ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

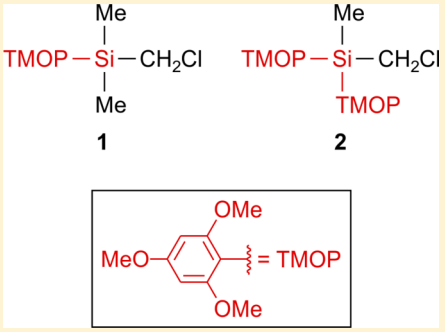
Synthesis of Silicon-Functionalized (Silylmethyl)silanes and α,ω-Dichlorocarbosilanes Using the TMOP (2,4,6-Trimethoxyphenyl) Protecting Group: (TMOP)Me_2SiCH_2Cl and $(TMOP)_2MeSiCH_2Cl$ as Reagents To Introduce the $ClMe_2SiCH_2$, $MeOMe_2SiCH_2$, or $Cl_2MeSiCH_2$ Group by Nucleophilic Substitution at Silicon

Nadine Laskowski, Eva-Maria Reis, Lisa Kötzner, Johannes A. Baus, Christian Burschka, and Reinhold Tacke*

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Supporting Information

ABSTRACT: In this study, the synthetic potential of the 2,4,6-trimethoxyphenyl (TMOP)-substituted (chloromethyl)silanes (TMOP)Me_2SiCH_2Cl (**1**) and $(TMOP)_2MeSiCH_2Cl$ (**2**) for the preparation of Si-functionalized (silylmethyl)-silanes and α,ω-dichlorocarbosilanes (with skeletons consisting of alternate carbon and silicon atoms) was investigated. Compounds **1** and **2** were used as reagents to introduce the $ClMe_2SiCH_2$, $MeOMe_2SiCH_2$, or $Cl_2MeSiCH_2$ group by nucleophilic substitution at silicon. The three-step synthetic method involves the (i) transformation of **1** and **2** into (TMOP)Me_2SiCH_2MgCl, (TMOP)-Me_2SiCH_2Li, $(TMOP)_2MeSiCH_2MgCl$, and $(TMOP)_2MeSiCH_2Li$, respectively, (ii) reaction of these nucleophiles with chloro- or methoxysilanes, and (iii) subsequent selective cleavage of the TMOP protecting group with HCl/Et_2O or $MeOH/[CF_3COOH]$. Using this method, the following compounds were prepared: $ClMe_2SiCH_2SiMe_3$ (**3**), $ClMe_2SiCH_2SiMe_2Cl$ (**4**), $ClMe_2SiCH_2SiMeCl_2$ (**5**), $ClMe_2SiCH_2SiCl_3$ (**6**), $ClMe_2SiCH_2Si(OMe)_3$ (**7**), $MeOMe_2SiCH_2Si(OMe)_3$ (**8**), $Cl_2MeSiCH_2SiMe_3$ (**9**), $Me_2Si(CH_2SiMe_2Cl)_2$ (**10**), and $Me_2Si(CH_2SiMe_2CH_2SiMe_2Cl)_2$ (**11**).



INTRODUCTION

In a series of recent publications, we have demonstrated that the 2,4,6-trimethoxyphenyl (TMOP) unit can be used effectively as a protecting group for silicon in synthetic organosilicon chemistry.[1] The TMOP group can be cleaved selectively under mild conditions using an ethereal hydrogen chloride solution to give the corresponding chlorosilane. Alternatively, deprotection with methanol, in the presence of catalytic amounts of trifluoroacetic acid, affords the corresponding methoxysilane.

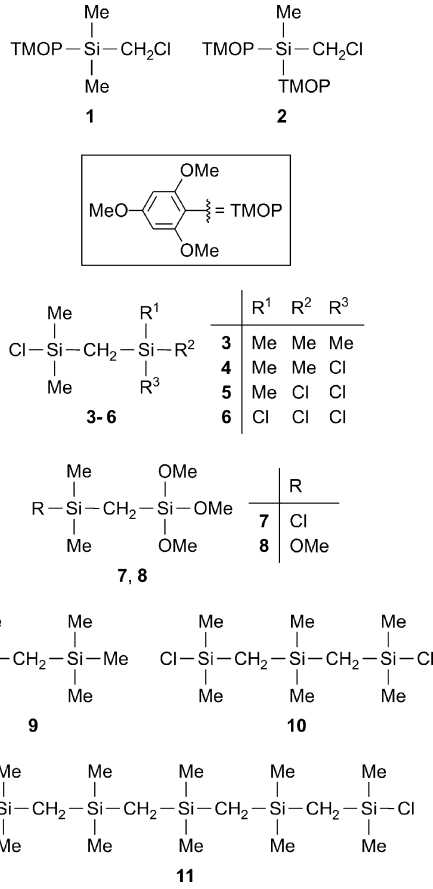
Si-functional (silylmethyl)silanes, such as **3**,[2] **4**,[3,4] **5**,[4] and **6**,[5] are versatile building blocks in synthetic organosilicon chemistry, which have been synthesized by various synthetic methods. In consideration of the growing demand for convenient, reliable, and generally applicable preparative methods for the synthesis of Si-functional (silylmethyl)silanes, we have developed a novel strategy for the preparation of compounds of this particular type by using the TMOP protecting group. This strategy is based on the use of the TMOP-substituted silanes **1** and **2** as reagents to introduce XMe_2SiCH_2 (X = Cl, OMe) or $Cl_2MeSiCH_2$ groups by nucleophilic substitution at the silicon atom of a given chloro- or methoxysilane using a three-step method. In the first step, the (chloromethyl)silanes **1** and **2** are transformed into the nucleophilic reagents (TMOP)Me_2SiCH_2MgCl, $(TMOP)_2MeSiCH_2MgCl$, and $(TMOP)_2MeSiCH_2Li$ (reaction with magnesium and lithium/naphthalene, respectively), which were then reacted in the second step with a chloro- or methoxysilane to introduce the (TMOP)Me_2SiCH_2 or $(TMOP)_2MeSiCH_2$ group by nucleophilic substitution at silicon. In the third step, the TMOP protecting group(s) is (are) cleaved selectively to furnish Si−Cl or Si−OMe moieties. To demonstrate the potential of this approach, we report here on the synthesis of compounds **1** and **2** and their use for the preparation of the Si-functionalized (silylmethyl)silanes **3**−**9** (Scheme 1).

To further demonstrate the potential of this synthetic method, we have also prepared the α,ω-dichlorocarbosilane **11**[6] via the intermediate **10**,[6,7] starting from dichlorodimethylsilane and using **1** as reagent to introduce $ClMe_2SiCH_2$ groups (Scheme 1).[8] In this case, we used the more reactive lithium reagent (TMOP)Me_2SiCH_2Li (obtained by reaction of **1** with lithium/naphthalene) instead of the corresponding Grignard reagent. The studies reported here were performed as part of

Received: March 11, 2013

   dx.doi.org/10.1021/om400190q | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 1. Chemical Structures of Compounds 1−11

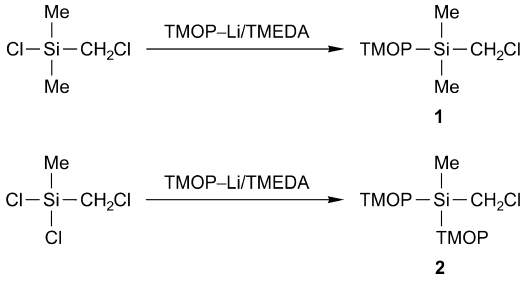


our systematic investigations on the chemistry of both (2,4,6-trimethoxyphenyl)silanes[1] and (chloromethyl)silanes.[9]

RESULTS AND DISCUSSION

Syntheses. (Chloromethyl)dimethyl(2,4,6-trimethoxyphenyl)silane (**1**) and (chloromethyl)methylbis(2,4,6-trimethoxyphenyl)silane (**2**) were synthesized according to Scheme 2, starting from chloro(chloromethyl)dimethylsilane

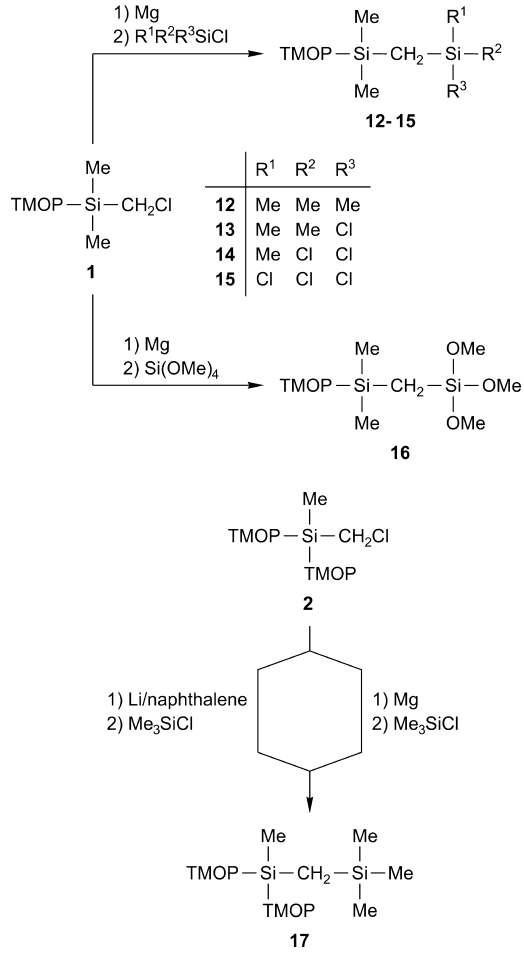
Scheme 2. Syntheses of Compounds 1 and 2



or dichloro(chloromethyl)methylsilane. Thus, reaction of $ClMe_2SiCH_2Cl$ and $Cl_2MeSiCH_2Cl$ with 1 or 2 molar equiv of (2,4,6-trimethoxyphenyl)lithium (TMOP-Li; obtained by reaction of 1,3,5-trimethoxybenzene with *n*-butyllithium in a mixture of hexanes and *n*-pentane, in the presence of *N,N,N′,N′*-tetramethylethane-1,2-diamine (TMEDA)) afforded **1** (82% yield) and **2** (80% yield), respectively.

The (2,4,6-trimethoxyphenyl)silanes **12**−**15** were synthesized according to Scheme 3. Thus, treatment of **1** with an

Scheme 3. Syntheses of Compounds 12−17

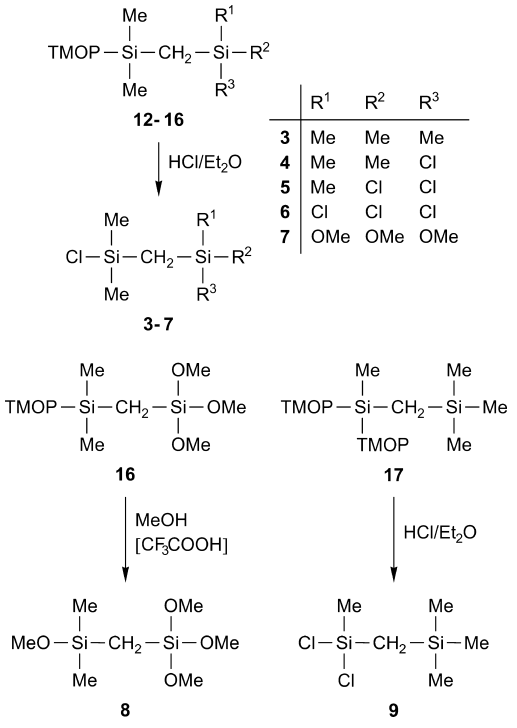


excess of magnesium turnings in tetrahydrofuran (THF) furnished the corresponding Grignard reagent (TMOP)-Me_2SiCH_2MgCl, which was then treated with 1 molar equiv of the corresponding chlorosilane to give compounds **12**−**15** (**12**, 87% yield; **13**, 78%; **14**, 71%; **15**, 64%). Compound **16** was prepared analogously by reaction of the Grignard reagent $(TMOP)Me_2SiCH_2MgCl$ with 1 molar equiv of tetramethoxysilane (54% yield; Scheme 3). Similarly, treatment of **2** with an excess of magnesium turnings in THF (formation of the Grignard reagent $(TMOP)_2MeSiCH_2MgCl$), followed by treatment with 1 molar equiv of chlorotrimethylsilane, gave the corresponding bis(2,4,6-trimethoxyphenyl)silane **17** (18% yield; Scheme 3). The yield of **17** could be significantly increased (→56%) by using the lithium reagent $(TMOP)_2MeSiCH_2Li$ instead of the Grignard reagent (Scheme 3). $(TMOP)_2MeSiCH_2Li$ was obtained by lithiation of **2** with lithium/naphthalene in THF.

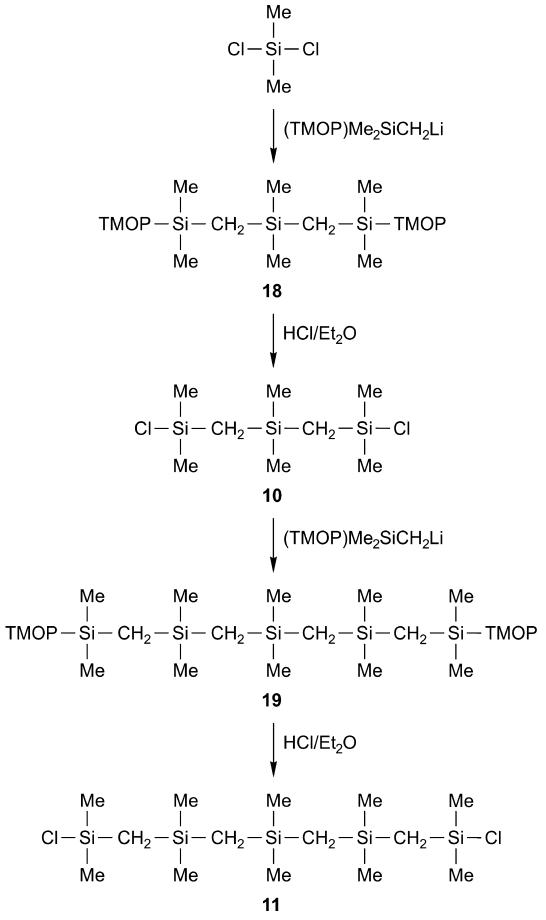
As already demonstrated in earlier studies,[1] the TMOP group can be cleaved selectively under mild conditions. Accordingly, treatment of the (2,4,6-trimethoxyphenyl)silanes **12**−**16** with 1 molar equiv of hydrogen chloride in diethyl ether at 0 °C furnished the corresponding chlorosilanes **3**−**7** (Scheme 4). In the case of **12**−**15**, these cleavage reactions occurred selectively and almost quantitatively, as monitored by gas chromatographic studies. In the case of **16**, however, byproducts (partial Si−O cleavage) were detected. Treatment of **16** with an excess of methanol in diethyl ether at 20 °C, in the presence of trifluoroacetic acid (7 mol %), afforded the corresponding

dx.doi.org/10.1021/om400190q | *Organometallics* XXXX, XXX, XXX−XXX

Scheme 4. Syntheses of Compounds 3−9



Scheme 5. Syntheses of Compounds 10, 11, 18, and 19



methoxysilane **8** (Scheme 4). As in the case of **12−15**, the cleavage reaction was selective and almost quantitative. Treatment of the bis(2,4,6-trimethoxyphenyl)silane **17** with 2 molar equiv of hydrogen chloride in diethyl ether at 0 °C furnished the corresponding dichlorosilane **9** (Scheme 4). Again, a selective and almost quantitative cleavage reaction was observed. Despite the quantitative reactions observed, compounds **3−6**, **8**, and **9** could be only isolated in 54−75% yield (**3**, 75% yield; **4**, 68%; **5**, 61%; **6**, 56%; **8**, 58%; **9**, 54%). This loss of yield can be explained by the fact that (i) the syntheses were performed on a 1−5 g scale and (ii) we mainly aimed at the preparation of analytically pure products. As the isolation of **3−9** implies a separation from the cleavage product 1,3,5-trimethoxybenzene by a combination of crystallization and distillation, higher yields could not be achieved. However, syntheses on a larger scale should lead to significantly higher yields. Furthermore, for compounds **3−9** to serve as intermediates in further syntheses, their isolation is not necessary, in so far as the reactivity profile of 1,3,5-trimethoxybenzene does not interfere with the reactions to be performed.

The carbosilane **11** was prepared by a four-step synthesis, starting from dichlorodimethylsilane (Scheme 5). In the first step, Cl_2SiMe_2 was treated with 2 molar equiv of (TMOP)-Me_2SiCH_2Li in THF at −30 °C (→20 °C) to give the 1,5-bis(2,4,6-trimethoxyphenyl)carbosilane **18** (78% yield).[10] Reaction of **18** with 2 molar equiv of hydrogen chloride in diethyl ether at 0 °C afforded the corresponding 1,5-dichlorocarbosilane **10** (48% yield), which upon reaction with 2 molar equiv of (TMOP)Me_2SiCH_2Li in THF at −30 °C (→20 °C) furnished the 1,9-bis(2,4,6-trimethoxyphenyl)carbosilane **19** (61% yield). Subsequent treatment of **19** with 2 molar equiv of hydrogen chloride in diethyl ether at 0 °C finally afforded the corresponding 1,9-dichlorocarbosilane **11** (62% yield). As observed for the analogous reactions described in Scheme 4, the cleavage reactions **18** → **10** and **19** → **11** were also selective and almost quantitative.

Compounds **1**, **2**, **12−15**, **17**, and **18** were isolated as colorless crystalline solids, whereas **3−11**, **16**, and **19** were obtained as colorless liquids. The identities of all these compounds were established by elemental analyses (C, H; except **7**) and NMR spectroscopic studies (^1H, ^{13}C, ^{29}Si). In addition, compounds **1**, **2**, **12−15**, **17**, and **18** were characterized by crystal structure analyses.

Crystal Structure Analyses. Compounds **1**, **2**, **12−15**, **17**, and **18** were structurally characterized by single-crystal X-ray diffraction. The molecular structures of **1**, **2**, **12−15**, **17**, and **18** are depicted in Figures 1−8, respectively; selected bond lengths and angles are given in the respective figure legends. The bond lengths and angles of all these compounds are in the expected ranges and therefore do not need any further discussion (for further details concerning the crystal structure analyses, see the Supporting Information).

■ CONCLUSIONS

With the synthesis of the Si-functionalized (silylmethyl)silanes **3−9** and the *α,ω*-dichlorocarbosilanes **10** and **11**, we have demonstrated once again the high synthetic potential of the TMOP (2,4,6-trimethoxyphenyl) moiety as a protecting group for silicon. In this study, we have synthesized the TMOP-substituted silanes (TMOP)Me_2SiCH_2Cl (**1**) and (TMOP)$_2$$MeSiCH_2Cl$ (**2**) and have used them to introduce the $ClMe_2SiCH_2$, $MeOMe_2SiCH_2$, or $Cl_2MeSiCH_2$ group by nucleophilic substitution at silicon. For this purpose, a three-

dx.doi.org/10.1021/om400190q | Organometallics XXXX, XXX, XXX−XXX

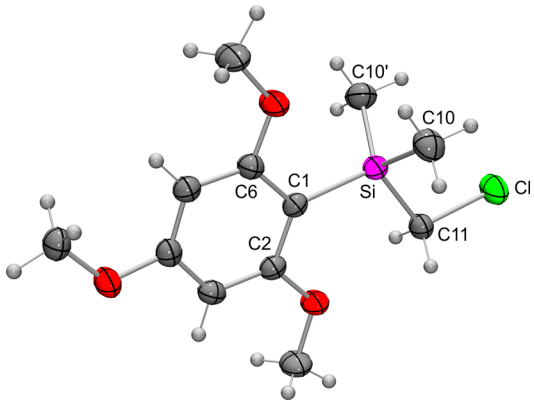


Figure 1. Molecular structure of **1** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si−C1 = 1.891(2), Si−C10 = 1.861(2), Si−C10′ = 1.861(2), Si−C11 = 1.891(3), Cl−C11 = 1.819(2); Si−C1−C2 = 126.58(16), Si−C1−C6 = 117.98(19), Si−C11−Cl = 108.31(14), C1−Si−C10 = 110.64(7), C1−Si−C10′ = 110.64(7), C1−Si−C11 = 110.03(11), C10−Si−C10′ = 110.17(14), C10−Si−C11 = 107.63(8), C10′−Si−C11 = 107.63(8).

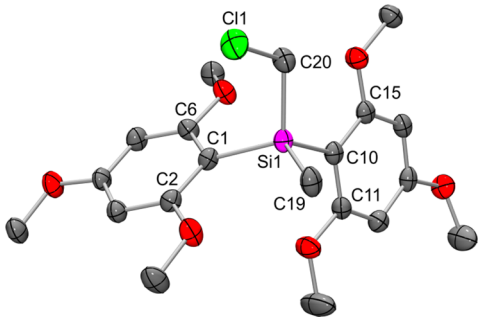


Figure 2. Molecular structure of one of the two crystallographically independent molecules of **2** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−C1 = 1.887(3), Si1−C10 = 1.893(3), Si1−C19 = 1.870(3), Si1−C20 = 1.898(3), Cl1−C20 = 1.811(3); Si1−C1−C2 = 126.70(19), Si1−C1−C6 = 117.44(19), Si1−C10−C11 = 117.81(18), Si1−C10−C15 = 125.8(2), Si1−C20−Cl1 = 110.24(14), C1−Si1−C10 = 109.87(11), C1−Si1−C19 = 115.74(12), C1−Si1−C20 = 107.40(13), C10−Si1−C19 = 108.46(13), C10−Si1−C20 = 109.52(12), C19−Si1−C20 = 105.67(13).

step synthetic method was developed: (i) transformation of **1** and **2** into (TMOP)Me_2SiCH_2MgCl, (TMOP)Me_2SiCH_2Li, (TMOP)$_2$$MeSiCH_2MgCl$, and (TMOP)$_2$$MeSiCH_2Li$, respectively, (ii) reaction of these nucleophilic reagents with a chloro- or methoxysilane, and (iii) selective cleavage of the TMOP protecting group using hydrogen chloride in diethyl ether or methanol in the presence of trifluoroacetic acid. With the synthesis of **3**−**11**, we have demonstrated the broad scope of this synthetic method, which should be applicable to the synthesis of a variety of other Si-functionalized (silylmethyl)-silanes and α,ω-dichlorocarbosilanes (with skeletons consisting of alternate carbon and silicon atoms).

EXPERIMENTAL SECTION

General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR-51 apparatus was used for the bulb-to-bulb distillations. Melting points

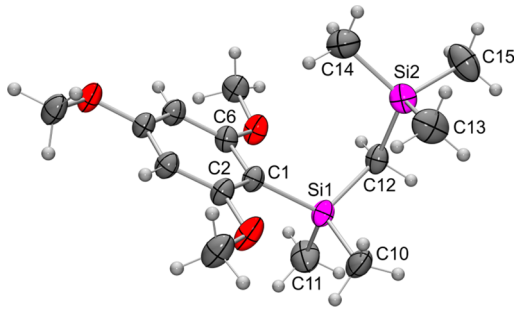


Figure 3. Molecular structure of **12** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si1−C1 = 1.9002(14), Si1−C10 = 1.8745(19), Si1−C11 = 1.8846(19), Si1−C12 = 1.8769(17), Si2−C12 = 1.8734(18), Si2−C13 = 1.871(2), Si2−C14 = 1.874(2), Si2−C15 = 1.880(2); Si1−C1−C2 = 126.39(11), Si1−C1−C6 = 118.42(10), Si1−C12−Si2 = 122.58(8), C1−Si1−C10 = 113.02(7), C1−Si1−C11 = 108.42(8), C1−Si1−C12 = 112.25(7), C10−Si1−C11 = 107.24(10), C10−Si1−C12 = 107.55(8), C11−Si1−C12 = 108.14(9), C12−Si2−C13 = 110.38(9), C12−Si2−C14 = 111.03(9), C12−Si2−C15 = 108.29(9), C13−Si2−C14 = 108.60(10), C13−Si2−C15 = 109.63(11), C14−Si2−C15 = 108.88(11).

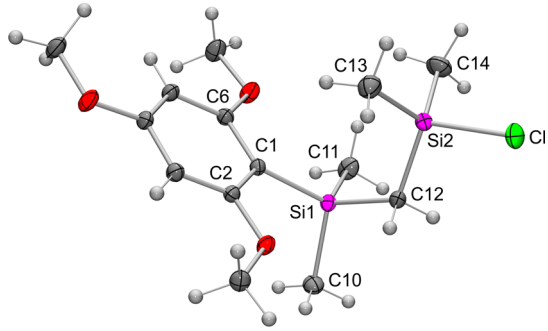


Figure 4. Molecular structure of **13** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si1−C1 = 1.8904(8), Si1−C10 = 1.8741(9), Si1−C11 = 1.8651(9), Si1−C12 = 1.8824(9), Si2−Cl = 2.1004(3), Si2−C12 = 1.8492(9), Si2−C13 = 1.8506(10), Si2−C14 = 1.8529(10); Si1−C1−C2 = 118.28(6), Si1−C1−C6 = 126.43(6), Si1−C12−Si2 = 119.26(5), C1−Si1−C10 = 109.75(4), C1−Si1−C11 = 113.53(4), C1−Si1−C12 = 110.58(4), C10−Si1−C11 = 106.13(5), C10−Si1−C12 = 107.31(4), C11−Si1−C12 = 109.27(4), Cl−Si2−C12 = 106.52(3), Cl−Si2−C13 = 105.72(4), Cl−Si2−C14 = 105.08(4), C12−Si2−C13 = 113.34(4), C12−Si2−C14 = 113.13(5), C13−Si2−C14 = 112.24(5).

were determined with a Büchi Melting Point B-540 apparatus using samples in sealed glass capillaries. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 23 °C on a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz) using $CDCl_3$ or C_6D_6 as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), internal $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), internal C_6HD_5 (^{1}H, δ 7.28; C_6D_6), internal C_6D_6 (^{13}C, δ 128.0; C_6D_6), or external TMS (^{29}Si, δ 0; C_6D_6). Analysis and assignment of the ^{1}H NMR data were supported by ^{1}H,^{1}H COSY, ^{13}C,^{1}H HMQC, ^{13}C,^{1}H HMBC, and ^{29}Si,^{1}H HMQC (optimized for $^2J_{SiH}$ = 7 Hz) experiments. Assignment of the ^{13}C NMR data was supported by DEPT 135, ^{13}C,^{1}H HMQC, and ^{13}C,^{1}H HMBC experiments. Gas chromatographic (GC) studies were performed using a Shimadzu GC-14B gas chromatograph with a capillary column from Phenomenex of the type Zebron ZB-1 (length, 15 m; inside diameter, 0.32 mm). The other experimental parameters were as follows: flow rate, 0.67 mL min^{-1}; injector, split 30 mL min^{-1}, split

dx.doi.org/10.1021/om400190q | Organometallics XXXX, XXX, XXX−XXX

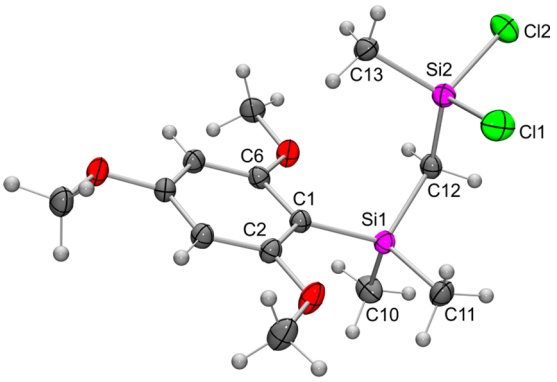


Figure 5. Molecular structure of **14** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si1−C1 = 1.8899(12), Si1−C10 = 1.8760(13), Si1−C11 = 1.8680(13), Si1−C12 = 1.8895(13), Si2−Cl1 = 2.0652(7), Si2−Cl2 = 2.0614(7), Si2−C12 = 1.8345(13), Si2−C13 = 1.8601(13); Si1−C1−C2 = 125.57(8), Si1−C1−C6 = 118.94(8), Si1−C12−Si2 = 120.49(6), C1−Si1−C10 = 107.94(6), C1−Si1−C11 = 113.96(5), C1−Si1−C12 = 111.74(5), C10−Si1−C11 = 108.25(7), C10−Si1−C12 = 107.72(6), C11−Si1−C12 = 107.02(6), Cl1−Si2−Cl2 = 105.52(4), Cl1−Si2−C12 = 109.82(5), Cl1−Si2−C13 = 107.47(5), Cl2−Si2−C12 = 109.33(5), Cl2−Si2−C13 = 107.34(5), C12−Si2−C13 = 116.75(6).

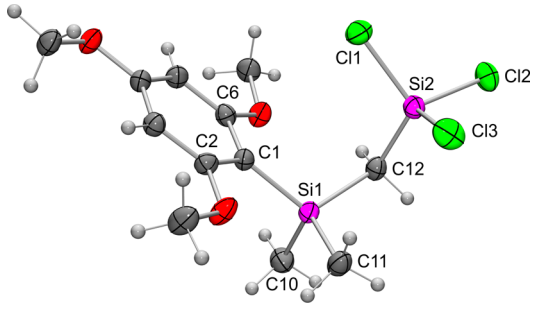


Figure 6. Molecular structure of **15** in the crystal (probability level of displacement ellipsoids 50%). Selected bond distances (Å) and angles (deg): Si1−C1 = 1.8820(18), Si1−C10 = 1.8720(19), Si1−C11 = 1.8685(19), Si1−C12 = 1.9067(19), Si2−Cl1 = 2.0329(9), Si2−Cl2 = 2.0539(12), Si2−Cl3 = 2.0432(9), Si2−C12 = 1.8205(18); Si1−C1−C2 = 125.41(12), Si1−C1−C6 = 119.17(12), Si1−C12−Si2 = 121.41(9), C1−Si1−C10 = 108.46(8), C1−Si1−C11 = 114.29(8), C1−Si1−C12 = 111.73(8), C10−Si1−C11 = 108.88(9), C10−Si1−C12 = 106.41(8), C11−Si1−C12 = 106.76(9), Cl1−Si2−Cl2 = 106.22(4), Cl1−Si2−Cl3 = 106.68(4), Cl1−Si2−C12 = 113.58(7), Cl2−Si2−Cl3 = 106.51(4), Cl2−Si2−C12 = 111.17(6), Cl3−Si2−C12 = 112.22(6).

ratio 1:10, 200 °C; detector, FID, 320 °C; carrier gas, N_2. The indicated retention times refer to the following temperature programs: program A, 40 °C (2 min)−280 °C (5 min) with 20 °C min^{-1} (compounds **3**−**9**); program B, 80 °C (2 min)−280 °C (5 min) with 20 °C min^{-1} (compounds **10** and **11**). Elemental analyses were carried out using a VarioMicro apparatus (Elementar Analysensysteme GmbH) or a EURO EA Elemental Analyzer (EuroVector).

Preparation of (Chloromethyl)dimethyl(2,4,6-trimethoxyphenyl)silane (1). This compound was synthesized according to ref 9l, using a slightly modified and optimized method: a 2.5 M solution of *n*-butyllithium in hexanes (24.0 mL, 60.0 mmol of *n*-BuLi) was added dropwise at 0 °C within 30 min to a stirred suspension of 1,3,5-trimethoxybenzene (10.0 g, 59.5 mmol) in a mixture of TMEDA (6.95 g, 59.8 mmol) and *n*-pentane (60 mL), and stirring was continued at 20 °C for a further 3 h. The resulting suspension was then added via a dropping funnel at 0 °C within 30 min to a stirred solution of chloro(chloromethyl)dimethylsilane (8.36 g, 58.4 mmol) in diethyl ether (50 mL). The mixture was stirred at 0 °C for 30 min and then at 20 °C for a further 17 h, followed by the addition of water (100 mL). The organic phase was separated, and the

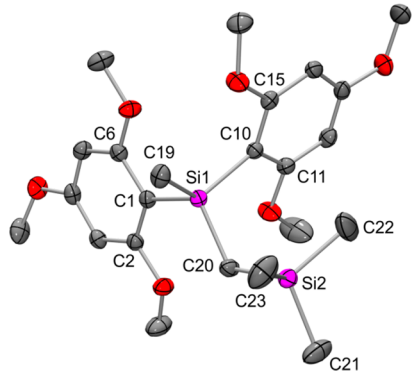


Figure 7. Molecular structure of one of the two crystallographically independent molecules of **17** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−C1 = 1.905(2), Si1−C10 = 1.890(2), Si1−C19 = 1.871(3), Si1−C20 = 1.877(2), Si2−C20 = 1.876(2), Si2−C21 = 1.861(3), Si2−C22 = 1.861(3), Si2−C23 = 1.873(4); Si1−C1−C2 = 126.76(16), Si1−C1−C6 = 118.43(17), Si1−C10−C11 = 117.89(16), Si1−C10−C15 = 126.80(17), Si1−C20−Si2 = 120.91(13), C1−Si1−C10 = 108.05(10), C1−Si1−C19 = 107.07(11), C1−Si1−C20 = 114.03(10), C10−Si1−C19 = 113.08(11), C10−Si1−C20 = 109.00(10), C19−Si1−C20 = 105.71(12), C20−Si2−C21 = 108.88(12), C20−Si2−C22 = 112.81(13), C20−Si2−C23 = 112.63(13), C21−Si2−C22 = 108.34(17), C21−Si2−C23 = 106.70(16), C22−Si2−C23 = 107.22(19).

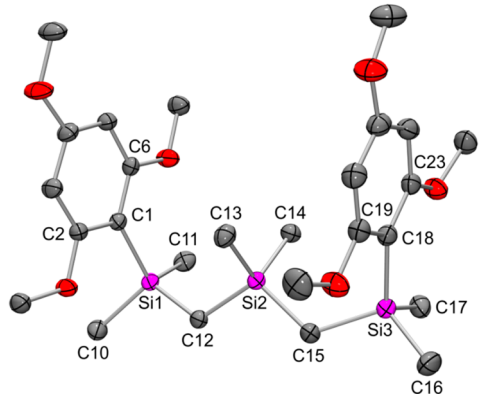


Figure 8. Molecular structure of **18** in the crystal (probability level of displacement ellipsoids 50%). The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si1−C1 = 1.8981(16), Si1−C10 = 1.8770(18), Si1−C11 = 1.870(2), Si1−C12 = 1.8733(17), Si2−C12 = 1.8799(16), Si2−C13 = 1.8708(19), Si2−C14 = 1.873(2), Si2−C15 = 1.8816(17), Si3−C15 = 1.8788(16), Si3−C16 = 1.8767(19), Si3−C17 = 1.872(2), Si3−C18 = 1.8982(17); Si1−C1−C2 = 118.32(12), Si1−C1−C6 = 125.78(13), Si1−C12−Si2 = 120.56(9), Si2−C15−Si3 = 119.11(9), Si3−C18−C19 = 117.37(13), Si3−C18−C23 = 126.93(14), C1−Si1−C10 = 110.94(8), C1−Si1−C11 = 112.66(9), C1−Si1−C12 = 109.48(8), C10−Si1−C11 = 104.51(10), C10−Si1−C12 = 108.57(8), C11−Si1−C12 = 110.53(8), C12−Si2−C13 = 108.88(8), C12−Si2−C14 = 110.17(8), C12−Si2−C15 = 109.38(7), C13−Si2−C14 = 108.29(9), C13−Si2−C15 = 110.39(9), C14−Si2−C15 = 109.72(8), C15−Si3−C16 = 110.60(9), C15−Si3−C17 = 107.30(9), C15−Si3−C18 = 110.45(8), C16−Si3−C17 = 106.35(10), C16−Si3−C18 = 108.07(9), C17−Si3−C18 = 114.01(9).

dx.doi.org/10.1021/om400190q | *Organometallics* XXXX, XXX, XXX−XXX

aqueous phase was extracted with diethyl ether (3 × 50 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the oily residue was purified by bulb-to-bulb distillation (120 °C/0.02 mbar) to give **1** in 82% yield as a colorless crystalline solid (crystallization of the distillate at room temperature; 13.1 g, 47.7 mmol); mp 32−33 °C. For the NMR data, see ref 9l. Anal. Calcd for $C_{12}H_{19}ClO_3Si$: C, 52.45; H, 6.97. Found: C, 52.6; H, 7.0.

Preparation of (Chloromethyl)methylbis(2,4,6-trimethoxyphenyl)silane (2). A 2.5 M solution of *n*-butyllithium in hexanes (24.0 mL, 60.0 mmol of *n*-BuLi) was added dropwise at 0 °C within 30 min to a stirred suspension of 1,3,5-trimethoxybenzene (10.0 g, 59.5 mmol) in a mixture of TMEDA (6.97 g, 60.0 mmol) and *n*-pentane (60 mL), and stirring was continued at 20 °C for a further 3 h. The resulting suspension was then added via a dropping funnel at 0 °C within 30 min to a stirred solution of dichloro(chloromethyl)-methylsilane (4.78 g, 29.2 mmol) in diethyl ether (50 mL). The mixture was stirred at 0 °C for 20 min and then at 20 °C for a further 17 h, followed by sequential addition of diethyl ether (200 mL) and water (100 mL). The organic layer was separated and washed with water (2 × 70 mL), and the combined aqueous layers were extracted with diethyl ether (3 × 50 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was dissolved in boiling diethyl ether (100 mL), and the solution was cooled to 20 °C within 20 min and then kept undisturbed at this temperature for 18 h. The resulting solid was isolated by filtration and dried in vacuo (20 °C/0.01 mbar, 3 h) to give **2** in 80% yield as a colorless crystalline solid (9.93 g, 23.3 mmol); mp 124−126 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 1.33 (s, 3 H; SiCH_3), 3.37 (s, 12 H; *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.47 (s, 6 H; *p*-OCH_3, $C_6H_2(OCH_3)_3$), 3.98 (s, 2 H; SiCH_2Cl), 6.15 (s, 4 H; *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −0.01 (SiCH_3), 35.2 (SiCH_2Cl), 54.6 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 55.0 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 91.2 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 105.6 (*C*-1, $C_6H_2(OCH_3)_3$), 163.6 (*C*-4, $C_6H_2(OCH_3)_3$), 166.6 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −14.3. Anal. Calcd for $C_{20}H_{27}ClO_6Si$: C, 56.26; H, 6.37. Found: C, 56.3; H, 6.6.

Preparation of Chlorodimethyl[(trimethylsilyl)methyl]silane (3). A 2.0 M solution of hydrogen chloride in diethyl ether (3.20 mL, 6.40 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **12** (2.00 g, 6.40 mmol) in diethyl ether (15 mL), and the resulting mixture was stirred for 2 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (5 mL). The solution was kept at −20 °C for 3 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by fractional distillation in vacuo (115−118 °C, 35 mbar) to give **3** in 75% yield as a colorless liquid (868 mg, 4.80 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.03 (s, 2 H; SiCH_2Si), 0.15 (s, 9 H; Si(CH_3)$_3$), 0.40 (s, 6 H; Si(CH_3)$_2$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 1.0 (SiCH_2Si), 4.6 (Si(CH_3)$_2$), 7.6 (Si(CH_3)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −0.5 (*Si*(CH$_3$)$_3$), 29.8 (*Si*(CH$_3$)$_2$). Anal. Calcd for $C_6H_{17}ClSi_2$: C, 39.85; H, 9.48. Found: C, 39.8; H, 9.5.

Preparation of Chloro[(chlorodimethylsilyl)methyl]-dimethylsilane (4). A 2.0 M solution of hydrogen chloride in diethyl ether (2.62 mL, 5.24 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **13** (1.74 g, 5.23 mmol) in diethyl ether (15 mL). The resulting mixture was stirred at 0 °C for 20 min, warmed to 20 °C, and then stirred at this temperature for 1.5 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (5 mL). The solution was kept at −20 °C for 2 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by fractional distillation in vacuo (96 °C, 10 mbar) to give **4** in 68% yield as a colorless liquid (716 mg, 3.56 mmol). ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.49 (s, 12 H; Si(CH_3)$_2$), 0.56 (s, 2 H; SiCH_2Si). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 4.4 (Si(CH$_3$)$_2$), 11.0 (SiCH_2Si). ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ 28.6. Anal. Calcd for $C_5H_{14}Cl_2Si_2$: C, 29.84; H, 7.01. Found: C, 30.1; H, 7.2.

Preparation of Dichloro[(chlorodimethylsilyl)methyl]-methylsilane (5). A 2.0 M solution of hydrogen chloride in diethyl ether (7.50 mL, 15.0 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **14** (5.20 g, 14.7 mmol) in diethyl ether (20 mL). The resulting mixture was stirred at 0 °C for 30 min, warmed to 20 °C, and then stirred at this temperature for 1.5 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (10 mL). The solution was kept at −20 °C for 3 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by fractional distillation in vacuo (57 °C, 4 mbar) to give **5** in 61% yield as a colorless liquid (1.99 g, 8.98 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.38 (s, 6 H; Si(CH_3)$_2$), 0.52 (s, 2 H; SiCH_2Si), 0.61 (s, 3 H; SiCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ 3.8 (Si(CH_3)$_2$), 7.5 (SiCH_3), 13.8 (SiCH_2Si). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 26.5 (*Si*(CH$_3$)$_2$), 28.4 (*Si*CH$_3$). Anal. Calcd for $C_4H_{11}Cl_3Si_2$: C, 21.67; H, 5.00. Found: C, 21.9; H, 5.1.

Preparation of Trichloro[(chlorodimethylsilyl)methyl]silane (6). A 2.0 M solution of hydrogen chloride in diethyl ether (3.00 mL, 6.00 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **15** (2.20 g, 5.89 mmol) in diethyl ether (12 mL). The resulting mixture was stirred at 0 °C for 20 min, warmed to 20 °C, and then stirred at this temperature for 1.5 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (12 mL). The solution was kept at −20 °C for 2 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (40 °C/1.5 mbar) to give **6** in 56% yield as a colorless liquid (798 mg, 3.30 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.33 (s, 6 H; Si(CH_3)$_2$), 0.69 (s, 2 H; SiCH_2Si). ^{13}C NMR (125.8 MHz, C_6D_6): δ 3.5 (Si(CH_3)$_2$), 16.5 (SiCH_2Si). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 7.9 (*Si*Cl$_3$), 25.1 (*Si*CH$_3$). Anal. Calcd for $C_3H_8Cl_4Si_2$: C, 14.88; H, 3.33. Found: C, 15.0; H, 3.3.

Preparation of Chlorodimethyl[(trimethoxysilyl)methyl]-silane (7). A 2.0 M solution of hydrogen chloride in diethyl ether (1.70 mL, 3.40 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **16** (1.21 g, 3.36 mmol) in diethyl ether (10 mL). The resulting mixture was stirred at 0 °C for 30 min, warmed to 20 °C, and then stirred at this temperature for 1.5 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (5 mL). The solution was kept at −20 °C for 3 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by fractional distillation in vacuo (87 °C, 5 mbar) to give **7** as a colorless liquid (431 mg; purity ca. 80%). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.33 (s, 2 H; SiCH_2Si), 0.58 (s, 6 H; Si(CH_3)$_2$), 3.46 (s, 9 H; Si(OCH_3)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 1.1 (SiCH_2Si), 3.8 (Si(CH_3)$_2$), 50.2 (Si(OCH_3)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −44.0 (*Si*OCH$_3$), 29.6 (*Si*CH$_3$).

Preparation of Methoxydimethyl[(trimethoxysilyl)methyl]-silane (8). Trifluoroacetic acid (73 mg, 640 μmol) was added at 0 °C in a single portion to a stirred mixture of **16** (3.30 g, 9.15 mmol), methanol (1.60 g, 49.9 mmol), and diethyl ether (7 mL), and the resulting mixture was then warmed to 20 °C and stirred at this temperature for 30 min. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (5 mL). The solution was kept at −20 °C for 2 h to crystallize the byproduct, 1,3,5-

dx.doi.org/10.1021/om400190q | *Organometallics* XXXX, XXX, XXX−XXX

trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (85 °C, 1 mbar) to give **8** in 58% yield as a colorless liquid (1.19 g, 5.30 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.12 (s, 2 H; SiCH_2Si), 0.39 (s, 6 H; Si(CH_3)$_2$), 3.44 (s, 3 H; SiOCH_3), 3.55 (s, 9 H; Si(OCH_3)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −2.9 (SiCH_2Si), −0.4 (Si(CH_3)$_2$), 49.9 (SiOCH_3), 50.2 (Si(OCH_3)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −41.4 (*Si*(OCH$_3$)$_3$), 16.5 (*Si*OCH$_3$). Anal. Calcd for $C_7H_{20}O_4Si_2$: C, 37.47; H, 8.98. Found: C, 37.3; H, 9.0.

Preparation of Dichloromethyl[(trimethylsilyl)methyl]silane (9). A 2.0 M solution of hydrogen chloride in diethyl ether (11.3 mL, 22.6 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **17** (5.26 g, 11.3 mmol) in diethyl ether (25 mL). The resulting mixture was stirred at 0 °C for 30 min, warmed to 20 °C, and then stirred at this temperature for 2 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (20 mL). The solution was kept at −20 °C for 3 h to crystallize the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (125 °C/100 mbar) to give **9** in 54% yield as a colorless liquid (1.23 g, 6.11 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.12 (s, 9 H; Si(CH_3)$_3$), 0.24 (s, 2 H; SiCH_2Si), 0.59 (s, 3 H; SiCH_3). ^{13}C NMR (125.8 MHz, C_6D_6): δ 0.6 (Si(CH_3)$_3$), 7.9 (SiCH_3), 10.8 (SiCH_2Si). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −0.5 (*Si*(CH_3)$_3$), 31.0 (*Si*CH_3). Anal. Calcd for $C_5H_{14}Cl_2Si_2$: C, 29.84; H, 7.01. Found: C, 29.9; H, 7.0.

Preparation of Bis[(chlorodimethylsilyl)methyl]-dimethylsilane (10). A 2.0 M solution of hydrogen chloride in diethyl ether (7.60 mL, 15.2 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **18** (4.05 g, 7.54 mmol) in diethyl ether (15 mL). The resulting mixture was stirred at 0 °C for 20 min, warmed to 20 °C, and then stirred at this temperature for 3 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (15 mL). The solution was kept at −20 °C for 2 h to crystallize most of the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, and the solvent was removed under reduced pressure. The residue was again dissolved in *n*-pentane (6 mL), and the solution was kept at −20 °C for 1 h to crystallize the remaining 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (110 °C/10 mbar) to give **10** in 48% yield as a colorless liquid (990 mg, 3.62 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.12 (s, 4 H; SiCH_2Si), 0.24 (s, 6 H; Si(CH_3)$_2$), 0.41 (s, 12 H; (Si(CH_3)$_2$Cl). ^{13}C NMR (125.8 MHz, C_6D_6): δ 1.9 (Si(CH_3)$_2$), 4.7 (Si(CH_3)$_2$Cl), 8.5 (SiCH_2Si). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −0.5 (*Si*(CH_2Si)$_2$), 29.5 (Si(CH_2*Si*)$_2$). Anal. Calcd for $C_8H_{22}Cl_2Si_3$: C, 35.14; H, 8.11. Found: C, 35.1; H, 8.2.

Preparation of Bis[[[(chlorodimethylsilyl)methyl]-dimethylsilyl]methyl]dimethylsilane (11). A 1.0 M solution of hydrogen chloride in diethyl ether (5.80 mL, 5.80 mmol of HCl) was added at 0 °C in a single portion to a stirred solution of **19** (1.95 g, 2.86 mmol) in diethyl ether (10 mL). The resulting mixture was stirred at 0 °C for 20 min, warmed to 20 °C, and then stirred at this temperature for 2 h. After the reaction was complete (quantitative and selective cleavage of the TMOP group as monitored by GC analysis), the solvent was removed by distillation under atmospheric pressure, and the residue was dissolved in *n*-pentane (8 mL). The solution was kept at −20 °C for 2 h to crystallize most of the byproduct, 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, and the solvent was removed under reduced pressure. The residue was again dissolved in *n*-pentane (6 mL), and the solution was kept at −20 °C for 1 h to crystallize the remaining 1,3,5-trimethoxybenzene. The mother liquor was separated with a syringe, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (150 °C/0.02 mbar) to give **11** in 62% yield as a colorless liquid (735 mg, 1.76 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ −0.05 (s, 4 H; Si(CH_2SiCH$_2$Si)$_2$), 0.16 (s, 4 H; Si(CH_2SiCH_2Si)$_2$), 0.25 (s, 6 H; Si(CH_3)$_2$), 0.27 (s, 12 H; Si(CH_2Si(CH_3)$_2$)$_2$), 0.46 (s, 12 H; Si(CH_3)$_2$Cl). ^{13}C NMR (125.8 MHz, C_6D_6): δ 2.4 (Si(CH_2Si-(CH_3)$_2$)$_2$), 2.7 (SiCH_3)$_2$), 4.8 (Si(CH_3)$_2$Cl), 7.0 (Si(CH_2SiCH$_2$Si)$_2$), 9.3 (Si(CH_2SiCH$_2$Si)$_2$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −0.2 (Si(CH_2*Si*CH$_2$Si)$_2$), 0.2 (*Si*(CH_2SiCH$_2$Si)$_2$), 29.7 (Si(CH_2SiCH$_2$*Si*)$_2$). Anal. Calcd for $C_{14}H_{38}Cl_2Si_5$: C, 40.25; H, 9.17. Found: C, 40.5; H, 9.1.

Preparation of Dimethyl(2,4,6-trimethoxyphenyl)-[(trimethylsilyl)methyl]silane (12). A solution of **1** (7.74 g, 28.2 mmol) in THF (15 mL) was added dropwise at 20 °C within 10 min to a stirred suspension of magnesium turnings (753 mg, 31.0 mmol)[11] in THF (10 mL), and the mixture was heated under reflux for 4 h. The Grignard reaction proceeded smoothly but required gentle heating to get started. The resulting dark-brown Grignard reagent was cooled to 20 °C, separated from the excess magnesium turnings with a syringe, and then added dropwise at 20 °C within 10 min to a stirred solution of chlorotrimethylsilane (3.06 g, 28.2 mmol) in THF (20 mL). The resulting mixture was then heated under reflux for 17 h, cooled to 20 °C, and concentrated under reduced pressure to a volume of ca. 10 mL. Diethyl ether (50 mL) and water (50 mL) were added sequentially, the organic layer was separated and washed with water (3 × 20 mL), and the combined aqueous layers were extracted with diethyl ether (3 × 30 mL). The organic extracts were combined and dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the oily residue was purified by bulb-to-bulb distillation (110 °C/0.02 mbar) to give **12** in 87% yield as a colorless crystalline solid (crystallization of the distillate at room temperature; 7.67 g, 24.5 mmol); mp 22−24 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.23 (s, 9 H; Si(CH_3)$_3$), 0.38 (s, 2 H; SiCH_2Si), 0.76 (s, 6 H; Si(CH_3)$_2$), 3.41 (s, 6 H; *o*-OCH_3, C_6H_2(OCH$_3$)$_3$), 3.48 (s, 3 H; *p*-OCH_3, C_6H_2(OCH$_3$)$_3$), 6.15 (s, 2 H; *H*-3/*H*-5, C_6H_2(OCH$_3$)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 1.4 (Si(CH_3)$_3$), 3.7 (Si(CH_3)$_2$), 4.9 (SiCH_2Si), 54.56 (*o*-OCH_3, C_6H_2(OCH$_3$)$_3$), 54.61 (*p*-OCH_3, C_6H_2(OCH$_3$)$_3$), 90.7 (*C*-3/*C*-5, C_6H_2(OCH$_3$)$_3$), 106.4 (*C*-1, C_6H_2(OCH$_3$)$_3$), 163.7 (*C*-4, C_6H_2(OCH$_3$)$_3$), 166.6 (*C*-2/*C*-6, C_6H_2(OCH$_3$)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −6.8 (*Si*(CH_3)$_2$), 0.2 (*Si*(CH_3)$_3$). Anal. Calcd for $C_{15}H_{28}O_3Si_2$: C, 57.64; H, 9.03. Found: C, 57.8; H, 9.1.

Preparation of Chlorodimethyl[[dimethyl(2,4,6-trimethoxyphenyl)silyl]methyl]silane (13). A solution of **1** (8.55 g, 31.1 mmol) in THF (15 mL) was added dropwise at 20 °C within 15 min to a stirred suspension of magnesium turnings (832 mg, 34.2 mmol)[11] in THF (10 mL), and the mixture was heated under reflux for 4 h. The Grignard reaction proceeded smoothly but required gentle heating to get started. The resulting dark-brown Grignard reagent was cooled to 20 °C, separated from the excess magnesium turnings with a syringe, and then added dropwise at 20 °C within 20 min to a stirred solution of dichlorodimethylsilane (3.81 g, 29.5 mmol) in THF (20 mL). The resulting mixture was then heated under reflux for 16 h, cooled to 20 °C, and concentrated under reduced pressure to a volume of ca. 10 mL. Subsequently, *n*-pentane (150 mL) was added, and the resulting suspension was stirred at 20 °C for 20 min. The precipitate was removed by filtration and washed with *n*-pentane (3 × 30 mL), the solvent of the filtrate (including the wash solutions) was removed under reduced pressure, and the oily residue was purified by bulb-to-bulb distillation (130 °C/0.03 mbar). The distillate was then crystallized from diethyl ether (35 mL) at −20 °C, and the product was isolated by filtration and dried in vacuo to give **13** in 78% yield as a colorless crystalline solid (7.66 g, 23.0 mmol); mp 53−55 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.47 (s, 6 H; Si(CH_3)$_2$Cl), 0.71 (s, 6 H; Si(CH_3)$_2$), 0.78 (s, 2 H; SiCH_2Si), 3.36 (s, 6 H; *o*-OCH_3, C_6H_2(OCH$_3$)$_3$), 3.46 (s, 3 H; *p*-OCH_3, C_6H_2(OCH$_3$)$_3$), 6.11 (s, 2 H; *H*-3/*H*-5, C_6H_2(OCH$_3$)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 3.2 (Si(CH_3)$_2$), 4.4 (Si(CH_3)$_2$Cl), 8.8 (SiCH_2Si), 54.5 (*o*-OCH_3, C_6H_2(OCH$_3$)$_3$), 54.6 (*p*-OCH_3, C_6H_2(OCH$_3$)$_3$), 90.7 (*C*-3/*C*-5, C_6H_2(OCH$_3$)$_3$), 105.0 (*C*-1, C_6H_2(OCH$_3$)$_3$), 164.0 (*C*-4, C_6H_2(OCH$_3$)$_3$), 166.6 (*C*-2/*C*-6, C_6H_2(OCH$_3$)$_3$). ^{29}Si NMR (99.4

dx.doi.org/10.1021/om400190q | *Organometallics* XXXX, XXX, XXX−XXX

MHz, C_6D_6): δ −8.0 ($Si(CH_3)_2$), 30.8 ($Si(CH_3)_2Cl$). Anal. Calcd for $C_{14}H_{25}ClO_3Si_2$: C, 50.50; H, 7.57. Found: C, 50.8; H, 7.8.

Preparation of Dichloromethyl[[dimethyl(2,4,6-trimethoxyphenyl)silyl]methyl]silane (14). A solution of **1** (2.43 g, 8.84 mmol) in THF (10 mL) was added dropwise at 20 °C within 5 min to a stirred suspension of magnesium turnings (237 mg, 9.75 mmol)[11] in THF (5 mL), and the mixture was heated under reflux for 4 h. The Grignard reaction proceeded smoothly but required gentle heating to get started. The resulting dark-brown Grignard reagent was cooled to 20 °C, separated from the excess magnesium turnings with a syringe, and then added dropwise at 20 °C within 10 min to a stirred solution of trichloromethylsilane (1.30 g, 8.70 mmol) in THF (10 mL). The resulting mixture was then heated under reflux for 17 h, cooled to 20 °C, and concentrated under reduced pressure to a volume of ca. 5 mL. Subsequently, *n*-pentane (100 mL) was added, and the resulting suspension was stirred at 20 °C for 20 min. The precipitate was removed by filtration and washed with *n*-pentane (3 × 30 mL), the solvent of the filtrate (including the wash solutions) was removed under reduced pressure, and the oily residue was purified by bulb-to-bulb distillation (135 °C/0.03 mbar). The distillate was then crystallized from *n*-pentane (15 mL) at −20 °C, and the product was isolated by filtration and dried in vacuo to give **14** in 71% yield as a colorless crystalline solid (2.18 g, 6.17 mmol); mp 38−40 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.67 (s, 3 H; SiCH_3), 0.71 (s, 6 H; Si(CH_3)$_2$), 1.06 (s, 2 H; SiCH_2Si), 3.34 (s, 6 H; *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.45 (s, 3 H; *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.09 (s, 2 H; *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 2.7 (Si(CH_3)$_2$), 7.6 (SiCH_3), 12.3 (SiCH_2Si), 54.56 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 54.64 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.7 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 104.1 (*C*-1, $C_6H_2(OCH_3)_3$), 164.2 (*C*-4, $C_6H_2(OCH_3)_3$), 166.6 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −8.3 ($Si(CH_3)_2$), 32.0 ($SiCH_3Cl_2$). Anal. Calcd for $C_{13}H_{22}Cl_2O_3Si_2$: C, 44.18; H, 6.27. Found: C, 44.5; H, 6.5.

Preparation of Trichloro[[dimethyl(2,4,6-trimethoxyphenyl)silyl]methyl]silane (15). A solution of **1** (4.90 g, 17.8 mmol) in THF (15 mL) was added dropwise at 20 °C within 10 min to a stirred suspension of magnesium turnings (477 mg, 19.6 mmol)[11] in THF (10 mL), and the mixture was heated under reflux for 2 h. The Grignard reaction proceeded smoothly but required gentle heating to get started. The resulting dark-brown Grignard reagent was cooled to 20 °C, separated from the excess magnesium turnings with a syringe, and then added dropwise at 20 °C within 15 min to a stirred solution of tetrachlorosilane (3.03 g, 17.8 mmol) in THF (20 mL), causing the mixture to boil under reflux. The mixture was then heated under reflux for 17 h, cooled to 20 °C, and concentrated under reduced pressure to a volume of ca. 15 mL. Subsequently, *n*-pentane (200 mL) was added, and the resulting suspension was stirred at 20 °C for 30 min. The precipitate was removed by filtration and washed with *n*-pentane (3 × 50 mL), the solvent of the filtrate (including the wash solutions) was removed under reduced pressure, and the oily residue was purified by bulb-to-bulb distillation (152 °C/0.05 mbar). The distillate was then crystallized from *n*-pentane (15 mL) at −20 °C, and the product was isolated by filtration and dried in vacuo to give **15** in 64% yield as a colorless crystalline solid (4.26 g, 11.4 mmol); mp 33−36 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.71 (s, 6 H; Si(CH_3)$_2$), 1.27 (s, 2 H; SiCH_2Si), 3.35 (s, 6 H; *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.45 (s, 3 H; *p*-OCH_3, $C_6H_2(OCH_3)_3$), 6.09 (s, 2 H; *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 2.3 (Si(CH_3)$_2$), 15.2 (SiCH_2Si), 54.57 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 54.64 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 90.7 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 103.2 (*C*-1, $C_6H_2(OCH_3)_3$), 164.3 (*C*-4, $C_6H_2(OCH_3)_3$), 166.6 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −8.2 ($Si(CH_3)_2$), 11.4 ($SiCl_3$). Anal. Calcd for $C_{12}H_{19}Cl_3O_3Si_2$: C, 38.56; H, 5.12. Found: C, 38.9; H, 5.3.

Preparation of Trimethoxy[[dimethyl(2,4,6-trimethoxyphenyl)silyl]methyl]silane (16). A solution of **1** (4.39 g, 16.0 mmol) in THF (10 mL) was added dropwise at 20 °C within 10 min to a stirred suspension of magnesium turnings (427 mg, 17.6 mmol)[11] in THF (10 mL), and the mixture was heated under reflux for 2 h. The Grignard reaction proceeded smoothly but required gentle heating to get started. The resulting dark-brown Grignard reagent was cooled to 20 °C, separated from the excess magnesium turnings with a syringe, and then added dropwise at 20 °C within 10 min to a stirred solution of tetramethoxysilane (2.43 g, 16.0 mmol) in THF (10 mL). The resulting mixture was then heated under reflux for 17 h, cooled to 20 °C, and concentrated under reduced pressure to a volume of ca. 10 mL. Subsequently, *n*-pentane (150 mL) was added, and the resulting suspension was stirred at 20 °C for 20 min. The precipitate was removed by filtration and washed with *n*-pentane (3 × 50 mL), the solvent of the filtrate (including the wash solutions) was removed under reduced pressure, and the oily residue was purified by column chromatography on silica gel (40−63 μm, 250 g (Merck); treated with concentrated aqueous ammonia solution (7% by weight related to the silica gel); eluent, *n*-hexane/ethyl acetate (90/10 v/v)). The relevant fractions (GC analysis) were combined, the solvents were removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 2 h) to give **16** in 54% yield as a colorless viscous liquid (3.12 g, 8.65 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.61 (s, 2 H; SiCH_2Si), 0.87 (s, 6 H; Si(CH_3)$_2$), 3.44 (s, 6 H; *o*-OCH_3, $C_6H_2(OCH_3)_3$), 3.51 (s, 3 H; *p*-OCH_3, $C_6H_2(OCH_3)_3$), 3.59 (s, 9 H; Si(OCH_3)$_3$), 6.17 (s, 2 H; *H*-3/*H*-5, $C_6H_2(OCH_3)_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ −2.3 (SiCH_2Si), 2.7 (Si(CH_3)$_2$), 50.1 (Si(OCH_3)$_3$), 54.65 (*p*-OCH_3, $C_6H_2(OCH_3)_3$), 54.71 (*o*-OCH_3, $C_6H_2(OCH_3)_3$), 90.8 (*C*-3/*C*-5, $C_6H_2(OCH_3)_3$), 106.4 (*C*-1, $C_6H_2(OCH_3)_3$), 163.7 (*C*-4, $C_6H_2(OCH_3)_3$), 166.7 (*C*-2/*C*-6, $C_6H_2(OCH_3)_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −39.8 ($Si(OCH_3)_3$), −6.6 ($Si(CH_3)_2$). Anal. Calcd for $C_{15}H_{28}O_6Si_2$: C, 49.97; H, 7.83. Found: C, 49.9; H, 7.8.

Preparation of Methylbis(2,4,6-trimethoxyphenyl)-[(trimethylsilyl)methyl]silane (17). *Method I.* A solution of **2** (2.29 g, 5.36 mmol) in THF (5 mL) was added dropwise at 20 °C within 5 min to a stirred suspension of magnesium turnings (143 mg, 5.88 mmol)[11] in THF (10 mL), and the mixture was heated under reflux for 4 h. The Grignard reaction proceeded smoothly but required gentle heating to get started. The resulting dark-brown Grignard reagent was cooled to 20 °C, separated from the excess magnesium turnings with a syringe, and then added dropwise at 20 °C within 10 min to a stirred solution of chlorotrimethylsilane (582 mg, 5.36 mmol) in THF (10 mL). The resulting mixture was then heated under reflux for 17 h, cooled to 20 °C, and concentrated under reduced pressure to a volume of ca. 10 mL. Subsequently, *n*-pentane (100 mL) was added, and the resulting suspension was stirred at 20 °C for 20 min. The precipitate was removed by filtration and washed with *n*-pentane (3 × 30 mL), the solvent of the filtrate (including the wash solutions) was removed under reduced pressure, and the oily residue was purified by column chromatography on silica gel (40−63 μm, 180 g (Merck); treated with concentrated aqueous ammonia solution (7% by weight related to the silica gel); eluent, *n*-pentane/ethyl acetate (10/1 v/v)). The relevant fractions (GC analysis) were combined, the solvents were removed under reduced pressure, and the residue was dried in vacuo (0.001 mbar, 20 °C, 3 h) to give **17** in 18% yield as a colorless solid (448 mg, 964 μmol).

Method II. Naphthalene (2.82 g, 22.0 mmol) was added in a single portion at 20 °C to a stirred suspension of lithium powder (153 mg, 22.0 mmol) in THF (10 mL), and the mixture was stirred at this temperature for 17 h. The resulting dark-green suspension was cooled to −30 °C, and a solution of **2** (4.64 g, 10.9 mmol) in THF (10 mL) was added dropwise at this temperature within 10 min. The reaction mixture was stirred at −30 °C for a further 1 h, and then a solution of chlorotrimethylsilane (1.18 g, 10.9 mmol) in THF (5 mL) was added dropwise at this temperature within 5 min. After it was stirred at −30 °C for 1 h, the mixture was warmed to 20 °C, followed by sequential addition of diethyl ether (50 mL) and water (50 mL). The organic layer was separated and washed with water (3 × 30 mL), and the combined aqueous layers were extracted with diethyl ether (3 × 30 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (40−63 μm, 260 g (Merck); treated with concentrated aqueous ammonia solution (7% by weight related to the silica gel);

dx.doi.org/10.1021/om400190q | *Organometallics* XXXX, XXX, XXX−XXX

eluent, *n*-pentane/ethyl acetate (10/1 v/v)). The relevant fractions (GC analysis) were combined, and the solvents were removed under reduced pressure. The residue was crystallized from *n*-pentane (20 mL) at −20 °C, and the product was isolated by filtration and dried in vacuo (0.001 mbar, 20 °C, 4 h) to give **17** in 56% yield as a colorless crystalline solid (2.84 g, 6.11 mmol); mp 79−81 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.32 (s, 9 H; Si(CH_3)$_3$), 1.00 (s, 2 H; SiCH_2Si), 1.20 (s, 3 H; SiCH_3), 3.43 (s, 12 H; *o*-OCH_3, C_6H_2(OCH_3)$_3$), 3.50 (s, 6 H; *p*-OCH_3, C_6H_2(OCH_3)$_3$), 6.20 (s, 4 H; *H*-3/*H*-5, C_6H_2(OCH_3)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 1.8 (Si(CH_3)$_3$), 4.6 (SiCH_3), 5.5 (SiCH_2Si), 54.6 (*p*-OCH_3, C_6H_2(OCH_3)$_3$), 54.9 (*o*-OCH_3, C_6H_2(OCH_3)$_3$), 91.1 (*C*-3/*C*-5, C_6H_2(OCH_3)$_3$), 109.7 (*C*-1, C_6H_2(OCH_3)$_3$), 162.9 (*C*-4, C_6H_2(OCH_3)$_3$), 166.3 (*C*-2/*C*-6, C_6H_2(OCH_3)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −14.4 (*Si*CH_3), 0.1 (*Si*(CH_3)$_3$). Anal. Calcd for $C_{23}H_{36}O_6Si_2$: C, 59.45; H, 7.81. Found: C, 59.5; H, 7.8.

Preparation of Bis[[dimethyl(2,4,6-trimethoxyphenyl)silyl]-methyl]dimethylsilane (18). Naphthalene (4.58 g, 35.7 mmol) was added in a single portion at 20 °C to a stirred suspension of lithium powder (248 mg, 35.7 mmol) in THF (20 mL), and the mixture was stirred at this temperature for 16 h. The resulting dark-green suspension was cooled to −30 °C, and a solution of **1** (4.68 g, 17.0 mmol) in THF (6 mL) was added dropwise at this temperature within 10 min. The reaction mixture was stirred at −30 °C for a further 2 h, and then dichlorodimethylsilane (1.10 g, 8.52 mmol) was added in a single portion at this temperature. After it was stirred at −30 °C for 1 h, the mixture was warmed to 20 °C, followed by sequential addition of diethyl ether (60 mL) and water (60 mL). The organic layer was separated and washed with water (3 × 30 mL), and the combined aqueous layers were extracted with diethyl ether (3 × 30 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (160 °C/0.01 mbar; removal of byproducts), followed by recrystallization of the remaining solid residue from *n*-pentane (15 mL) to give **18** in 78% yield as a colorless crystalline solid (3.57 g, 6.65 mmol); mp 68−70 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.29 (s, 6 H; Si(CH_3)$_2$), 0.48 (s, 4 H; SiCH_2Si), 0.78 (s, 12 H; Si(CH_2Si(CH_3)$_2$)$_2$), 3.44 (s, 12 H; *o*-OCH_3, C_6H_2(OCH_3)$_3$), 3.49 (s, 6 H; *p*-OCH_3, C_6H_2(OCH_3)$_3$), 6.16 (s, 4 H; *H*-3/*H*-5, C_6H_2(OCH_3)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 2.2 (Si(CH_3)$_2$), 3.8 (Si(CH_2Si(CH_3)$_2$)$_2$), 6.4 (SiCH_2Si), 54.5 (*o*-OCH_3, C_6H_2(OCH_3)$_3$), 54.6 (*p*-OCH_3, C_6H_2(OCH_3)$_3$), 90.7 (*C*-3/*C*-5, C_6H_2(OCH_3)$_3$), 106.9 (*C*-1, C_6H_2(OCH_3)$_3$), 163.6 (*C*-4, C_6H_2(OCH_3)$_3$), 166.6 (*C*-2/*C*-6, C_6H_2(OCH_3)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −6.8 (Si(CH_2Si)$_2$), 0.8 (*Si*(CH_2Si)$_2$). Anal. Calcd for $C_{26}H_{44}O_6Si_3$: C, 58.17; H, 8.26. Found: C, 58.0; H, 8.4.

Preparation of Bis[[[[dimethyl(2,4,6-trimethoxyphenyl)silyl]-methyl]dimethylsilyl]methyl]dimethylsilane (19). Naphthalene (1.92 g, 15.0 mmol) was added in a single portion at 20 °C to a stirred suspension of lithium powder (104 mg, 15.0 mmol) in THF (10 mL), and the mixture was stirred at this temperature for 17 h. The resulting dark-green suspension was cooled to −30 °C, and a solution of **1** (2.00 g, 7.28 mmol) in THF (5 mL) was added dropwise at this temperature within 2 min. The reaction mixture was stirred at −30 °C for a further 1 h, and then **10** (995 mg, 3.64 mmol) was added in a single portion at this temperature. After it was stirred at −30 °C for 1 h, the mixture was warmed to 20 °C, followed by sequential addition of diethyl ether (50 mL) and water (50 mL). The organic layer was separated and washed with water (3 × 20 mL), and the combined aqueous layers were extracted with diethyl ether (3 × 20 mL) and discarded. The combined organic extracts were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (220 °C/0.3 mbar; removal of byproducts), followed by further purification of the remaining residue by column chromatography on silica gel (40−63 μm, 140 g (Merck); treated with concentrated aqueous ammonia solution (7% by weight related to the silica gel); *n*-pentane/ethyl acetate (10/1 v/v)). The relevant fractions (GC analysis) were combined, the solvents were removed under reduced pressure, and the residue was dried in vacuo (0.01 mbar, 20 °C, 5 h) to give **19** in 61% yield as a colorless viscous liquid (1.51 g, 2.22 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ 0.00 (s, 4 H; Si(CH_2SiCH_2Si)$_2$), 0.32 (s, 18 H; Si(CH_3)$_2$(CH_2Si-(CH_3)$_2$CH_2Si)$_2$), 0.46 (s, 4 H; Si(CH_2SiCH_2Si)$_2$), 0.79 (s, 12 H; Si(CH_2Si(CH_3)$_2$CH_2Si(CH_3)$_2$)$_2$), 3.46 (s, 12 H; *o*-OCH_3, C_6H_2(OCH_3)$_3$), 3.50 (s, 6 H; *p*-OCH_3, C_6H_2(OCH_3)$_3$), 6.17 (s, 4 H; *H*-3/*H*-5, C_6H_2(OCH_3)$_3$). ^{13}C NMR (125.8 MHz, C_6D_6): δ 2.7 (Si(CH_2Si(CH_3)$_2$CH_2Si)$_2$), 2.9 (Si(CH_3)$_2$(CH_2SiCH_2Si)$_2$), 3.9 (Si-(CH_2SiCH_2Si(CH_3)$_2$)$_2$), 6.5 (SiCH_2SiCH_2Si), 7.4 (SiCH_2SiCH_2Si), 54.6 (*o*-OCH_3, C_6H_2(OCH_3)$_3$), 54.7 (*p*-OCH_3, C_6H_2(OCH_3)$_3$), 90.7 (*C*-3/*C*-5, C_6H_2(OCH_3)$_3$), 106.5 (*C*-1, C_6H_2(OCH_3)$_3$), 163.7 (*C*-4, C_6H_2(OCH_3)$_3$), 166.6 (*C*-2/*C*-6, C_6H_2(OCH_3)$_3$). ^{29}Si NMR (99.4 MHz, C_6D_6): δ −6.9 (Si(CH_2SiCH_2Si)$_2$), 0.2 (*Si*(CH_2SiCH_2Si)$_2$), 0.5 (Si(CH_2SiCH_2Si)$_2$). Anal. Calcd for $C_{32}H_{60}O_6Si_5$: C, 56.42; H, 8.88. Found: C, 56.3; H, 9.2.

Crystal Structure Analyses. Suitable single crystals of **1**, **2**, **12**−**15**, **17**, and **18** were obtained by crystallization from diethyl ether at −20 °C (**1**, **2**, **12**, **13**) or from *n*-pentane at −20 °C (**14**, **15**, **17**, **18**). The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (**1**, **2**, **12**, **15**, **17**, **18**, Stoe IPDS, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); **13**, **14**, Bruker Nonius KAPPA APEX II, Montel mirror, Mo Kα radiation (λ = 0.71073 Å)). The structures were solved by direct methods (SHELXS-97).[12] All non-hydrogen atoms were refined anisotropically (SHELXL-97).[12] A riding model was employed in the refinement of the C*H* hydrogen atoms. CCDC-928119 (**1**), CCDC-928120 (**2**), CCDC-928121 (**12**), CCDC-928122 (**13**), CCDC-928123 (**14**), CCDC-928124 (**15**), CCDC-928125 (**17**), and CCDC-928126 (**18**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for compounds **1**, **2**, **12**−**15**, **17**, and **18** (Tables S1 and S2 and CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: r.tacke@uni-wuerzburg.de.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Publications dealing with (2,4,6-trimethoxyphenyl)silanes and their use in synthesis: (a) Daiss, J. O.; Penka, M.; Burschka, C.; Tacke, R. *Organometallics* **2004**, *23*, 4987−4994. (b) Daiss, J. O.; Barth, K. A.; Burschka, C.; Hey, P.; Ilg, R.; Klemm, K.; Richter, I.; Wagner, S. A.; Tacke, R. *Organometallics* **2004**, *23*, 5193−5197. (c) Popp, F.; Nätscher, J. B.; Daiss, J. O.; Burschka, C.; Tacke, R. *Organometallics* **2007**, *26*, 6014−6028. (d) Tacke, R.; Popp, F.; Müller, B.; Theis, B.; Burschka, C.; Hamacher, A.; Kassack, M. U.; Schepmann, D.; Wünsch, B.; Jurva, U.; Wellner, E. *ChemMedChem* **2008**, *3*, 152−164. (e) Troegel, D.; Walter, T.; Burschka, C.; Tacke, R. *Organometallics* **2009**, *28*, 2756−2761. (f) Tacke, R.; Nguyen, B.; Burschka, C.; Lippert, W. P.; Hamacher, A.; Urban, C.; Kassack, M. U. *Organometallics* **2010**, *29*, 1652−1660.

(2) Synthesis of $ClMe_2SiCH_2SiMe_3$: (a) Kumada, M.; Nakajima, J.-I.; Ishikawa, M.; Yamamoto, Y. *J. Org. Chem.* **1958**, *23*, 292−295. (b) Fritz, G.; Ksinsik, D. *Z. Anorg. Allg. Chem.* **1963**, *322*, 46−57. (c) Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 4478−4479. (d) West, R.; Gornowicz, G. A. *J. Organomet. Chem.* **1971**, *28*, 25−35.

(3) Synthesis of $ClMe_2SiCH_2SiMe_2Cl$: (a) Greber, G.; Degler, G. *Makromol. Chem* **1962**, *52*, 174−183. (b) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, *45*, 5493−5497.

(c) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63−69. (d) Herzog, U.; Rheinwald, G. *J. Organomet. Chem.* **2001**, *628*, 133−143.

(4) Synthesis of $ClMe_2SiCH_2SiMeCl_2$: (a) See ref 2b. (b) Roark, D. N.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1972**, *94*, 5837−5841. (c) See ref 3d.

(5) Synthesis of $ClMe_2SiCH_2SiCl_3$: (a) Jung, I. N.; Lee, G.-H.; Yeon, S.-H.; Suk, M.-Y. *Bull. Korean Chem. Soc.* **1991**, *12*, 445−449. (b) Jung, I. N.; Yeon, S.-H.; Joon, S.-H. *Organometallics* **1993**, *12*, 2360−2362. (c) Kang, S.-H.; Han, J. S.; Yoo, B. R.; Lee, M. E.; Jung, I. N. *Organometallics* **2003**, *22*, 529−534.

(6) Greber, G.; Degler, G. DE 1257434, December 28, 1967.

(7) Cho, Y. S.; Yoo, B. R.; Ahn, S.; Jung, I. N. *Bull. Korean Chem. Soc.* **1999**, *20*, 427−430.

(8) For selected reviews dealing with carbosilanes, see: (a) Fritz, G. *Angew. Chem.* **1967**, *79*, 657−663; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 677−683. (b) Fritz, G. *Angew. Chem.* **1987**, *99*, 1150−1171; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1111−1132. (c) Birot, M.; Pillot, J.-P.; Dunoguès, J. *Chem. Rev.* **1995**, *95*, 1443−1477.

(9) Publications dealing with (chloromethyl)silanes and their use in synthesis: (a) Daiss, J. O.; Barth, K. A.; Burschka, C.; Hey, P.; Ilg, R.; Klemm, K.; Richter, I.; Wagner, S. A.; Tacke, R. *Organometallics* **2004**, *23*, 5193−5197. (b) Ilg, R.; Troegel, D.; Burschka, C.; Tacke, R. *Organometallics* **2006**, *25*, 548−551. (c) Klapötke, T. M.; Krumm, B.; Ilg, R.; Troegel, D.; Tacke, R. *J. Am. Chem. Soc.* **2007**, *129*, 6908−6915. (d) See ref 1e. (e) Troegel, D.; Möller, F.; Burschka, C.; Tacke, R. *Organometallics* **2009**, *28*, 5765−5770. (f) Falgner, S.; Burschka, C.; Wagner, S.; Böhm, A.; Daiss, J. O.; Tacke, R. *Organometallics* **2009**, *28*, 6059−6066. (g) Weidner, T.; Ballav, N.; Siemeling, U.; Troegel, D.; Walter, T.; Tacke, R.; Castner, D. G.; Zharnikov, M. *J. Phys. Chem. C* **2009**, *113*, 19609−19617. (h) Evangelisti, C.; Klapötke, T. M.; Krumm, B.; Nieder, A.; Berger, R. J. F.; Hayes, S. A.; Mitzel, N. W.; Troegel, D.; Tacke, R. *Inorg. Chem.* **2010**, *49*, 4865−4880. (i) Apfel, U.-P.; Troegel, D.; Halpin, Y.; Tschierlei, S.; Uhlemann, U.; Görls, H.; Schmitt, M.; Popp, J.; Dunne, P.; Venkatesan, M.; Coey, M.; Rudolph, M.; Vos, J. G.; Tacke, R.; Weigand, W. *Inorg. Chem.* **2010**, *49*, 10117−10132. (j) Sunderkötter, A.; Lorenzen, S.; Tacke, R.; Kraft, P. *Chem. Eur. J.* **2010**, *16*, 7404−7421. (k) Troegel, D.; Lippert, W. P.; Möller, F.; Burschka, C.; Tacke, R. *J. Organomet. Chem.* **2010**, *695*, 1700−1707. (l) Berkefeld, A.; Troegel, D.; Burschka, C.; Tacke, R. *Organometallics* **2010**, *29*, 4548−4554.

(10) When using (TMOP)Me_2SiCH_2MgCl instead of (TMOP)-Me_2SiCH_2Li, compound **18** was not obtained.

(11) Prior to use, the magnesium turnings were activated with 0.01 mol equiv of iodine in a sealed 5 mL glass vessel at 80 °C for 30 min.

(12) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.