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Oligosilylanions and their Reactions with Zirconocene and Hafnocene Dichlorides

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Summary. New group 4 metallocene oligosilyl compounds (RSi(SiMe$_3$)$_2$$MCp_2$Cl; $M = $ Zr, $R = $ H, Me, SiMe$_3$, SiMe$_2{}^t$Bu, SiMe$_2$CMe$_2$CHMe$_2$, SiMe$_2$Si(SiMe$_3$)$_3$; $M = $ Hf, $R = $ H, SiMe$_3$) have been synthesized by reaction of the respective oligosilyl potassium compounds with zirconocene or hafnocene dichloride.

Keywords. Oligsilylanions; Transition metal silicon complexes.

Oligosilylanionen und ihre Reaktionen mit Zirkonocen- und Hafnocendichlorid

Zusammenfassung. Eine Reihe neuer Übergangsmetall-Siliciumverbindungen der 4. Nebengruppe (RSi(SiMe$_3$)$_2$$M$(C$_5H_5$)$_2$Cl; ($M = $ Zr, $R = $ H, Me, SiMe$_3$, SiMe$_2{}^t$Bu, SiMe$_2$CMe$_2$CHMe$_2$, SiMe$_2$Si (SiMe$_3$)$_3$; $M = $ Hf, $R = $ H, SiMe$_3$) wurde durch Umsetzung der entsprechenden Oligosilylkalium-verbindungen mit Zirconocen- oder Hafnocendichlorid synthetisiert.

Introduction

The chemistry of transition metal silicon compounds [1, 2] has long been limited mainly to monosilyl ligands and the ubiquitous *tris*(trimethylsilyl)silyl group [3]. Based on our interest in the use of transition metal compounds for the functionalization and transformation of polysilanes we are currently exploring the possibilities to obtain transition metal compounds with other polysilyl ligands. Recently, we have reported the synthesis of tertiary, secondary, and primary polysilyl potassium compounds [4]. Herein we present a number of zirconocene and hafnocene complexes with various new oligosilyl ligands.

Results and Discussion

During our studies on polysilylanions we found that potassium *tert*-butoxide does not only react with *tetrakis*(trimethylsilyl)silane, but also with higher and differently substituted polysilanes in a clean and almost quantitative way (Scheme 1) [4].

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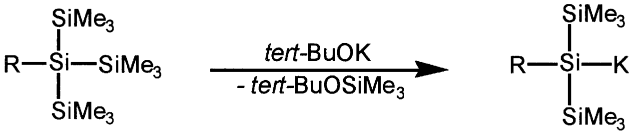
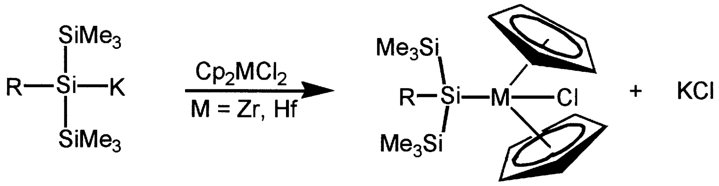


1 : R = H	**8**
2 : R = Me	**9**
3 : R = $SiMe_3$	**10**
4 : R = $SiMe_2{}^tBu$	**11**
5 : R = $SiMe_2CMe_2CHMe_2$	**12**
6 : R = $Si(SiMe_3)_3$	**13**
7 : R = $SiMe_2Si(SiMe_3)_3$	**14**

Scheme 1. Synthesis of polysilyl potassium compounds



8 : R = H	**15, 16** (M = Hf)
9 : R = Me	**17**
10 : R = $SiMe_3$	**18, 19** (M = Hf)
11 : R = $SiMe_2{}^tBu$	**20**
12 : R = $SiMe_2CMe_2CHMe_2$	**21**
14 : R = $SiMe_2Si(SiMe_3)_3$	**21**

Scheme 2. Synthesis of polysilyl group 4 metallocenes[a]; $M = Zr$ if not stated otherwise

With this set bulky polysilylanions at hand, we decided to investigate its use for the synthesis of silyl complexes of group 4 transition metals. Reactions of silyl potassium compounds were expected to proceed analogously to the reactions with silyl lithium compounds described by *Tilley et al.* some years ago [5, 6] (Scheme 2).

Unfortunately, hydrosilane **1** does not react with potassium *tert*-butoxide in a completely selective manner. The reaction mixture consists of the products **8** and **10**, the latter of which is probably formed by some sort of deprotonation reaction, in a 70:30 ratio. This mixture was used for the reaction with the metallocene chlorides. As a result, mixtures of **15** and **18** ($M = Zr$) as well as **16** and **19** ($M = Hf$) were obtained. Separation by means of recrystallization could not be achieved so far. A hafnocene with the same ligand has been synthesized recently by

Tilley et al. by means of metathesis reaction with 1,1,1,3,3,3-hexamethyltrisilane [7].

The secondary silyl potassium compound **9**, containing only two stabilizing trimethylsilyl groups attached to the silicon atom bearing the negative charge, is expected to be less stable and thus more reactive. Therefore, in contrast to all other silyl potassium compounds used in this study, **9** could not be used as an *in situ* generated solution in *THF*. In order to obtain a reasonably clean reaction with the metal chlorides, toluene had to be used instead of *THF*.

The synthetic problems encountered in the reactions with silyl anions **11**–**14** reflect the increasing steric influence of the polysilyl groups. Whereas clean reactions occur with the smaller anions **8** and **10** leading to products **15**, **16** and **18**, **19** [5] in high yields, compounds **20**–**22** are formed in slightly lower yields and are difficult to purify. Besides other side reactions, slow decomposition to the respective hydrosilanes occurs almost from the beginning of the reaction. A particularly sluggish reaction takes place between the metallocene chlorides and **13**, the sterically most demanding *pentakis*(trimethylsilyl)disilanyl potassium compound. Whereas some signals in the ^{29}Si NMR spectrum possibly can be attributed to the expected product, a definite statement on what is actually formed cannot be made at the present state of investigation.

Currently, we are studying the reactivity of compounds **15**–**22**. We are especially interested in the use of these compounds for the selective functionalization of polysilanes.

Experimental

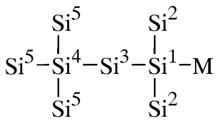
All reactions were carried out in flame-dried glassware under an inert atmosphere of dry argon or nitrogen. Solvents were distilled prior to use from either sodium or sodium potassium alloy. Starting materials **1**, **3**, **6**, and **7** were prepared as reported previously [4]. In a similar way, compounds **4** and **5** were obtained from the reaction of *tris*(trimethylsilyl)silyl potassium with the respective chlorosilanes. **2** was obtained by the reaction of *tris*(trimethylsilyl)silyl potassium with dimethylsulfate.

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded with a Bruker MSL 300 instrument at the indicated frequencies. ^{29}Si NMR spectra were measured in C_6D_6. In all cases the INEPT pulse sequence was employed [8].

General procedure for the synthesis of transition metal silyl complexes:

Starting material and one equivalent of potassium *tert*-butoxide were mixed in a flask and *THF* was added. Almost immediately the solution turned yellow and after some time sometimes orange. Complete formation of the silyl potassium compound was checked by derivatization with ethyl bromide and subsequent GC/MS analysis. The obtained solution was added dropwise over a period of 20 min to a stirred suspension of either Cp_2ZrCl_2 or Cp_2HfCl_2 in pentane at 0°C (in the case of **9**, *THF* was removed prior to addition and replaced by toluene). After complete addition, the reaction mixture was stirred at 0°C for another 60 min after which volatile compounds were removed *in vacuo*. Extraction with 10 ml of pentane, followed by filtration and crystallization on concentrating and cooling, gave the desired products as air sensitive red ($M = \mathrm{Zr}$) or yellow ($M = \mathrm{Hf}$) crystals in 60–80% yields. Yields and selected spectroscopical data (in ppm relative to *TMS* as external standard) are given in Table 1.

Table 1. Selected ^{29}Si NMR data of synthesized polysilyl group 4 metallocenes (δ in ppm, J in Hz)



$\mathrm{Si^5{-}\overset{Si^5}{\underset{Si^5}{Si^4}}{-}Si^3{-}\overset{Si^2}{\underset{Si^2}{Si^1}}{-}M}$

	Si^1	Si^2	Si^3	Si^4	Si^5	Yield (%)
15	-55.6, $J_{Si,H} = 129$	-7.9				80[a]
16	-49.6, $J_{Si,H} = 130$	-6.1				78[a]
17	-29.9	-7.9				68
18	-85.5	-6.1				85
19	-79.7	-5.3				78
20	-85.6	-7.1	10.4			60
21	-83.7	-6.9	13.8			72
22	-63.0,	-6.9	-17.8	-114.1	-9.0	79

[a] Yield calculation based on a 70% pure solution of starting material

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