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Synthesis of the First Organometallic Monosubstituted Octanuclear Silasesquioxane

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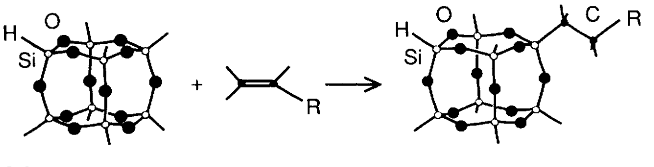
The hexachloroplatinic acid-catalysed hydrosilylation of vinylferrocene by octahydrosilasesquioxane $H_8Si_8O_{12}$ to the first organometallic monosubstituted octasilasesquioxane $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CH_2CH_2)]H_7Si_8O_{12}$ has been achieved.

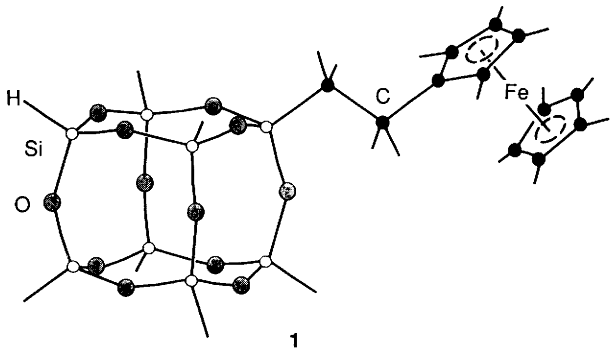
The structure of the highly symmetrical octahydrosilasesquioxane $H_8Si_8O_{12}$ was first determined by Larsson[1a] and has lately been reinvestigated.[1b] It is one of the most appealing members of the class of silasesquioxanes of the type $(RSiO_{\frac{3}{2}})_{2n}$, n = 1, 2, 3, *etc.*, and can be prepared in good yields by the polycondensation of $SiHCl_3$ in a biphasic solution.[2] This class of substances[3] seemed to be forgotten for a long time. Structurally well defined silasesquioxanes and silicate clusters have, however, recently attracted interest as 'building blocks' for the preparation of highly siliceous materials.[4] Agaskar[5] has developed an elegant simple procedure for the synthesis of a wide variety of silylated spherosilicates, many of which offer interesting possibilities as precursors to organolithic macromolecular material. New organosiliceous polymeric materials have been prepared by Hoebbel *et al.*[6] Feher *et al.*[7a] followed a different route by using an incompletely condensed hepamer trisilanol as a model for a silicon surface on which they examined metal catalysed reactions. These investigations led to the synthesis of some new metallasilasesquioxanes with important implications for the chemistry of silica surfaces.[7b]

Our interest for the silasesquioxanes has been attracted by the resemblance of $H_8Si_8O_{12}$ to the double-four ring of the secondary building unit of zeolite A and by the appealing polycyclic structure which makes these compounds attractive as models for vibrational spectroscopy.[8] Furthermore, the possible use of $H_8Si_8O_{12}$ as a framework for building donor–acceptor systems encouraged us to explore the chemistry of this substance. After the palladium-catalysed deuterium exchange and the substitution of all H atoms by alkyl groups, we recently found a way to prepare $RH_7Si_8O_{12}$.[9] It became clear that a great number of interesting compounds would become accessible if a route to organometallic monosubstituted octasilasesquioxanes could be found. Two main ways seemed to be within reach. One was to start with $RH_7Si_8O_{12}$, *e.g.* R = $(CH_2)_2Ph$, and to treat it with *e.g.* $[Cr(CO)_6]$. The other possibility was to try hydrosilylation by treating $H_8Si_8O_{12}$ with a vinylmetalloorganic compound as shown in Scheme 1. To test the second reaction path, we tried a hexachloroplatinic acid-catalysed hydrosilylation of the well understood vinylferrocene by $H_8Si_8O_{12}$ and found that an easy one-flask reaction leads to the desired monosubstituted organometallic octasilasesquioxane $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CH_2CH_2)]H_7Si_8O_{12}$ **1**.†



Scheme 1 Hydrosilylation, a reaction path to monosubstituted organometallic silasesquioxanes; *e.g.* R = ferrocenyl

We assume that the mechanism of this reaction is dictated by the rigidity and cage size of $H_8Si_8O_{12}$ and that it proceeds *via* five-co-ordinated Si similar to the reaction path for the palladium-catalysed deuterium exchange of $H_8Si_8O_{12}$ to $D_8Si_8O_{12}$.[11] The structure of compound **1** is unequivocally demonstrated by ^1H, ^{13}C and ^{29}Si NMR and mass spectroscopy. The ^1H NMR spectrum shows the expected splitting pattern, especially two singlets for the SiH protons with relative intensities of 4:3. The CH_2CH_2 bridge between the octa-



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† The compound $H_8Si_8O_{12}$ (100 mg, 0.24 mmol)[2] was dissolved in a round-bottom flask (25 cm^3) in toluene (15 cm^3), vinylferrocene (50 mg, 0.24 mmol) (Aldrich) and H_2PtCl_6 solution (10 µl, 0.01 mol dm^{-3} in Pr^iOH) were added in toluene (4 cm^3) and the mixture heated at reflux for 20 h under N_2. After evaporation of the solvent a yellow solid precipitated which was suspended in hexanes (Romil Chemicals), filtered and the remaining yellow solution injected on a 600 × 25 mm PolymerLab (pore size 50 Å, particle size 10 µm) size-exclusion liquid chromatography column. The yield of compound **1** was 21 mg (0.035 mmol, 14%). IR: see lit.,[10] NMR ($CDCl_3$, standard $SiMe_4$: ^1H (300 MHz), δ 1.01 (m, 2 H, $SiCH_2$), 2.46 (m, 2 H, $CH_2C_5H_4$), 4.06 (m, 4 H, $CH_2C_5H_4$), 4.11 (s, 5 H, C_5H_5), 4.23 (s, 3 H, SiH) and 4.25 (s, 4 H, SiH); ^{13}C (75 MHz), δ 13.0 (1 C, $SiCH_2$), 22.3 (1 C, $CH_2C_5H_4$), 67.3, 67.8 (4 C, $CH_2C_5H_4$), 68.5 (5 C, C_5H_5) and 90.8 (1 C, $CH_2C_5H_4$); ^{29}Si (60 MHz, inverse gated, external standard), δ −66.7 (1 Si, $SiCH_2$), −84.58 (3 Si), −84.60 (3 Si) and −84.64 (1 Si). Solutions of **1** in chlorinated solvents should be kept in the dark. Mass spectrum (70 eV, *ca.* 1.12×10^{-17} J): *m*/*z* 636 (100, M^+), 423 (16, $[M - C_{12}H_{13}Fe]^+$), 199 (20, $[C_{11}H_{11}Fe]^+$) and 121 (27%, $[C_5H_5Fe]^+$).

silasesquioxane and the ferrocene forms an AA′XX′ system which is responsible for the multiplets in the corresponding regions. The ^{29}Si NMR spectrum shows four peaks with relative intensities of 1:3:3:1. The three Si atoms in the direct neighbourhood of the substituted Si atoms have the largest shift with respect to unsubstituted $H_8Si_8O_{12}$. The IR spectrum in the range 350–4000 cm^{-1} shows the expected pattern to be discussed later.[10]

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