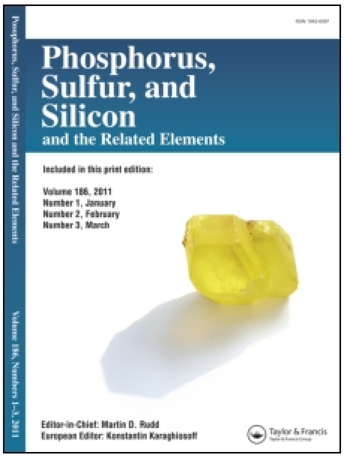

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Synthesis and NMR-Spectroscopic Studies of Substituted Cyclohexasilanes

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SYNTHESIS AND NMR-SPECTROSCOPIC STUDIES OF SUBSTITUTED CYCLOHEXASILANES

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Abstract Synthesis of di- and tri-functionel derivatized cyclohexasilanes of the type 1,3-$X_2Si_6Me_{10}$ (X = Cl, Br, H, $Fe(CO)_2Cp$), 1,3,5-$Y_3Si_6Me_9$ (Y = F, Cl, Br, Ph) and 1-$[Fe(CO)_2Cp]$-4-XSi_6Me_{10} (X = H, Cl, $Co(CO)_3PPh_3$).

INTRODUCTION

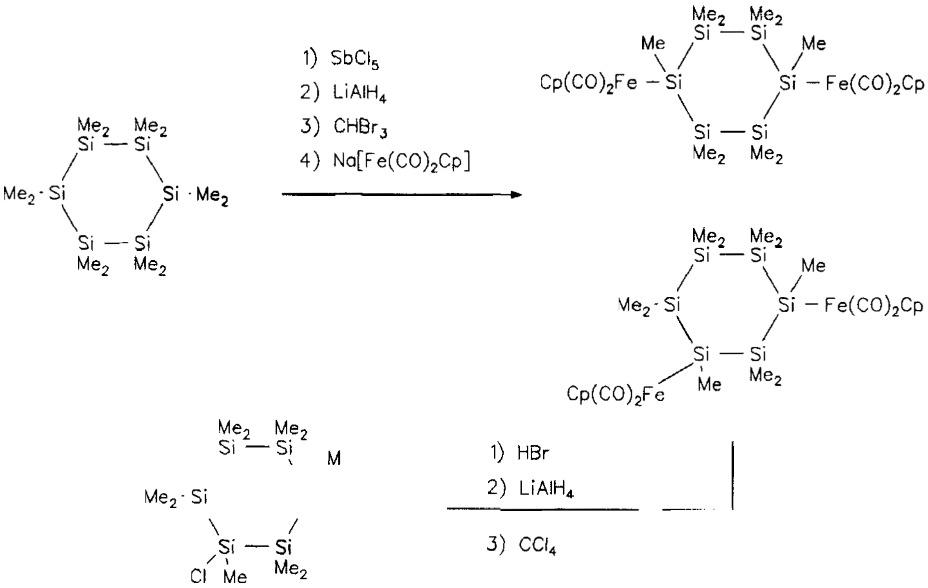
Di- and tri-functional derivatized cyclopolysilanes are useful starting materials for building oligocyclosilanes or cage-like oligosilane structures. 1,4-$Cl_2Si_6Me_{10}$ has been synthesized as the only isomer by reaction of $SbCl_5$ with Si_6Me_{12} [1,2] . Up to now it was presumed that there is a marked effect of the first chlorine on the position of substitution by the second [3].

We present thorough investigations leading to the conclusion that there is no directing effect upon oligochlorination of $ClSi_6Me_{11}$. The new compounds 1,3-$X_2Si_6Me_9$ (X = Cl, Br, H, $Fe(CO)_2Cp$) and 1,3,5-$Y_3Si_6Me_9$ (Y = F, Cl, Br, Ph) were isolated and characterized. In addition, the first examples of cyclohexasilanes bearing two different substituents except methyl were prepared.

All compounds were characterized by ^1H, ^{13}C, ^{31}P, ^{29}Si-NMR, C/H-analysis and IR-,MS-spectroscopy.

SYNTHESIS

For the synthesis and isolation of the 1,3-disubstituted decamethylcyclohexasilane derivatives the following reaction sequence was used:

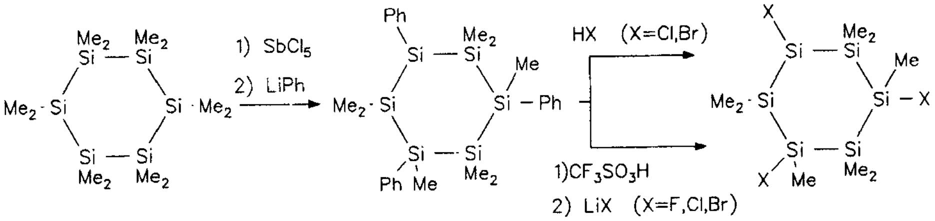


The isomers 1,3-$Cl_2Si_6Me_{10}$ and 1,4-$Cl_2Si_6Me_{10}$ cannot be separated by chromatography, sublimation or recrystallization. Therefore a mixture of 1,3-$Br_2Si_6Me_{10}$ and 1,4-$Br_2Si_6Me_{10}$ is derivatized with Na[Fe(CO)$_2$Cp]. The resulting two [Fe(CO)$_2$Cp]$_2$$Si_6Me_{10}$-derivatives can be separated by recrystallization from benzene. 1,3-[Fe(CO)$_2$Cp]$_2$$Si_6Me_{10}$ reacts with HBr to 1,3-$Br_2Si_6Me_{10}$. After preparing the 1,3-$H_2Si_6Me_{10}$ from 1,3-$Br_2Si_6Me_{10}$ with $LiAlH_4$, in the reaction with CCl_4 the 1,3-$Cl_2Si_6Me_{10}$ is formed. The structure of the cyclohexasilanes could be assigned by ^{29}Si-INEPT-INADEQUATE.

TABLE 1 ^{29}Si-NMR chemical shifts of 1,3-$X_2Si_6Me_{10}$ derivatives:

X	Si(1)	Si(2)	Si(3)	Si(4)
Cl	16.02	-36.99	-38.93	-44.53
	15.51	-37.52	-39.29	-42.43
Br	8.65	-37.64	-38.94	-43.73
	7.41	-38.27	-39.33	-42.02
H	-66.88	-40.31	-40.95	-41.36
	-67.73	-40.81	-41.81	-41.74
Fe(CO)$_2$Cp	-13.13	-17.16	-30.90	-39.12

The isolation of the 1,3,5-trisubstituted nonamethylcyclohexasilanes was achieved by following reaction sequence:



The separation of $Ph_2Si_6Me_{10}$ and $Ph_3Si_6Me_9$ easily is possible by Kugelrohr distillation.

X-ray structure of 1,3,5-$Ph_3Si_6Me_9$:

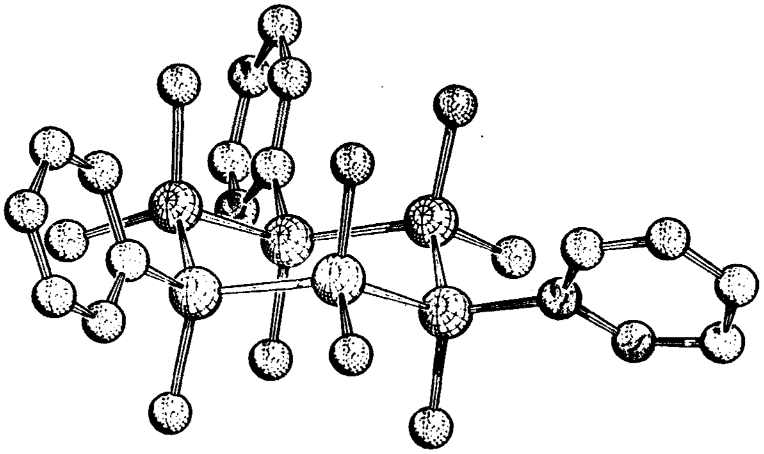
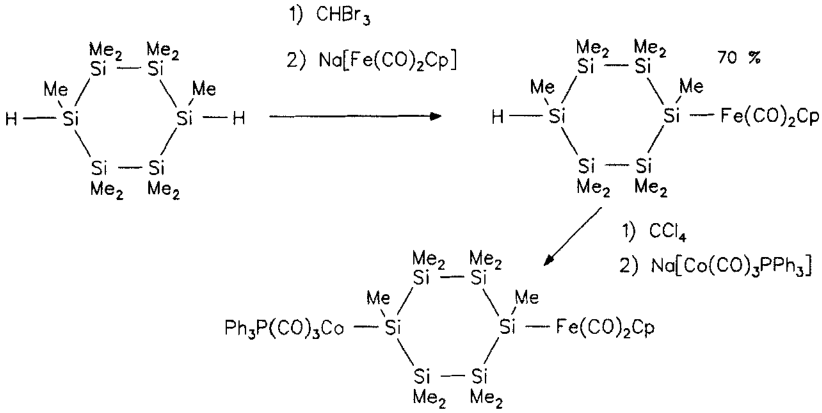


TABLE 2 ^{29}Si-NMR chemical shifts of 1,3,5-$X_3Si_6Me_9$ derivatives:

X	Si(1)	Si(2)
Cl	14.92 / 11.93	-37.13 / -37.45
Br	7.27 / 2.37	-37.41 / -38.99
Ph	-40.50	-40.57
F	43.38 m / 37.71 m	-45.8 m

$1,4\text{-}Cl_2Si_6Me_{10}$, the starting material for the disubstituted decamethylcyclohexasilanes with two different substituents in 1,4-position, was prepared via 1,2,2,3,3,4,5,5,6,6-decamethyl-7-thio-1,2,3,4,5,6-hexasilanorbornan. The following reaction pathway gives $1\text{-}[Fe(CO)_2Cp]\text{-}4\text{-}[Co(CO)_3PPh_3]Si_6Me_{10}$ in good yield:



Separation of $1,4\text{-}H_2Si_6Me_{10}$, $1\text{-}Br\text{-}4\text{-}HSi_6Me_{10}$ and $1,4\text{-}Br_2Si_6Me_{10}$ only can be achieved by preparative gas chromatography. Fortunately, $1,4\text{-}H_2Si_6Me_{10}$, $1\text{-}[Fe(CO)_2Cp]\text{-}4\text{-}HSi_6Me_{10}$ and $1,4\text{-}[Fe(CO)_2Cp]_2Si_6Me_{10}$ exhibit completely different solubilities in benzene or pentane and therefore easily can be separated by simple recrystallization.

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