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Journal of Organometallic Chemistry 584 (1999) 11–15

Journal of Organo metallic Chemistry

Octakis-(dimethylphosphanoethyl)-octasilsesquioxane–synthesis, characterization and reactivity

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Received 23 November 1998

Abstract

The addition of $HPMe_2$ to the vinyl-T_8 silsesquioxane quantitatively yields the novel octakis-(dimethylphosphanoethyl)-octasilsesquioxane (**1**) which can easily be converted into the thio-derivative $(Me_2P(S)CH_2CH_2)_8Si_8O_{12}$ (**2**) via mild oxidation with sulfur in CS_2. Reaction of **1** with transition metal complexes such as $W(CO)_5THF$, $CpMn(CO)_3$ or $Cp^*Rh(CO)_2$ offers an interesting synthetic access to supramolecular organometallic compounds. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Silsesquioxanes; Multidentate phosphane ligands; Transition metal complexes

1. Introduction

Fully condensed polyhedral silsesquioxanes $(RSiO_{1.5})_n$ ($n =$ even integer ≥ 6) are a highly interesting class of organosilicon compounds. Their unique polyhedral Si–O framework makes them an attractive model system to mimic the surface properties of silicas [1], alumosilicates [2] or SiO_2-supported heterogeneous catalysts [3]. Besides these applications, silsesquioxanes are highly used as molecular building blocks in material science, opening new synthetic pathways to ceramics or liquid crystalline supramolecular compounds [4].

Much attention has recently been paid to the synthesis of functional octasilsesquioxanes such as $(XCH_2CH_2CH_2)_8Si_8O_{12}$ (X = Cl, Br, I) which allow easy conversion into a variety of derivatives via nucleophilic substitution [5]. Our current studies on polyhedral silsesquioxanes aim at the preparation and use of phosphane-substituted octasilsesquioxanes of the general type $(R_2P(CH_2)_n)_8Si_8O_{12}$. Molecular compounds of this type are promising precursors to organometallic gels [6], branched dendritic macromolecules [7] as well as classical ligands in transition metal complex chemistry. Here we report on the preparation of the novel octasilsesquioxane $(Me_2PCH_2CH_2)_8Si_8O_{12}$ (**1**) and its reaction with sulfur and transition metal complexes.

The first experimental step is the formation of the known vinyl-T_8 $(CH_2{=}CH)_8Si_8O_{12}$ utilizing a modified hydrolytic polycondensation first published by Agaskar [8]. The $FeCl_3$-catalyzed reaction of vinyltrichlorosilane in a biphasic solvent system affords the cubic silsesquioxane product in the form of a white powder, easily soluble in pentane. The X-ray structure has been reported elsewhere [9]. Reaction of the octavinylsilsesquioxane with dimethylphosphane quantitatively leads to the octakis-(dimethylphosphanoethyl)-octasilsesquioxane (**1**) in the form of a white microcrystalline powder (Fig. 1).

Although the novel silsesquioxane **1** is extremely sensitive to oxygen, crystals suited for X-ray structural analysis can be obtained via recrystallization from pentane. The crystal data given in Tables 1 and 2 clearly indicate the presence of eight $CH_2CH_2PMe_2$ groups attached to an intact Si_8O_{12} core (Fig. 2).

In contrast to octasilsequioxane molecules reported in the literature [10], all Si–O bond lengths are in the rather narrow range of 1.594 ± 0.005 Å, suggesting that the distortion of the Si_8O_{12} cage which is generally observed for T_8-silsesquioxanes is negligible in this new phosphano-derivative. Nonetheless, the X-ray data of **1** also indicate crystal disorder in the $Me_2PCH_2CH_2$ groups attached to Si(4). However, the quantitative formation of **1** is doubtless from the NMR spectroscopic studies. Most importantly, the ^{31}P-NMR spec-

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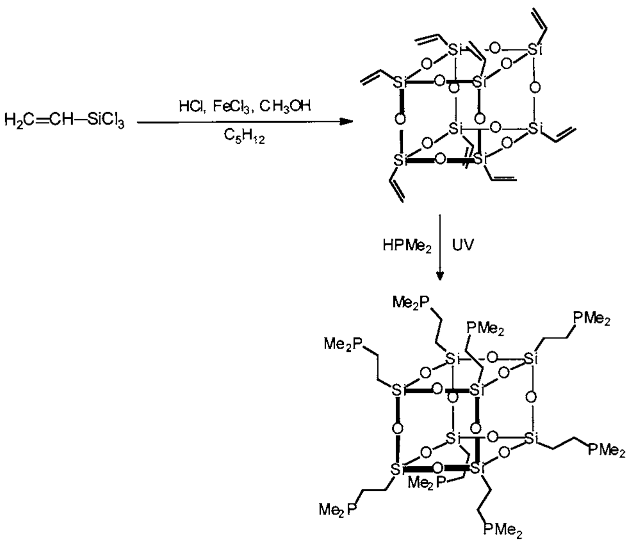
PII: S0022-328X(99)00079-0



(1)

Fig. 1.

trum exhibits a sharp single resonance at $\delta_P = -45.5$ ppm, very specific for the dimethylphosphano group [11]. The ^{13}C-NMR spectrum of the product shows characteristic resonances as well as typical coupling constants for the $Me_2PCH_2CH_2$ moiety ($\delta_C = 7.1$ ppm ($^1J_{PC} = 9.7$ Hz; $Me_2PCH_2\underline{C}H_2$), 13.5 ppm ($^2J_{PC} = 13.5$ Hz; $P(\underline{C}H_3)_2$); 24.1 ppm ($^1J_{PC} = 10.7$ Hz; $CH_2\underline{C}H_2PMe_2$)). Furthermore, the ^1H-NMR spectrum underlines the presence of eight equivalent $Me_2PCH_2CH_2$ groups with the Me_2P doublet resonance at $\delta_H = 1$ ppm and a coupling constant of 1.2 Hz.

Table 1
Crystal data and structure refinement for octakis-(dimethylphosphinoethyl)-octasilsesquioxane (**1**)

Empirical formula	$C_{32}H_{80}P_8Si_8O_{12}$
Formula weight (g mol^{-1})	1029.44
Temperature (K)	213(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	12.439(3)
b (Å)	12.269(3)
c (Å)	19.108(4)
α (°)	90
β (°)	96.97(3)
γ (°)	90
V (Å^3)	2894.6(10)
Z	2
$D_{calc.}$ (Mg m^{-3})	1.296
Absorption coefficient (mm^{-1})	0.454
$F(000)$	1200
Theta range for data collection (°)	5.44–26.00
Index ranges	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-23 \leq l \leq 23$
Reflections collected	22 463
Independent reflections	5595 [$R_{int} = 0.1188$]
Completeness to $\theta = 26.00°$ (%)	98.3
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5595/0/283
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0569$, $wR_2 = 0.1510$
R indices (all data)	$R_1 = 0.0708$, $wR_2 = 0.1659$
Largest difference peak and hole (e Å^{-3})	0.761 and -0.534

Table 2
Bond lengths (Å) and angles (°) for octakis-(dimethylphosphinoethyl)-octasilsesquioxane (**1**) [a]

Bond lengths			
Si(1)–O(5)	1.588(2)	Si(1)–O(4)	1.591(2)
Si(1)–O(1)	1.597(2)	Si(1)–C(11)	1.810(3)
Si(2)–O(1)	1.594(2)	Si(2)–O(2)	1.591(2)
Si(2)–O(6)	1.595(2)	Si(2)–C(21)	1.821(3)
Si(3)–O(2)	1.595(2)	Si(3)–O(3)	1.593(2)
Si(3)–O(5) # 1	1.595(2)	Si(3)–C(31)	1.814(3)
Si(4)–O(3)	1.598(2)	Si(4)–O(4)	1.595(2)
Si(4)–O(6) # 1	1.598(2)	Si(4)–C(412)	1.81(2)
Si(4)–C(411)	1.822(8)	Si(3) # 1–O(5)	1.595(2)
Si(4) # 1–O(6)	1.598(2)		
P(1)–C(12)	1.800(5)	P(41)–C(441)	1.828(11)
C(412)–C(422)	1.49(3)	P(42)–C(422)	1.87(2)
P(42)–C(432)	1.66(3)	P(42)–C(442)	1.79(5)
Bond angles			
O(5)–Si(1)–O(4)	108.47(14)	O(5)–Si(1)–O(1)	109.56(14)
O(4)–Si(1)–O(1)	109.12(13)	O(5)–Si(1)–C(11)	106.68(15)
O(4)–Si(1)–C(11)	113.37(16)	O(1)–Si(1)–C(11)	109.56(15)
Si(2)–O(1)–Si(1)	145.44(17)	O(2)–Si(2)–O(1)	109.70(13)
O(2)–Si(2)–O(6)	108.88(14)	O(1)–Si(2)–O(6)	109.31(13)
O(2)–Si(2)–C(21)	109.10(14)	O(1)–Si(2)–C(21)	109.03(15)
O(6)–Si(2)–C(21)	110.81(15)	Si(2)–O(2)–Si(3)	149.78(16)
O(3)–Si(3)–O(2)	109.25(13)	O(3)–Si(3)–O(5) # 1	108.98(13)
O(2)–Si(3)–O(5) # 1	108.71(13)	O(3)–Si(3)–C(31)	111.42(14)
O(2)–Si(3)–C(31)	109.79(15)	O(5) # 1–Si(3)–C(31)	108.64(15)
Si(3)–O(3)–Si(4)	145.73(15)	O(4)–Si(4)–O(6) # 1	109.68(14)
O(4)–Si(4)–O(3)	109.24(14)	O(6) # 1–Si(4)–O(3)	109.35(14)
O(4)–Si(4)–C(412)	108.5(8)	O(6) # 1–Si(4)–C(412)	104.3(8)
O(3)–Si(4)–C(412)	115.6(8)	O(4)–Si(4)–C(411)	109.8(3)
O(6) # 1–Si(4)–C(411)	111.2(3)	O(3)–Si(4)–C(411)	107.5(3)
Si(1)–O(4)–Si(4)	149.63(17)	Si(1)–O(5)–Si(3) # 1	152.37(17)
Si(2)–O(6)–Si(4) # 1	150.83(17)		

[a] Symmetry transformations used to generate equivalent atoms # 1: $-x+2$, $-y-1$, $-z+2$.

The UV-inserted addition of Me_2PH was also carried out with the corresponding allyl-T_8 obtained via hydrolytic polycondensation of $CH_2{=}CH{-}CH_2SiCl_3$ following the Agaskar method. In accordance with the vinyl-derivative, this novel octakis(dimethylphosphanopropyl)-octasilsesquioxane shows one single resonance in the ^{31}P-NMR spectrum ($\delta_P = -45.6$ ppm). Although the formation of the $(Me_2PCH_2CH_2CH_2)_8Si_8O_{12}$ is doubtless from the ^1H-, ^{13}C- and ^{29}Si-NMR data, crystals suited for X-ray analysis have not been obtained so far.

In order to obtain a more stable derivative of **1**, we synthesized the corresponding thiophosphano cage **2**

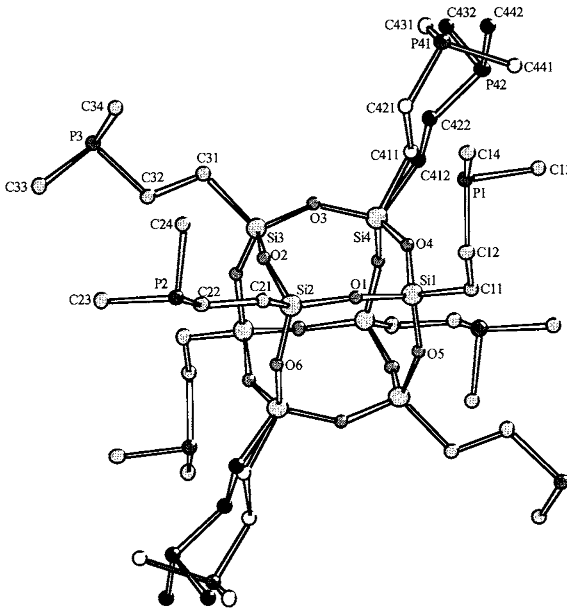


Fig. 2.

(Fig. 3). Reaction of **1** with an excess of sulfur in CS_2 proceeds rapidly and quantitatively yields a red microcrystalline precipitate. The complete oxidation of the Me_2P– to $Me_2P(S)$–groups is evident from the NMR data obtained for compound **2**: The $^{31}P\{^1H\}$-NMR spectrum exhibits a single resonance at $\delta_P = +40.9$ ppm, whereas the ^1H-NMR spectrum shows a doublet resonance at 1.7 ppm with a spin–spin coupling of 12.7 Hz, typical for compounds of the type $Me_2P(S)R$ [12]. Despite the fact that the thio-derivative **2** is significantly more stable towards oxidation, no crystals suitable for X-ray structural analysis could yet be obtained.

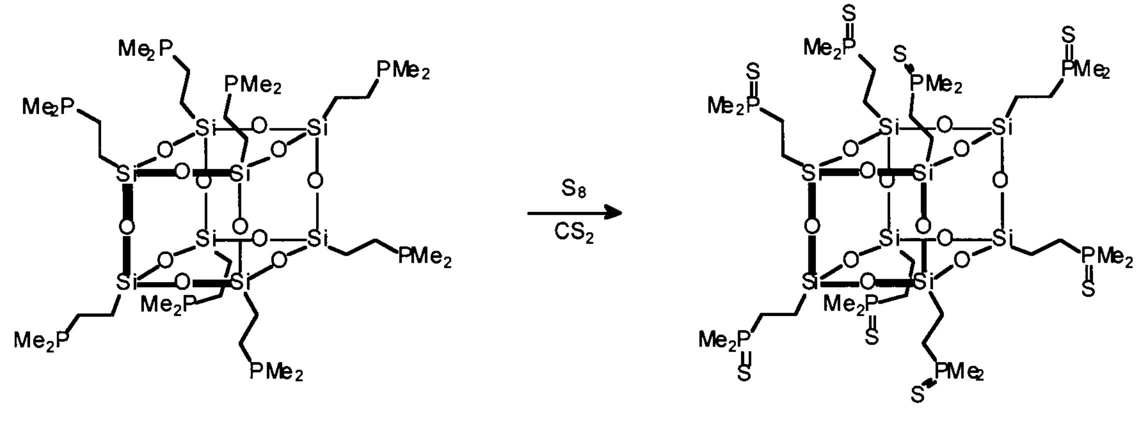
In order to study the ligand properties of the Me_2P groups in **1**, a series of reactions with different transition metal–carbonyl complexes was carried out (Fig. 4), leading to microcrystalline solids.

The exclusive formation of the octakis-[(L_mM)-dimethylphophanoethyl]-octasilsesquioxanes [$L_mM = (CO)_5W$ (**3a**), $Cp(CO)_2Mn$ (**3b**), $Cp(CO)Co$ (**3c**), $Cp^*(CO)Rh$ (**3d**)] **3a**–**3d** is doubtless from the NMR spectroscopic investigation. In the case of the tungsten-pentacarbonyl complex, the only detectable ^{31}P resonance at $\delta_P = -19.9$ ppm is accompanied by characteristic tungsten satellites with a coupling constant of $^1J_{WP} = 250$ Hz. The ^1H-NMR spectrum exhibits a resonance for the $P(CH_3)_2$ group at $\delta_H = 1.2$ ppm, the coupling $^2J_{PH}$ constant here is about 5.5 Hz. In the case of the ^{13}C-NMR ($\delta_C = 17.3$ ppm ($Me_2PCH_2\underline{C}H_2$), 25.6 ppm ($P(\underline{C}H_3)_2$); 29.7 ppm ($Me_2P\underline{C}H_2CH_2$)), the spin–spin coupling produces a very complex spectrum which will not be explained here in detail. The manganese compound **3b** similarly shows a single ^{31}P resonance at $\delta_P = +61.4$ ppm and the cobalt compound **3c** at $\delta_P = 37.7$ ppm whereas for the corresponding rhodium complex **3c** a typical doublet is observed ($\delta_P = 14.6$ ppm) showing a $^1J_{RhP}$ coupling of 192.3 Hz.

In addition to NMR spectroscopic studies, IR analysis was used to follow the progress of the reaction by monitoring the characteristic ν(C=O) vibrational modes. In the case of the silsesquioxane **3a**, three distinct absorption bands for the eight equivalent $W(CO)_5$ fragments were observable (local symmetry C_{4v}, vibrational modes $2\ A_1 + E$).

2. Conclusions

UV-activated addition of $HPMe_2$ to the C=C double bonds of the vinyl-T_8 and allyl-T_8 cages represents a smooth and powerful route for the synthetic preparation of phosphane-substituted octasilsesquioxanes. Due to the high reactivity of the Me_2P group, the mild oxidation with sulfur as well as the reactions with



(1)

(2)

Fig. 3.

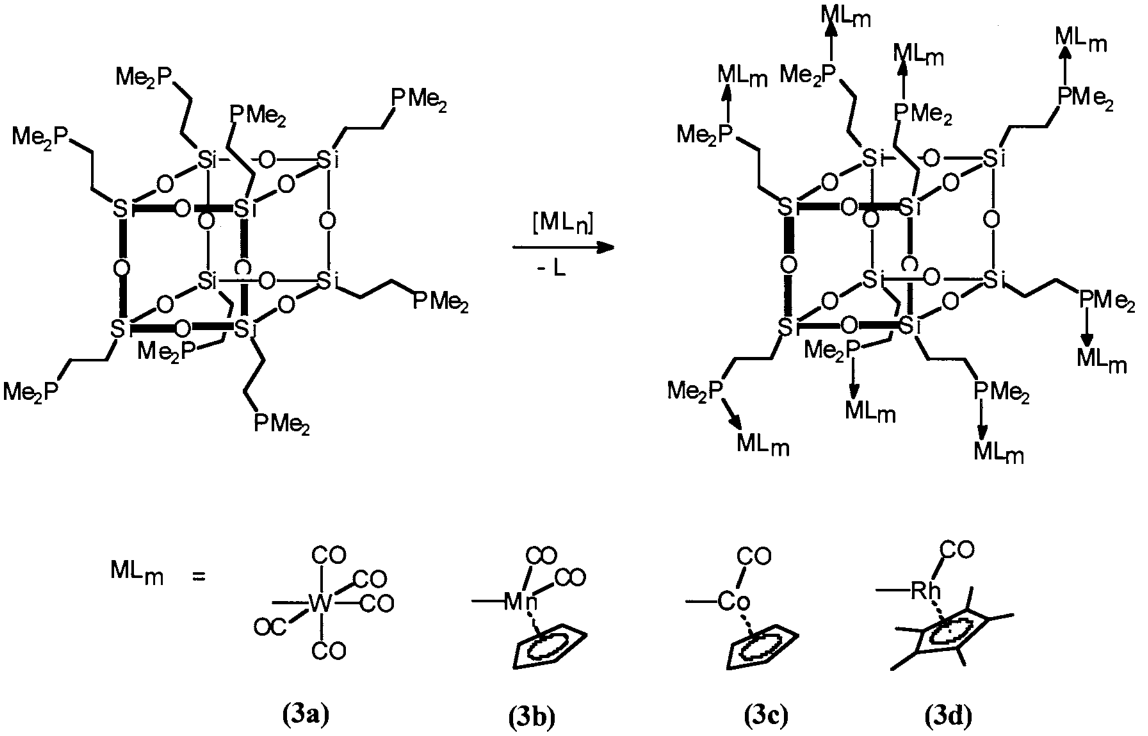


Fig. 4.

transition metal carbonyls such as $W(CO)_5THF$, $CpMn(CO)_3$, $CpCo(CO)_2$ and $Cp^*Rh(CO)_2$ quantitatively lead to new functional silsesquioxanes of high practical interest. Particularly in this respect, their application in organometallic gels as catalysts is quite promising. Future work in this area, therefore, has to address the introduction of other phosphanes R_2PH, the reaction with other transition metal fragments as well as investigation of the catalytic activity of these novel octasilsesquioxanes.

3. Experimental

All reactions were performed under dry argon using standard Schlenk techniques. Solvents were freshly distilled under argon from the usual drying agents prior to use. ^1H-, ^{13}C- and ^{31}P- chemical shifts are recorded in $CDCl_3$.

3.1. Synthesis of *1*

A 633.8 mg (1 mmol) mass of $(CH{=}CH_2)_8Si_8O_{12}$ was dissolved in pentane (50 ml) and 0.56 g (9 mmol) of Me_2PH was condensed into the flask. The educts were irradiated by a UV-lamp for 3 days. Pentane and unreacted Me_2PH were removed in vacuo. The final product **1** was obtained as a white powder (1.13 g; 100%). NMR: $\delta_H = 0.6–0.9$ ppm (m, br, 2H, $Me_2PCH_2C\underline{H}_2$), 1.0 ppm (d, $^2J_{PH} = 1.2$ Hz, 6H, $P(C\underline{H}_3)_2$), 1.2–1.4 ppm (m, br., 2H, $Me_2PC\underline{H}_2CH_2$), $\delta_C = 7.1$ ppm ($^2J_{PC} = 9.7$ Hz; $Me_2PCH_2\underline{C}H_2$), 13.5 ppm ($^1J_{PC} = 13.5$ Hz; $P(\underline{C}H_3)_2$); 24.1 ppm ($^1J_{PC} = 10.7$ Hz; $Me_2P\underline{C}H_2CH_2$); $\delta_P = -45.5$ ppm.

3.2. Synthesis of *2*

Solid **1** (300 mg; 0.26 mmol) was added whilst stirring to a solution of sulfur (67 mg; 2.1 mmol) in 20 ml CS_2. An immediate color change from white to pale-red was observed and the solution was stirred for a further 5 min. The silsesquioxane **2** was obtained as a pale-red powder (360 mg, 100%). NMR: $\delta_H = 1.7$ ppm (d, $^2J_{PH} = 12.7$ Hz; $P(C\underline{H}_3)_2$), $\delta_C = 3.7$ ppm ($Me_2PCH_2\underline{C}H_2$), 20.0 ppm ($^1J_{PC} = 54$ Hz; $P(\underline{C}H_3)_2$); 28.3 ppm ($^1J_{PC} = 55$ Hz; $Me_2P\underline{C}H_2CH_2$); $\delta_P = 40.9$ ppm.

3.3. Synthesis of *3a*

Solid **1** (255 mg, 0.23 mmol) was dissolved in pentane and then added to a solution of 705 mg (1.8 mmol) $W(CO)_5THF$ in THF using an oxygen-free Schlenk line. The tungsten–THF complex was generated from the tungsten hexacarbonyl $W(CO)_6$ and THF in a falling film photo reactor. The reagents were irradiated by a UV-lamp for two days before the unreacted educts were removed. The crude product (**3**) was obtained as a white to pale yellow microcrystalline material, soluble in $CDCl_3$. NMR: 1.2 ppm ($^2J_{PH} = 5.5$ Hz; $P(C\underline{H}_3)_2$);

$\delta_P = -19.9$ ppm ($^1J_{WP} = 250$ Hz); $\delta_C = 17.3$ ppm ($Me_2PCH_2\underline{C}H_2$), 25.6 ppm ($P(\underline{C}H_3)_2$); 29.7 ppm ($Me_2P\underline{C}H_2CH_2$).

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