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Preparation and Characterization of a Bis(silsesquioxane)tungsten Complex

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By reaction of tungsten(VI) chloride with the trisilanolic silsesquioxane $(C_6H_{11})_7Si_7O_9(OH)_3$ (**1**), the bis(silsesquioxane)tungsten $[(C_6H_{11})_7Si_7O_9(O)_3]_2W$ (**3**) complex is formed. This is evidenced by proton and carbon NMR and X-ray diffraction. Compound **3** crystallizes in the orthorhombic space group *Cmca* with $a = 19.407(7)$ Å, $b = 25.163(6)$ Å, $c = 22.176(3)$ Å, $V = 10829(5)$ Å^3, and $Z = 4$. In addition, the analysis of silsesquioxanes by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), a technique initially developed for the characterization of biomolecules, has been successfully applied.

Introduction

In recent years, the interest in silsesquioxanes has grown tremendously. The incompletely condensed trisilanol **1** can react with a variety of compounds of the type R_nMCl_m (M being a main group element) or with transition metal complexes, to form completely condensed silsesquioxanes.[1−5]

Substituted silsesquioxanes can be used as models for silica surfaces,[6−7] Wittig reagents,[8] heterogeneous silica-supported transition-metal catalysts,[9−11] and many other applications.

We report here the synthesis and characterization of a new monomeric tungsten−silsesquioxane complex in which two ligands are attached to the transition metal.

Experimental Section

Tungsten(VI) chloride was used as purchased from ACROS Chemical Co. Toluene was dried and distilled over sodium wire in an inert atmosphere immediately before use.

Infrared spectra were recorded on a Mattson Research FTIR spectrometer using a resolution of 4 cm^{-1} in KBr. NMR spectra were recorded on a Bruker AM-500 for proton resonance (500 MHz) and a Bruker AM-360 for carbon NMR (90 MHz). Chemical shifts are reported in parts per million.

Table 1. Crystallographic Data for **3**

$C_{84}\,H_{154}\,O_{24}\,Si_{14}\,W$	fw = 2125.49
$a = 19.407(7)$ Å	space group = *Cmca*
$b = 25.163(6)$ Å	$T = 299(2)$ K
$c = 22.176(3)$ Å	$\lambda = 0.710\,93$ Å
$\alpha, \beta, \gamma = 90, 90, 90$ (deg)	$\rho_{calc} = 1.304$ Mg m^{-3}
$V = 10829(5)$ Å^3	$\mu = 1.29$ mm^{-1}
$Z = 4$	$R^a = 0.0916$
	$R_w{}^b = 0.2551$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w(F_o2 - F_c{}^2)^2)^{1/2}$, $w^{-1} = \sigma^2F^2 + (x(F_o{}^2 + 2F_c{}^2)/3)^2 + y(F_o{}^2 + 2F_c{}^2)/3$; $x = 0.1996$; $y = 0.0000$.

MALDI-TOF MS analyses were performed on a VG Tofspec SE, equipped with a nitrogen UV laser and time-lag focusing (Micromass, Wythenshaw, U.K.). The instrument was used in the linear and reflectron mode. In both configurations, 25 kV was applied to the source. When used, the reflectron voltage was set at 28.5 kV. The signals obtained from approximately 20 laser shots were averaged and processed using the software delivered with the instrument. External calibration of the mass spectrometer was performed by preliminary analysis of a mixture of peptides of known molecular weight.

Crystals suitable for an X-ray diffraction study were obtained by crystallization from toluene. Crystal data for **3** $\{[(C_6H_{11})_7Si_7O_9(O)_3]_2W$ (FW 2125.49)$\}$ are as follows: orthorhombic *Cmca*, $a = 19.407(7)$ Å, $b = 25.163(6)$ Å, $c = 22.176(3)$ Å, $V = 10829(5)$ Å^3, $D_{calc} = 1.304$ Mg/m^3 ($Z = 4$). A total of 5470 independent reflections with $1.61 \leq 2\theta \leq 25.98°$ were collected on a Nonius CAD4 device at 299(2) K with use of graphite-monochromated Mo Kα radiation. The structure was solved by direct methods. Full-matrix least-squares refinement of positional and thermal parameters led to convergence with a final *R* factor of 0.0916 with $|F_0| > 2.0\sigma(|F_0|)$. Crystallographic data for **3** are summarized in Table 1. All other details regarding the crystal structure are reported in the Supporting Information.

Molecular mechanics calculations were performed by using the PC SPARTAN Plus software (Wavefunction, Inc.).

Synthesis of Compound 1. Trisilanol **1** was prepared according to literature procedure developed by Feher et al.[7] The proton NMR spectrum is shown in Figure 1a.

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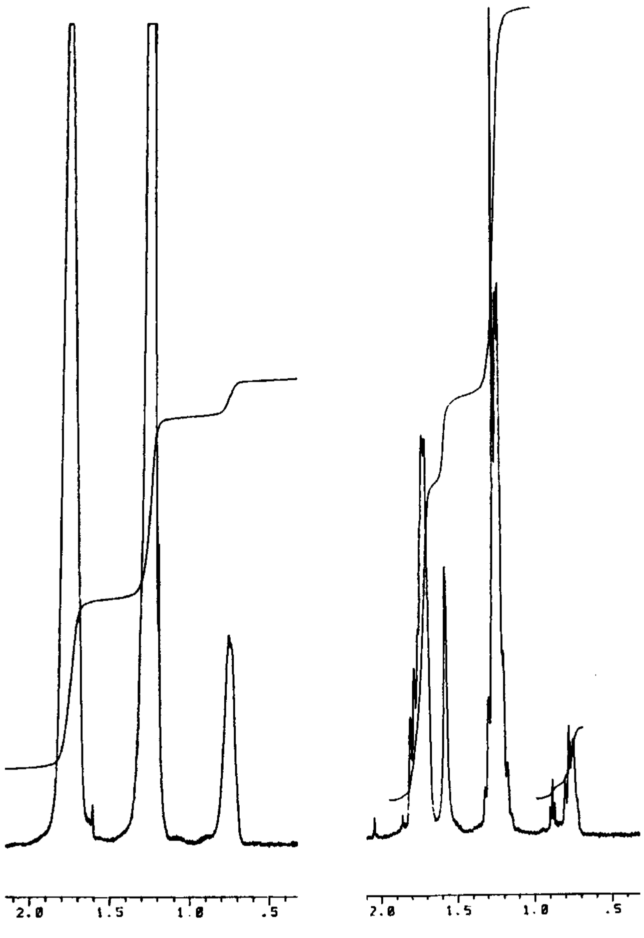

(a) (b)

Figure 1. ^1H NMR spectra of (a) compound **1** and (b) compound **3**. For **1**, the figure represents only a part of the spectrum as the OH resonance is omitted.

Synthesis of Compound 3. In a typical reaction, WCl_6 (0.64 g, 1.62 mmol) is dissolved in 10 mL toluene. To this is added a solution of silsesquioxane **1** (3.16 g, 1.62 mmol) in 30 mL of toluene over a period of 10 min. This mixture was allowed to reflux for about 10 h. After filtering and evaporation of the solvent an amorphous foam was obtained, which was crystallized from a concentrated toluene solution, resulting in the formation of colorless crystals.

The same procedure applies when using 2 equiv of the trisilanolic compound **1**. In both cases the same compound **3** is formed (yield 62%). No evidence for the presence of compound **2** (Scheme 1) is found. The ^1H spectrum is depicted in Figure 1b. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) data for **3**: δ 1.73 (vbr m, 28H), 1.57 (Br m, 7H), 1.23 (vbr m, 35H), 0.89 (t, 1H), 0.73 (vbr m, 6H). $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$, 25 °C) data for **3**: δ 27.83, 27.61, 27.03, 26.97, 26.92, 26.84, 26.74 (s, CH_2), 23.91, 23.30, 23.15 (s, 3:1:3, CH).

Results and Discussion

The reaction of $(C_6H_{11})_7Si_7O_9(OH)_3$ (**1**) with 1 and 2 equiv of tungsten(VI) chloride (Scheme 1) was followed by infrared spectroscopy. The spectrum of compound **1** shows an absorption band near 3201 cm^{-1}. This signal can be ascribed to OH stretching vibrations and should disappear upon complete reaction with WCl_6. After about 10 h reaction time, the OH absorption was no longer observed. The amorphous product, which was obtained after filtration and evaporation of the solvent from the crude product mixture, was crystallized from a concentrated toluene solution. Stable transparent colorless crystals have been obtained.

Table 2. Methine (ipso) Carbon NMR Data for Both the Starting Material **1** and the Tungsten Complex

	chemical shifts (ppm)		
	for **1**	for the complex	relative intensity
R_a	23.11	23.30	1
R_b	23.54	23.91	3
R_c	23.88	23.15	3

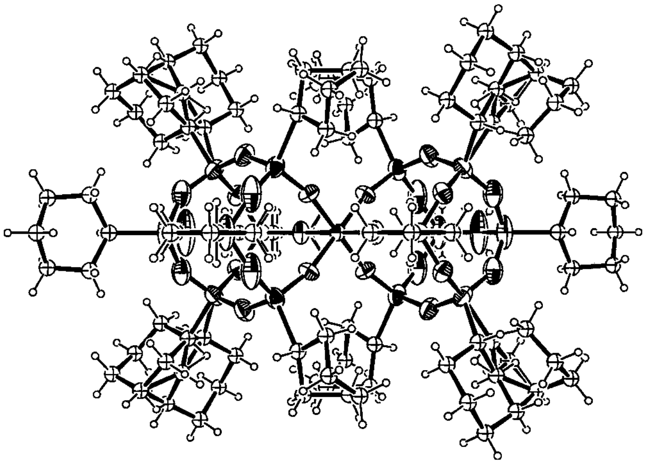

Figure 2. Perspective ORTEP plot of **3**. Cyclohexyl groups are also depicted.

The ^1H NMR spectrum of **1** shows three distinct signals originating from the cyclohexyl proton resonances[7] (Figure 1a). On complexation with WCl_6 a higher number of unresolved ^1H signals is observed (Figure 1b). This is probably due to the high steric hindrance around the tungsten center, which induces a deformation of the original chair conformation in the strained (see further) cyclohexyl groups.

In the ^{13}C NMR spectra of both the ligand **1**[7] and tungsten complex **3**, three signals are observed for the methine (C_1) carbons of the cyclohexyl groups in the expected 1:3:3 ratio. This indicates that the original C_{3v} symmetry of the framework is preserved after reaction with WCl_6. However the chemical shifts are interchanged (Table 2) on complexation. The C_1 of R_a (relative intensity 1) and R_b undergo a high-frequency shift while for the R_c groups a low frequency shift is observed. Probably the chemical shift of the R_c carbons, in the near neighborhood of the W−O bonds, are influenced by neighbor anisotropy effects (see Scheme 1 for designation of R_a, R_b, and R_c).

Recently the complexation of $Ti(OPr^i)_4$ with 1 and 2 equiv of silsesquioxane resulting in respectively a mono- and bis(silsesquioxane)titanium complex has been described by Crocker et al.[14]

To decide about the composition of the corresponding tungsten complex, MALDI-TOF mass spectrometry and X-ray diffraction analysis have been performed.

Although the silsesquioxane is insoluble in an acetonitrile/water/TFA mixture, we found that mixing a suspension with the matrix solution (50 mM α-cyano-4-hydroxycinnamic acid in ethanol/acetonitrile, 1:1) was effective in obtaining MALDI-TOF spectra of remarkably high quality.[15] The spectrum of the silsesquioxane ligand **1** yields a major peak with a

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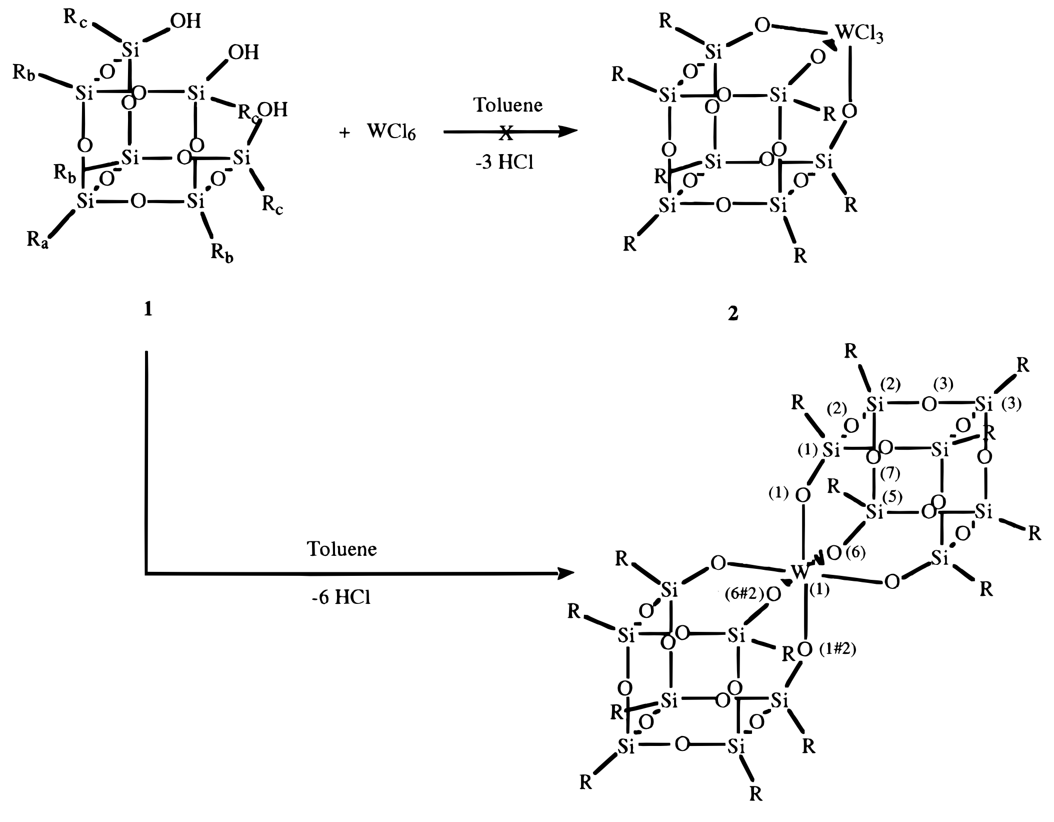
Scheme 1 . Synthetic Route to the Tungsten Bis(silsesquioxane) Complex **3**



1 **2** **3**

Table 3. Summary of Selected Bond Distances (Å) for **3**[a]

O(1)−W(1)	1.86(2)	C(2)−C(3)	1.47(3)
O(6)−W(1)	1.891(13)	C(2)−H(2A)	0.97
O(1)−Si(1)	1.64(2)	C(2)−H(2B)	0.97
O(6)−Si(5)	1.578(14)	C(3)−C(4)	1.46(3)
O(2)−Si(1)	1.62(2)	C(3)−H(3A)	0.97
O(7)−Si(5)	1.61(2)	C(3)−H(3B)	0.97
O(2)−Si(2)	1.57(2)	C(4)−C(5)	1.47(3)
O(7)−Si(2)	1.62(2)	C(4)−H(4A)	0.97
O(3)−Si(2)	1.55(2)	C(4)−H(4B)	0.97
O(3)−Si(3)	1.64(2)	C(5)−C(6)	1.48(3)
C(1)−Si(1)	1.87(3)	C(5)−H(5A)	0.97
C(13)−Si(3)	1.91(4)	C(5)−H(5B)	0.97
C(1)−C(6)	1.47(3)	C(6)−H(6A)	0.97
C(1)−C(2)	1.47(3)	C(6)−H(6B)	0.97
C(1)−H(1)	0.98		

[a] For numbering of the atoms, see Scheme 1, compound **3**. C(1) to C(6) are the carbon atoms of the cyclohexyl group attached to Si(1).

Table 4. Summary of Selected Bond Angles (deg) for **3**

Si(1)−O(1)−W(1)	161.9(12)	C(6)−C(1)−C(2)	121(2)
Si(2)−O(2)−Si(1)	152.1(11)	C(6)−C(1)−Si(1)	110(3)
Si(2)−O(3)−Si(3)	151.9(13)	C(2)−C(1)−Si(1)	129(3)
Si(5)−O(6)−W(1)	165.3(10)	C(6)−C(1)−H(1)	90.000(9)
Si(5)−O(7)−Si(2)	147.8(13)	C(2)−C(1)−H(1)	90.00(2)
O(2)−Si(1)−C(1)	111.9(8)	Si(1)−C(1)−H(1)	90.000(7)
O(1)−Si(1)−C(1)	107.6(13)	C(1)−C(2)−C(3)	120(2)
O(3)−Si(2)−O(2)	109.7(10)	C(4)−C(3)−C(2)	120(2)
O(3)−Si(2)−O(7)	108.3(10)	C(3)−C(4)−C(5)	121(2)
O(2)−Si(2)−O(7)	107.7(9)	C(3)−C(4)−H(4A)	107.2(10)
O(1)−W(1)−O(1)#2	180.000(2)	C(5)−C(4)−H(4A)	107.0(10)
O(1)−W(1)−O(6)	90.3(6)	C(3)−C(4)−H(4B)	107.2(10)
O(1)#2−W(1)−O(6)	89.7(6)	C(5)−C(4)−H(4B)	107.0(11)
O(6)#2−W(1)−O(6)	180.000(2)	H(4A)−C(4)−H(4B)	106.78(6)
		C(4)−C(5)−C(6)	120(2)
		C(1)−C(6)−C(5)	119(2)

monoisotopic mass of 995.0 Da, which is in good agreement with the calculated mass of the sodium derivate (995.4 Da). The spectra of the tungsten complex are more complex. In the linear TOF spectrum a major peak is observed at 2041.96 Da. This peak corresponds to structure **3**, minus one cyclohexyl group (2042.0 Da). It is currently uncertain what induces the loss of a single cyclohexyl group, but this phenomenon may be caused by in-source fragmentation. The molecular ion of **3** is found as a minor peak at 2125.6 Da (2125.2 Da). These findings are undoubtedly in favor of the bis(silsesquioxane)tungsten complex **3**.

Decisive proof for the presence of 2 silsesquioxane ligands on a single tungsten center is provided by a single-crystal X-ray diffraction study. The ORTEP plot of **3** is shown in Figure 2, and Tables 3 and 4 contain respectively selected bond distances and bond angles. The complex **3** crystallizes in the orthorhombic space group *Cmca* with W−O bond lengths of 1.891 and 1.86(2) Å. The coordination geometry around W is nearly octahedral, with O−W−O interbond angles of 89.6(9)−90.4(9)°. Interatomic Si−O distances and intrabond angles for atoms within the silsesquioxane framework are normal.[6,7,12,13] Also depicted in Figure 2 are the cyclohexyl groups, attached to the silicon atoms of the skeleton. Noteworthy is the high degree of deformation in some of these rings, especially those in the neighborhood of the tungsten center. The bond angles for the cyclohexyl ring on Si(1) are summarized in Table 4. Steric hindrance lies at the basis of these deformations as a result of the limited space which is available in the central periphery of the molecule. We also assume that this decrease of symmetry in the cyclohexyl groups leads to an increase in multiplicity in the PMR spectrum, as was already stated (see Figure 1b).

Also, molecular mechanics calculations have been carried out on structure **3** with a simplified framework (R=CH_3)—in order

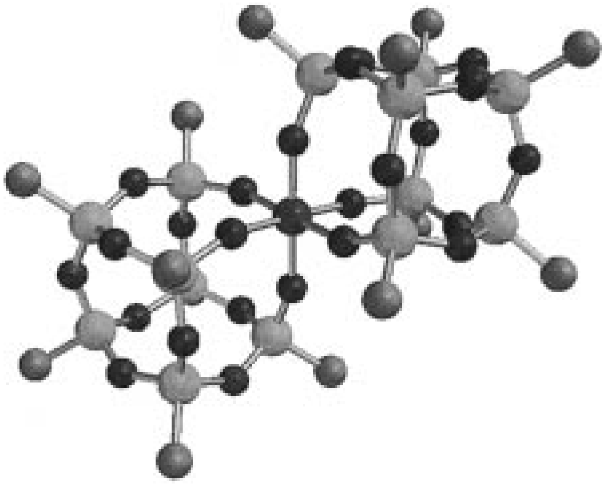


Figure 3. Calculated structure for **3** (R = CH_3; H atoms omitted for clarity).

to stay within the semiempirical limit—using a PM3 semiempirical molecular orbital model (Figure 3). After optimization, a slightly distorted octahedral geometry of the tungsten center is obtained, and selected bond angles and distances are collected in Table 5. These results are in excellent agreement with the values obtained from the X-ray crystal analysis. This is quite interesting, since it is now possible to obtain a reliable picture of the structure by an easily accessible calculation method.

Table 5. Selected Bond Distances and Angles of Structure **3** Obtained after Molecular Mechanics Calculations

O(1)−W(1)	1.92	Si(1)−O(1)−W(1)	157.4
O(6)−W(1)	1.92	Si(2)−O(2)−Si(1)	144.8
O(1)−Si(1)	1.67	Si(2)−O(3)−Si(3)	141.8
O(6)−Si(5)	1.67	Si(5)−O(6)−W(1)	157.4
O(2)−Si(1)	1.65	Si(5)−O(7)−Si(2)	140
O(7)−Si(5)	1.66	O(2)−Si(1)−C(1)	107.4
O(2)−Si(2)	1.66	O(1)−Si(1)−C(1)	109.9
O(7)−Si(2)	1.66	O(3)−Si(2)−O(2)	111.8
O(3)−Si(2)	1.66	O(3)−Si(2)−O(7)	111.3
O(3)−Si(3)	1.66	O(2)−Si(2)−O(7)	113.8
C(1)−Si(1)	1.91	O(1)−W(1)−O(1)#2	177.4
		O(1)−W(1)−O(6)	92.5
		O(1)#2−W(1)−O(6)	85.6
		O(6)#2−W(1)−O(6)	177.4

Conclusion

By a simple synthetic route, a new bis(silsesquioxane)tungsten complex **3** has been synthesized. Infrared spectroscopy and ^{1}H NMR have been used in order to follow the reaction course. ^{13}C NMR showed that the symmetry of the reaction product **3** was the same as for the starting material **1**, i.e., C_{3v}, indicating that three identical Si−O−W bridges were formed. Single-crystal X-ray analysis and MALDI-TOF mass spectrometry both provide full evidence for the formation of complex **3**. Finally, by means of molecular mechanics, a remarkably good picture of **3** was obtained, prior to any spectroscopic analysis.

Currently, the utility of matrixes other than α-cyano-4-hydroxycinnamic acid, their effects on the fragmentation of the silsesquioxane and methods for sample preparation are in progress. Also the activity toward oxidation reactions is under investigation.

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Supporting Information Available: X-ray crystal data for **3** including atomic coordinates, bond lengths, and bond angles (14 pages). Ordering information is given on any current masthead page.

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