are difficult intermediates in the synthesis of precursors because of the high reactivity of the $-SiX_3$ (X = Cl, OR) groups towards H_2O and other nucleophiles which make them incompatible with many experimental procedures of synthesis and separation. The hydrosilylation reaction [3] constitutes a general and selective route to trifunctional silicon compounds from olefins. The reaction of $ClSi(OMe)_3$ also allows the preparation of trimethoxysilyl derivatives [4,5] via silylation of organometallic intermediates or via an extension of the Calas–Dunoguès silylation reaction [6]. The cross-coupling reaction of the stable (triisopropyloxysilyl)methyl Grignard reagent with organic bromides [7] affords a facile access to trifunctional organosilicon compounds. Other methods of preparation of trifunctional silicon-containing molecules include silylation with $HSiCl_3$–NEt_3 [8], triethoxysilylation of aromatic iodides [9], nucleophilic substitution of tetramethoxysilane by an organometallic precursor [10]. We were also interested in the synthesis of bis(dimethoxymethysilyl) precursors. In the same way, very few methods have been described in literature concerning the methyldialkoxysilylation of aromatic compounds: (i) nucleophilic substitution of an aromatic Grignard reagent on methyltrialkoxysilane [11]; (ii) the methanolysis of methylaryldichlorosilanes in the presence of pyridine or triethylamine [12], or catalyzed by PPh_3CuH [13]; (iii) the nucleophilic substitution by sodium methoxide on a bulky alkoxysilane through the elimination of phenolate as the leaving group [14]; (iv) the methyldiethoxysilylation of 1,4-dibromobenzene [15,16].

We report here an extension of the Heck type reaction [17] permitting the synthesis of bis(trimethoxysilyl)arene and bis(dimethoxymethylsilyl)arene

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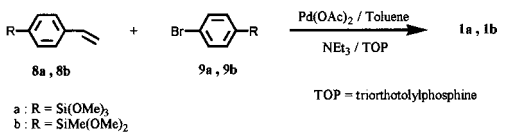
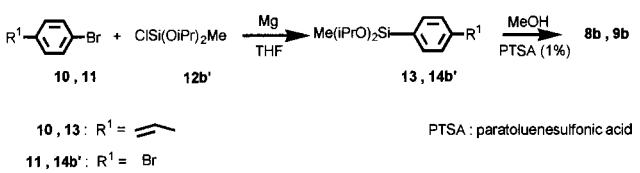
derivatives containing rigid organic groups, such as stilbenyl **1a**, **1b**, diphenylacetylene **2a**, **2b** or diphenylbut-1,3-diyne **3a**, **3b** (Table 1). The Pd-catalyzed cross-coupling reactions of halogenoarenes with styrene derivatives (Heck reaction) [17] are a convenient route to obtaining of stilbene derivatives. The extension of Heck reaction [18,19] is a useful reaction for the synthesis of acetylenic compounds under mild conditions. The new compounds presented here were synthesized using this coupling reaction which appeared very convenient for obtaining reactive trimethoxy and dimethoxysilyl derivatives.

Table 1

X–[ ]–X	X
1a	$Si(OMe)_3$
1b	$SiMe(OMe)_2$
2a	$Si(OMe)_3$
2b	$SiMe(OMe)_2$
3a	$Si(OMe)_3$
3b	$SiMe(OMe)_2$
4	$Si(OMe)_3$
5	$Si(OMe)_3$
6	$SiMe(OMe)_2$
7	$SiMe(OMe)_2$



Scheme 1.



Scheme 2.

2. Results

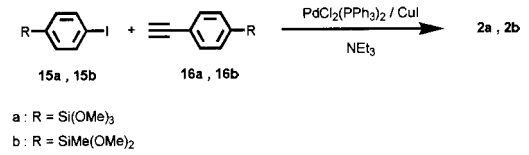
2.1. Synthesis of stilbene derivatives *1a* and *1b*

Compound 4,4′-bis(trimethoxysilyl)stilbene (**1a**) was obtained by Pd-catalyzed cross-coupling reaction of 4-(trimethoxysilyl)styrene (**8a**) [20] with 4-bromo-1-(trimethoxysilyl)benzene (**9a**) [21] (Heck reaction) [17]. The reaction was carried out in toluene in the presence of palladium(II) acetate, triethylamine and tri-ortho-tolylphosphine (Scheme 1). 4,4′-Bis(trimethoxysilyl)stilbene (**1a**) was isolated in almost quantitative yield. Attempts to direct silylation of 4,4′-dibromostilbene with chlorotrimethoxysilane in the presence of magnesium according to the extension of Calas–Dunoguès reaction [5] was not complete and led to a mixture of products.

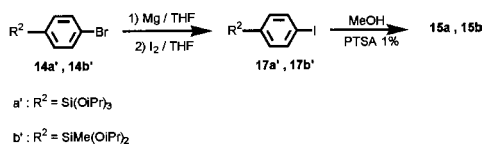
Compound 4,4′-bis(dimethoxymethylsilyl)stilbene (**1b**) was obtained using the same reaction conditions by coupling 4-(dimethoxymethylsilyl)styrene (**8b**) and 4-bromo-1-(dimethoxymethylsilyl)benzene (**9b**) (Scheme 1). Compound **8b** was obtained by silylation reaction of 4-bromostyrene **10** with chlorodiisopropyloxymethylsilane **12b′** using the extension of Calas–Dunoguès reaction [6], which gave **13**, and was followed by exchange of alkoxyde groups (Scheme 2). In a same way, **9b** was obtained starting from 1,4-dibromobenzene (**11**) (Scheme 2). Chlorodiisopropyloxymethylsilane **12b′** was prepared by treatment of one equivalent of methyltrichlorosilane with 2.2 equivalents of dry isopropanol in pentane.

2.2. Synthesis of diphenylacetylene compounds *2a* and *2b*

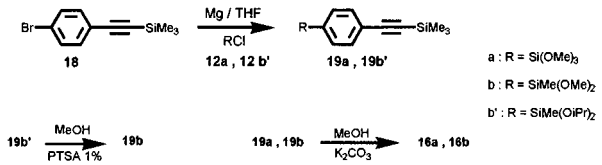
Compound 4,4′-bis(trimethoxysilyl)diphenylacetylene (**2a**) was obtained by coupling reaction of 4-iodo-1-(trimethoxysilyl)benzene (**15a**) with the alkyne 4-(trimethoxysilyl)phenylacetylene (**16a**) in the presence of a catalytic amount of bis(triphenylphosphine)palladium dichloride–cuprous iodide in triethylamine [18] (Scheme 3). An almost quantitative yield of 4,4′-bis(trimethoxysilyl)diphenylacetylene (**2a**) was recovered. The direct silylation of 4,4′-dibromodiphenylacetylene with chlorotrimethoxysilane in the presence



Scheme 3.



Scheme 4.



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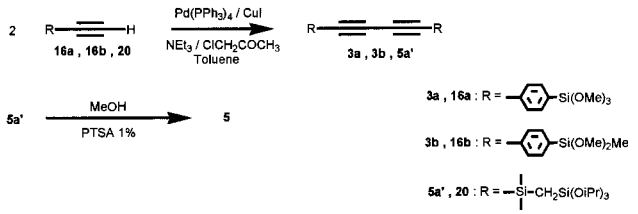

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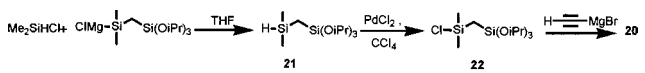
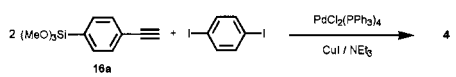


Scheme 7.



Scheme 8.

of magnesium (extension of Calas–Dunoguès reaction [5]) was not complete and led to a mixture of products.

Similarly 4,4′-(dimethoxymethylsilyl)diphenylacetylene (**2b**) was prepared following the same reaction starting from 4-iodo-1-(dimethoxymethylsilyl)benzene (**15b**) and 4-(dimethoxymethylsilyl)phenylacetylene (**16b**) (Scheme 3).

The synthesis of compounds **15a**, **15b**, **16a**, **16b** has been achieved. The 4-iodo-1-(trimethoxysilyl)benzene (**15a**) was obtained starting from 4-bromo-1-(triisopropyloxysilyl) benzene (**14a′**) which bears the bulky isopropyloxysilyl group [21]. The corresponding Grignard reagent was easily prepared [21] and reacted with iodine to give **17a′** in 88% yield. The compound **15a** was finally obtained from **17a′** by exchange reaction of alkoxyde groups in the presence of a catalytic amount of *p*-toluenesulfonic acid in anhydrous methanol (Scheme 4). Compound **15b** was synthesized following the same route (Scheme 4). [4-(Trimethoxysilyl)phenyl]acetylene (**16a**) and [4-(dimethoxymethylsilyl)phenyl]acetylene (**16b**) were obtained by alkoxysilylation of (4-bromophenyl)acetylene (**18**) following the extension of Calas–Dunoguès reaction. Compound **18** was prepared according to literature procedure [22]. The trimethylsilyl protecting group [23] was then easily removed by treatment of **19a** and **19b** with K_2CO_3 in anhydrous methanol [22,24] (Scheme 5).

*2.3. Synthesis of diphenylbut-1,3-diyne derivatives **3a**, **3b** and **5***

4,4′-Bis(trimethoxysilyl)diphenylbut-1,3-diyne (**3a**) and 4,4′-bis(dimethoxymethylsilyl)diphenylbut-1,3-diyne (**3b**) were obtained by homocondensation of **16a** and **16b**, respectively, in the presence of tetrakis-(triphenylphosphine)palladium(0), cuprous iodide and chloroacetone in triethylamine [25,26] (Scheme 6).

Bis[(triisopropyloxysilylmethyl)dimethylsilyl]but - 1,3-diyne (**5**) was prepared from **20** in the same conditions.

The synthesis of **20** has been achieved according to Scheme 7. Dimethylchlorosilane was treated by the (triisopropyloxysilyl)methyl Grignard reagent [7] to give **21**, which was converted into chloro compound **22** by reaction with $PdCl_2$ in CCl_4 [27]. The addition of the monoacetylene Grignard reagent to **22** yielded the intermediate **20**.

*2.4. Synthesis of 1,4-bis[2-(4-trimethoxysilylphenyl)ethynyl]benzene (**4**)*

The coupling reaction of two equivalents of the acetylenic compound **16a** with one equivalent of 1,4-diiodobenzene in the presence of a catalytic amount of bis(triphenylphosphine)palladium dichloride–cuprous iodide in triethylamine [18] afforded **4** in almost quantitative yield (Scheme 8).

*2.5. Synthesis of arene derivatives **6** and **7***

The synthesis of 1,4-(bis(dimethoxymethylsilyl)-benzene (**6**) and 4,4′-bis(dimethoxymethylsilyl)biphenyl (**7**) was investigated using a method reported in literature [16] in the case of the preparation of bis(alkyldiethoxysilyl)benzene. This reaction, which consisted in the dimethoxymethylsilylation of 1,4-dibromobenzene or 4,4-dibromobiphenyl in the presence of magnesium and methyltrimethoxysilane in THF, was not selective and afforded a mixture of unreacted dibromide, the product of monosubstitution and the ex-

pected compound. Compounds **6** and **7** were isolated in low yields (25 and 10%, respectively) after distillation.

Another route to **7** was developed which consisted in an extension of the Calas–Dunoguès reaction [5], using chlorodiisopropyloxymethylsilane **12b′** (Scheme 9). The intermediate **23** was obtained in 35% yield and was converted into **7** in 85% yield.

3. Conclusions

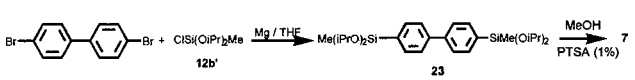
The Heck type reaction constitutes a convenient route to rigid bis(trimethoxy) or bis(dimethoxy) silanes. Such compounds constitute an interesting class of products since rigid molecules have been reported as precursors to nanostructured hybrid materials, which exhibit a self organization of the organic units in the solid. This arrangement has been detected by X-ray at a short range and by birefringence experiments for mesogenic properties [5,28,29]. The organization is important for possible physical and chemical properties. The experimental conditions and the reagents involved in the synthetic pathway appeared to be compatible with the presence of $Si(OR)_3$ groups.

4. Experimental

All reactions were carried out under Ar using a vacuum line and Schlenk techniques. Solvents were dried and distilled just before use. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR data were obtained on a Perkin–Elmer 1600FTIR spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker DPX-200 spectrometer and the ^{29}Si-NMR spectra were recorded on a Bruker WP-200 SY spectrometer. Chemical shifts are given relative to tetramethylsilane. Elemental analyses were carried out by the 'Service Central de Micro-Analyse du CNRS'.

4.1. 4,4′-Bis(trimethoxysilyl)stilbene (*1a*)

A mixture of 4-(trimethoxysilyl)styrene (**8a**) [20] (1.5 g, 6.7 mmol) and 4-bromo-1-(trimethoxysilyl)benzene (**9a**) [21] (1.85 g, 6.7 mmol) was dissolved in dry toluene (15 ml). Palladium acetate (10 mg, 4.45×10^{-5} mol), dry triethylamine (1.35 g, 13.3 mmol) and tri-orthotolylphosphine (TOP) (0.08 g, 2.67×10^{-5} mol) were added all at once successively. The brown suspension was heated during 24 h at 110°C. The yellow suspension was filtered at room temperature (r.t.) under silanized silica. The solvent was pumped off under vacuum and a yellow powder was obtained in quantitative yield (2.97 g, 6.7 mmol). ^{1}H-NMR ($CDCl_3$, δ): 7.69 (4H, d), 7.58 (4H, d), 7.20 (2H, s), 3.65 (18H, s). ^{13}C-NMR ($CDCl_3$, δ): 55.1, 111.9, 114.0, 125.2, 129.6, 139.7. ^{29}Si-NMR ($CDCl_3$, δ): −55.4. Anal. Calc. for $C_{20}H_{28}O_6Si_2$: C, 57.12; H, 6.71. Found: C, 57.86; H, 6.48%.



Scheme 9.

4.2. 4,4′-Bis(dimethoxymethylsilyl)stilbene (*1b*)

A mixture of 4-(dimethoxymethylsilyl)styrene (**8b**) (1.52 g, 7.2 mmol) and 4-bromo-1-(diisopropyloxymethylsilyl)benzene (**9b**) (1.9 g, 7.2 mmol) was dissolved in toluene (15 ml). Palladium acetate (81 mg, 3.6×10^{-4} mol), dry triethylamine (4.39 g, 43.2 mmol) and tri-orthotolylphosphine (TOP) (438 mg, 1.5×10^{-3} mol) were added all at once successively. The suspension was heated during 24 h at 120°C. The resulting suspension was filtered at r.t. over silanized silica. The solvent was pumped off under vacuum and a yellow powder was recovered. It was recrystallized in pentane. 4,4′-bis(dimethoxymethylsilyl)stilbene (**1b**) (1.54 g, 3.96 mmol) was obtained (yield 55%). ^{1}H-NMR ($CDCl_3$, δ): 7.65 (4H, d), 7.61 (4H, d),7.19 (2H, s), 3.60 (12H, s), 0.39 (3H, s).

4.3. 4-(Dimethoxymethylsilyl)styrene (*8b*)

A solution of 4-bromostyrene (**10**) (10 g, 55 mmol) in anhydrous THF (40 ml), was added dropwise to a suspension of magnesium chips (2.07 g, 86.4 mmol) and chloromethyldiisopropyloxysilane (**12b′**) (17.03 g, 109 mmol) in anhydrous THF (50 ml) at 0°C. The suspension was then stirred 24 h at 20°C. The solvent was pumped off under vacuum (2 mBar), the reaction mixture was then taken up with dry pentane (200 ml). The suspension was filtered. The filtrate was evaporated under vacuum (2 mBar) to give an oil which was distilled. (b.p. 70–75°C, 5×10^{-2} mBar) (8.23 g, 31 mmol) of 4-(diisopropyloxymethylsilyl)styrene (**13**) were obtained as a colorless oil in 56% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.65 (2H, d), 7.44 (2H, d), 6.75 (1H, dd), 5.80 (1H, d), 5.30 (1H, d), 4.22 (2H, hept), 1.22 (12H, d), 0.39 (3H, s).

Compound 4-(diisopropyloxymethylsilyl)styrene (**13**) (8.23 g, 31 mmol) was dissolved in dry MeOH (10 ml). 1% M *p*-toluene sulfonic acid (17 mg) was added all at once. The yellow suspension was stirred for 4 h. The organic solvent was pumped off and the corresponding crude oil was distilled under vacuum (b.p. 70–80°C, 5×10^{-2} mBar) to afford 4-(dimethoxymethylsilyl)styrene (**8b**) as a yellow oil (4 g, 20 mmol) in 65% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.64 (2H, d), 7.49 (2H, d), 6.77 (1H, dd), 5.84 (1H, d), 5.33 (1H, d), 3.60 (6H,s), 0.39 (3H, s).

4.4. 4-Bromo-1-(diisopropyloxymethylsilyl)benzene (14b′)

A solution of 4-bromophenyl magnesium bromide (7.82 g, 50 mmol) in THF (100 ml) was added at 0°C to a solution of chloromethyldiisopropyloxysilane (**12b′**) (10 g, 48 mmol). The mixture was stirred at r.t. for 24 h. After evaporation of the solvent, the yellow solid was extracted by 200 ml of dry pentane and filtered. The solvent was then pumped off to afford a yellow oil. Residual 1,4-dibromobenzene (**11**) was sublimated under vacuum at 80°C to give 4-bromo-1-(diisopropyloxymethylsilyl)benzene (**14b′**) as a colorless oil in 33% yield (5.1 g, 16 mmol). ^{1}H-NMR ($CDCl_3$, δ): 7.52 (4H, m), 4.22 (2H, hept), 1.24 (12H, d), 0.39 (3H, s). ^{13}C-NMR ($CDCl_3$, δ): 136.1, 134.5, 131.3, 125.1, 65.8, 26.1, −2.8. ^{29}Si-NMR ($CDCl_3$, δ): −21.8.

4.5. 4-Bromo-1-(dimethoxymethylsilyl)benzene (9b)

Compound 4-bromo-1-(diisopropyloxymethylsilyl)benzene (**14b′**) (5 g, 16 mmol) was dissolved in dry MeOH (20 ml). 1% M *p*-toluene sulfonic acid (30 mg) was added all at once. The suspension was stirred for 4 h. The organic solvent was pumped off and the corresponding crude oil was 4-bromo-1-(dimethoxymethylsilyl)benzene (**9b**) (2 g, 8 mmol) in 50% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.56 (4H, m), 3.59 (6H,s), 0.38 (3H, s).

4.6. Chloromethyldiisopropyloxysilane (12b′)

A solution of trichloromethylsilane (29.9 g, 200 mmol) in 200 ml of anhydrous pentane was placed in a Schlenck tube under an Ar atmosphere at 0°C. A solution of 2.2 equivalents of dry isopropanol (26.4 g, 440 mmol) was then added dropwise. The evolution of HCl was trapped by a concentrated solution of NaOH. At the end of addition, the reaction mixture was allowed to warm to r.t. and then stirred for 24 h. After this time the colorless solution was evaporated under vacuum (2 mBar) to give a colorless oil (36 g). It consisted in a mixture of chloromethyldiisopropyloxysilane (**12b′**) (∼80%) and methyltriisopropyloxysilane (∼20%).^{1}H-NMR ($CDCl_3$, δ): 4.37 (2H, hept), 1.26 (12H, d), 0.48 (3H, s).

4.7. 4,4′-Bis(trimethoxysilyl)diphenylacetylene (2a)

A solution of 4-(trimethoxysilyl)phenylacetylene (**16a**) (1.03 g, 4.62 mmol) in dry triethylamine (13.5 ml) with a stoichiometric amount of 4-iodo-1-(trimethoxysilyl)benzene (**15a**) (1.5 g, 4.62 mmol) was stirred for a few minutes. 3% M CuI (26 mg, 0.138 mmol) and bis-(triphenylphosphine)palladium chloride(II) (100 mg, 0.138 mmol) were added all at once, and the final brown suspension was stirred vigorously for 8 h at ∼20°C. The brown suspension was concentrated under vacuum and the dark residue was extracted with 50 ml of dry toluene. The yellow suspension was filtered on silanized silica and concentrated under vacuum. The expected product **2a** was obtained as a fine yellow powder (1.88 g, 4.49 mmol) in 97% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.68 (4H, m), 7.59 (4H, d), 3.67 (18H, s). ^{13}C-NMR ($CDCl_3$, δ): 135.1, 131.4, 130.2, 125.7, 90.9, 51.3. ^{29}Si-NMR ($CDCl_3$, δ): −54.8. Anal. Calc. for $C_{20}H_{26}O_6Si_2$: C, 57.39; H, 6.16; Si, 13.42. Found: C, 57.23; H, 5.85; Si, 13.45%.

4.8. 1-[4-(Trimethoxysilyl)phenyl]-2-trimethylsilylacetylene (19a)

A solution of [1-(4-bromophenyl)-2-trimethylsilyl]acetylene (**18**) [22] (17 g, 0.067 mol) in dry THF (60 ml) was added dropwise to a suspension of chlorotrimethoxysilane **12a** (16 g, 0.1 mol) and magnesium chips (2.45 g, 0.1 mol) in dry THF (60 ml) at 10°C. The mixture was then stirred at r.t. for 1 day. After evaporation of the solvent, the brown mixture was extracted with 200 ml of dry pentane and filtered. The solvent was then pumped off and the brown oil was distilled under vacuum (b.p. 78–81°C, 10^{-1} mBar) to afford a colorless oil **19a** in 46% yield (9 g, 0.031 mol). ^{1}H-NMR ($CDCl_3$, δ): 7.60 (2H, d), 7.47 (2H, d), 3.65 (9H, s), 0.28 (9H, s). ^{13}C-NMR ($CDCl_3$, δ): 134.9, 131.7, 130.8, 125.7, 105.3, 96.0, 51.2; 0.3. ^{29}Si-NMR ($CDCl_3$, δ): −17.32, −54.8. Anal. Calc. for $C_{14}H_{22}O_3Si_2$: C, 57.08; H, 7.52. Found: C, 57.07; H, 7.52%.

4.9. [4-(Trimethoxysilyl)phenyl]acetylene (16a)

A solution of 1-[4-(trimethoxysilyl)phenyl]-2-trimethylsilylacetylene (**19a**) (19.80 g, 0.067 mol) in 41.8 ml of dry MeOH was stirred for 4 h with potassium carbonate (0.84 g, 6.07 mmol) at r.t. The white suspension was concentrated under vacuum and the residue was extracted with 50 ml of dry pentane. After filtration, the solvent was removed under vacuum to give a crystalline beige powder. This crude solid was crystallized in dry hexane and afforded white crystals of [4-(trimethoxysilyl)phenyl]acetylene (**16a**) in 72% yield (10.76 g, 0.048 mol). m.p. 38–39°C. ^{1}H-NMR ($CDCl_3$, δ): 7.62 (2H, d), 7.53 (2H, d), 3.65 (9H, s), 3.17 (1H, s). ^{13}C-NMR ($CDCl_3$, δ): 135.0, 131.9, 130.8, 124.7, 83.8, 78.8, 51.3. ^{29}Si-NMR ($CDCl_3$, δ): −55.03. Anal. Calc. for $C_{11}H_{14}O_3Si$: C, 59.44; H, 6.34, Si, 12.64. Found: C, 59.85; H, 6.30, Si, 13.30%.

4.10. 4,4′-(Dimethoxymethylsilyl)diphenylacetylene (2b)

A solution of [4-(dimethoxymethylsilyl)phenyl]-acetylene (**16b**) (0.96 g, 4.64 mmol) in dry triethylamine

(15 ml) with a stoichiometric amount of 4-iodo-1-(dimethoxymethylsilyl)benzene (**15b**) (1.43 g, 4.64 mmol) was stirred for few minutes. 2.5% M CuI (23 mg, 0.12 mmol) and bis-(triphenylphosphine)palladium chloride(II) (82 mg, 0.12 mmol) were added all at once, and the final beige suspension was stirred vigorously for 15 h at ~20°C. The corresponding suspension was filtered on silanized silica and concentrated under vacuum. The expected product 4,4′-(dimethoxymethylsilyl)diphenylacetylene (**2b**) was obtained as an orange oil (1.72 g, 4.44 mmol) in 96% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.65 (4H, m), 7.57 (4H, d), 3.60 (12H, s), 0.40 (6H, s). ^{13}C-NMR ($CDCl_3$, δ): 134.69, 134.32, 131.35, 112.24, 90.73, 50.98, −4.79. ^{29}Si-NMR ($CDCl_3$, δ): −14.46.

4.11. 4-Iodo-1-(diisopropyloxymethylsilyl)benzene (17b′)

A solution of 4-bromo-1-(diisopropyloxymethylsilyl)-benzene (**14b′**) (13.35 g, 42.1 mmol) in THF (85 ml) was added slowly dropwise at 0°C to a suspension of magnesium chips (1.53 g, 63.1 mmol) in THF (10 ml). After 1 h, the Grignard reagent of 4-bromo-1-(diisopropyloxymethylsilyl)benzene was added dropwise at 0°C to iodine (13.87 g, 54 mmol) dissolved in 50 ml of dry THF. After stirring during 4 h, the solvent was pumped off and the residue was extracted with dry pentane (200 ml) and filtered. The yellow solution was concentrated to afford 4-iodo-1-(diisopropyloxymethylsilyl)benzene (**17b′**) as a yellow oil in 84% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.76 (2H, d), 7.42 (2H, d), 4.21 (2H, hept), 1.23 (12H, t), 0.37 (3H, s).

4.12. 4-Iodo-1-(dimethoxymethylsilyl)benzene (15b)

Compound 4-iodo-1-(diisopropyloxymethylsilyl)-benzene (**17b′**) (11.27 g, 35.5 mmol) was dissolved in dry MeOH (12.87 g, 400 mmol). 1% M *p*-toluene sulfonic acid (53 mg, 0.3 mmol) was added all at once. The yellow suspension was stirred for 4 h. The organic solvent was pumped off and the corresponding crude orange oil was distilled under vacuum (b.p. 59–69°C, 3×10^{-1} mBar) to afford 4-iodo-1-(dimethoxymethylsilyl)benzene (**15b**) as a colorless oil (9 g, 30 mmol) in 82% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.78 (2H, d), 7.37 (2H, d), 3.58 (6H,s), 0.37 (3H, s).

4.13. 1-[4-(Diisopropyloxymethylsilyl)phenyl]-2-trimethylsilylacetylene (19b′)

A solution of the Grignard reagent prepared from 1-(4-bromophenyl)-2-trimethylsilylacetylene (13.85 g, 50 mmol) in THF (100 ml) was added at 0°C to a solution of chloromethyldiisopropyloxysilane (**12b′**) (12 g, 60 mmol). The mixture was stirred at r.t. for 24 h. After evaporation of the solvent, the gray solid was extracted by 200 ml of dry pentane and filtered. The solvent was then pumped off to afford a yellow oil. This oil was distilled under vacuum (b.p. 80–85°C, 10^{-2} mBar) to afford **19b′** as a colorless oil in 66% yield (11 g, 33 mmol). ^{1}H-NMR ($CDCl_3$, δ): 7.63 (2H, d), 7.46 (2H, d), 4.21 (2H, hept), 1.20 (12H, m), 0.28 (9H, s).

4.14. 1-[4-(Dimethoxmethylsilyl)phenyl]-2-trimethylsilylacetylene (19b)

Compound 1-[4-(diisopropoxymethylsilyl)phenyl]-2-trimethylsilylacetylene (**19b′**) (5.01 g, 15 mmol) was dissolved in dry MeOH (4.29 g, 130 mmol). 1% M *p*-toluene sulfonic acid (17 mg, 0.1 mmol) was added all at once. The suspension was stirred for 4 h. The organic solvent was pumped off and the corresponding crude orange oil was distilled under vacuum (b.p. 75–80°C, 10^{-2} mBar) to afford 1-[4-(dimethoxymethylsilyl)phenyl]-2-trimethylsilylacetylene (**19b**) as a colorless oil (3.3 g, 11.7 mmol) in 78% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.58 (4H, m), 3.65 (12H,s), 0.40 (6H, s), 0.27 (9H, s).

4.15. 4-(Dimethoxymethylsilyl)phenylacetylene (16b)

A solution of 1-[4-(dimethoxymethylsilyl)phenyl]-2-trimethylsilylacetylene (**19b**) (5 g, 17.80 mmol) in 25 ml of dry MeOH was stirred for 2 h with potassium carbonate (120 mg, 0.80 mmol) at r.t. The dark suspension was concentrated under vacuum and the residue was extracted with 60 ml of dry hexane. After filtration, the solvent was removed under vacuum to give [4-(dimethoxymethylsilyl)phenyl]acetylene (**16b**) as a colorless oil (3.4 g, 16.5 mmol) in 93% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.59 (2H, d), 7.55 (2H, d), 3.59 (6H, s), 3.16 (1 H, s), 0.39 (3H, s).

4.16. 4,4′-Bis-(trimethoxysilyl)diphenylbut-1,3-diyne (3a)

[4-(Trimethoxysilyl)phenyl]acetylene (**16a**) (2 g, 9 mmol), one equivalent of chloroacetone (0.67 g, 9 mmol), two equivalents of dry triethylamine (2.51 ml), 7.6% M CuI (130 mg, 0.68 mmol) and 3% M tetrakis-(triphenylphosphine)palladium (312 mg, 27 mmol) were added all at once. The final black solution was stirred for 24 h at 20°C. The resulting black suspension was concentrated under vacuum and the dark residue was extracted with 50 ml of dry pentane. The residual dark suspension was filtered on silanized silica and concentrated under vacuum. The black crude oil was crystallized twice in dry pentane and afforded the expected product **3a** as a yellow fine powder in 67% yield (1.58 g, 3.31 mmol) (m.p. 57–59°C). ^{1}H-NMR ($CDCl_3$, δ): 7.66 (4H, d), 7.56 (4H, d), 3.66 (18H, s). ^{13}C-NMR ($CDCl_3$, δ): 135.1, 132.2, 131.5, 124.2, 82.2, 75.3, 51.3. ^{29}Si-NMR ($CDCl_3$, δ): −55.3. Anal. Calc. for $C_{25}H_{26}O_6Si_2$: C, 62.74; H, 5.40; Si, 11.73. Found: C, 60.05; H, 5.56; Si, 13.20%.

4.17. 4,4′-Bis-(dimethoxymethylsilyl)diphenylbut-1,3-diyne (3b)

In a Schlenk tube under Ar, 1.66 g (8.04 mmol) of [4-(dimethoxymethylsilyl)phenyl]acetylene (**16b**), one equivalent of chloroacetone (0.745 g, 8.04 mmol), two equivalents of dry ethylamine (2.3 ml), 7.6% M CuI (116 mg, 0.61 mmol) and tetrakis-(triphenylphosphine) palladium(0) (280 mg, 0.61 mmol) were added all at once. The final black solution was stirred for 4.5 h at ~20°C. The residual dark suspension was filtered on silanized silica and concentrated under vacuum to afford a crude yellow oil. It was crystallized twice in dry pentane and afforded 4,4′-bis-(dimethoxymethylsilyl)diphenylbut-1,3-diyne (**3b**) as a yellow fine powder (1 g, 2.43 mmol) (m.p. 85–86°C) in 61% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.64 (4H, d), 7.57 (4H, d), 3.60 (12H, s), 0.39 (6H, s). ^{29}Si-NMR ($CDCl_3$, δ): −14.80.

4.18. 1,4-Bis-[2-(4-trimethoxysilylphenyl)ethynyl]-benzene (4)

A solution of [4-(trimethoxysilyl)phenyl]acetylene (**16a**) (1 g, 4.50 mmol) in dry triethylamine (12.5 ml) with a 0.5 equivalent of 1,4-diodobenzene (0.74 g, 2.25 mmol) was stirred for few minutes. 5% M CuI (21 mg, 0.112 mmol) and bis-(triphenylphosphine)palladium chloride(II) (80 mg, 0.112 mmol) were added all at once, the final brown suspension was stirred vigorously for 8 h at ~20°C. The brown suspension was concentrated under vacuum and the dark residue was extracted with 50 ml of dry toluene. The yellow suspension was filtered on silanized silica and concentrated under vacuum. The expected product was obtained as a fine yellow–orange powder. Crystallization in hexane–dichloromethane (1:1) gave the expected product **4** as an orange powder (1.88 g, 4.49 mmol) in 97% yield. m.p. 164–166°C. ^{1}H-NMR ($CDCl_3$, δ): 7.69 (4H, d), 7.59 (4H, d), 7.55 (4H, s), 3.67 (18 H, s). ^{13}C-NMR ($CDCl_3$, δ): 135.1, 132.0, 131.4, 130.4, 125.6, 123.5, 91.6, 90.8, 51.3. ^{29}Si-NMR ($CDCl_3$, δ): −55.9. Anal. Calc. for $C_{28}H_{30}O_6Si_2$: C, 64.48; H, 5.78; Si, 10.83. Found: C, 63.42; H, 5.73; Si, 11.75%.

4.19. Bis[(triisopropyloxysilylmethyl)dimethylsilyl]-but-1,3-diyne (5)

In a Schlenk tube under argon, 1.5 g (5 mmol) of [(triisopropyloxysilylmethyl)(dimethyl)(ethynyl)]silane (**20**), one equivalent of chloroacetone (0.46 g, 5 mmol), two equivalents of dry ethylamine (1.3 ml), 7.6% M CuI (72 mg, 0.38 mmol) and tetrakis-(triphenylphosphine)palladium(0) (173 mg, 0.38 mmol) were added all at once. The final black solution was stirred for 10 h at r.t. The residual dark suspension was filtered on silanized silica and concentrated under vacuum to afford a crude yellow oil distilled under vacuum (b.p. 120–130°C, 5×10^{-2} mbar). The expected product **5** was obtained as an oil (0.75 g, 1.25 mmol) (55% yield). ^{1}H-NMR ($CDCl_3$, δ): 4.23 (hept, 3H, hept), 1.21 (8H, d), −0.27 (6H, s), 0,00 (2H, s). ^{13}C-NMR ($CDCl_3$, δ): 88.30, 87.39, 65.38, 29.96, 0.60, 0.57. ^{29}Si-NMR ($CDCl_3$, δ): −15.94, −50.13.

4.20. (Triisopropyloxysilylmethyl)dimethylsilane (21)

The Grignard reagent of chloromethyltriisopropyloxysilane (0.045 mol) was added dropwise at 0°C to chlorodimethylsilane (3.76 g, 0.040 mol) dissolved in 150 ml of THF. The mixture was stirred at 30°C for about 24 h. After evaporation of THF the residue was extracted with 400 ml of dry pentane and filtrated. Pentane was then pumped off to give a yellow oil. The distillation of this oil (b.p. 74–77°C, 5×10^{-1} mBar) afforded 7.04 g (0.027 mol) of (triisopropyloxysilylmethyl)dimethylsilane (**21**) (67% yield). ^{1}H-NMR ($CDCl_3$,δ): 4.24 (3H, hept), 4.05 (1H, hept), 1.23 (18H, d), 0.16 (6H, d), −0.12 (2H, d). ^{13}C-NMR (δ): 65.22, 25.95, −1.47, −2.78. ^{29}Si-NMR ($CDCl_3$,δ): 15.57, −48.46.

4.21. (Triisopropyloxysilylmethyl)dimethylchlorosilane (22)

The compound (triisopropyloxysilylmethyl)dimethylsilane (**21**) (10.4 g, 0.037 mol) was added dropwise at r.t. to a solution of CCl_4 (60 ml) containing $PdCl_2$ (66×10^{-3} g, 74×10^{-4} mol). The dark mixture was stirred at 80°C for 24 h. The solvent was then evaporated under vacuo to give a yellow oil. The distillation of the residue (b.p. 80°C, 2 mBar) afforded 10.01 g (0.032 mol) of (triisopropyloxysilylmethyl)dimethylchlorosilane (**22**) (88% yield). ^{1}H-NMR: 4.25 (3H, hept), 1.23 (18H, d), 0.54 (6H, s), 0.30 (2H, s). ^{13}C-NMR ($CDCl_3$, δ): 65.52, 25.61, 4.28, 1.56.

4.22. [(Triisopropyloxysilylmethyl)(dimethyl)-(ethynyl)]silane (20)

A solution of ethynylmagnesiumbromide (0.035 mol) was added dropwise at 0°C to (triisopropyloxysilylmethyl)dimethylchlorosilane (**22**) (9.26 g, 0.030 mol) dissolved in 40 ml of THF. The mixture was stirred at r.t. for about 18 h. After evaporation of THF, the residue was extracted with 200 ml of dry pentane and filtrated. The organic solvent was then pumped off to give an oil. Distillation of the residue (b.p. 73°C, 2 mBar) afforded 7.1 g (0.024 mol, 67% yield) of [(triisopropyloxysilylmethyl)(dimethyl)(ethynyl)]silane (**20**). ^{1}H-NMR ($CDCl_3$, δ): 4.24 (3H, hept), 2.41 (1H, s), 1.22 (18H, d), 0.31 (1H, s), 0.03 (1H, s).

4.23. 1,4-Bis-(dimethoxymethylsilyl)benzene (6)

A solution of 1,4-dibromobenzene (24.75 g, 105 mmol) in 60 ml of anhydrous THF, was added dropwise to a suspension of magnesium (12.60 g, 518 mmol) and methyltrimethoxysilane (28.60 g, 210 mmol) in 20 ml of anhydrous THF at 0°C. The suspension was then stirred 24 h at 20°C. The solvent was pumped off under vacuum (2 mBar), the reaction mixture was then taken up with 250 ml of dry pentane. The green suspension was filtered. The filtrate was evaporated under vacuum (2 mBar) to give a pale yellow oil which was distilled (b.p. 105–110°C, 5×10^{-1} mBar). Product 1,4-bis-(dimethoxymethylsilyl)benzene (**6**) (7.38 g, 26.5 mmol) was obtained as a colorless oil which crystallized at r.t. in 25% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.67 (4H, s), 3.60 (12H, s), 0.39 (6H, s). ^{29}Si-NMR ($CDCl_3$, δ): -14.90. Anal. Calc. for $C_{12}H_{22}O_4Si_2$: C, 50.35; H, 7.69; Si, 19.58. Found: C, 50.30; H, 7.64; Si, 20.01%.

4.24. 4,4′-Bis(dimethoxymethylsilyl)biphenyl (7)

Compound 4,4′-bis(diisopropyloxymethylsilyl)-diphenyl (**23**) (7.1 g, 15 mmol) was dissolved in dry MeOH (4.29 g, 130 mmol). 1% M *p*-toluene sulfonic acid (17 mg, 0.1 mmol) was added all at once. The suspension was stirred for 4 h. The organic solvent was pumped off and the corresponding crude orange oil was distilled under vacuum (b.p. 110–115°C, 10^{-2} mBar) to afford 4,4-bis-(dimethoxymethylsilyl)biphenyl (**7**) as a colorless oil (3.83 g, 12.75 mmol) in 85% yield. ^{1}H-NMR ($CDCl_3$, δ): 7.72 (4H, d), 7.67 (4H, d), 3.65 (12H, s), 0.44 (6H, s). ^{29}Si-NMR ($CDCl_3$, δ): -14.7.

4.25. 4,4′-Bis(diisopropyloxymethylsilyl)diphenyl (23)

A solution of diGrignard reagent of 4,4′-dibromobiphenyl (18.03 g, 50 mmol) in THF (100 ml) was added at 0°C to a solution of chloromethyldiisopropyloxysilane (**12b′**) (22 g, 110 mmol). The mixture was stirred at r.t. for 24 h. After evaporation of the solvent, the gray solid was extracted with 200 ml of dry pentane and filtered. The solvent was then pumped off to afford a yellow oil. Residual 4,4′-dibromobiphenyl was sublimated under vacuum at 100°C. The resulting oil was distilled under vacuum (b.p. 120–130°C, 10^{-1} mbar) to afford **23** as a colorless oil in 35% yield (8.29 g, 17.5 mmol). ^{1}H-NMR ($CDCl_3$, δ): 7.70 (4H, m), 7.67 (4H, m), 4.25 (4H, hept), 1.26 (12H, m), 0.39 (3H, s).

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