# Synthesis of Some New Functionalized Octasilsesquioxane Hybrid Nanoclusters. III. Potential of the Octameric Clusters as Hydraulic Lubricating Fluids

**Enock O. DARE**
*Department of Chemistry, University of Agriculture, P. O. Box 28,*
*UNAAB post office, Abeokuta-NIGERIA*
*e-mail: dare3160@hotmail.com*

The reaction of suitable organic compounds such as $\omega$-halo-1-alkenes, allyltrichlorosilane or 2-methyl-3-butyn-2-ol in combination with a well-defined inorganic silsesquioxane, $H_8Si_8O_{12}$ A cores, leads to covalently bound organic-inorganic hybrid materials in high yields.

The hydraulic fluid properties of these viscous hybrid materials were evaluated and compared with those of some commercially available hydraulic fluids: Mobil EAL 224H, Super-V (AP) and Puroil SHO. The results showed that most silsesquioxane semi-liquids possess hydraulic fluid properties comparable to those of the 3 commercial lubricants.

**Key Words:** Hydraulic fluid property, hybrid material, nanocluster, octasilsesquioxane.

## Introduction

Topologically spherically silsesquioxanes (i.e. $[RSiO_{1.5}]_n$} and silicates {i.e. $[ROSiO_{1.5}]_n$) have attracted widespread attention as precursors to a variety of interesting compounds and materials, and the number of known frameworks bearing synthetically useful functional groups is growing at an increasingly rapid pace [1,2].

In some earlier work, our goal was to develop novel silsesquioxane-based precursors on which material chemists could work upon, and that prompted research in the direction of various functionalized silsesquioxanes[3−5]. Despite the fact that the possibility of producing alkyl-functionalized silsesquioxane was brought about in 1991 by the Calzaferri group[6] using a hydrosilylation reaction, interest in them has recently arisen again, especially when a longer alkyl carbon (up to $(-CH_2)_8X$, X = Cl, Br) is attached at cubane vertices. Interest in alkyl-functionalized oligoorganylsilsesquioxanes is explained by the determination of the area of practical use such as electrooptics[7] and microelectronics[8]. However, persistence shape, size (0.5-0.7 nm)[9] and high viscosity of some semi-liquid silsesquioxanes [4,5] have not been taken into consideration as factors that should suggest their potential in some hydraulic applications.

Most commercial synthetic hydraulic lubricants are usually formulated from linear organosilicon/silanes having Si-O-Si functionality in their framework, for example, $CH_3$-$Si(CH_3)_2$-O-$Si(CH_3)_2$-O-$Si(CH_3)_2$-O-$Si(CH_3)_3$ [10]. The reason behind their adoption is the fact that they are considered high quality base stocks exhibiting unmatched performance, good thermal stability and environmental compatibility.

Herein, a report of the synthesis of some new alkylsilsesquioxanes whose alkyl carbon arms are up to $-(CH_2)_8X$ attached at the vertices of the octasilsesquioxane framework by hydrosilylation is presented. In this work, results of the preliminary investigation into the hydraulic lubricating fluid properties of some alkylsilsesquioxanes are also presented.

# Experimental

**General.** All reactions were carried out in an inert atmosphere unless otherwise noted. Commercial source reagents (Aldrich and Fluka chemicals) were used without further purification.

IR spectra were recorded in $CH_2Cl_2$ unless otherwise stated, using $CaF_2$ optic on a Perkin-Elmer 882 spectrophotometer. The $^1$H-NMR and $^{13}$C-NMR and $^{29}$Si-NMR were obtained on a Bruker AC 300 spectrometer. Chemical shifts are reported in $\delta$ values relative to the residual solvent resonance of $CDCl_3$ ($^1$H, $\delta$ 7.24; $^{13}$C, $\delta$ 77.0.), $(CD_3)_2CO$ ($^1$H, $\delta$ 2.05). Low-resolution mass spectra were recorded on a VG 70-250s mass spectrometer using FAB. Micro-analytical data were obtained with the use of a Perkin-Elmer 240C elemental analyzer.

The procedures used in the determination of the physico-chemical characteristic of the viscous alkyl-silsesquioxanes are in accordance with the American Society for Testing and Materials (ASTM) standards, except otherwise stated.

## Synthesis of A, D and H

Compounds **A**, **D** and **H** were synthesized following some literature procedures[4,5]. **D** and **H** are colorless viscous liquids.

## Synthesis of B

Hydrogen-$T_8$ **A** (0.125 g, 2.89 x $10^{-4}$ mol) ($T_8$ = $Si_8O_{12}$ = silsesquioxane cubic framework) was added to 7-bromo-1-heptene (1.0 mL, 6.5 x $10^{-3}$ mol) in a 5.0 mL flask. Eight drops of 0.1 M $H_2PtCl_6$ solution in *i*-prOH were added to the mixture and it was heated under reflux for 5 h. The excess reactant was removed under vacuum to give a clear colorless viscous liquid **B**. Yield = 90%. $^1$H-NMR ($CDCl_3$): $\delta$: 0.58 ppm ($SiCH_2$, 2H); 1.30-1.37 ppm (m, $-CH_2-$, 8H); 1.78 ppm ($CH_2$, 2H); 3.36 ppm ($-CH_2Br$, 2H). $^{13}$C-NMR ($CDCl_3$): $\delta$: 11.87 ppm ($CH_2$); 22.64 ppm ($CH_2$); 28.03 ppm ($CH_2$); 28.40 ppm ($CH_2$); 32.38 ppm ($CH_2$); 32.78 ppm ($CH_2$); 33.97 ppm ($CH_2$). IR ($CaF_2$, $cm^{-1}$): 3685.2 (C-H), 1449.0 (Si-$CH_2$), 1118.3 (Si-O-Si). MS (FAB): 1841.41 ($M^+$, parent ion). Elemental analysis: calcd. for $C_{56}H_{112}O_{12}Si_8Br_8$ : C 36.43%, H 6.13%; found C 35.45%, H 5.84%.

## Synthesis of C

8-Bromo-1-octene (1.5 mL 8.9 x $10^{-3}$ mol) was added to hydrogen-$T_8$ (0.25 g, 5.7 x $10^{-4}$ mol). Eight drops of 0.1 M $H_2PtCl_6$ solution in $i$-PrOH were added and the mixture heated at reflux for 7 h. It was vacuum-dried to give a light brown viscous liquid **C** with a yield of 96%. $^1$H-NMR (CHCl$_3$): $\delta$: 0.55 ppm (SiCH$_2$, 2H); 1.27 ppm (-CH$_2$-, 10H); 1.78 ppm (CH$_2$, 2H); 3.35 ppm (CH$_2$Br, 2H). $^{13}$C-NMR (CDCl$_3$): $\delta$: 11.80, 22.60, 28.10, 28.58, 29.00, 32.40, 32.73 & 33.83 ppm (all CH$_2$). MS (FAB): 1952.2 (M$^+$, parent ion). Elemental analysis: calcd. for C$_{64}$H$_{128}$O$_{12}$Si$_8$Br$_8$: C 39.37%, H 6.56%; found C 39.26%, H 6.49%.

## Synthesis of E

Hydrogen-$T_8$ (0.125 g, 2.89 x $10^{-4}$ mol) dissolved in toluene (8.0 mL) and allyltrichlorosilane (3.0 mL, 2.1 x $10^{-2}$ mol) were measured into a 25.0 mL flask, and 8 drops of 0.1 M $H_2PtCl_6$ solution in $i$-prOH were added and the mixture heated under reflux for 16 h. The excess reactant was removed under vacuum to give a brown viscous liquid, which was highly air sensitive. $^1$H NMR (CDCl$_3$): 0.789 (t, SiCH$_2$, 2H); 1.438 (m, -CH$_2$-, 2H); 1.669 (t, -CH$_2$Si, 2H). $^{13}$C NMR (CDCl$_3$): 8.8 ppm (-CH$_2$-); 22.1 ppm (—SiCH$_2$-); 25.4 ppm (-CH$_2$-Si—).

## Synthesis of F

Hydrogen-$T_8$ (0.25 g, 5.7 x $10^{-4}$ mol) was dissolved in toluene (5.0 mL) containing excess of 2-methyl-3-butyn-2-ol, followed by the addition of 6 drops of 0.1 M $H_2PtCl_6$ solution in $i$-PrOH. The mixture was heated under reflux for 13 h, during which yellowish brown precipitate was formed. The yellowish brown precipitate was filtered and washed with hexane to give a mixture of silylated (C-silylation + O-silylation) products **F**. $^1$H-NMR [(CD$_3$)$_2$CO]: $\delta$: 1.23 ppm (CH$_3$, 6H); 1.36 ppm (CH$_3$, 6H); 3.71 ppm (OH, 1H); 5.75 ppm (CH, 1H); 6.59 ppm (CH, 1H); 2.87 ppm (-CCH, 1H). $^{29}$Si NMR [(CD$_3$)$_2$CO]: $\delta$: -64.2 ppm. IR (acetone): 3405.7-3603.8 (-OH), 2977.0 (C-H), 1118.8 (Si-O-Si).

### Test Methods for Determining Kinematic Viscosity (Kv) and Viscosity Index (Vi)

ASTM standard test procedure D445 was followed for determining the viscosities[11] of compounds **B, C, D** and **H** using a Universal Torsion Viscometer VHA-200-M at the temperature range 30 to 120 °C.

A 50-mL flask containing the viscous liquid silsesquioxane was suspended in a water bath with a temperature controller. After determining the kinematic viscosity (Kv) of the viscous liquids at various temperature ranges, ASTM test procedure D2270 was followed for calculating the viscosity index (Vi)[12] at 40 and 100 °C.

# Results and Discussion

This study was undertaken with 2 objectives in mind: (1) to synthesize some known[4,5] and new functionalized octasilsesquioxanes, and (2) to take advantage of the viscous nature of some of these products and their Si-O functionality to evaluate their hydraulic fluid properties; the properties were compared with 3 commercially

available hydraulic fluids: Mobil EAL 224H (vegetable oil based), Super-V (AP) (petroleum based) and Puroil SHO (synthetic product).

The synthesis of the functionalized molecules was accomplished according to the Scheme using hydrosilylation and alkylation. The latter procedure is the same as one previously published[4]. Hydrosilylation of octahydridosilsesquioxane **A** using 7-bromo-1-heptene, 8-bromo-1-octene, allyltrichlorosilane and 2-methyl-3-butyn-2-ol gave $Si_8O_{12}(CH_2)_7Br$ **B**, $Si_8O_{12}(CH_2)_8Br$ **C**, $Si_8O_{12}(CH_2)_3Si_8Cl_{24}$ **E** and (C-silylated + O-silylated) products **F**, respectively. These new compounds were obtained in high yields usually in the presence of hexachloroplatinic acid as catalyst and excess of various unsaturated substrates. Toluene was used as solvent during the synthesis of **E** and **F**.

**B** and **C** exist as colorless viscous liquids whose kinematic viscosities at 20 °C are 47 and 50 cSt, respectively. In a recent report[5], the carbon chain length of the alkyl substrate placed on the silsesquioxane cores contained up to 6 carbons. Therefore, it was thought that increasing the number of carbons on the alkyl chain to 8 might have an effect on the physical characteristic of the products. The effect on physical property in **B** and **C** can be seen by noting differences in their kv at 20 °C. Similar variations in physical properties have been reported for other carbosilane products, where varying the length of alkenylating agents from $C_2$ to $C_{10}$ gave products varying markedly in physical propertie[13]. In contrast, $Si_8O_{12}(CH_2)_6Cl$ **D** with a smaller carbon length has higher kv (52 cSt) at 20 °C, presumably due to a stronger electronegative influence of the terminal chlorine atom. **E** is a brown viscous liquid sensitive to air. It has the potential to be used as an intermediate to a starburst dendrimer under a repetitive hydrosilylation/alkenylation reaction [14]. Paul and Morris[13] hydrosilylated vinyltrichlorosilane with **1** to produce a 72-Cl dendrimer[14] under a repetitive procedure.

In order to make a contribution towards the study of silica, which retains reactive Si—-OH functionality that can be exploited as a ligand in a wide variety of complexations, a report of the synthesis of **F** is presented. C-silylation and O-silylation products resulted from a reaction of **1** with an excess of $CH{\equiv}CC(CH_3)_2OH$. NMR spectroscopy analysis indicates that the majority of the products resulted from C-silylation (89%); only 11% of the products resulted from O-silylation. This result, however, contradicts a 100% C-silylation product resulting from the hydrosilylation of **1** with $H_2C{=}CHC(CH_3)_2OH$ reported by Roesky et al. [15]. The main feature of interest of the octameric clusters **F**, especially C-silylation product when separated from the mixture, is the presence of the hydrogen bond, which is useful in the formation of new supramolecular assemblies [15]. Moreover, Endo et al. have shown self-assembly in the porous organic structure through the formation of hydrogen bonds [16].

Characterization of $Si_8O_{12}(CH_2)_7Br$ **B** and $Si_8O_{12}(CH_2)_8Br$ **C** was accomplished by $^1H$ and $^{13}C$ NMR spectroscopy and elemental analysis. The results obtained are in good agreement with the products' structure. **B** and **C** are almost the same structurally, except that the latter contains an extra –CH_2- on its arms. $^1H$- and $^{13}C$-NMR spectra of **B** (Figures 1 and 2) clearly reflect the respective proton and carbon signals in the cluster. For example, on the $^1H$-NMR spectra, $-SiCH_2-$ (2H), $-CH_2Br$ (2H), $-(CH_2)_4-$ (8H) and $-CH_2CH_2Br$ (2H) resonate at 0.58, 3.36, 1.30 and 1.78 ppm, respectively. Almost the same spectral patterns with slight changes in chemical shifts were observed on the spectra of cluster **C** except that the resonance at 1.27 ppm is assigned to $-SiCH_2(C\underline{H}_2)_5CH_2Br$ (10H). **E** and **F** were characterized using $^1H$, $^{29}Si$, and $^{13}C$ NMR spectroscopy as well as IR spectroscopy. The results are quite satisfactory. Further characterization of **E** and **F** was not pursued.

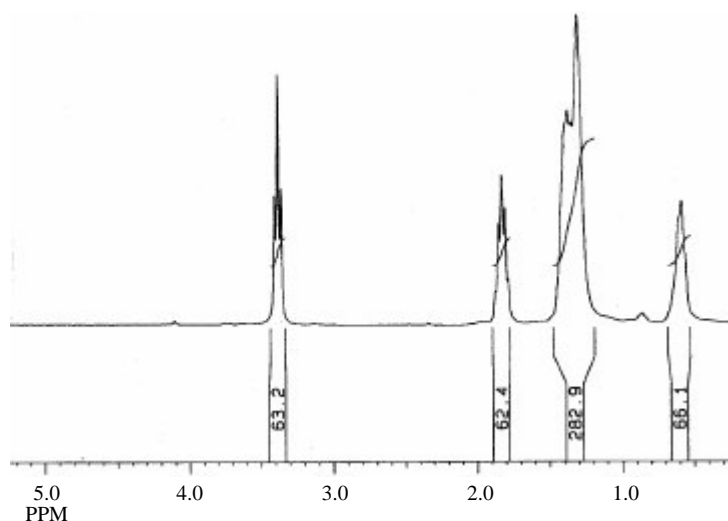**Scheme.** Synthetic outline for B, C, D, E, F and H.

C-silylation has been studied extensively since the 1950s. The widely accepted mechanism of hydrosilylation (Chalk-Harrod)[17] was studied in 1964. S-H alcoholysis resulting in O-silylation has also been studied[18]. Most mechanistic studies suggest transition metal activation of Si-H bonds, either through oxidative addition or formation of a $\sigma$ complex, which favors attack of the alcohol on Si.

**Figure 1.** $^1$H-NMR spectra of **B** $Si_8O_{12}(CH_2)_7Br$.
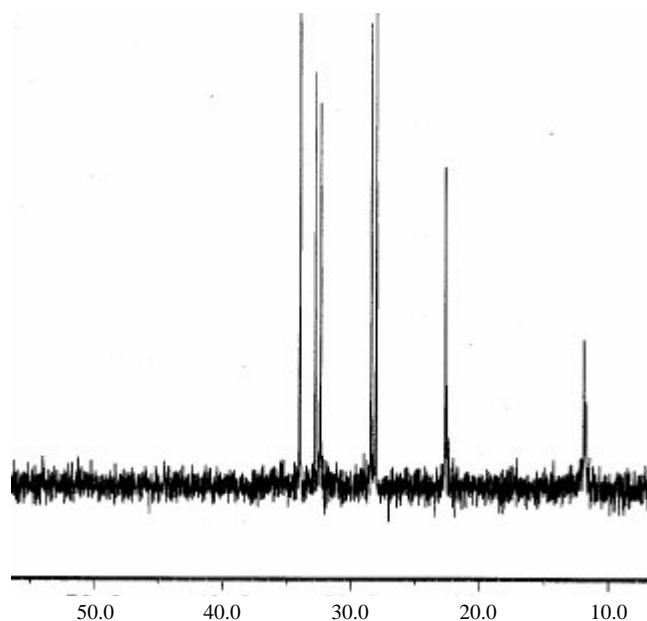


**Figure 2**. $^{13}$C-NMR spectra of **B** $Si_8O_{12}(CH_2)_7Br$.

## Hydraulic Fluid Properties of B, C, D and H

The oil/fluid in a hydraulic system that may be petroleum-based, vegetable-based[19] or synthetic-based (silicon)[10] serves as the power transmission medium, lubricant and coolant. Hydraulic fluids have been rated on their viscosity[19,20] and anti-wear [19] properties. In this report, the former has been considered on a preliminary scale. Therefore, **B**, **C**, **D** and **H** were evaluated by measuring their kv, Vi and pour point.

The Kv at 40 °C of **B** (35 cSt), **C** (38 cSt), **D** (cSt) and **H** (48 cSt) is quite reasonable and is higher than that of Super-v, a petroleum-based commercial product (Figure 3). The kv at 100 °C of Super-v was the highest among the tested fluids (Figure 4). For most industrial applications, lubricating oils with viscosities ranging from 5 to 15 cSt at 100 °C cover the requirements[19]. **H** has a high kv (11 cSt) at 100 °C, notably

higher than that of Mobil EAL and Puroil SHO, and therefore its utility as a base stock is encouraging. Its ability to possess good lubricity power even at high temperature is plausibly attributed to the terminal phenyl group on **H**. It has been stated that the presence of a phenyl group in a silicon lubricant[10] increases the load-bearing capacity and enhances its stability at high temperature.
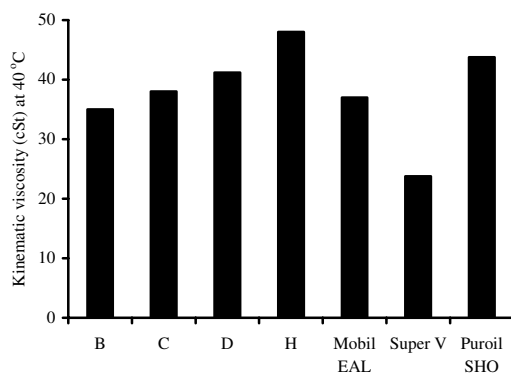
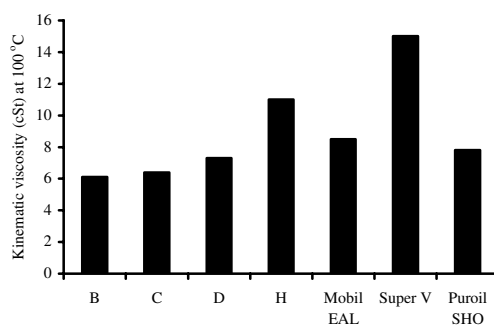**Figure 3.** Kinematic viscosity (Kv) at 40 °C for silsesquioxane liquids and commercial products.

**Figure 4.** Kinematic viscosity (Kv) at 100 °C for silsesquioxane liquids and commercial products.

The viscosity index indicates the ability of an oil/fluid to maintain its fluidity or viscosity over a range of temperature. In other words, it is the ratio of the change in viscosity with temperature. The viscosity-temperature graph of the results obtained (Figure 5) for **B**, **C**, **D**, and **H** clearly shows that viscosity changes at a very low rate compared to temperature.
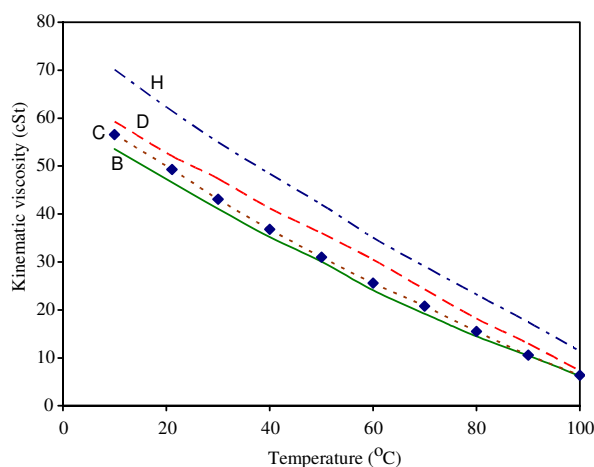
**Figure 5.** Viscosity-temperature graph for B, C, D and H.

However, the graph for **H** is quite distinct from the others: evidence of high Vi. Further clarification is shown in Figure 6 with **H** having the highest Vi (233) when compared with other silsesquioxanes and commercial lubricants. **B**, **C** and **D** compare favorably with other commercial lubricants.
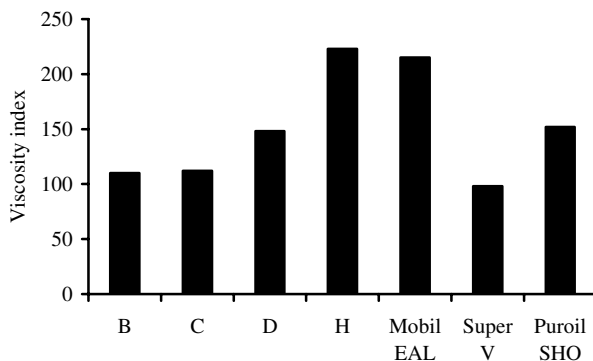


**Figure 6.** Viscosity index for silsesquioxane and commercial fluids.

The fluid characteristic of silsesquioxanes was determined at low temperature. In a cold-storage study, **B** showed onset of solidification at 0 °C, **C** at +8 °C, **D** at –5 °C and **H** at –20 °C. The pour points of **B** and **C** are quite high and this may limit its utilization as a hydraulic base stock. If this property could be enhanced, the scope of its application in hydraulic systems may be widened[21]. No attempt was made to improve the properties of **B** and **C**. The pour points of **D** (-38 °C) and **H** (-25 °C) are low and fall within the typical range for mineral oils (+6 to –40)[19] even without pour point depressant[10].

In conclusion, an easy and straightforward synthetic procedure was used to prepare some functionalized octasilsesquioxanes in quantitative yields. Using the same hydrosilylation procedure, it was possible to synthesize 2 different mixed compounds; the one with reactive $SiCH=CHC(CH_3)_2$-OH functionality constitutes the majority. This compound is expected to play an essential role in the construction of a new supramolecular network through intermolecular hydrogen bonds[15]. Moreover, in the presence of allyltrichlorosilane, synthesis of a 24-Cl dendrimer is established. This compound may serve as an intermediate for a more complex dendrimer with unusual molecular architecture.

The test results on the hydraulic properties of viscous silsesquioxanes show that they have the potential to be used in hydraulic fluid formulations and they compared favorably with commercial fluids. However, it is obvious that the commercial fluids mentioned have additional additives. The shortcoming in the pour point of some of silsesquioxanes may be overcome, perhaps, in the presence of additives[20]. Therefore, the full recommendation of silsesquioxane liquids as potentially useful substitutes for petroleum- and vegetable-based hydraulic fluids may be suspended until outstanding properties such as anti-wear, flash point, mist spray flammability and biodegradability are evaluated.

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