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Undecamethylcyclohexasilane derivatives of group IV elements and manganese

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Summary – The early transition metal silyl complexes $(\eta^5\text{-}C_5H_5)_2M(Si_6Me_{11})Cl$ (M = Ti, Zr) were prepared from the dichlorides $(\eta^5\text{-}C_5H_5)_2MCl_2$ and KSi_6Me_{11}. The manganese-silyl complex $Si_6Me_{11}Mn(CO)_5$ was also synthesized from $(CO)_5MnBr$ and KSi_6Me_{11}. The zirconium derivative reacted with MeLi to give $(\eta^5\text{-}C_5H_5)_2Zr(Si_6Me_{11})Me$, O_2 to give the silylether $(Si_6Me_{11})_2O$ and with H_2O/CH_3OH to produce $Si_6Me_{11}H$ and $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$. The spectroscopic properties of these derivatives are reported.

cyclosilane / group IV elements / NMR

Introduction

In 1956 Piper and Wilkinson [1] synthesized $Me_3Si\text{-}Fe(CO)_2Cp$, the first compound containing a transition element-silicon σ-bond. Since this time different methods have been used to prepare a substantial number of compounds of this class. The major routes are : oxidative additions; reactions with bis(silyl)mercury compounds; reactions with acidic transition metal hydrides; and salt eliminations.

The selection of a suitable method depends mainly on the reagents used. In the case of the most frequently employed synthetic route, salt elimination, two general routes are possible. The most usual route uses the transition element component as the negative part (salts of transition metal carbonyl acids) and the silyl component as the positive part (silyl halides, triflates etc).

It has been shown in some cases that an "inverse" operation is more effective. The transition metal part contains the positive charge (*eg* carbonyl halides) and the negative charge is situated on the silicon component.

salt elimination

$$\rightarrow \text{Si-X} + \text{M}'[\text{TM}] \xrightarrow[-\text{M}'\text{X}]{} \rightarrow \text{Si-[TM]} \qquad (1)$$

"inverse" salt elimination

$$\rightarrow \text{Si-M}' + \text{X-[TM]} \xrightarrow[-\text{M}'\text{X}]{} \rightarrow \text{Si-[TM]} \qquad (2)$$

M′ = alkali metal; X = halogen, triflate; [TM] = transition metal complex

This last method, however, is limited by the availability of the silylalkali metal component. Only a few silylalkali metal compounds are known and stable enough for this reaction.

Recently, we have reported a new method for the synthesis of undecamethylcyclohexasilanyl potassium [2]. This compound was first synthesized many years ago in our group by the reaction of bis(undecamethylcyclohexasilane)mercury with sodium/potassium alloy. However, this method is dangerous and difficult.

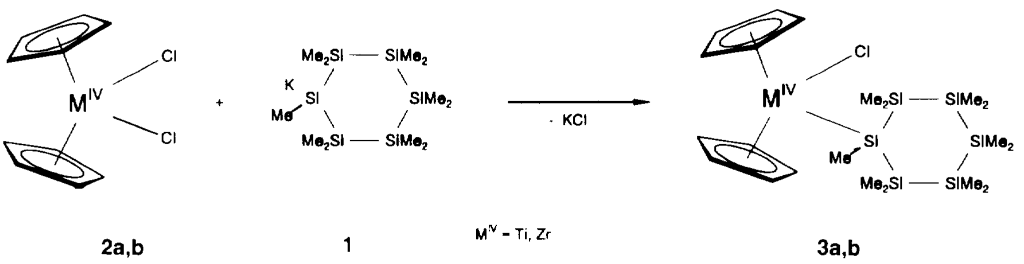
Our new synthesis starts with dodecamethylcyclohexasilane, prepared following the procedure of West [3]. Reaction with potassium *t*-butoxide leads to undecamethylcyclohexasilanylpotassium which is formed very easily in good yield without poisonous (mercury) and dangerous (Na/K alloy) reagents.

The availability of undecamethylcyclohexasilanylpotassium allows the synthesis of new transition element cyclosilanyl compounds. This is important, for example, for synthesizing transition metal-silicon compounds of group IV elements. With these elements only a few stable anions exist [4]. On the other hand, these compounds are possible catalysts for polymerization reactions, such as the polymerization of hydrosilanes to polysilanes [5]. Therefore, we are interested in the synthesis of this class of components.

Synthesis of group IV transition element cyclosilanyl compounds

Undecamethylcyclohexasilanyl potassium reacted with dicyclopentadienyl titanium or zirconium dichlorides **2a** or **2b** with a color change to dark green (Ti) or red (Zr), respectively. The ^{29}Si-NMR spectra showed the formation of a transition metal-silicon bond in both cases.

We have not been able to isolate the titanium compound **3a** in a pure form so far. It was always mixed with the by-product bis(undecamethylcyclohexasilanyl)



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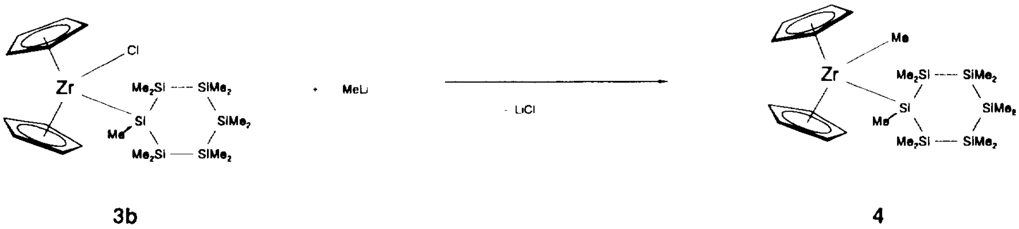

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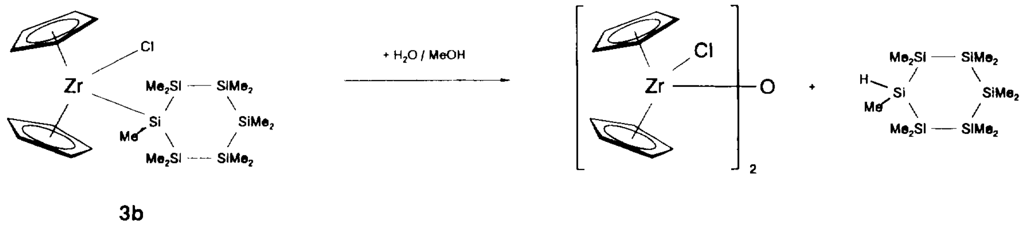

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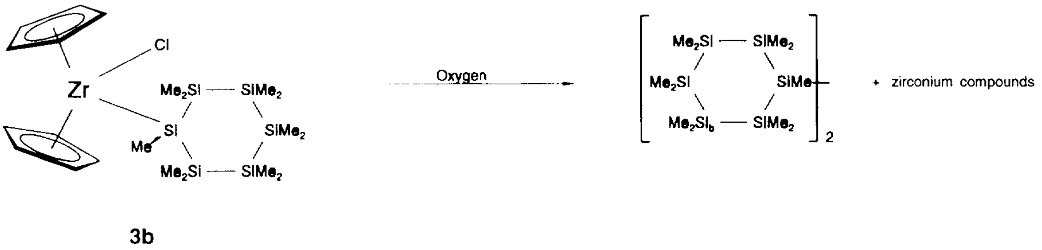

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and we have not yet found a method to separate these two compounds. In the case of zirconium, the isolation was possible because the side reaction to the bicyclic compound did not take place and the reaction yielded nearly quantitatively undecamethylcyclohexasilanyl(dicyclopentadienyl) zirconium chloride **3b**.

Compound **3b** is the first known example of an "early" transition metal cyclosilane. Compound **3b** is a red compound, which is extremely air sensitive but stable for a long time under a nitrogen or argon atmosphere. The general reactivity is similar to the other known Zr-Si compounds [6]. Reaction of **3b** with a second equivalent of **1** has not yet yielded the expected bis(undecamethylcyclohexasilanyl)dicyclopentadienyl zirconium. At low temperatures (−70 to −30°C) no reaction occurred; at higher temperatures decomposition to the zirconium-free Si-bicyclic compound and silicon-free zirconium compound took place. Similar results were observed in the reaction of **2b** with two equivalents of **1**.

Reaction of **3b** with methyllithium afforded the methylated complex undecamethylcyclohexasilanyl(dicyclopentadienyl) methyl zirconium **4**.

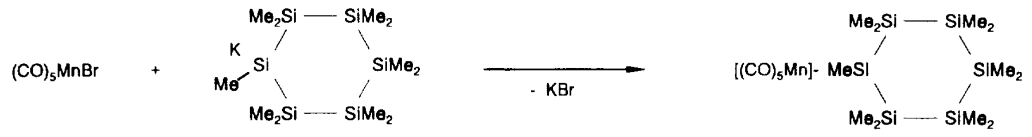
Compound **4** is a yellow crystalline solid with similar sensitivity to **3b**.

A methanol/water mixture hydrolyzed the silicon-zirconium bond of **3b**, forming undecamethylcyclohexasilane.

Oxidation without influence of water with oxygen or dry air resulted in the formation of bis(undecamethylcyclohexasilanyl)ether.

Thermolysis yielded bis(undecamethylcyclohexasilanyl) and unidentified zirconium compounds.

Similar results were achieved with late transition elements. It was not possible to synthesize a compound with a manganese-silicon bond by use of the normal salt



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elimination. Complicated transmetallation reactions were observed in the reaction of monochloroundecamethylcyclohexasilane and potassiumpentacarbonylmanganese. No compound with a silicon-manganese-bond was found. With undecamethylcyclohexasilanylpotassium **1** and $(CO)_5MnBr$, the formation of expected undecamethylcyclohexasilanylpentacarbonylmanganese **5** occurred.

The easy availability of the cyclosilanylalkalimetal compounds opens a wide field of syntheses for new cyclic silicon compounds with main group elements as well as transition metal elements.

Experimental section

General Data

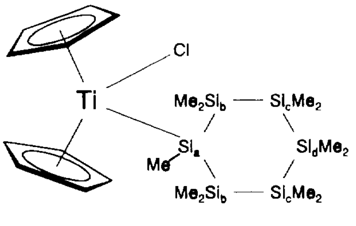
All manipulations involving air-sensitive materials were performed under nitrogen using standard Schlenk techniques. All solvents were dried with Na/K alloy under nitrogen and distilled prior to use. Titanocene dichloride (**2a**) [7], zirconocene dichloride (**2b**) [8] and undecamethylcyclohexasilanyl potassium (**1**) [2] were prepared according to published procedures.

All NMR spectra were recorded with a Bruker MSL 300 spectrometer (^1H, 300.13 MHz; ^{29}Si, 59.627 MHz; ^{13}C, 75.47 MHz). IR spectra were recorded with a Perkin-Elmer 883 IR spectrometer. Mass spectra were recorded with a Kratos profile spectrometer. C, H analyses were performed on a Heraeus-Mikro-K1 apparatus.

$Cp_2M^{IV}(Si_6Me_{11})Cl$

A two-necked flask was charged with $Cp_2M^{IV}Cl_2$ (5.82 mmol) and 20 mL diethyl ether.The stirred solution was cooled to −78°C and **1** (5,82 mmol) in 25 mL DME was added. The reaction mixture was allowed to warm to room temperature over 2 h with stirring.

Preparation of $(\eta^5\text{-}C_5H_5)_2Ti(Si_6Me_{11})Cl$ **3a**

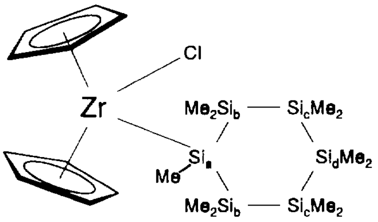


The starting materials were 1.45 g (5.82 mmol) **2a** and 2.17 g (5.82 mmol) **1**. The green solution was investigated by ^{29}Si NMR. Yield : $Cp_2TiCl(Si_6Me_{11})$ (30%). The other product is bis(undecamethylcyclohexasilanyl) [9] (60%).

^{29}Si NMR of $Cp_2TiCl(Si_6Me_{11})$ [ppm, D_2O external standard] : Si_a = −20.0; Si_b = −37.0; Si_c = −40,3; Si_d = −43,3.

Solvent exchange and recrystallization did not afford pure **3a**.

Preparation of $(\eta^5\text{-}C_5H_5)_2Zr(Si_6Me_{11})Cl$ **3b**



Starting materials were 1.70 g (5.82 mmol) **2b** and 2.17 g (5.82 mmol) **1**. The solution was evaporated to dryness and the residue was extracted with pentane (2 x 20 mL). The combined extracts were concentrated by removing 50% of the solvent by recondensation and cooled to −30°C. After 2 days red crystals were formed in 60% yield (2.07 g, 3.5 mmol). Purification by fractional crystallization in pentane.

mp = 188-190°C.

Anal found : C, 42.79 ; H 7.43. $C_{21}H_{43}ClSi_6Zr$ calc : C, 42.69 ; H, 7.34%.

IR (Nujol, CsBr, cm^{-1}) : 1 245 s, 1 145 w, 1 065 s, 1 018 m, 969 m, 825 m, 798 s, 767 m, 729 s, 685 m, 649 s, 454 m, 398 w, 353 m.

Mass spectrum (*m/e* (relative intensities)) : 590.1 (M^+, 9); 462.9 ($S_i6Me_{11}ZrCl$, 5); 334.1 (Si_6Me_{11}, 71); 73,0 ($SiMe_3$, 100).

^{29}Si NMR [ppm, C_6D_6] : Si_a = −22.3; Si_b = −31.5; Si_c = −39.7; Si_d = −42.7.

Si-Si coupling constants are given in Hz :

$^1J_{Si_a-Si_b}$ = 40; $^1J_{Si_b-Si_c}$ = 57; $^1J_{Si_c-Si_d}$ = 61; $^2J_{Si_a-Si_c}$ = 2.0; $^2J_{Si_b-Si_d}$ = 10.5.

^1H NMR [ppm, C_6D_6] : 5.89 (Cp/10H); 0.60 (CH_{3a}/3H); 0.47 (CH_3/12H); 0.31 (CH_3/12H); 0.30 (CH_{3d}/6H).

^{13}C NMR [ppm in C_6D_6] : 110.9 (2×C_5H_5); −0.64 (2×Me); −0.99 (1 × Me); −2.9 (2 × Me); −3.66 (2 × Me); −4.4 (1 × Me); −5.7 (2 × Me); −5.9 (1 × Me).

Preparation of $(\eta^5\text{-}C_5H_5)_2Zr(Si_6Me_{11})Me$ **4**

Compound **3b** (0.60 g (1.02 mmol) was dissolved in diethyl ether (15 mL) and cooled to −70°C. To this stirred solution was added 3.1 mL of 0.33 M MeLi. After 1 h the reaction mixture was allowed to warm to room temperature. During this period the color changed from red to yellow-orange. After another hour the solvent was removed by recondensation and the product extracted with pentane (20 mL). This solution was concentrated to 10 mL by recondensation. A yellow-orange crystalline product was isolated to give a yield of 80% (0.47 g, 0.82 mmol).

^{29}Si NMR [ppm, D_2O external standard] : $Si_a = -45.8$; $Si_b = -31.1$; $Si_c = -40.2$; $Si_d = -43.2$.

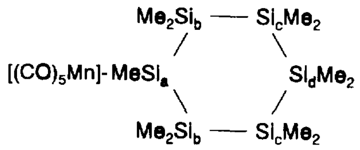
^{13}C NMR [ppm in C_6D_6] : 108.5 (2 × C_5H_5); 75.4 (Zr-Me); −0.45 (2 × Me); −2.13 (1 × Me); −2.22 (2 × Me); −3.52 (2×Me); −4.35 (1×Me); −5.21 (2×Me); −5.73 (1×Me).

^{1}H NMR [ppm in C_6D_6] : 5.81 (2 × C_5H_5/10H); 0.51 (Me/3H); 0.47 (Me/6H); 0.41 (Me/12H); 0.41(Me/12H).

Reaction of **3b** *with CH_3OH/H_2O*

Compound **3b** (1.00 g; 1.69 mmol) was added to a 1:1 mixture of 10 mL CH_3OH/H_2O at room temperature. The color of the solution changed from red to colorless within a few minutes. ^{29}Si NMR and ^{1}H NMR showed that the only products of the hydrolysis of **3b** are $Si_6Me_{11}H$ [1, 2] (0.57 g, 1.69 mmol) and $(Cp_2ZrCl)_2O$.

Pentacarbonylundecamethylcyclohexasilanylmanganese 5



$BrMn(CO)_5$ (1.04 g, 3.78 mmol) was dissolved in 30 mL of tetrahydrofuran (THF) and cooled to −60°C. Compound **1** (1.41 g, 3.78 mmol) in 50 mL diethyleneglycoldimethylether/THF (1:1) was slowly added over a period of 2 h. The reaction mixture was stirred 1 h at −60°C and was then allowed to warm to room temperature.

After evaporation of the solvent, the residue was extracted with 100 mL pentane. The solution was filtered and concentrated (20 mL). The mixture was cooled to −20°C. Filtration and recrystallization with 10 mL pentane gave 0.57 g (0.95 mmol) (25.0%) of $[Si_6Me_{11}Mn(CO)_5 \times THF]$.

^{29}Si NMR [ppm, D_2O external standard] : $Si_a = -21.5$; $Si_b = -28.9$; $Si_c = -39.8$; $Si_d = -43.3$.

IR (cm^{-1}) : υ_{CO} = 2 095, 2 015, 1 960.

MS (*m/e*) : 599 (M^+ + THF); 528 (M^+).

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