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Journal of Organometallic Chemistry 551 (1998) 125–131

Journal of Organometallic Chemistry

Reactions of thiol-functionalized silsesquioxanes with metal carbonyl clusters: syntheses and characterization of $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)M_3(\mu\text{-}H)(CO)_{10}\}]$ (M = Ru, Os; $Pr^n = C_3H_7$), $[Si_8O_{12}(Pr^n)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ and $[Si_8O_{12}(C_3H_6SH)_x\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_{8-x}]$ ($x = 6, 0$) [1]

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Received 26 February 1997

Abstract

The thiol-functionalised silsesquioxanes, $[Si_8O_{12}(Pr^n)_7(C_3H_6SH)]$, **1**, and $[Si_8O_{12}(Pr^n)_6\{o\text{-}(C_3H_6SH)_2\}]$, **2**, ($Pr^n = C_3H_7$) readily react with the activated metal clusters $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru, Os) to form cluster-substituted silsesquioxanes. The compounds $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)M_3(\mu\text{-}H)(CO)_{10}\}]$ (M = Ru, **4**; M = Os, **5**) and $[Si_8O_{12}(Pr^n)_6\{o\text{-}(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ **6** have been prepared and characterized. The octa-substituted silsesquioxane, $[Si_8O_{12}(C_3H_6SH)_8]$, **3**, may be partially or completely substituted at its thiol functionalities depending on the reaction stoichiometry employed; $[Si_8O_{12}(C_3H_6SH)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$, **7**, and $[Si_8O_{12}\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_8]$, **8**, have been prepared. © 1998 Elsevier Science S.A.

Keywords: silsesquioxanes; metal cluster; thiol functionalities

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1. Introduction

Molecular clusters have been used as homogeneous catalysts for a variety of reactions [1], although in the majority of cases it is probable that the active catalyst has a different nuclearity from that of the precursor cluster. Therefore, bridging ligands have been employed to prevent fragmentation of the metal core, which may occur under the conditions required for catalysis [2]. Further, several attempts have been made to circumvent the technological problems associated with a homogeneous catalytic system by attaching molecular cluster compounds with ‘clamped’ cores onto chemically functionalized supports, such as polymers and silica [3]. Initial attempts made use of phosphinated supports [4,5], although the often labile nature of the transition metal–phosphine interaction prompted investigations into the reactions of cluster compounds with thiol modified silica supports [6].

Much attention has recently been paid to the synthesis and investigation of ‘octopus’ molecules, which are based on cage silsesquioxane cores with eight pendant molecular ‘arms’. Through their eight Si vertices, these cubes may be covalently linked to a plethora of organic or organometallic groups which may serve as precursors to inorganic–organic hybrid materials and inorganic gels [7].

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[1] Dedicated to Professor P.M. Maitlis on the occasion of his 65th birthday with our sincere congratulations and best wishes.

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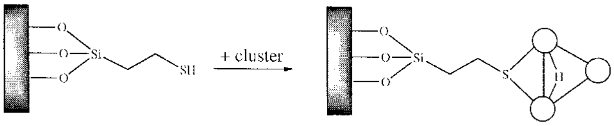


Fig. 1. Pictorial representation of the preparation of silica-tethered molecular clusters.

The synthesis of $[M_3(\mu\text{-}H)(\mu_2\text{-}SR)(CO)_{10}]$ clusters, M = Ru or Os, R = alkyl or aryl, anchored to silica has been achieved either by: (1) reaction of thiol-functionalized silica with an appropriate cluster compound (Fig. 1) or (2) preparation of a cluster bridged by a thiolate ligand containing a pendant alkoxysilyl group, which may be incorporated into a silica polymer. With these considerations in mind, the series of clusters encompassing $[M_3(\mu\text{-}H)(\mu_2\text{-}SR)(CO)_{10}]$ [8,9], $[M_3(\mu\text{-}H)\{\mu_2\text{-}S(CH_2)_3Si(OMe)Me_2\}(CO)_{10}]$ and $[M_3(\mu\text{-}H)\{\mu_2\text{-}S(CH_2)_3SiMe_2O(anchored)\}(CO)_{10}]$ (M = Ru, Os) [7] has been previously synthesized and spectroscopically characterized.

Models for silica-tethered organometallic catalysts may be synthesized by functionalizing thiol-substituted silsesquioxanes with organometallic clusters. These species are discrete molecules, soluble in readily available solvents and thus easily characterized and studied. Here we report the synthesis of $[Si_8O_{12}R_8]$-type silsesquioxanes containing *covalently bonded* metal carbonyl clusters.

2. Experimental

2.1. General data

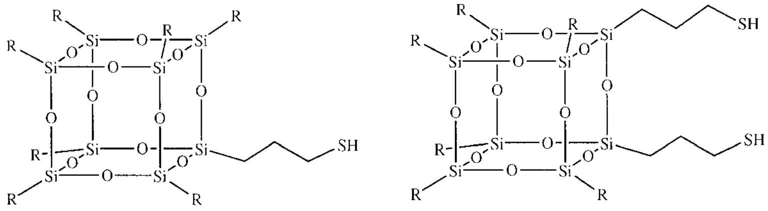
All reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from the usual drying agents prior to use. Separations were carried out by thin layer chromatography in air with Kieselgel 60-PF-254 (Merck). The starting materials $[Ru_3(CO)_{10}(NCMe)_2]$ [10], $[Os_3(CO)_{10}(NCMe)_2]$ [11], $[Si_8O_{12}(Pr^n)_7(C_3H_6SH)]$ **1** [12], $[Si_8O_{12}(Pr^n)_6\{o\text{-}(C_3H_6SH)_2\}]$ **2** [12], and $[Si_8O_{12}(C_3H_6SH)_8]$ **3** [13], were prepared according to the literature. NMR spectra were recorded either on Bruker AM 300 (^1H at 300 MHz, ^{13}C at 75.5 MHz) or Varian Unity AM 500 (^{29}Si 99.3 MHz) spectrometers; ^1H, ^{13}C and ^{29}Si shifts are reported with respect to $\delta = 0$ ppm for $SiMe_4$ and all downfield shifts are positive. Infrared spectra were obtained using Bruker IFS66 or Perkin-Elmer FT 1710 spectrophotometers; laser desorption mass spectra were obtained using a LaserTec (TOF) instrument (α cinnamic acid as matrix) or by Dr. Ballantine at the EPSRC facility at the University of Swansea (for +FAB) on a Varian E 109 instrument. Microanalyses were obtained from the Service Central de Microanalysis du CNRS and the microanalytical department of the Inorganic Chemistry Laboratory, University of Oxford.

3. Preparations

$[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}]$ **4**: $[Ru_3(CO)_{10}(NCMe)_2]$ (67 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (80 cm^3) and MeCN (20 cm^3) and then filtered through silica into a flask containing $[Si_8O_{12}(Pr^n)_7(C_3H_6SH)]$ (79 mg, 0.10 mmol). An immediate colour change from orange–yellow to yellow was observed. The solution was stirred for a further 15 min until no S–H absorptions were visible by IR spectroscopy. The solvent was removed in vacuo, the yellow solid dissolved in hexane and then filtered through silica to give yellow $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}]$ **4**. Yield 110 mg, 80%. The reaction also yielded small amounts ($< 10\%$) of $[H_2Ru_3(CO)_9S]$ [14]. The compound **4** can be also be purified by TLC using hexane as eluent.

$[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)Os_3(\mu\text{-}H)(CO)_{10}\}]$ **5** was prepared as a yellow powder by the same method from $[Os_3(CO)_{10}(NCMe)_2]$ (93 mg, 0.10 mmol) and $[Si_8O_{12}(Pr^n)_7(C_3H_6SH)]$ (79 mg, 0.10 mmol). Yield 141 mg, 86%. Small amounts of $[H_4Os_4(CO)_{12}]$ were produced in the reaction and identified in a ^1H NMR spectrum of the crude reaction mixture.

$[Si_8O_{12}(Pr^n)_6\{o\text{-}(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ **6**: $[Ru_3(CO)_{10}(NCMe)_2]$ (71 mg, 0.106 mmol) was dissolved in CH_2Cl_2 (160 cm^3) and MeCN (20 cm^3) and then filtered through silica into a flask containing $[Si_8O_{12}(Pr^n)_6\{o\text{-}(C_3H_6SH)_2\}]$ **2**, (45 mg, 0.054 mmol). An immediate colour change from orange–yellow to yellow was observed and the solution stirred for a further 15 min until no S–H absorptions were visible by IR spectroscopy. The solvent was



$R = C_3H_7$, **1**

$R = C_3H_6SH$, **3**

$R = C_3H_7$, **2**

Fig. 2. Schematic representation of silsesquioxanes **1**, **2**, and **3**.

removed in vacuo, the yellow solid dissolved in hexane and then filtered through silica to yield $[Si_8O_{12}(Pr^n)_6\{o\text{-}(\mu_2\text{-}C_3H_6S)Ru_3(\mu\text{-H})(CO)_{10}\}_2]$ **6**. Yield 88 mg, 82%. Compound **6** may also be purified by TLC using hexane as eluent.

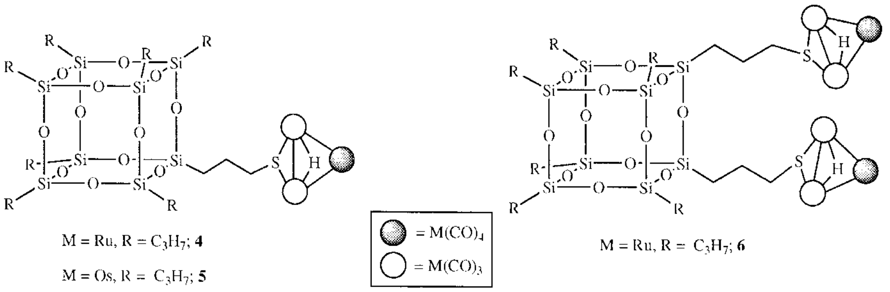
$[Si_8O_{12}(C_3H_6SH)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-H})(CO)_{10}\}_2]$ **7**: $[Ru_3(CO)_{10}(NCMe)_2]$ (133 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (160 cm^3) and MeCN (20 cm^3) and then filtered through silica into a flask containing $[Si_8O_{12}(C_3H_6SH)_8]$ (102 mg, 0.10 mmol). An immediate colour change from orange–yellow to yellow was observed and the solution stirred for a further 1 h. The solvent was removed in vacuo to yield $[Si_8O_{12}(C_3H_6SH)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-H})(CO)_{10}\}_2]$ **7**. Yield 161 mg, 74%.

$[Si_8O_{12}\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-H})(CO)_{10}\}_8]$ **8**: $[Ru_3(CO)_{10}(NCMe)_2]$ (1.064 g, 1.6 mmol) was dissolved in CH_2Cl_2 (200 cm^3) and MeCN (30 cm^3) and then filtered through silica into a flask containing $[Si_8O_{12}(C_3H_6SH)_8]$ (204 mg, 0.2 mmol). An immediate colour change from orange–yellow to orange–red was observed and this deepened to dark red whilst being stirred for 3 h. The solvent was removed in vacuo and the residue washed with petroleum ether (40/60) and then ether. The orange–brown residue was pumped to dryness and characterized as $[Si_8O_{12}\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-H})(CO)_{10}\}_8]$ **8**. Yield 874 mg, 77%.

4. Results and discussion

The thiol-substituted silsesquioxanes $[Si_8O_{12}(Pr^n)_7(C_3H_6SH)]$, **1**, $[Si_8O_{12}(Pr^n)_6\{o\text{-}(C_3H_6SH)_2\}]$, **2** and $[Si_8O_{12}(C_3H_6SH)_8]$, **3**, (Fig. 2) react rapidly with activated clusters of the type $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru, Os). In each case oxidative addition of the SH moiety to the metal cluster occurs, with concomitant loss of the labile MeCN ligands, resulting in the formation of $[M_3(\mu\text{-H})(\mu_2\text{-SR})(CO)_{10}]$ clusters (R = silsesquioxane). This transformation is readily observed by IR spectroscopy as the species $[M_3(\mu\text{-H})(\mu_2\text{-SR})(CO)_{10}]$ exhibit a distinctive pattern of absorptions in the CO stretching region, which is virtually independent of R [8,9], shifting slightly upon changing the metal from ruthenium to osmium. Reaction of the thiol functionality is also evidenced by the absence of any S–H stretches in the IR spectra of metal carbonyl substituted silsesquioxanes.

The monothiol-substituted silsesquioxane, **1**, can be converted to $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)M_3(\mu\text{-H})(CO)_{10}\}]$ (Fig. 3) by reaction with one equivalent of $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru, **4**, or M = Os, **5**). Spectroscopic and analytical data for compounds **4** and **5** are detailed in Table 1. The ^1H NMR spectra display two sets of signals, in the ratio 1:7, assignable to the $M_3(\mu_2\text{-}SCH_2CH_2CH_2)$ and $\text{-}CH_2CH_2CH_3$ linkages, respectively. Transfer of the thiol proton to the metal cluster framework is confirmed by the presence of a high frequency resonance typical for this



$M = Ru, R = C_3H_7$; **4**

$M = Os, R = C_3H_7$; **5**

$M = Ru, R = C_3H_7$; **6**

Fig. 3. Schematic representation of the cluster-substituted silsesquioxanes **4**, **5** and **6**.

Table 1
Analytical and spectroscopic data for compounds **4**, **5**, **6**, **7** and **8**

Complex[a]	Spectroscopic Data[b]
4 $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}]$ C, 29.5 (29.7); H, 3.90 (4.07); S, 2.2 (2.32) Mass: m/z 1376 [**4**], 1348 [**4**-CO], 1321 [**4**-2CO]	IR: 2950–2850 w, 2104 w, 2064 vs, 2056 m, 2041 w, 2025 vs, 2006 m, 1994 w, 1103 vs ^{1}H: 2.17 [2H, t J7 Hz, $C\mathbf{H_2}S$], 1.77 [2H, tt J7, 7 Hz, $C\mathbf{H_2}CH_2S$], 1.49 [14H, m, $C\mathbf{H_2}CH_3$), 0.98 [21H, m, $C\mathbf{H_3}$], 0.76 [2H, t, $C\mathbf{H_2}CH_2CH_2S$], 0.63 [14H, m, $SiC\mathbf{H_2}$], -15.43 [1H, s, Ru–**H**–Ru] ^{13}C: 204.33 [s, CO], 202.64 [s, CO], 198.18 [s, CO], 192.95 [s, CO], 191.72 [s, CO], 185.54 [s, CO], 56.98 [s, $\mathbf{C}H_2S$], 26.71 [s, $\mathbf{C}H_2CH_2S$], 17.25 [s, $Si\mathbf{C}H_2CH_2CH_3$], 16.29 [s, $SiCH_2\mathbf{C}H_2CH_3$], 14.34 [s, $SiCH_2CH_2\mathbf{C}H_3$], 11.71 [s, $\mathbf{C}H_2CH_2CH_2S$] ^{29}Si: -67.22 [d, J5 Hz], -67.37 [d, J10 Hz], -67.42 [d, J11 Hz]
5 $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)Os_3(\mu\text{-}H)(CO)_{10}\}]$ C, 24.6 (24.8); H, 3.3 (3.4); S, 1.8 (1.95) Mass: m/z 1642 [**5**]	IR: 2950–2850 w, 2108 w, 2066 vs, 2058 m, 2019 vs, 1998 m, 1983 w, 1112 vs ^{1}H: 2.42 [2H, t J7 Hz, $SC\mathbf{H_2}$], 1.73 [2H, tt J7, 7 Hz, $C\mathbf{H_2}CH_2S$], 1.45 [14H, m, $SiCH_2C\mathbf{H_2}$], 0.97 [21H, m, $C\mathbf{H_3}$], 0.73 [2H, t, J7 Hz, $C\mathbf{H_2}CH_2CH_2S$], 0.65 [14 H, m, $SiC\mathbf{H_2}CH_2CH_3$], -17.36 [1H, s, Os–**H**–Os] ^{13}C: 180.68 [s, CO], 180.33 [s, CO], 176.26 [s, CO], 173.71 [s, CO], 170.46 [s, CO], 169.25 [s, CO], 58.02 [s, $\mathbf{C}H_2S$], 26.21 [s, $\mathbf{C}H_2CH_2S$], 17.35 [s, $Si\mathbf{C}H_2CH_2CH_3$], 16.35 [s, $SiCH_2\mathbf{C}H_2CH_3$], 14.33 [s, $SiCH_2CH_2\mathbf{C}H_3$], 11.43 [s, $\mathbf{C}H_2CH_2CH_2S$]
6 $[Si_8O_{12}(Pr^n)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ C, 26.3 (26.5); H, 2.7 (2.81); S, 3.1 (3.22) Mass: m/z 1990 [**5**], 1971 [**5**-CO], 1944 [**5**-2CO], 1903 [**5**-3CO], 1875 [**5**-4CO], 1850 [**5**-5CO]	IR: 2934 m, 2860 w, 2104 w, 2064 vs, 2055 s, 2025 vs, 2006 m, 1997 w, 1100 vs ^{1}H: 2.66 [4H, t, $SC\mathbf{H_2}$], 1.90 [4H, m, $CH_2C\mathbf{H_2}CH_2S$), 1.63 [12H, m, $SiCH_2C\mathbf{H_2}CH_3$), 1.03 [18H, m, $C\mathbf{H_3}$], 0.85 [16H, m, $SiC\mathbf{H_2}$), -15.41 [2H, s, Ru–**H**–Ru]
7 $[Si_8O_{12}(C_3H_6SH)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ C, 25.4 (25.2); H, 2.8 (2.67); S, 12.0 (12.2) Mass: m/z 2097 [**7**-3CO], 2069 [**7**-4CO], 2097 [**7**-5CO], 2040 [**7**-5CO]	IR:[c] 2960 w, 2920 m, 2892 w, 2554 w, 2103 w, 2064 vs, 2055 s, 2021 vs, 2006 m, 1970 w, 1265 m, 1115 vs ^{1}H: 2.55 [12H, td J7, 7 Hz, $C\mathbf{H_2}SH$], 2.16 [4H, t J7 Hz, $C\mathbf{H_2}SRu_3$], 1.73 [16H, m, $SiCH_2C\mathbf{H_2}$], 1.36 [6H, t J7 Hz, S**H**], 0.76 [16H, m, $SiC\mathbf{H_2}$], -15.35 [2H, s, Ru–**H**–Ru]
8 $[Si_8O_{12}\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_8]$ C, 22.1 (22.0); H, 1.04 (0.99); S, 4.63 (4.51)	IR:[d] 2963 w, 2940 w, 2555 w, 2106 w, 2056 vs, 2017 vs, 2001 vs, 1996 m(sh), 1262 m, 1105 s(br) ^{1}H: 2.54 [16H, s(br), $C\mathbf{H_2}SRu$], 1.76 [16H, s(br), $SiCH_2C\mathbf{H_2}$], 0.77 [16H, m, $SiC\mathbf{H_2}$], -15.32 [8H, s, Ru–**H**–Ru]

[a] Analytical data given as found (calculated) in percent. Mass spectra data given as: m/z [assignment], Fast Atom Bombardment (NOBA matrix).
[b] IR data (cm^{-1}) determined in hexane solution, unless otherwise stated. NMR data ($CDCl_3$, 298 K), unless otherwise stated, given as: chemical shift (δ) [relative intensity, multiplicity (J in Hz), assignment].
[c] CH_2Cl_2.
[d] KBr disc.

family of molecules (Table 2). Further evidence that the S–H bond has oxidatively added to the M_3 core is manifest in the low frequency region of the ^{1}H NMR spectra; the triplet of doublets signal assigned to the $C\mathbf{H_2}SH$ protons (δ 2.55 in compound **1**) becomes a triplet (δ 2.16, compound **4**; δ 2.42, compound **5**) once reaction has occurred. The ^{29}Si{^{1}H} NMR spectrum of compound **4** is not very informative and exhibits three overlapping doublet resonances at δ -67.22, -67.37 and -67.42 ppm. This can be compared to the spectrum of the monosubstituted silsesquioxane **1** which exhibits resonances at δ -66.05, -66.13 and -66.60 ppm [12]. In both cases two of the four Si resonances are superimposed. The *bis*-substituted derivative, $[Si_8O_{12}(Pr^n)_6\{o\text{-}(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$, **6**, has also been

Table 2
Highfield ^{1}H NMR spectroscopic data for $[M_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}SR)]$ clusters

Compound	^{1}H NMR δ (ppm)
$[Ru_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}SEt)]^8$	−15.40
$[(Si_8O_{12})(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}]$ **4**	−15.43
$[(Si_8O_{12})(Pr^n)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ **6**	−15.41
$[(Si_8O_{12})(C_3H_6SH)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$ **7**	−15.35
$[(Si_8O_{12})\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_8]$ **8**	−15.32
$[Os_3(\mu\text{-}H)(CO)_{10}(\mu_2\text{-}SEt)]^9$	−17.50
$[(Si_8O_{12})(Pr^n)_7\{\mu_2\text{-}S(C_3H_6)Os_3(\mu\text{-}H)(CO)_{10}\}]$ **5**	−17.36

synthesized by the same route from $[Si_8O_{12}(Pr^n)_6\{o\text{-}(C_3H_6SH)_2\}]$, **2**, and displays similar spectroscopic properties (Table 1).

Rather surprisingly, despite their high molecular weights, compounds **4**, **5** and **6** are readily soluble in hexane and can be purified by TLC using hexane as eluent. This is in stark contrast to the behaviour of silsesquioxanes **1** and **2**, which are sparingly soluble in acetone and CH_2Cl_2. Presumably, this difference can be ascribed to the polar -SH units present in the latter silsesquioxanes. The large bulk of the silicon–oxygen cage does not appear to perturb the chemical environment of the cluster moiety in these compounds. The propyl chain is obviously a sufficiently long spacer to prevent steric interactions between the metal cluster and the $\{Si_8O_{12}\}$ cage portions of the molecule. The most likely candidate in which to observe steric effects in solution is the disubstituted silsesquioxane, **6**, where the $\{Ru_3\}$ clusters are tethered to adjacent corners of the $\{Si_8O_{12}\}$ cage. However, the spectral data for this molecule exhibits no unusual features, indicating that the propyl chains are sufficiently flexible to allow the two $\{Ru_3\}$ cluster units to remain distinct. These reactions are very ‘clean’ and, in addition to the desired products, only trace amounts of $[H_2Ru_3(CO)_9S]$ [14] and $[H_4Os_4(CO)_{12}]$ [15] were detected and identified by ^{1}H NMR spectroscopy.

The octathiol-substituted silsesquioxane, **3**, also behaves in a similar fashion to its mono- and di-substituted congeners. When $[Si_8O_{12}(C_3H_6SH)_8]$, **3**, is reacted with two equivalents of $[Ru_3(CO)_{10}(NCMe)_2]$ a yellow–orange powder is obtained, the spectroscopic data of which are in good agreement with the formula $[Si_8O_{12}(C_3H_6SH)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$, **7**, (Table 1). In the ^{1}H NMR spectrum signals assignable to two distinct propyl chains, $SiCH_2CH_2CH_2SX$ ($X = H$ or $\{Ru_3(\mu\text{-}H)(CO)_{10}\}$) are visible. Integration of the relative intensities of the resonances due to the $C\mathbf{H_2}SX$ protons confirms that metal carbonyl cluster substitution has occurred at two thiol functionalities; δ 2.55 (12*H*, td, $CH_2CH_2C\mathbf{H_2}SH$), 2.16 (4H, t, $Ru_3(\mu\text{-}SC\mathbf{H_2}CH_2CH_2)$). As can be seen from the ^{1}H NMR spectra of monosubstituted silsesquioxanes, incorporation of the cluster moiety has little effect upon the propyl chains occupying the *ortho*, *meta* and *para* positions and the signals assigned to these protons are indiscernible. Thus, although the simplicity of the ^{1}H NMR spectrum of compound **7** is consistent with the selective formation of the *para* isomer, we are unwilling to rule out the possibility that the spectrum is due to a mixture of isomers. Attempts to crystallize compound **7** by dissolution in CH_2Cl_2 and cooling to 0°C resulted in the formation of a white solid, **3**, and an orange–brown insoluble precipitate. An IR spectrum of the orange–brown solid (KBr disc) indicates that the cluster motif, $[Ru_3(\mu\text{-}H)(\mu_2\text{-}SR)(CO)_{10}]$, is retained and that no S–H linkages remain. These results are consistent with a redistribution of the organometallic clusters (Eq. (1)):

$$\begin{tikzcd} \underset{\mathbf{3}}{4\,[Si_8O_{12}(C_3H_6SH)_8]} + 8\,[Ru_3(CO)_{10}(NCMe)_2] \arrow[r] & \underset{\mathbf{7}}{4[Si_8O_{12}(C_3H_6SH)_6\{\mu_2\text{-}S(C_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]} \arrow[d, "CH_2Cl_2"] \\ & \underset{\mathbf{3}}{3\,[Si_8O_{12}(C_3H_6SH)_8]} + \underset{\mathbf{8}}{[Si_8O_{12}\{\mu_2\text{-}S(C_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_8]} \end{tikzcd} \qquad (1)$$

to form the octasubstituted species, $[Si_8O_{12}\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_8]$, in addition to silsesquioxane **3**. This suggests that the thermodynamics governing oxidative addition of RSH across the M–M bond are very favourable.

Reaction of $[Si_8O_{12}(C_3H_6SH)_8]$ with eight equivalents of $[Ru_3(CO)_{10}(NCMe)_2]$ leads to the formation of a orange–brown solid. The IR spectroscopic data and elemental analyses of this species are consistent with a molecular formula of $[Si_8O_{12}\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_8]$, **8**. The ^1H NMR spectrum of compound **8** exhibits a single high frequency signal at δ −15.32 ppm, concordant with the proposed formula although the propyl resonances were very broad and their multiplicities could not be resolved, even using extended relaxation times. This may be due to restricted tumbling of the propyl chains once an outer shell of eight $\{Ru_3(\mu\text{-}H)(\mu_2\text{-}S)(CO)_{10}\}$ units has been formed around the Si_8O_{12} core. Nevertheless, the absence of any S–H functionalities combined with good elemental analyses supports the proposed formula.

5. Conclusion

The mono-, di- and octathiol-functionalised silsesquioxanes rapidly react with $[M_3(CO)_{10}(NCMe)_2]$, R = Ru, Os, to yield products of the type $[M_3(\mu\text{-}H)(\mu_2\text{-}SR)(CO)_{10}]$ where R contains the silsesquioxane cage. The size of the silsesquioxane cage has little effect on the spectroscopic properties of the cluster moiety compared to analogous species where R = alkyl, aryl. The mono- and bis-derivatives are stable, readily soluble and easy to handle compounds and consequently provide convenient models for silica tethered clusters.

6. Summary

The thiol-functionalized silsesquioxanes, $[Si_8O_{12}(Pr^n)_{8-x}(C_3H_6SH)_x]$ ($x = 1$, 2 or 8; $Pr^n = C_3H_7$) readily react with the activated clusters $[M_3(CO)_{10}(NCMe)_2]$ (M = Ru, Os) to form metal carbonyl cluster substituted silsesquioxanes. The compounds $[Si_8O_{12}(Pr^n)_7\{(\mu_2\text{-}SC_3H_6)M_3(\mu\text{-}H)(CO)_{10}\}]$, $[Si_8O_{12}(Pr^n)_6\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_2]$, and $[Si_8O_{12}(C_3H_6SH)_x\{(\mu_2\text{-}SC_3H_6)Ru_3(\mu\text{-}H)(CO)_{10}\}_{8-x}]$ ($x = 6$, 0) have been synthesized and characterized by IR, NMR spectroscopies and elemental analyses.

Acknowledgements

We are grateful to the Royal Society/CNRS Exchange Programme for a post-doctoral grant to J.R.G., and to the CNRS and the European Commission (CHRX-CT93-0277) for financial support.

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