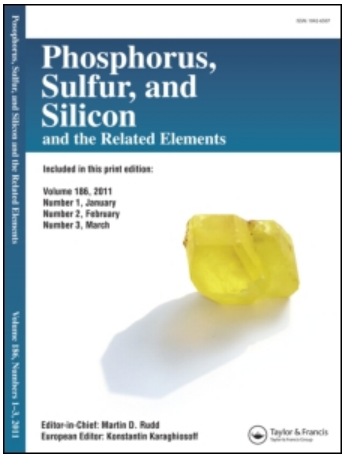

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New Organosilicon Precursors for the Formation of Porous Structures

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Mono- and disilane substituted arene-centered star molecules are prepared via reactions of halogenodialkylaminosilanes with lithium aryl acetylides. After complete coupling of both chlorosilane and acetylenic synthon the dialkyl-amino substituent can be replaced by halogenes. Reactive sites at the silicon atoms allow an enlargement of the system by coupling and cross-linking to build up a permanent cavity structure. All compounds have been characterized by NMR-spectroscopy.

Keywords: Aryl acetylides; Silicon

1. Introduction The gradual building up of well defined porous structures is of high interest both in basic research and industry due to the great variety of inherent applications [1]. Usually, porous clathrate frameworks are held together by weak inter-molecular interactions. Therefore the resulting frame-works are rather labile. On the other hand inforce of such weak cohesions by strong covalent bonds may create a permanent hollow structure. Along this line we are interested in methodologies to develop the synthesis of silicon-rich star as well as dendritic compounds, which may be used as precursors to construct new porous solid materials. Aromatic units as connecting building blocks between rigid organo-silanes are promising. They offer the possibility to

get to dendrimers by making use of the protecting group concept and functionalized silicon atoms in the target molecule. The stepwise synthesis of porous structures containing both inorganic and organic units requires a rigid structure containig organic moiety which should be able to react with the silane molecule.

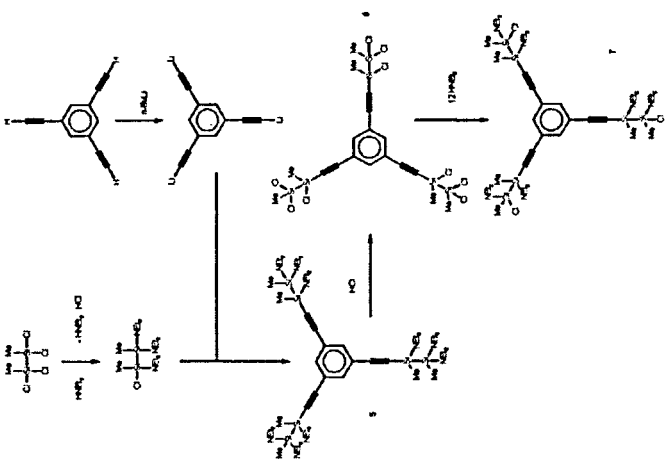
2. Results All organosilanes of the generell formula 1,3,5-$(RC{\equiv}C)_3C_6H_3$ (R=silyl rest) were prepared via reaction of lithiumarylacetylides ($(LiC{\equiv}C)_3C_6H_3$), which resulted from treatment of 1,3,5-triethynylbenzene[2] with ^{n}BuLi in THF, and the chloro-(diethylamino)silanes.

^{n}BuLi (1.6 M in ^{n}hexane; 12.5 ml, 20 mmol) was added dropwise to 1,3,5-triethynylbenzene (1 g, 6.7 mmol) in THF (100 mL) at 253 K. This mixture was stirred for 20 min then 20 mmol of the appropriate halogenosilyl derivative was added. The solution became bright yellow and was stirred for 5 h at room temperature. The solvent was drained off and the LiCl salt was eliminated by stirring of the crude product with ^{n}hexane and filtration. ^{n}Hexane was removed under vacuum to give yellow to pale brown residues (**1-3, 5**).

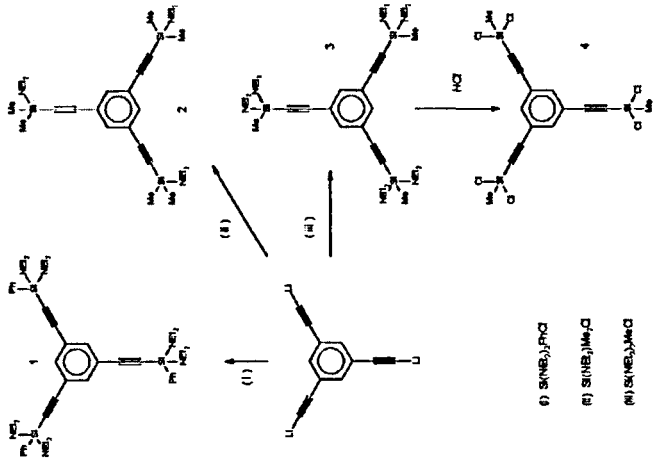
To take advantage of diethylamino functions as protecting groups, the aminosilanes were synthesized from the corresponding chlorosilanes by treatment with diethylamine [3]. The preparations of monosilyl substituted ethynylbenzenes have given an insight to understand the peculiarities of analytical data interpretation. Our hopeful results have stimulated us to extend the synthesis including also methylchlorodisilanes and -trisilanes.

All prepared molecules were characterized by ^{1}H-, ^{13}C- and ^{29}Si NMR spectroscopy (Tables 1 and 2). Exchange of the chlorine atom against an acetylenic unit in aminochlorosilanes causes a characteristic upfield shift of the ^{29}Si NMR resonances of about 10 to 20 ppm for the substituted silicon atom. The chemical shift value of the other silicon atom in the disilanes are insignificantly influenced (up to 3 ppm). In the ^{13}C NMR spectra the linkage between silicon and C≡C sequence is indicated by the down field shift for the acetylenic carbons. In case of resulting stereoisomers, the signal of the carbon atom bonded to silicon is split into two peaks.

To replace the amino function against chlorine, dried HCl gas was passed through a solution of the compounds **3** and **5** in tetrachloromethane. Completness of the conversion is indicated by



SCHEME 2.

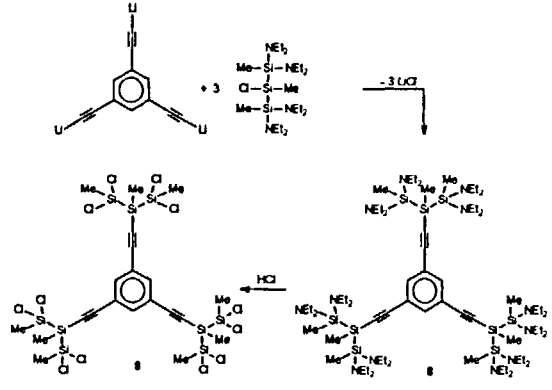


SCHEME 1.

decreasing of the temperature in the solution. The resulting ammonium salt CCl_4 complex was eliminated and the CCl_4 was removed under vacuum. A bright oil in case of **4** and a bright solid of **6** could be isolated.

For selective reamination, $HNEt_2$ (1.74 ml, 16.67 mmol) was added dropwise to a solution of **6** (1 g, 1.39 mmol) in ^{n}hexane (100 mL). The mixture was stirred for 4 h. The resulting ammonium salt was eliminated by filtration and the solvent was removed under vacuum to give a pale yellow residue of **7**.

The Bis-[bis(diethylamino)chloromethylsilyl]chloromethylsilane was prepared by the reaction of bis(dichloromethylsilyl)chloromethylsilan [4] and diethylamine in ^{n}hexane [5].



SCHEME 3.

A solution of 5.82 g (12.8 mmol) bis(diethylamino)-chloromethylsilyl-chloromethylsilane in ^{n}hexane was treated with a solution prepared from ^{n}BuLi (1.6 M in ^{n}hexane; 10.7 ml, 17.12 mmol), 1,3,5-triethynylbenzene (0.64 g, 4.28 mmol) and 100 mL THF. The mixture was stirred for 12 h at ambient temperature and solvents were removed in vacuo. The yellow product was dissolved with ^{n}hexane and filtered off. The solvent was removed under reduced pressure and a pale yellow solid (**8**) was obtained.

TABLE 1. ^{29}Si and ^{1}H NMR data of silane substituted 1,3,5-triethynylbenzene, in ppm, (* stereoisomers)

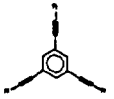
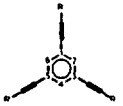
 R	δ(^{29}Si)	δ(^{1}H)				
		Si^{A}-Me	Si^{B}-Me	N-Me	N-CH_2	
-$Si^{A}MeCl$-$Si^{B}MeCl_2$	-17.11A; 21.08 B	0.85	1.01			7.65
-$Si^{A}MeN$-$Si^{B}MeClN$ *	-30.4 / -30.9A; 3.8 / 4.4 B	0.47; 0.51	0.59; 0.64	1.07	2.97	7.45
-$Si^{A}MeN$-$Si^{B}MeN_2$	-30.84 A; -11.39 B	0.24	0.34	1.02	2.94	7.34
-$Si^{A}Me(Si^{B}MeCl_2)_2$	-58.09 A; 27.78 B	0.53	1.05			7.58
-$Si^{A}Me(Si^{B}MeN_2)_2$	-74.11 A; -5.46 B	0.33	0.48	1.1	3.0	7.3 / 7.4
-$SiMeN_2$	-28.62	0.39		1.17	3.05	7.52
-$SiMe_2N$	-17.59	0.20		0.98	2.81	7.40
-$SiPhN_2$	-34.52	1.03		1.20	2.98	7.32; 7.58-7.75 (Si-Ph)
-$SiMeCl_2$	-7.35	0.89				

TABLE 2. ^{13}C NMR data of silane substituted 1,3,5-triethynylbenzene, in ppm, (* stereoisomers)

 R	8	7	1, 3, 5	2, 4, 6	Si^AMe	Si^BMe
$-Si^AMeCl-Si^BMeCl_2$	88,40	107,70	122,48	136,42	1,28	5,58
$-Si^AMeN-Si^BMeClN$*	93,80/94,0	104,84	123,82	134,83	-1,28 / -0,95	2,12 / 2,23
$-Si^AMeN-Si^BMeN_2$	97,38	103,7	124,32	133,96	-0,59	0,12
$-Si^AMe(Si^BMeCl_2)_2$	89,44	108,19	123,12	135,95	-8,10	7,60
$-Si^AMe(Si^BMeN_2)_2$	96,22	106,66	124,87	133,42	-4,70	0,23
$-SiMeN_2$	94,94	101,42	124,40	134,34	-0,72	
$-SiMe_2N$	98,04	104,45	126,85	137,12	2,79	
$-SiPhN_2$	94,01	102,61	124,13	136,40		
$-SiMeCl_2$	89,51	103,92	122,03	136,75	-0,02	

To replace the amino functions against chlorine the procedure described above was applied to prepare compound **9**. A detailed characterization of **8** and **9** has been carried out by ^{1}H-, ^{13}C- and ^{29}Si NMR spectroscopy. The ^{13}C-NMR spectra for **8** and **9** exhibit the typical peaks of the 1,3,5-triethynylbenzene unit and the methyl groups (see Table 2).

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