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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

## Synthesis and NMR-Spectroscopic Studies of Substituted Cyclohexasilanes

Markus Eib<sup>a</sup>; Ulrike Katzenbeisser<sup>a</sup>; Edwin Hengge<sup>a</sup>

<sup>a</sup> Institut für Anorganische Chemie, TU-Graz, Austria

**To cite this Article** Eib, Markus , Katzenbeisser, Ulrike and Hengge, Edwin(1992) 'Synthesis and NMR-Spectroscopic Studies of Substituted Cyclohexasilanes', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 65: 1, 43 – 46

**To link to this Article:** DOI: 10.1080/10426509208055313

**URL:** <http://dx.doi.org/10.1080/10426509208055313>

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## SYNTHESIS AND NMR-SPECTROSCOPIC STUDIES OF SUBSTITUTED CYCLOHEXASILANES

Markus Eibl, Ulrike Katzenbeisser and Edwin Hengge  
Institut für Anorganische Chemie TU-Graz Austria

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  $Si_6Me_{12}$ <sup>1,2</sup>. Up to now it was presumed that there is a marked effect of the first chlorine on the position of substitution by the second<sup>3</sup>.

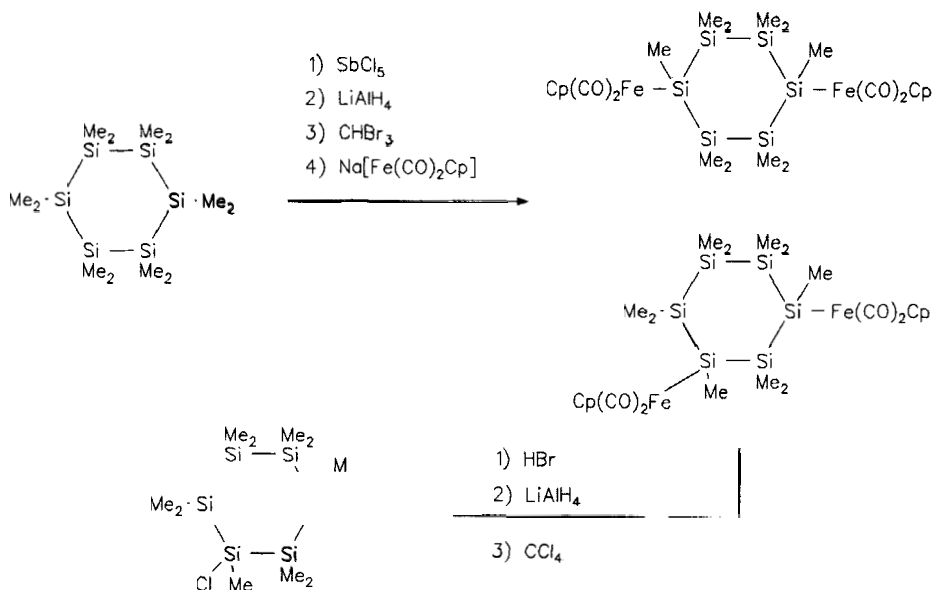
We present thorough investigations leading to the conclusion that there is no directing effect upon oligochlorination of  $ClSi_6Me_{11}$ . The new compounds 1,3- $X_2Si_6Me_9$  ( $X = Cl, Br, H, Fe(CO)_2Cp$ ) and 1,3,5- $Y_3Si_6Me_9$  ( $Y = F, Cl, Br, Ph$ ) were isolated and characterized. In addition,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

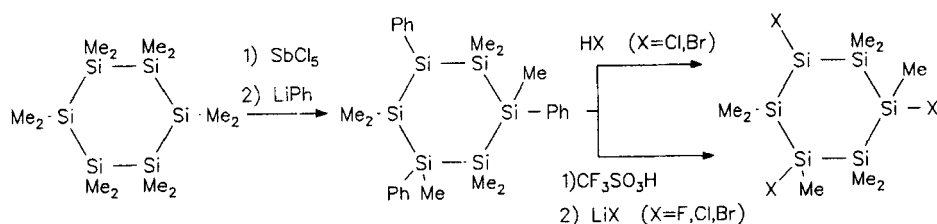


The isomers  $1,3\text{-Cl}_2\text{Si}_6\text{Me}_{10}$  and  $1,4\text{-Cl}_2\text{Si}_6\text{Me}_{10}$  cannot be separated by chromatography, sublimation or recrystallization. Therefore a mixture of  $1,3\text{-Br}_2\text{Si}_6\text{Me}_{10}$  and  $1,4\text{-Br}_2\text{Si}_6\text{Me}_{10}$  is derivatized with  $\text{Na}[\text{Fe}(\text{CO})_2\text{Cp}]$ . The resulting two  $[\text{Fe}(\text{CO})_2\text{Cp}]_2\text{Si}_6\text{Me}_{10}$ -derivatives can be separated by recrystallization from benzene.  $1,3\text{-}[\text{Fe}(\text{CO})_2\text{Cp}]_2\text{Si}_6\text{Me}_{10}$  reacts with  $\text{HBr}$  to  $1,3\text{-Br}_2\text{Si}_6\text{Me}_{10}$ . After preparing the  $1,3\text{-H}_2\text{Si}_6\text{Me}_{10}$  from  $1,3\text{-Br}_2\text{Si}_6\text{Me}_{10}$  with  $\text{LiAlH}_4$ , in the reaction with  $\text{CCl}_4$  the  $1,3\text{-Cl}_2\text{Si}_6\text{Me}_{10}$  is formed. The structure of the cyclohexasilanes could be assigned by  $^{29}\text{Si}$ -INEPT-INADEQUATE.

TABLE 1  $^{29}\text{Si}$ -NMR chemical shifts of  $1,3\text{-X}_2\text{Si}_6\text{Me}_{10}$  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
$\text{Fe}(\text{CO})_2\text{Cp}$	-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  $\text{Ph}_2\text{Si}_6\text{Me}_{10}$  and  $\text{Ph}_3\text{Si}_6\text{Me}_9$  easily is possible by Kugelrohr distillation.

X-ray structure of 1,3,5- $\text{Ph}_3\text{Si}_6\text{Me}_9$ :

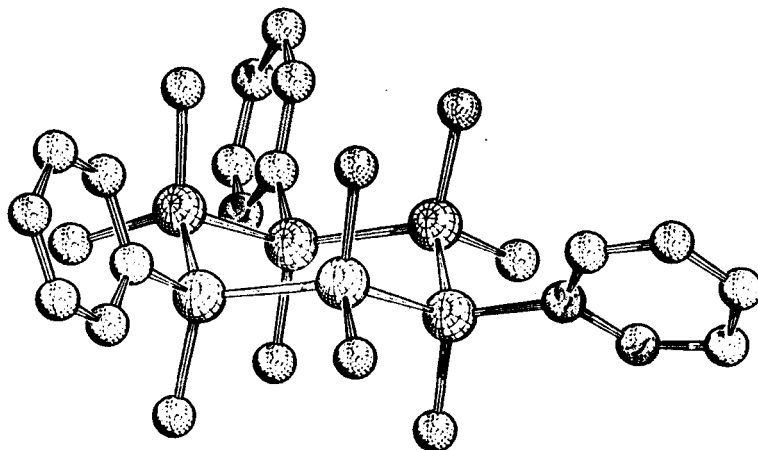
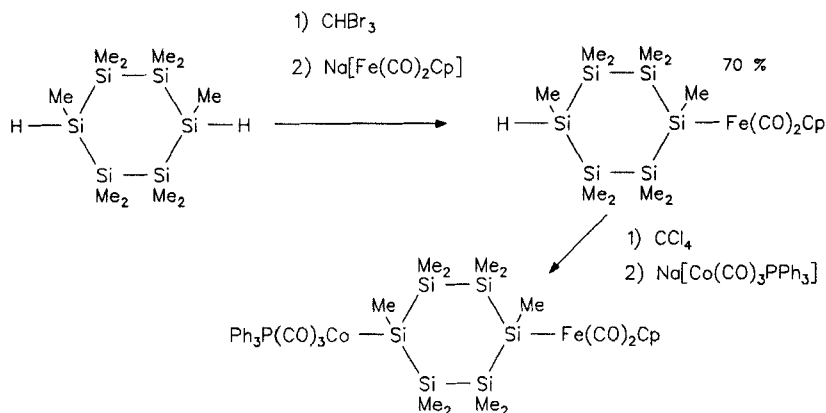


TABLE 2  $^{29}\text{Si}$ -NMR chemical shifts of 1,3,5- $\text{X}_3\text{Si}_6\text{Me}_9$  derivatives:

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-Cl<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub>, 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-[Fe(CO)<sub>2</sub>Cp]-4-[Co(CO)<sub>3</sub>PPh<sub>3</sub>]Si<sub>6</sub>Me<sub>10</sub> in good yield:



Separation of 1,4-H<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub>, 1-Br-4-HSi<sub>6</sub>Me<sub>10</sub> and 1,4-Br<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub> only can be achieved by preparative gas chromatography. Fortunately, 1,4-H<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub>, 1-[Fe(CO)<sub>2</sub>Cp]-4-HSi<sub>6</sub>Me<sub>10</sub> and 1,4-[Fe(CO)<sub>2</sub>Cp]<sub>2</sub>Si<sub>6</sub>Me<sub>10</sub> exhibit completely different solubilities in benzene or pentane and therefore easily can be separated by simple recrystallization.

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