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Synthesis, Structural Characterization, and Transmetalation Reactions of a Tetranuclear Magnesium Silsesquioxane Complex

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The reaction of a silsesquioxane trisilanol with methylmagnesium chloride leads to an unprecedented tetranuclear magnesium silsesquioxane complex **1** in high yield. The crystal structure shows an unusually short Mg−Cl bond, indicative of an electron-deficient magnesium atom; **1** has been used as transmetalation agent for the synthesis of metal silsesquioxane complexes. Transmetalation activity was low, but can easily be followed by multinuclear NMR. Crystal data for **1**: $C_{78}H_{142}Cl_2Mg_4O_{26}Si_{14}\cdot 6(C_4H_8O)$, $a = 15.744(1)$ Å, $b = 26.526(2)$ Å, $c = 16.917(1)$ Å, $\beta = 113.229(2)°$, monoclinic, $P2_1/n$, , $Z = 2$.

Introduction

Over the past several years, silsesquioxane metal complexes[1] have been used to mimic silica surfaces[2−5] and silica-supported metal catalysts[6−8] and to synthesize new porous materials.[9] The key to success in all of the areas aforementioned is the development of efficient synthesis methodologies. Although the chemistry of silsesquioxane ligands and their complexes has seen a great evolution over the last years, it still may meet with complications.[10,11] As a result there is clearly a demand for suitable transmetalation reagents. Feher et al. found new transmetalation reagents based on thallium and antimony complexes, but these approaches involved the use of the synthetically not readily available pentamethylantimony[12] or toxic thallium compounds.[13,14] Aspinall et al. explored the use of silsesquioxane lithium complexes as transmetalating agents.[15] The use of magnesium as transmetalating ion has, however, not yet been explored in silsesquioxane chemistry, although being widely used in many areas of organometallic chemistry. In this paper we report the synthesis and structural characterization of a new tetranuclear magnesium silsesquioxane complex that can easily be synthesized by the protolysis of methylmagnesium chloride and an incompletely condensed silsesquioxane trisilanol. The magnesium silsesquioxane complex was demonstrated to be useful in transmetalation reactions.

Experimental Section

General Remarks. All operations involving air and moisture sensitive materials were performed in an inert atmosphere using standard Schlenk techniques and an argon-filled glovebox. Solvents were dried over Na/K alloy (THF) or 4 Å molecular sieves ($CDCl_3$) and were degassed before use. Methylmagnesium chloride (3.0 M solution in THF, Merck), $SiCl_4$ (99.8+%, Acros), and $Cr(acac)_3$ (97%, Jansen-Chimica) were used as purchased. The silsesquioxane silanols[16,17] as well as $(\eta^5\text{-}C_5H_5)TiCl_3$[18] and $O{=}ReCl_3(PPh_3)_2$[19] were prepared according to literature procedures. NMR spectra were recorded on VARIAN Mercury 400 and VARIAN Inova 500 spectrometers and referred to residual solvent resonances (^{1}H, ^{13}C) or $SiMe_4$ (^{29}Si). Transmission IR spectra were measured on a Nicolet AVATAR 360 FT-IR. The Organic Chemistry Department of the Eindhoven University carried out the elemental analyses.

Synthesis of $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2Mg_4Cl_2(THF)_2\}\cdot 4THF$ (1). Methylmagnesium chloride (7.20 mmol, 2.4 mL of a 3.0 M solution in THF) was added to a solution of the trisilanol silsesquioxane $(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ (2.10 g, 2.40 mmol) in THF (15 mL). Immediately after the addition of the Grignard reagent, a vigorous gas evolution took place. The resulting clear solution was stirred for 5 min and was subsequently left standing. After 2 h spectroscopically pure **1** (2.18 g, 1.05 mmol, 87%) had crystallized from the solution. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.05 (m, THF-α-CH_2, 24H), 1.95 (m, THF-β-CH_2, 24H), 1.9−1.3 (m, CH_2-C_5H_9, 112H), 1.1−0.7 (CH, C_5H_9, 14H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 69.07 (s, THF-α-CH_2) 28.04, 27.97, 27.78, 27.62, 27.56, 27.12, 27.03, 26.96, 26.89 (s, CH_2-C_5H_9), 25.42 (s, THF-β-CH_2),

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Table 1. Crystal Data and Details of the Structure Determination for **1**

formula	$C_{78}H_{142}Cl_2Mg_4O_{26}Si_{14}\cdot 6(C_4H_8O)$
fw, g·mol^{-1}	2489.93
space group	$P2_1/n$ (No. 14)
a, Å	15.744(1)
b, Å	26.526(2)
c, Å	16.917(1)
β, deg	113.229(2)
V, Å^3	6492.3(8)
Z	2
T, °C	−100
ρ_{calc}, g·cm^{-3}	1.274
λ(Mo Kα),	0.71073
μ, cm^{-1}	2.7
$R(F)^a$	0.0628
$R_w(F^2)^b$	0.1732

[a] $R(F) = \sum(||F_o| - |F_c||)/\sum|F_o|$ for 6327 reflections obeying $F_o \geq 4.0\sigma(F_o)$. [b] $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for 11045 reflections with $F_o^2 \geq 0$.

24.49, 24.13, 23.79, 22.53, 22.07 (s, *C*H−C_5H_9, ratio 1:2:1:2:1). ^{29}Si-{^{1}H} NMR (99.3 MHz, $CDCl_3$, 0.02 M Cr(acac)$_3$, δ): −63.83, −68.59, −70.01, −70.65, −75.52 (s, C_5H_9*Si*O_3, ratio 2:1:1:2:1). Anal. Calcd for $C_{78}H_{142}Cl_2Mg_4O_{26}Si_{14}\cdot 2(C_4H_8O)$: C, 45.54; H 6.96. Found: C, 42.90; H, 6.37 (possibly due to formation of silicon carbides, no satisfactory elemental analyses could be obtained).

Transmetalation Reactions. All transmetalations studied were performed in a similar fashion. About 30 mg of complex **1** and an equimolar amount of the other reactant were weighed out in a glovebox and dissolved in 1 mL of $CDCl_3$. This solution was transferred to an NMR tube, which was then sealed to prevent contact with air. Multinuclear NMR (^{1}H and ^{13}C) was used to follow the reaction. The reaction of (η^5-C_5H_5)$TiCl_3$ with **1** could be followed by the resonance of the cyclopentadienyl ligand. ^{1}H NMR (400 MHz, $CDCl_3$, δ): $t = 0$, 7.05 (s, η^5-C_5*H_5*$TiCl_3$); $t = 20$ min, 7.05 (s, η^5-C_5*H_5*$TiCl_3$), 6.92, 6.73, 6.58, 6.47, 6.44 (all s, intermediate products); $t = 16$ h, 7.05 (s, η^5-C_5*H_5*$TiCl_3$), 6.92, 6.86, 6.77, 6.75, 6.73, 6.66, 6.68, 6.60, 6.55, 6.47, 6.44 (all s, intermediate products); $t = 2$ days, 6.48 (s, η^5-C_5*H_5*TiO_3). Products of the reaction of **1** with $SiCl_4$ or O=$ReCl_3(PPh_3)_2$ were identical to those prepared in an alternative way, viz., via amine hydrochloride elimination.[20,21]

X-ray Diffraction: Crystal and Molecular Structure of 1. Diffraction data were collected on a Bruker SMART CCD area detector diffractometer. The structure was solved by direct methods using the program SHELXTL.[22] Hydrogen atoms were included in the final refinement riding on their carrier atoms. The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures. Crystal data and numerical details on data collection and refinement are given in Table 1.

Results and Discussion

The reaction of the silsesquioxane trisilanol (c-C_5H_9)$_7Si_7O_9$(OH)$_3$ with 3 equiv of methylmagnesium chloride in THF proceeds rapidly, with the vigorous release of methane gas, even when performed at −40 °C (Scheme 1, step i). Concentration of the solution and crystallization by subsequent heating and slow cooling yields large colorless cubelike crystals of **1**, as a moderately air and moisture stable compound.

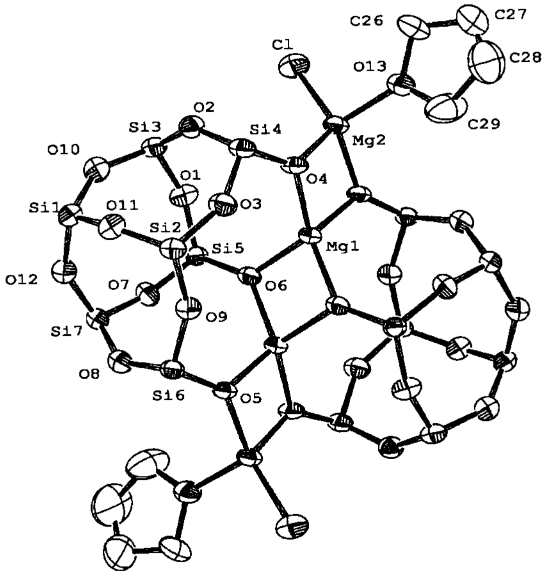
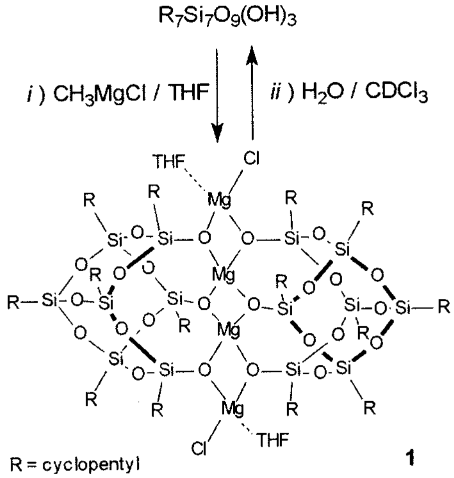


Figure 1. Structure of [(c-C_5H_9)$_7Si_7O_{12}$]$_2Mg_4Cl_2$(THF)$_2$ (**1**) in the crystal (ORTEP drawing with 50% probability ellipsoids). The cyclopentyl groups have been omitted for clarity.

Scheme 1. Synthesis of the Tetranuclear Silsesquioxane Magnesium Complex **1**



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Reaction of **1** with H_2O in an NMR tube yields the starting silsesquioxane trisilanol in quantitative yield, together with a white powder that was insoluble in the NMR solvent (Scheme 1, step ii). Dissolving **1** in a $CDCl_3$/pyridine-d_5 mixture results in THF−pyridine exchange, as indicated by the presence of free THF observed by ^{1}H NMR. Addition of acetone-d_6 to a $CDCl_3$ solution of **1** resulted in THF−acetone exchange. Complex **1** is very soluble in chloroform and dichloromethane while it is moderately soluble in THF, benzene, and toluene. Attempts to prepare complexes with other than two magnesium atoms per silsesquioxane ligand by Grignard addition all yield complex **1**.

Since an unambiguous assignment of the structure of the magnesium complex could not be established on the basis of the spectroscopic data alone, a single-crystal X-ray diffraction study was performed on **1**. Details of the data acquisition are given in Table 1. An ORTEP drawing of **1** is shown in Figure 1. Selected bond lengths and bond angles are given in Table 2. The monoclinic unit cell contains two units of the title compound and 12 THF solvent molecules, of which two are highly disordered.

The structure determination shows **1** to be an inversion symmetric, tetranuclear, tetracoordinated magnesium species, with two chemically different magnesium atoms. One magnesium atom (denoted as Mg1) is connected to two silsesquioxane

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

	Bond Lengths		
Mg2−Cl	2.255(2)[a]	Mg1−O5a	1.968(3)
Mg2−O13	1.989(4)	Mg1−O6	1.964(3)
Mg2−O4	1.962(3)	Si4−O4	1.614(3)
Mg2−O5a	1.945(3)	Si5−O6	1.600(3)
Mg1−O4	1.969(3)	Si6−O5	1.605(3)
	Bond Angles		
Cl−Mg2−O13	104.00(12)	Si4−O4−Mg2	132.01(19)
Cl−Mg2−O4	120.28(12)	Si4−O4−Mg1	128.92(19)
Mg2−O4−Mg1	93.37(13)	Si5−O6−Mg1	130.76(19)
Mg2−O5a−Mg1	93.96(13)	Si5−O6−Mg1a	135.65(19)
Mg1−O6−Mg1a	92.95(13)	Si6−O5−Mg1a	126.71(18)
O4−Mg2−O5a	86.16(13)	Si6−O5−Mg2a	137.66(19)
O4−Mg1−O5a	85.37(13)	O4−Mg1−O6	118.84(14)
O6−Mg1−O6a	87.05(13)	O5a−Mg1−O6a	117.26(13)

[a] Standard deviations in the last decimal place are given in parentheses.

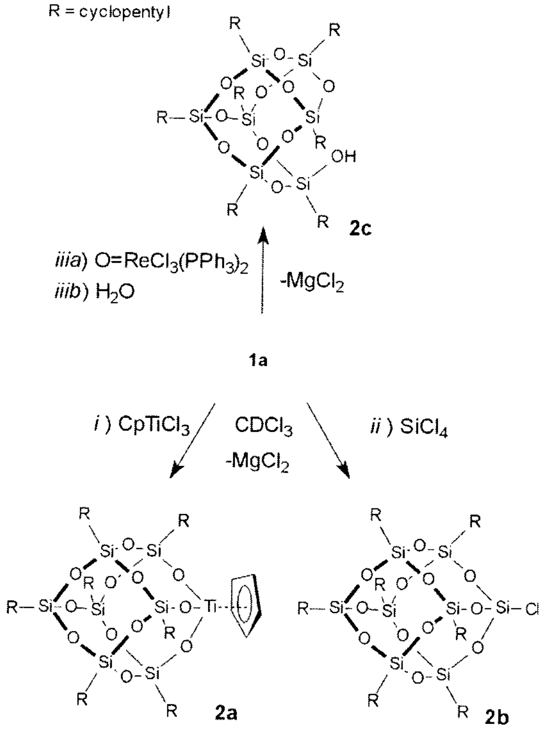
ligands via three crystallographically different oxygen atoms, of which one oxygen atom (O6) is μ_3-bonded to the magnesium atom and two oxygen atoms (O4, O5) are μ_3-bonded to both magnesium atoms. The magnesium atom (Mg2) is connected to one chloride and to two silsesquioxane ligands via two oxygen atoms. To complete the tetrahedral coordination sphere of Mg2, this Mg atom also has one THF molecule coordinated.

The four magnesium atoms are incorporated in an interlayer between the two trianionic silsesquioxide ligands. This interlayer consists of three almost planar four-membered metallaoxocycles, alternatingly perpendicular to each other, in which the four magnesium atoms are in a linear structure (the dihedral angle of Mg2a−Mg1a−Mg1−Mg2 is 180°). The two outer metallaoxocycles are virtually planar (the sum of all angles is 359°), and the oxygen atoms are bent slightly out of plane toward the coordinated THF molecule. The inner metallaoxocycle is perfectly planar (sum of all angles is 360.0°).

The tetrahedral coordination of the magnesium atoms is highly distorted with an average O−Mg−O angle of 86.2°. This was also found for other Mg(μ_3-O)$_2$Mg complexes with angles ranging from 79.1° in $\{(4\text{-}^i\text{PrPhO})(\text{Br})(\text{Et}_2\text{O})\text{Mg}(\mu_3\text{-OPh})\}_2$[23] to 95.1° in $\{(\text{Br})(\text{Et}_2\text{O})\text{Mg}(\mu_3$-O-(2,2-dimethylpent-3-en-3-olato))$\}_2$.[24] The Mg−O bond lengths (average 1.96 Å) are consistent with those compiled by Holloway and Melnik for tetracoordinated magnesium compounds (1.819−2.219 Å).[25] However, the magnesium−chloride bond is exceptionally short (2.255 Å) in comparison to other similar magnesium complexes, suggesting a highly electron-deficient magnesium atom.[26,27] The distance between Mg2 and O13 (O−THF) is in the normal range (1.989 Å), but reasonably short, which could also be explained by a relatively high electron deficiency on the magnesium atom.

The silsesquioxane magnesium complex **1** was subjected to transmetalation reactions, leading to various known silsesquioxane complexes. In 48 h the NMR tube reaction of **1** with (η^5-C_5H_5)$TiCl_3$ in $CDCl_3$ leads to the corned-capped cyclopentadienyl titanium silsesquioxane complex **2a** together with precipitation of $MgCl_2$ (Scheme 2, step i).[8,12] However, this reaction proceeds slowly compared to the conventional reaction conditions, viz., amine hydrochloride elimination.[5] Yet the low rate of the reaction offers the opportunity to follow it by NMR. Immediately after addition of (η^5-C_5H_5)$TiCl_3$, signals in the low-field resonances for Cp in the ^{1}H NMR are observed (δ 7.05 to δ 6.44 ppm). In time, other resonances appear while the original peaks decrease and eventually disappear. After 48 h, only resonances of the cyclopentadienyl titanium silsesquioxane are observed (i.e., one resonance at 6.48 ppm). This indicates that the transmetalation reaction proceeds via numerous intermediates, possibly being one-, two-, and three-bonded silsesquioxane titanium complexes and their $MgCl_2$ adducts.[28] The reaction of **1** with $SiCl_4$ in $CDCl_3$ (Scheme 2, reaction ii) also proceeded slowly, but led to the expected product **2b**[29] overnight. The absence of a characteristic ^{1}H NMR signal in the reacting moieties frustrates the observation of intermediate products and prohibits a clear assignment of the resonances, but it is likely that reaction ii proceeds in analogy via numerous intermediates.

Scheme 2. Transmetalation Reactions with Complex **1**



However, the NMR tube reaction of **1** with O=$ReCl_3(PPh_3)_2$ in $CDCl_3$ met with complications (Scheme 2, step iiia). In 1 day of reaction, a single product was observed by NMR. After careful hydrolysis (Scheme 2, step iiib), the cyclodehydration product **2c** was identified.[30] This behavior was observed in many experiments by Feher *et al.*[12,31] in which they tried to react silsesquioxane trisilanols and silsesquioxide tetramethyl antimony complexes with high valent metal halides such as MoO_2Cl_2 or WO_2Cl_2, and $POCl_3$.[5] It indicates that **1** has a transmetalation behavior similar to that of the tetramethyl antimony substituted silsesquioxane complexes, and is therefore useful only in a limited amount of reactions, not involving high valent metal species. In contrast to the tetramethyl antimony substituted silsesquioxane complexes, however, magnesium complex **1** is easily available. It also has some advantage against the

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tetramethyl antimony silsesquioxide complexes, i.e., the transmetalation byproduct $MgCl_2$ is almost completely insoluble in noncoordinating solvents, while Me_4SbCl is soluble in a variety of solvents, which could lead to equilibrium mixtures of transmetalated and nontransmetalated products. The absence of metal−carbon bonds in **1**, as opposed to tetramethyl antimony silsesquioxide complexes, also eliminates the chance of alkyl transfer, which could happen with late transition metals.

Conclusions

We have reported the synthesis and structural characterization of the novel silsesquioxane magnesium complex $\{[(c\text{-}C_5H_9)_7Si_7O_{12}]_2Mg_4Cl_2(THF)_2\}\cdot 4THF$, **1**. An X-ray diffraction study showed **1** to be a tetranuclear magnesium silsesquioxane dimer, with unusually short magnesium−chloride bonds, indicating a highly electron deficient magnesium atom. The magnesium complex was tested in transmetalation reactions and seemed to have a chemistry similar to that oftetramethyl antimony substituted silsesquioxane complexes. Transmetalation could be followed by multinuclear NMR.

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Supporting Information Available: One X-ray crystallography file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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