1560 *Organometallics* **2002,** *21,* 1560−1564

Synthesis and Characterization of New Stable α,ω-Organo(bis-silanetriols)

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Received November 27, 2001

Synthesis and characterization of the first stable α,ω-bis(silanetriols) containing phenylene, biphenylene, α,ω-bis(phenylene)vinylene, α,ω-bis(phenylene)ethynylene, and α,ω-bis(phenylene)buta-1,3-diynylene organic bridging groups are described. They were obtained by controlled hydrolysis of the corresponding bis(trialkoxysilyl) precursors. An alternative route involving phase-transfer catalysis is also reported. These solids were organized as layers. The triol end groups formed hydrophilic layers, whereas the body of the sheets corresponded to hydrophobic layers. The distance between two neighboring hydrophilic layers was directly related to the length of the organic group; nevertheless, the packing was induced by the hydrogen-bond network.

Introduction

For many years the chemistry of silanetriols has received less attention than that of silanols and silanediols[1] because of their very facile polycondensation.[2] Most of the silanetriols reported in the literature contain only one $Si(OH)_3$ group[3−18] and are stabilized by a combination of steric and electronic effects. A general feature of silanetriols is their high tendency to self-organization and their relatively good stability, especially in the solid state because of intermolecular hydrogen bonding. As a result, a large variety of networks can be obtained and classified with respect to the balance between the tightness of the hydrogen-bond network and the steric constraints due to the organic substituent on the silicon atom. In the case of lipophilic molecules, one can find the following: (i) a double-sheet structure in which the molecules arrange themselves head-to-head and tail-to-tail, the alkyl and OH groups forming alternating hydrophobic and hydrophilic double sheets, respectively;[5−7] (ii) tubular structures with a hydrophilic axis and hydrophobic outer shell;[10,13] (iii) hexameric and octameric cage structures as found for the silanetriols containing a hydrophilic core which is sterically shielded by a hydrophobic outer layer;[8,9] (iv) tetrameric structures.[2] Finally, in the case of the very bulky ligand $OsCl(CO)(PPh_3)_2$, there is no intermolecular hydrogen bonding at all.[4] Thus for mono(silanetriols), it is possible to isolate organized structures in which the hydrogen bonds tighten the structure in a balance with the steric hindrance or the lipophilicity. The mono(silanetriols) reported in the literature have a silicon atom bonded to carbon, nitrogen, oxygen, or a transition metal.

We have recently reported the structure of the first stable bis(silanetriol) which featured a strong hydrogen-bond network.[19] We report here the synthesis and characterization of a new class of layered structures of silanetriols containing two $Si(OH)_3$ groups in the same molecule.

Results and Discussion

Relatively few silanetriols have been isolated up to now because of the increasing tendency of silanols to condense as the number of OH groups at silicon increases. The two main routes to organosilanetriols described in the literature consist on one hand of a controlled hydrolysis of trimethoxysilyl precursors in

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† E-mail: gcerveau@crit.univ-montp2.fr. Fax: +33(0)467143852.

(1) Murugavel, R.; Bhattacharjee, M.; Roesky, H. W. *Appl. Organomet. Chem.* **1999**, *13*, 227 and references therein.

(2) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147 and references cited therein.

(3) Tyler, L. *J. Am. Chem. Soc.* **1955**, *77*, 770.

(4) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. *J. Am. Chem. Soc.* **1992**, *114*, 9682.

(5) Winkhofer, N.; Roesky, H. W.; Noltemeyer, M.; Robinson, W. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 599.

(6) Jutzi, P.; Strassburger, G.; Schneider, M.; Stammler, H. G.; Neumann, B. *Organometallics* **1996**, *15*, 2842.

(7) Ishida, H.; Koenig, J. L.; Gardner, K. G. *J. Chem. Phys.* **1982**, *77*, 5748.

(8) Ritter, U.; Winkhofer, N.; Schmidt, H. G.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 524.

(9) Al-Juaid, S. S.; Buttrus, N. H.; Damja, R. I.; Derouiche, Y.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1989**, *371*, 287.

(10) Murugavel, R.; Chandrasekhar, V.; Voigt, A.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **1995**, *14*, 5298.

(11) Takigushi, T. *J. Am. Chem. Soc.* **1959**, *81*, 2359.

(12) Michalska, Z.; Lasocki, Z. *Bull. Acad. Pol. Ser. Sci. Chim.* **1971**, *19*, 757.

(13) Jutzi, P.; Schneider, M.; Stammler, H. G.; Neumann, B. *Organometallics* **1997**, *16*, 5377.

(14) Winkhofer, N.; Voigt, A.; Dorn, H.; Roesky, H. W.; Steiner, A.; Stalke, D.; Reller, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1352.

(15) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205.

(16) Schneider, M.; Neumann, B.; Stammler, H. G.; Jutzi, P. *Monatsh. Chem.* **1999**, *130*, 33.

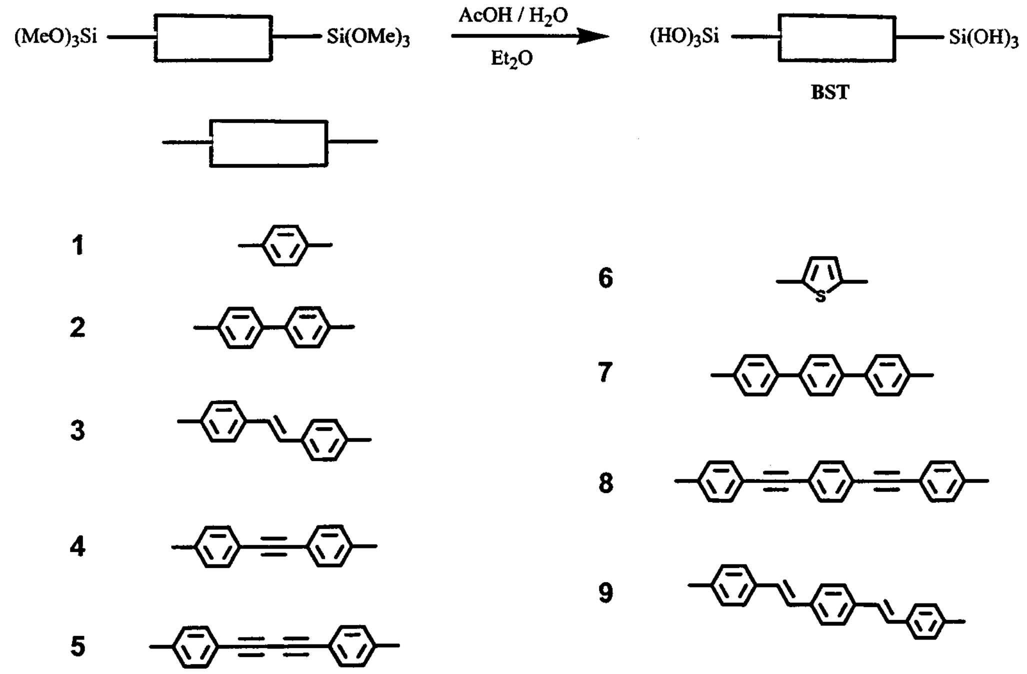
(17) Klemp, A.; Hatop, H.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. *Inorg. Chem.* **1999**, *38*, 5832.

(18) Malish, W.; Lankat, R.; Schmitzer, S.; Reising, J. *Inorg. Chem.* **1995**, *34*, 5701.

(19) Cerveau, G.; Corriu, R. J. P.; Dabiens, B.; Le Bideau, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4533.

10.1021/om0110179 CCC: $22.00
Publication on Web 03/16/2002

Scheme 1



aqueous acetic acid at low temperature[3] and on the other hand of the hydrolysis of trichlorosilanes in the presence of a base at 0 °C.[11] For our purposes we have selected the hydrolysis of alkoxysilanes, which results in formation of the alcohol instead of HCl, which accelerates the condensation reaction.

The bis(silanetriols) (**BST**) reported here were prepared by controlled hydrolysis of the corresponding bis(trimethoxysilyl) precursors **1**−**5** under mild conditions according to Scheme 1. The original procedure reported by Tyler[3] for the phenyl(trimethoxy)silane precursor was modified, since these conditions led always to organosilsesquioxane solids in the case of bis(trialkoxysilyl) precursors. The bis(silanetriols) **BST1-BST5** were obtained in a *biphasic medium (diethyl ether/water)* at room temperature in the presence of acetic acid as catalyst. The reaction mixture was stirred thoroughly until the resulting organobis(silanetriol) precipitated out in the aqueous phase. The progress of the reaction was followed by ^{1}H NMR spectroscopy in DMSO-d_6. The intensity of the signal at ∼3.56 ppm (OCH_3) decreased, whereas a new singlet at ∼6.36 ppm due to hydrogens of hydroxy groups appeared. In each case, the reaction was stopped when the singlet at ∼3.56 ppm had completely disappeared. After filtration and drying overnight at 25 °C under vacuum, the bis(silanetriols) were recovered. After longer reaction times, some polycondensation occurred. The experimental conditions and the yields of **BST1**−**BST5** are reported in Table 1. The use of diethyl ether as cosolvent allowed thorough solubilization of the bis(trialkoxysilyl) precursors and permitted the hydrolysis to occur at the interface of the biphasic medium. The bis(silanetriols) **BST1**−**BST5** were stable in the atmosphere in the solid state. In the case of precursors **6, 8**, and **9** it was not possible to isolate the corresponding pure bis(silanetriols): **6** gave the polysilsesquioxane **PS6**, whatever the ratio of the number of moles of precursor (np) over the number of moles of acetic acid (na) was; the bis(trialkoxysilyl) compounds **8** and **9** led in all cases to a mixture of silsesquioxane and bis(silanetriol), as shown by IR and NMR spectroscopy. In all cases the solid isolated in the reaction was sparingly soluble in DMSO. The ^{1}H NMR and ^{29}Si NMR spectra of this soluble part exhibited singlets at respectively 6.55 ppm (OH groups) and −55.2 ppm ($Si(OH)_3$ groups), in agreement with the values reported in the literature for silanetriols.[20] It is noteworthy that the terphenyl compound **7** did not react under the same experimental conditions, and **7** was recovered unchanged.

Table 1. Experimental Conditions and Yields for BST1−**BST5**

precursor	molar ratio:[a] np/na	reacn time (days)	yield (%)
1	26	1	93
2	26	1	95
3	3	10	70
4	1.5	27	77
5	2.2	34	65

[a] np/na = number of moles of precursor versus number of moles of acetic acid.

In some cases, very long reaction times were required (Table 1). To shorten them, some attempts at liquid−liquid phase-transfer catalysis were investigated. This process is well-known to favor reactions between a lipophilic substrate dissolved in an organic phase, with a hydrophilic reactant solubilized in water.[21] Several catalysts were investigated in the case of **1** and **3**: tetrabutylammonium chloride (TBACl), tetrabutylammonium bromide (TBABr), tris(3,6-dioxaheptyl)amine (TDA-1), tetrabutylammonium hydrosulfate (TBAHSO$_4$), tetrabutylammonium acetate (TBAA), and tetraethylammonium *p*-toluenesulfonate (TEApTS) (Table 2). It appears that for precursors **1** and **3**, using the same amount of acetic acid, the most efficient catalyst was TEApTS. We extended this synthesis to the other

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[20] Voigt, A.; Murugavel, R.; Ritter, U.; Roesky, H. W. *J. Organomet. Chem.* **1996**, *521*, 279.

[21] Starks, C. M.; Liotta, C. In *Phase Transfer Catalysis: Principles and Techniques*; Academic Press: New York, 1978.

Table 2. Comparison between Various Phase Transfer Catalysts

precursor	molar ratio: np/na	PTC[a] (%)	reacn time (h)	product	yield (%)
1	26	TBACl (1)	36	*b*	
1	26	TBACl (5)	24	*c*	
1	26	TDA-1 (1)	18	*c*	
1	26	$TBAHSO_4$ (10)	24	*c*	
1	26	TBAA (10)	15	**BST1**	20
1	26	TEApTS (10)	2	**BST1**	95
3	2.95	TBABr (10)	120	*c*	
3	2.95	TBACl (5)	216	**BST3**	60
3	5.7	TEApTS (15)	192	**BST3**	78

[a] PTC: phase transfer catalyst (mol % given in parentheses). [b] Starting precursor. [c] Mixture of bis(silanetriol) and poly(silsesquioxane).

Table 3. Experimental Conditions and Yields with TEApTS as Catalyst

precursor	molar ratio: np/na	TEApTS (%)	reacn time (days)	yield (%)
1	26	10	0.08[a]	95
3	5.7	15	8	78
4	2.9	15	15	73
5	2.4	15	17	62

[a] 2 h.

Table 4. Maximum Temperature for Endothermic Peak of BST1−BST5

temp (°C)				
BST1	**BST2**	**BST3**	**BST4**	**BST5**
196	152	136	137	141

Table 5. Cell Parameters, Interlamellar Distances, and Tilt Angles for BST1−BST5

compd	a/Å	b/Å	c/Å	β/deg	d_{int}/Å	~α/deg
BST1	10.056(2)	6.879(2)	6.937(2)	95.71(3)	10.0	18
BST2	14.030(7)	6.953(4)	6.86(1)	92.80(8)	14.0	21
BST3	15.88(2)	6.91(1)	6.73(3)	98.6(2)	15.7	23
BST4	16.41(4)	6.73(10)	7.04(12)	99.0(4)	16.2	20
BST5	18.48(2)	6.90(1)	6.83(1)	99.5(1)	18.2	23

precursors, as shown in Table 3. In the case of **5** the reaction time was halved with respect to the reaction time without phase transfer catalyst.

The bis(silanetriols) **BST1**−**BST5** were insoluble in the usual polar organic solvents such as methanol, ethanol, 2-propanol, THF, acetone, diethyl ether, and acetonitrile. In contrast, they were very soluble in DMSO, certainly because of strong hydrogen bonding between DMSO and OH groups. They were identified by IR and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. For all samples, the FTIR spectra exhibited a broad absorption band centered at 3200 cm^{-1}, attributed to hydrogen-bonded OH groups, and a broad band centered at ~890 cm^{-1}, due to the Si−O(H) bond vibration modes. No absorption bands at ~1050 cm^{-1} which would correspond to Si−O−Si bond vibrations were detected. The NMR spectra were recorded in DMSO-d_6. The ^{1}H and ^{13}C NMR spectra of **BST1**−**BST5** exhibited the expected resonances for the organic moiety in each case. The OH groups displayed a sharp singlet at about 6.36−6.58 ppm (see Experimental Section). In all cases the ^{29}Si NMR spectra exhibited a sharp resonance at ~−55 ppm, in agreement with the values reported in the literature for silanetriols.[20]

The thermal stability of the bis(silanetriols) was studied by differential scanning calorimetry (DSC). The curves exhibited very broad and highly asymmetric endothermic signals. The maxima ranged between 136 °C (**BST3**) and 196 °C (**BST1**). The values are reported in Table 4. The bis(silanetriols) appeared to be relatively stable, despite the presence of six OH functional groups per molecule. These signals corresponded to the polycondensation reaction. Interestingly, when the length of the organic bridging fragment increased, the temperature corresponding to the maximum decreased. The thermal stability of the bis(silanetriols) seemed to be directly related to the length of the organic bridging group.

We have reported the crystal structure of the phenylene derivative **BST1** along with the cell parameters of the biphenylene derivative **BST2**.[19] This structure consists of bis(silanetriol) molecules arranged as layers; the molecules are almost orthogonal to the plane of these layers. The triol end groups form hydrophilic sheets within which a hydrogen-bond network sets up the cohesion of the solid. The X-ray powder diffraction patterns obtained for **BST1**−**BST5** were very similar. Attempts to find cell parameters for each sample led us to the data gathered in Table 5. Except for the phenylene and biphenylene cases, the pattern showed relatively wide and overlapped peaks; with the best-resolved peaks (13, 11, and 16 peaks for **BST3**, **BST4**, and **BST5**, respectively), the automatic powder indexing software DICVOL[22] was run. The best cell parameters found were in the monoclinic system with the Figure of Merit[23] M(13), M(11) and M(16) for **BST3**, **BST4**, and **BST5** at 7.7, 8.6, and 8.8, respectively. Along with the similarities between all patterns and the consistency with **BST1** and **BST2**, these cell parameters were reliable. The b and c parameters, as shown for the bis(trihydroxysilyl)benzene **BST1**, described the plane parallel to the hydroxy layers and are similar in the whole family. The a parameter (a^* was along the stacking axis), was directly related to the length of the organic bridging group and increased from the smallest, **BST1**, up to the longest, **BST5**. Interlamellar distances increased monotonically, and calculations of the tilting angle of the molecule with respect to the layers' stacking axis showed results between 18 and 23°. Since we have reported the crystal structure determination of **BST1**,[19] it seemed possible to attribute the same structural arrangement to **BST3**−**BST5.** It is noteworthy that the tilting angle of the molecules seemed related to the hydrogen-bond network: for **BST1**, as a result of this tilting angle, one oxygen atom (O3) of one triol extremity is directed toward a neighboring molecule of the same sheet, whereas the two other oxygen atoms of the same triol extremity are directed toward a molecule of the neighboring sheet (Figure 1). Therefore, this tilting angle would permit a higher packing of the molecules as well as the structural organization. Moreover, the value of the tilting angle would thus be related more to the geometry of the triol end group rather than to the length of the molecule. This is consistent with small variations of the tilting angles observed for **BST1** up to **BST5**, although the length of the molecules increases drastically. The TEM images of bis(silanetriols) **BST1**−**BST5** showed the presence of the superposition of thin plates.

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(22) Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, *24*, 987.
(23) De Wolff, P. M. *J. Appl. Crystallogr.* **1968**, *1*, 108.

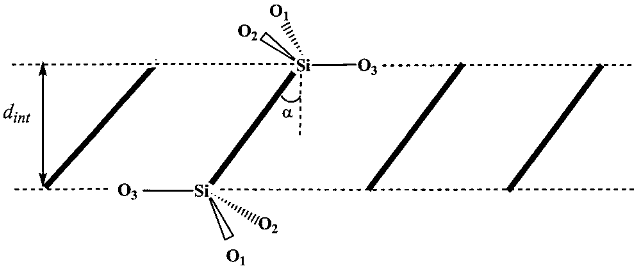

Figure 1. Schematic representation of the tilting angle and oxygen atom arrangement within a sheet.

The organization of the bis(silanetriols) **BST1**−**BST5** as layers may be explained by a preferential organization of the organic spacers during the hydrolysis step. The organization of the organic pillars can be favored by van der Waals type interactions between the organic units before the formation of the hydrogen-bond network. Interestingly, these types of layered structures have been reported in the case of the hydrolysis−polycondensation of alkyl(trialkoxy)silanes containing long-chain alkyl groups.[24] The octadecylsilanetriol is organized as alternating hydrophilic−hydrophobic sheets. This arrangement as sheets is favored and stabilized by the hydrophobic interactions between the saturated aliphatic chains. In this case the high lipophilicity is certainly slowing down the polycondensation at silicon, allowing the stabilization of the material by hydrogen bonding.

In the case of the bis(silanetriols) presented here, the stabilization of organized structures could be the result of the presence of strong hydrogen bonds, which would be the driving force for the organization of the hydrophobic organic bridging groups. The hydrophilic layer was formed in the aqueous phase and allowed the formation of the bis(silanetriols) by slowing down the polycondensation reaction. Furthermore, the presence of silicon directly bonded to the aromatic group is of fundamental importance, since all attempts to isolate silanetriols from 1,4-bis((trimethoxysilyl)ethyl)benzene failed and yielded the corresponding silsesquioxanes. Another requirement is the geometry of the organic bridging group. That a bis(silanetriol) is obtained implies the presence of rigid-rod organic bridging units. The monothiophene **6** did not yield a bis(silanetriol). This behavior could be explained by the competition occurring between polycondensation at silicon, which is the expected reaction between polysilanol groups, and the formation of the layered structure controlled by hydrogen bonding. Only the very favorable cases with an appropriate geometry for the formation of the layers of a hydrogen-bond network permit the formation of layered solids. Thus, the rigidity of the precursor is more favorable to hydrogen-bond network formation than a flexible one. The fact that the bis(silylated) monothiophene **6** did not permit bis(silanetriol) formation confirms this hypothesis. Although its structure is rigid, the geometry is not favorable to the formation of the layered hydrogen bond network, the angle between the two Si−C bonds being 168° instead of the favorable angle of 180°.

Conclusion

In conclusion, we have obtained for the first time layers of bis(trihydroxysilylated) organic units using a new synthesis route. In the methods used for the synthesis of silanetriols, there is always a competition between the kinetics of polycondensation leading to the formation of the Si−O−Si network and the possilibity of thermodynamic stabilization by hydrogen bonding able to give a structural organization. In the case of bis(silanetriols), the polycondensation is very fast, since it occurs at the two silylated end groups. The use of biphasic systems allowed us to slow the polycondensation and to accelerate and favor the formation of layered structures in the aqueous phase. The systems obtained are the result of strong hydrogen bonding and bidimensional structural arrangement. The solutions of silanetriols in DMSO are very stable, because of the strong hydrogen bonding between DMSO and the OH groups, whereas the solubilization in formamide led to the destruction of the crystalline network and to polycondensation reaction.

These bis(silanetriols) would constitute precursors for the preparation of hybrid organic−inorganic silicon-based materials.[25−30] Further work is in progress in order to use these systems for the preparation of hybrid materials.

Experimental Section

All reactions were carried out under argon using a vacuum line and Schlenk techniques. Solvents were dried and distilled just before use. IR data were obtained on a Perkin-Elmer 1600 FTIR 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. Differential scanning calorimetry was carried out on a Mettler DSC 30 instrument. The X-ray powder patterns were recorded on a Seifert MZ4 diffractometer from 4 to 60° 2θ, 0.04° 2θ/step, 2.5 s/step. The electronic transmission microscopy was carried out on a Cambridge Stereoscan 360. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS". The bis(trialkoxysilyl)precursors **1**−**9** were prepared according to literature procedures: **1**, **2** and **7**,[31,32] **3**−**5** and **8**,[33] **6**,[34] **9**.[35]

The preparation of bis(silanetriols) **BST1**−**BST5** was carried out according to the following general procedure: the synthesis of **BST1** is given as an example.

1,4-Bis(trihydroxysilyl)benzene (BST1). A mixture of 1,4-bis(trimethoxysilyl)benzene (**1**; 1.6 g, 5 mmol) in 2.3 mL of ether and 2.2 mL of 0.5% aqueous acetic acid solution was

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[24] Shimojima, A.; Suguhara, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2847.

[25] *New J. Chem.* **1994**, *18* (special issue).

[26] Loy, D. A.; Shea, K. J. *Chem. Rev.* **1995**, *95*, 1431.

[27] Lindner, D. A.; Schneller, T.; Auer, F.; Mayer, H. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2154.

[28] Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376.

[29] Sanchez, C.; Ribot, F. *Comments Inorg. Chem.* **1999**, *30*, 327.

[30] Brinker, C. J.; Scherer, G. W. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: San Diego, CA, 1990.

[31] Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.* **1992**, *114*, 6700.

[32] Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217.

[33] Cerveau, G.; Chappellet, S.; Corriu, R. J. P.; Dabiens, B. *J. Organomet. Chem.* **2001**, *626*, 92.

[34] Corriu, R. J. P.; Moreau, J. J. E.; Thépot, P.; Wong Chi Man, M.; Chorro, C.; Lère Porte, J. P.; Sauvajol, J. L. *Chem. Mater.* **1994**, *6*, 640.

[35] Corriu, R. J. P.; Hesemann, P.; Lanneau, G. *Chem. Commun.* **1996**, 1845.

stirred vigorously for 1 day at 25 °C. During this period a white solid precipitated in the aqueous phase. The white suspension was filtered, and the resulting solid was washed three times with ethanol, acetone, and ether. The white powder was dried overnight under vacuum at 20 °C to give the white, crystalline solid **BST1** in 93% yield (1.09 g, 4.65 mmol).

Phase-Transfer Catalysis (PTC) Route. Tetraethylammonium *p*-toluenesulfonate (TEApTS; 0.150 g, 0.5 mmol) was added to a solution of **1** (1.6 g, 5 mmol) in 2.3 mL of ether and 2.2 mL of 0.5% aqueous acetic acid solution with vigorous stirring. The white biphasic mixture was stirred for 2 h at 25 °C. A white solid precipitated. The suspension was filtered, and the resulting solid was washed three times with ethanol, acetone, and ether. The powder was dried overnight under vacuum at 20 °C to give **BST1** in 95% yield (1.12 g, 4.75 mmol).

^{1}H NMR (DMSO-d_6; δ, ppm): 7.55 (4H, s), 6.36 (6H, s). ^{13}C NMR (DMSO-d_6; δ, ppm) 138.7, 133.7. ^{29}Si NMR (DMSO-d_6; δ, ppm) −54.3. Anal. Calcd for $C_6H_{10}O_6Si_2$: C, 30.16; H, 4.30; Si, 23.95. Found; C, 30.86; H, 4.39; Si, 24.20.

4,4′-Bis(trihydroxysilyl)biphenyl (BST2). A solution of 4,4′-bis(trimethoxysilyl)biphenyl (**2**; 1 g, 2.53 mmol) in 3 mL of ether and 1.10 mL of a 0.5% aqueous acetic acid solution was vigorously stirred for a period of 24 h at a temperature of 20 °C. The usual treament gave the white, crystalline solid **BST2** in 95% yield (0.61 g, 2.40 mmol).

^{1}H NMR (DMSO-d_6; δ, ppm): 7.69 (4H, d), 7.63 (4H, d), 6.43 (6H, s). ^{13}C NMR (DMSO-d_6; δ, ppm): 141.2, 136.8, 135.5, 126.3. ^{29}Si NMR (DMSO-d_6; δ, ppm): −54.3. Anal. Calcd for $C_{12}H_{14}O_6Si_2$: C, 46.44; H, 4.54; Si, 18.09. Found: C, 45.44; H, 4.70; Si, 18.20.

4,4′-Bis(trihydroxysilyl)stilbene (BST3). Similarly, a mixture of 9 mL of a 1% aqueous acetic acid solution and 4,4′-bis(trimethoxysilyl)stilbene (**3**; 2 g, 4.76 mmol) dissolved in 10 mL of ether was stirred for a period of 10 days. The yellow powder **BST3** was recovered in 70% yield (1.12 g, 3.32 mmol).

PTC Route. 3 (1.26 g, 3 mmol) in 10 mL of ether, 6 mL of 1% aqueous acetic acid solution, and TEApTS (0.136 g, 0.45 mmol) yielded **BST3** (0.786 g, 2.34 mmol, 78%).

^{1}H NMR (DMSO-d_6; δ, ppm): 7.69 (4H, d), 7.63 (4H, d), 7.28 (2H, s), 6.41 (6H, s). ^{13}C NMR (DMSO-d_6; δ, ppm): 138.1, 137.5, 135.1, 129.3, 126.0. ^{29}Si NMR (DMSO-d_6; δ, ppm): −54.3. Anal. Calcd for $C_{14}H_{16}O_6Si_2$: C, 49.98; H, 4.80; Si, 16.70. Found: C, 50.46; H, 4.95; Si, 16.90.

4,4′-Bis(trihydroxysilyl)diphenylacetylene (BST4). A solution of 4,4′-bis(trimethoxysilyl)diphenylacetylene (**4**; 1.58 g, 3.77 mmol) in 10 mL of ether was stirred vigorously with 29 mL of 0.5% aqueous acetic acid solution for 27 days. The usual treatment gave a beige solid of **BST4** (0.970 g, 2.9 mmol, 77%).

PTC Route. 4 (0.280 g, 0.67 mmol) in 2.2 mL of ether, 2.65 mL of 0.5% aqueous acetic acid solution, and TEApTS (0.030 g, 0.1 mmol) yielded **BST4** (0.164 g, 0.49 mmol, 73%).

^{1}H NMR (DMSO-d_6; δ, ppm): 7.63 (4H, d); 7.50 (4H, d), 6.52 (6H, s). ^{13}C NMR (DMSO-d_6; δ, ppm): 139.3, 135.2, 130.9, 123.6, 90.7. ^{29}Si NMR (DMSO-d_6; δ, ppm): −55.2. Anal. Calcd for $C_{14}H_{14}O_6Si_2$: C, 50.24; H, 4.22; Si, 16.70. Found: C, 48.99; H, 3.96; Si, 15.00.

4,4′-Bis(trihydroxysilyl)diphenylbut-1,3-diyne (BST5). A solution of 4,4′-bis(trimethoxysilyl)diphenylbut-1,3-diyne (**5**; 1.15 g, 2.60 mmol) in 10 mL of ether was stirred vigorously with 13.70 mL of 0.5% aqueous acetic acid solution for 34 days. The resulting beige, crystalline solid **BST5** was obtained in 65% yield (0.605 g, 1.69 mmol).

PTC Route. 5 (1 g, 2.26 mmol) in 7 mL of ether, 12.5 mL of 0.5% aqueous acetic acid solution, and TEApTS (0.103 g, 0.34 mmol) yielded **BST5** (0.500 g, 1.4 mmol, 62%).

^{1}H NMR (DMSO-d_6; δ, ppm): 7.65 (4H, d), 7.57 (4H, d), 6.58 (6H, s). ^{13}C NMR (DMSO-d_6; δ, ppm): 140.9, 135.2, 131.9, 121.6, 83.1, 74.7. ^{29}Si NMR (DMSO-d_6; δ, ppm): −55.6. Anal. Calcd for $C_{16}H_{14}O_6Si_2$: C, 53.62; H, 3.93; Si, 15.67. Found: C, 53.04; H, 3.75; Si, 16.35.

Acknowledgment. We acknowledge the Dow Corning Corp. for supporting this research and thank Dr. Pierre Chevalier from Dow Corning (Barry, U.K.) for fruitful discussions.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM0110179