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Study of transition metals and F-Elements

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Abstract
This paper will focus mainly on the field disiloxanediolates and matellasiloxanes. May industrially and commercially important processes are catalysed by transition metal complexes immobilized this paper.
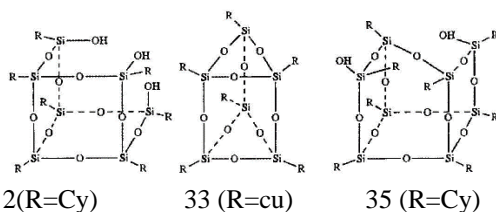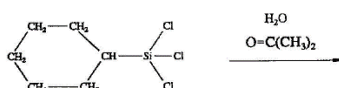
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Introduction

The chemistry of metallasiloxanes, including synthetic and structural aspects, has been extensively covered in excellent recent review articles [1–3] and a book [4]. More specialized reviews covering the chemistry of silanols, disilanols, and silanetriols [5], silicate cages [6], and silsesquioxanes [7-9] are also available. Thus this article will focus mainly on the most recent work in the field of disiloxanediolates and metallasilsesquioxanes. It is divided into two parts. In the first part early transition metal and f-element complexes derived from tetraphenyldisiloxanediol, $Ph_2Si(OH)OSiPh_2(OH)$ (1), will be surveyed. The second part deals with early transition metal and f-element derivatives of the incompletely condensed silsesquioxane cage molecule $Cy_7Si_7O_9(OH)3$ (2) (Cy=cyclohexyl). In addition to polyhedral metallasilsesquioxanes, a number of highly interesting transition metal and lanthanide complexes containing cyclo(poly)siloxanolate ligands have been reported. However, these are not within the scope of this review as their preparation and structural characterization have been surveyed elsewhere.

Metallasilsesquioxanes Analysis

Silsesquioxanes are silicon—oxygen cage compounds of the general formula $(RSiO15)n$ which can be prepared by hydrolysis of the corresponding trifunctional organosilicon monomers $RSiCl_3$ or $RSKOMe)_3$. Various aspects of their chemistry, including the preparation and structure of metallasilsesquioxanes, have been documented in a number of review articles. Among the fully condensed silsesquioxane polyhedra are trigonal prisms ($R_6Si_6O_9$, n=6), cubes ($R_8Si_8O_{12}$, n=8), and drum-shaped frameworks ($R_{10}Si_{10}O_{15}$, n=10; D_{2d}–$R_{12}Si_{12}O_{18}$, n=12). Especially interesting for the preparation of metallasilsesquioxanes and other functional derivatives are incompletely condensed silsesquioxanes which can be regarded as intermediates in the formation of the fully condensed frameworks. The most prominent representative of this class of organosilicon compounds is the trisilanol derivative $Cy_7Si_7O_9(OH)_3$ (2), which was first reported by Brown and Vogt [10–11] and more recently investigated in great detail by Feher and coworkers [9]. An improved synthetic route developed by the latter research group involves kinetically controlled hydrolysis of trichlorocyclohexylsilane according to Eq. (1).

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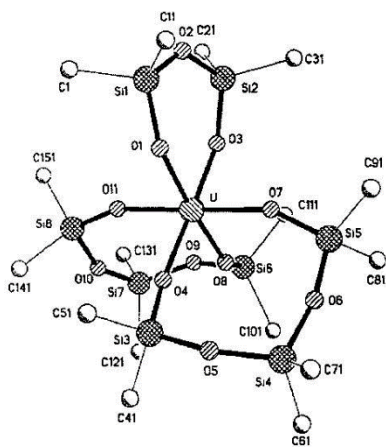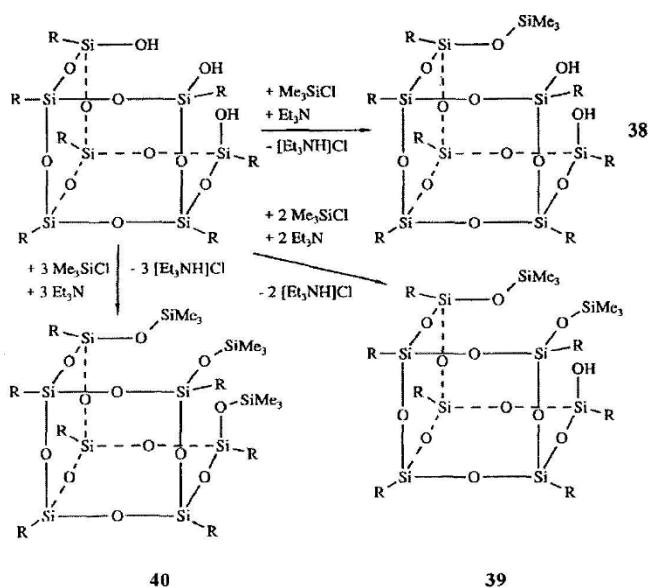
(1)

2(R=Cy)   33 (R=cu)   35 (R=Cy)

Fig 1: Molecular structure of 32.

Scheme 1: Synthesis of the silylated silsesquioxanes 38-40 (R=Cy). Reagents and conditions: Me₃SiCl: NEt₃, THF, r.t.

Other products resulting from this reaction are the fully condensed silsesquioxane 33 and the disilanol derivative 34, from which 2 can be readily separated by an extraction procedure. A certain drawback of this synthesis is that the kinetically controlled hydrolytic polycondensation of the in situ formed cyclohexylsilanetriol, $CySi(OH)_3$ (35), takes up
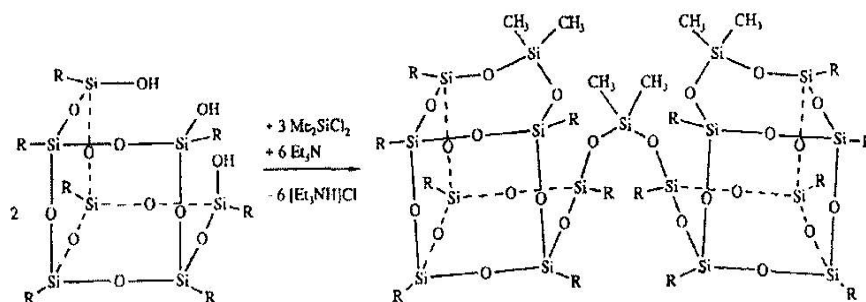
to 3 years to proceed to completion. However, synthetically useful quantities of 2 can already be isolated after a reaction time of several months. Related trisilanols based on a silsesquioxane cube have been isolated with R=cyclopentyl (36) and cycloheptyl (37) [12]. In these cases, and quite in contrast to the formation of 2, the rates of the hydrolysis reactions can be dramatically improved by refluxing the reaction mixtures.

The derivative chemistry of 2 and especially the study of related metallasilsesquioxanes as molecular models for silica-supported metal catalysts have been pioneered by Feher *et al*. [13]. Synthesis, characterization, and reactivity of these compounds have been surveyed in a recent review article. Thus the present contribution focuses mainly on new results published after 1995. The preparation of metal derivatives of 2 generally involves treatment of the parent trisilanol with the appropriate metal halide in the presence of a base such as triethylamine. In addition, Feher *et al*. have demonstrated that the reactivity of 2 can be modified and tuned by silylation of the Si-OH functions or by preparing the corresponding thallium silanolates [14]. The latter offer the advantage that thallium reagents are non-reducing and thus allow the preparation of transition metal derivatives in high oxidation states. On the other hand, silylation is an effective way to protect one or two Si-OH functions and thus prepare the corresponding mono- and disilanol derivatives. Scheme 3 illustrates the selective preparation of mono-, di- and trisilylated silsesquioxanes starting from 2.

The silylated products 38 and 40 can be readily isolated as pure materials by fractional crystallization from pentane or hexane. The disilylated silsesquioxane 39 is not as easily prepared as it is very soluble in hydrocarbon solvents and thus somewhat difficult to purify. Recently an analytically pure sample of 39 was obtained by repeated crystallization from acetonitrile and this enabled us to determine its molecular structure. Figure 2 depicts how the single Si-OH function is sterically shielded by a cyclohexyl substituent and two - $OSiMe_3$ units.

In contrast to the monomeric nature of 39, the parent trisilanol 2 had previously been reported to crystallize as a hydrogen-bonded dimer.

In an extension of this chemistry the reaction of 2 with the difunctional reagent dichlorodimethylsilane was studied [88]. A pure reaction product, the bis(-silsesquioxane) derivative 41, can be isolated when the reaction is carried out in a 2:3 molar ratio according to Eq. (2).

41 (R=Cy)

The white crystalline solid was structurally characterized by X-ray diffraction (Fig. 3). In this molecule one corner of the original incompletely condensed silsesquioxane is capped

$$\text{(2)}$$

by a Me_2Si unit. A third Me_2Si group connects two of these partially closed silsesquioxane cages.

Lithium, sodium or potassium silanolates derived from the trisilanol 2 would be of paramount interest as they could also serve as useful. starting materials for the preparation of

other polyhedral metallasilsesquioxanes. In fact, it was first demonstrated by Feher *et al*. that deprotonation of the trisilanols 2, 36 or 37 with one equivalent of sodium t-butoxide cleanly affords the corresponding mono-sodium derivatives, but these products were found to be stable only for short periods of time in solution and could not be isolated as crystalline materials. Another
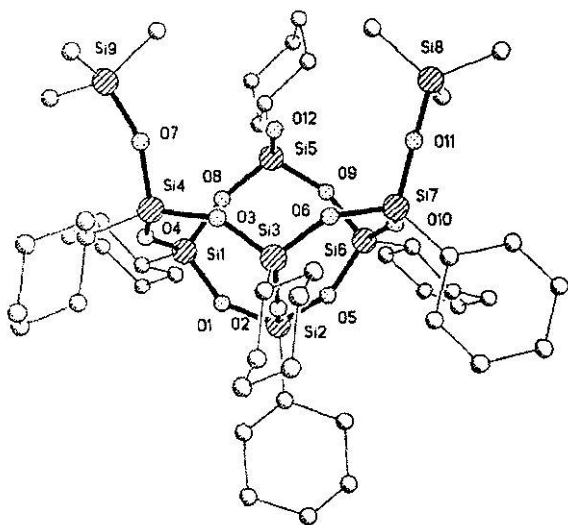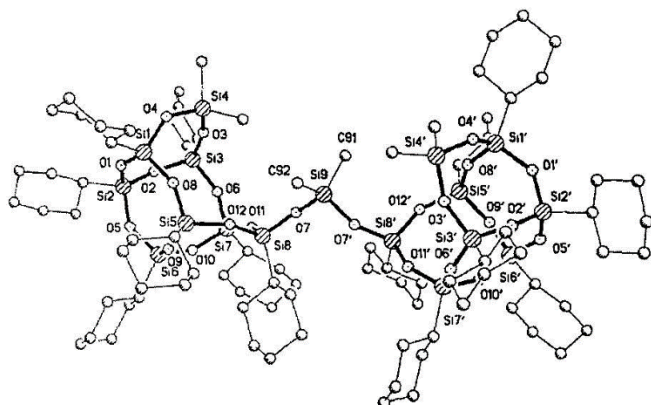

Fig 2: Molecular structure of 39.

Fig 3: Molecular structure of 41.

route to remarkably stable mono-anionic derivatives involves the comproportionation reaction of 2 with $Cy_7Si_7O_9(OT1)_3$ (42) followed by reaction with [PPh$_4$]Cl, [PnBu$_4$]C1, or [NnBu$_4$]Br to produce the corresponding salts of $[Cy_7Si_7O_{10}(OH)_2]^-$, i.e. the monoanion derived from deprotonation of 2. A single-crystal X-ray diffraction study revealed that the salt $[NnBu_4][Cy_7Si_7O_{10}(OH)_2]$ (43) exists in the solid state as isolated ion pairs with strong intramolecular hydrogen bonding [15].

Result and Discussion

Quite in contrast, early attempts to exhaustively deprotonate the Si–OH functions with the use of strong bases such as NaOtBu resulted in decomposition, presumably owing to skeletal degradation of the silsesquioxane cage. Recently it was discovered that a successful preparation of fully deprotonated trisilanols strongly depends on the proper choice of the base [89b,c]. It was found that the silsesquioxane cage remains intact and all thee Si–OH functions are deprotonated when 2 is treated with three

equivalents of LiN(SiMe$_3$)$_2$. Diethyl ether, THF or toluene are suitable solvents for these reactions. When the deprotonation reaction between 2 and LiN(SiMe$_3$)$_2$ (21) is carried out in toluene, the unsolvated lithium silanolate $Cy_7Si_7O_9(OLi)_3$ (44) precipitates as an amorphous, presumably polymeric material. However, crystalline adducts are readily obtained in the presence of suitable Lewis bases. Eq. (3) illustrates the preparation of the acetone solvate $[Cy_7Si_7O9(OLi)_3]_2 \cdot 3Me_2CO$ (45), which was the first adduct of this type to be isolated and structurally characterized.
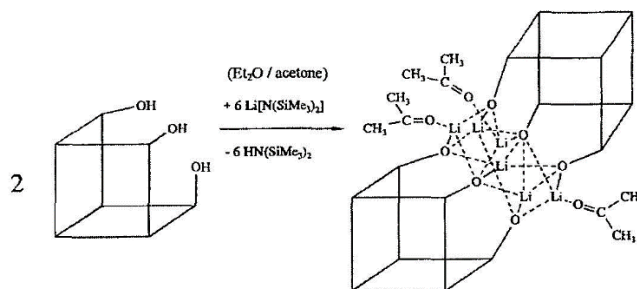
As shown by X-ray diffraction, supramolecular self-assembly of 45 leads to the formation of an unsymmetrical dimer in the solid state. The central structural unit of 45 consists of a box-shaped Li_6O_6 polyhedron.

Acetone ligands are coordinated to three lithium ions while the other three interact with framework oxygen atoms of the silsesquioxane cages. This results in tetracoordination around each lithium. Structurally related box-shaped Li_6O_6 or Li_6S_6 polyhedra have previously been reported for some hexameric lithium phenoxides or
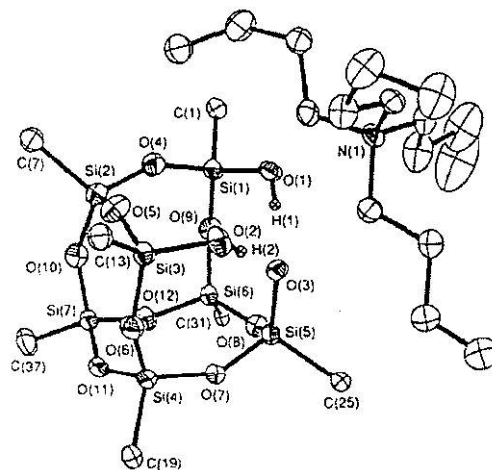

Fig 4: Molecular structure of 43.

arenethiolates. The structural investigation of 45 clearly demonstrated that fully deprotonated trisilanols can be generated without concomitant break-down of the silsesquioxane cage structure and that the products can be isolated as stable crystalline solids. In a similar manner the well-defined adducts $[Cy_7Si_2O_9(OLi_3]_2 \cdot 3Et_2O$ (46) and $[Cy_7Si_7O_9(OLi)_{32} \cdot 3TFIF$ (47) have been isolated in high yields and fully characterized..

Conclusion

A heterogeneous epoxidation catalyst has been obtained by Abbenhuis *et al*. though immobilization of $Cy_7Si_7O_{12}TiCp$

(59) on silica or MCM-41 molecular sieve. Finally, a silica-supported vanadium-containing silsesquioxane catalyst was prepared from 127. This material showed excellent activity towards the selective photo-assisted catalytic oxidation of methane to formaldehyde.

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