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Octakis(tetracarbonylcobaltio)octasilsesquioxane: Synthesis, Structure, and Reactivity

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Summary: The reaction of octacarbonyldicobalt with octahydridosilsesquioxane (4:1 stoichiometry) in hexane leads to octakis(tetracarbonylcobaltio)octasilsesquioxane ***(1)****, the first octasilsesquioxane in which eight metals are directly bound to the silicon atoms of the siloxane cage. The product has been characterized by* ^{29}*Si CP-MAS NMR, IR, and Raman spectroscopy as well as elemental analysis and MALDI TOF spectrometry. The molecular structure of* ***1*** *has been determined by single-crystal X-ray diffraction. In combination with triphenylphosphine,* ***1*** *shows catalytic activity in the hydroformylation of 1-hexene.*

Introduction

Eightfold organo-functionalized octasilsesquioxanes have attained much interest as precursors for the preparation of highly siliceous materials or organolithic macromolecular compounds.[1] They are useful core molecules in dendrimer chemistry[2] and alternative precursors for the generation of low-dielectric-constant materials[3] as well as dry resists[4] in microelectronics.

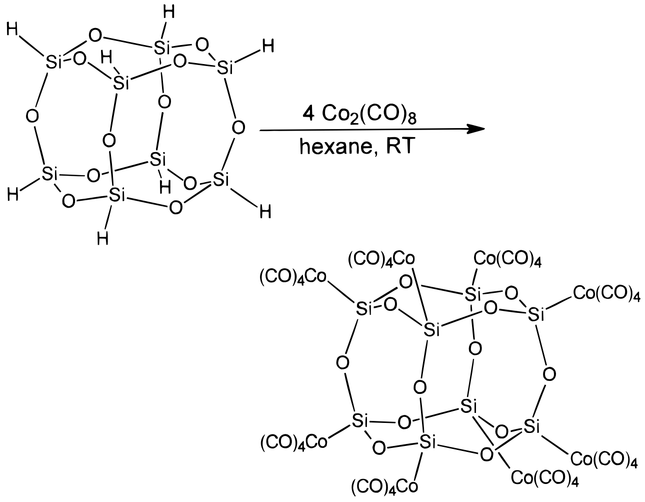
Calzaferri et al. prepared the first monosubstituted octasilsesquioxane with a silicon−cobalt bond.[5] The reaction of $H_8Si_8O_{12}$ and $Co_2(CO)_8$ in a 1:0.5 molar ratio led to the formation of $[Co(CO)_4]H_7Si_8O_{12}$ in 10% yield. Harrison and Kannengiesser claimed the isolation of the disubstituted octasilsesquioxane $[Co(CO)_4]_2H_6Si_8O_{12}$, using the same reaction procedure with a 1:1 molar ratio of $H_8Si_8O_{12}$ and $Co_2(CO)_8$.[6] Whereas $[Co(CO)_4]H_7Si_8O_{12}$ was characterized by single-crystal X-ray diffraction, the disubstituted species was characterized by its ^{1}H NMR and mass spectra.

We report here the isolation of octakis(tetracarbonylcobaltio)octasilsesquioxane and describe its crystal structure. Furthermore, we present the first results of an investigation of the catalytic activity of this compound in hydroformylation reactions.

Results and Discussion

Synthesis. When a hexane solution of octahydridosilsesquioxane and octacarbonyldicobalt in a 1:4 molar ratio is allowed to stand at ambient temperature, highly refractive millimeter-sized colorless crystals of **1** are formed on the wall of the reaction flask (Scheme 1). The formation of **1** is complete within 48 h and was monitored through the evolution of hydrogen. The product was isolated in an analytically pure form and characterized by X-ray structure analysis, elemental analysis, IR, Raman, ^{29}Si CP-MAS NMR spectroscopy, and MALDI TOF (matrix-assisted laser desorption ionization time of flight) spectrometry.

Scheme 1



Structure. Compound **1** crystallizes in the cubic space group $P2_1/3$. The molecular structure of **1** in the solid state with the atom-labeling scheme is shown in Figure 1. Selected structural parameters are listed in Table 1.

The molecule contains a cubic Si_8O_{12} framework with a $Co(CO)_4$ substituent bound to each of the silicon atoms. The silicon atoms are approximately tetrahedrally surrounded by three oxygen atoms of the Si−O framework and the cobalt atom of the $Co(CO)_4$ substituent.

1 shows a remarkable stretching of the Si−O framework along its C_3 symmetry axis which results in an arrangement of overall C_3 symmetry. This is shown by the increased Si(6)···Si(8) nonbonding distance (5.469(2) Å) in comparison to the values of the other body diagonals (Si(5)···Si(7) = 5.431(5) Å). The same tendency is observed for the respective O···O and Si···Si (Si_8-cube edges) nonbonding distances presented in Table 1.

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(1) Harrison, P. G. *J. Organomet. Chem.* **1997**, *542*, 141.
(2) Bassindale, A. R.; Gentle, T. E. *J. Mater. Chem.* **1993**, *3*, 1319.
(3) Hacker, N. P. *MRS Bull.* **1997**, *22*, 33.
(4) Schmidt, A.; Babin, S.; Böhmer, K.; Koops, H. W. P. *Microelectron. Eng.* **1997**, *35*, 129.
(5) Calzaferri, G.; Imhof, R.; Törnroos, K. W. *J. Chem. Soc., Dalton Trans.* **1993**, 3741.
(6) Harrison, P. G.; Kannengiesser, R. *J. Chem. Soc., Chem. Commun.* **1996**, 2065.

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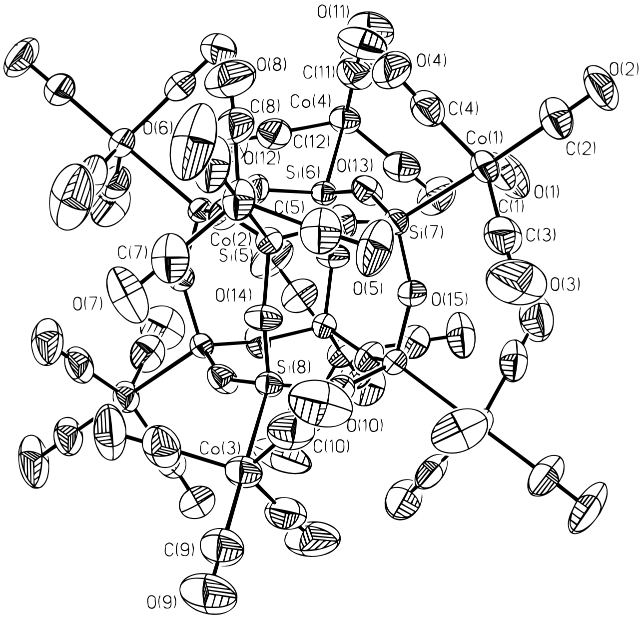

Figure 1. Molecular structure of **1**.

Table 1. Selected Bond Lengths (Å), Angles (deg), and Nonbonding Distances (Å) for 1

	min value	max value
Si−O	1.610(4)	1.637(4)
Co−Si	2.282(3)	2.293(3)
$(C-O)_{ax}$	1.105(15)	1.128(8)
$(C-O)_{eq}$	1.127(9)	1.168(9)
$Co-C_{ax}$	1.817(7)	1.851(12)
$Co-C_{eq}$	1.768(9)	1.809(7)
Si−O−Si	147.6(2)	154.1(3)
O−Si−O	107.5(2)	108.5(2)
$Si-Co-C_{ax}$	178.0(2)	180.0(2)
$Si-Co-C_{eq}$	82.2(2)	84.3(2)
$C_{eq}-Co-C_{eq}$	95.5(4)	98.1(3)
$C_{eq}-Co-C_{ax}$	117.3(4)	119.9(3)
Si···Si (body diagonal)	5.431(5)	5.469(2)
Si···Si (Si_8-cube edge)	3.120(1)	3.164(3)
O···O	3.557(5)	3.865(3)

The coordination geometry at the cobalt centers corresponds to a distorted-trigonal-bipyramidal arrangement with significant deviation from local C_{3v} symmetry. This is mainly due to the differing angles between the equatorial carbon atoms and to the deviation of the $Si-Co-C_{eq}$ and $C_{eq}-Co-C_{ap}$ angles from 90°. The equatorial carbonyl groups bend out of the trigonal plane toward the silicon atoms.

The bond lengths as well as the bond angles within the $Co(CO)_4$ units do not differ significantly from those in $[Co(CO)_4]H_7Si_8O_{12}$.[5] As a consequence, intramolecular interactions of the eight $Co(CO)_4$ groups of **1** are negligible. This is reflected in the high flexibility of the Si_8O_{12} framework, which seems to be able to compensate for the steric demand of eight $Co(CO)_4$ substituents.

In the ^{29}Si CP-MAS NMR spectrum of **1** a signal at −55 ppm is observed. The signal does not show any cross polarization but exhibits a remarkable anisotropy which is in good agreement with the determined solid-state structure.

In the IR and Raman spectrum of **1** the deviation from a local C_{3v} symmetry at the cobalt centers results in the observation of six vibrations in the $\nu(CO)$ region.

The MALDI TOF spectrum of **1** shows the $[M + K]^+$ peak as well as the $[(M - Co(CO)_4) + K]^+$ peak. The insolubility of **1** in common solvents does not allow a routine NMR analysis (^{13}C, ^{29}Si) in solution.

Reactivity. Due to its highly metal functionalized Si−O framework **1** can be seen as a model compound for Si−O-supported transition-metal catalysts. In initial experiments we studied the catalytic activity of **1** in hydroformylation reactions. All experiments in the present study were performed at 120 °C with a reaction time of 18 h. The initial CO/H_2 pressure at room temperature was 70 bar. Owing to the insolubility of **1** in toluene, all experiments were performed with stirring in the heterogeneous phase. In these experiments **1** did not show any catalytic activity at all and was recovered unchanged after a reaction time of 18 h. However, the use of a catalyst formulation of **1** and triphenylphosphine in a 1:8 stoichiometry led to complete conversion of 1-hexene to the corresponding aldehydes (98% yield). NMR and GC analyses of the hydroformylation products showed that a 3:1 mixture of 1-heptanal and 2-methylhexanal had been formed.

Filtration of the reaction mixture led to the isolation of a brownish solid, which still showed catalytic activity. According to IR spectroscopic results it is thought that the catalytically active species formed *in situ* is a substitution product of **1** and triphenylphosphine.

The mechanistic pathway of this catalysis is not yet understood. Experiments leading to a further understanding are under investigation.

In comparison to hydroformylation of 1-hexene performed under the same reaction conditions with $Co_2(CO)_8$ as catalyst,[7] our system shows higher chemoselectivity (no formation of alcohols) as well as higher stereoselectivity.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. The elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of the chemistry faculty at the University of Bielefeld. The cobalt analysis was carried out by means of flame emission spectroscopy on a Unicam SP 1900 atomic absorption spectrophotometer. IR spectra were recorded with a Bruker Vector 22 spectrometer. The Raman spectrum was recorded with a Bruker FRA 106 spectrometer (Nd:YAG-laser, 1064 nm).

Materials. Octahydridosilsesquioxane, $H_8Si_8O_{12}$, was prepared according to the method of Agaskar[8] and recrystallized from hot cyclohexane. The recrystallized $H_8Si_8O_{12}$ was sublimed prior to use. Octacarbonyldicobalt was obtained commercially from Fluka and was purified by sublimation and stored refrigerated under exclusion of light. 1-Hexene (Fluka) and triphenylphosphine (Riedel de Haën) were used as received.

$[(CO)_4Co]_8Si_8O_{12}$ (1). A solution of 250 mg (0.59 mmol) of octahydridosilsesquioxane, $H_8Si_8O_{12}$, in 80 mL of *n*-hexane was added to a solution of 800 mg (2.34 mmol) of octacarbonyldicobalt in 100 mL of *n*-hexane at ambient temperature with exclusion of light. After 1 min of stirring, the reaction mixture was placed under a slow stream of argon. After a few hours the first colorless crystals precipitated, and after 48 h crystallization was complete. The dark brown solution was separated from the crystals and discarded. The precipitate was washed

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[7] Ritter, U.; Winkhofer, N.; Schmidt, H. G.; Roesky, H. W. *Angew. Chem.* **1996**, *108*, 591.

[8] Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2708.

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with three portions of *n*-pentane and dried. $[(CO)_4Co]_8Si_8O_{12}$ **(1)** was isolated as colorless trigonal prisms in a yield of 87% (919 mg). IR (CsI): 2116, 2110, 2053, 2022, 2001, 1084, 562, 547, 512, 490, 463, 403 cm^{-1}. Raman (powder, 70 mW): 2116, 2039, 2022, 2002, 442, 421, 255, 176, 110 cm^{-1}. ^{29}Si CP-MAS NMR: δ −55 ppm. Anal. Calcd for $C_{32}Co_8O_{44}Si_8$: C, 21.53; Co, 26.42. Found: C, 21.38; Co, 26.46.

Catalysis. All hydroformylation reactions were carried out in a 200 mL stainless steel autoclave (Roth). The reaction products were analyzed by ^1H and ^{13}C NMR spectroscopy and analytical GC. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (^1H, 500.1 MHz; $^{13}C\{^1H\}$, 125.8 MHz). Analytical GC was performed on a Carlo Erba Fractovap 4200 (Macherey and Nagel OV 17 column, 80/100 mesh, 3 m; carrier gas nitrogen, FID detector) using diethyl ether and toluene as internal standards. The hydroformylation reactions were run with solutions of 16 mL of toluene and 4 mL (32.0 mmol) of 1-hexene. A 65.0 mg (36.4 μmol) portion of octakis(tetracarbonylcobaltio)octasilsesquioxane and 82.0 mg (313 μmol) of triphenylphosphine were added under a stream of argon. The reaction solutions were pressurized at room temperature to 70 bar with a mixture of hydrogen and carbon monoxide (partial pressures: 1:1) and then heated to 120 °C for 18 h.

Crystal Structure Determination. Data for **1**: $[(CO)_4Co]_8Si_8O_{12}$, $M_r = 1784.48$, cubic, space group $P2_3/1$, $a = b = c = 18.321(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6149.3(12)$ Å^3, $Z = 4$, $\rho_{calc} = 1.928$ Mg m^{-3}, $F(000) = 3488$, $\lambda = 0.710\,73$ Å, $T = 190(2)$ K, μ(Mo Kα) = 2.365 mm^{-1}, $2.49° < 2\theta < 25.87°$, 16 652 total reflections, 3947 independent reflections (R(int) = 0.0632), R1 (for $I > 2\sigma(I)$) = 0.0413, $wR_2 = 0.0922$. The data were collected on a STOE IPDS diffractometer. The structure was solved by direct methods (SHELXS-97) and refined using the least-squares method on F^2.

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Supporting Information Available: Figures giving additional views and tables giving crystal data and structure refinement details, atomic coordinates, bond distances and angles, and thermal parameters for **1** (7 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1998, Volume 17

Fernando Canales, Silvia Canales, Olga Crespo, M. Concepción Gimeno, Peter G. Jones, and Antonio Laguna*: Synthesis and Reactivity of the First (Hydrosulfido)gold(III) Complex. Crystal Structure of the Derivatives $NBu_4[\{Au(C_6F_5)_3\}_2SR]$ with the Isolobal Fragments R = H, $AuPPh_3$, $AgPPh_3$.

Page 1617. Reference 4 should read as follows.

(4) Vicente, J.; Chicote, M. T.; González-Herrero, P.; Grünwald, C.; Jones, P. G. *Organometallics* **1997**, *16*, 3381.

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