Silsesquioxanes as Ligands for Gold Clusters☆

Günter Schmid*[a], Raphael Pugin[a], Jan-Olle Malm[b], and Jan-Olov Bovin[b]

Institut für Anorganische Chemie, Universität Essen[a],
Universitätsstrasse 5−7, D-45117 Essen, Germany
Fax: (internat.) + 49(0)201/183-2402
E-mail: guenter.schmid@uni-essen.de

National Center for HREM, Inorganic Chemistry 2, Lund University[b],
P.O. Box 124, S-22100 Lund, Sweden
Fax: (internat.) + 46(0)46/2224012
E-mail: jan-olle.malm@oorg2.lth.se

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A new type of gold cluster has been synthesized using the silsesquioxane derivative (cyclopentyl)$_7$Si$_8$O$_{12}$(CH$_2$)$_3$SH (T_8-OSS−SH) to exchange the PPh_3 ligands in $(PPh_3)_{12}Au_{55}Cl_6$ by T_8-OSS−SH quantitatively. This exchange causes several important changes in the physical and chemical behavior of the compound. Owing to the presence of cyclopentyl substituents, the cluster becomes soluble in non-polar solvents such as pentane. The stability of this compound compared with that of the PPh_3-protected cluster is considerably higher meaning that decomposition in solution, and even under the high-energetic irradiation in the microscope, is not observed over longer periods of time. The increase in the total diameter from 2.1 to ca. 4.4 nm is probably responsible for these advantageous properties, supported by strong S−Au bonds. The increase in size is also expressed as an increase in the activation energy for electron-tunneling processes through the ligand shells of neighboring clusters in a densely packed pellet. This increase is from 0.16 eV for $(PPh_3)_{12}Au_{55}Cl_6$ to 0.26 eV for the T_8-OSS−SH-protected cluster.

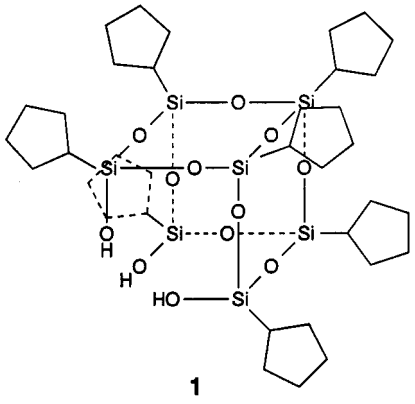
Introduction

In nanoscale structures, the effect of size on the electronic properties (Quantum Size Effect) is an active area of research.[1][2] The main motivation for this work is to understand the change in the electronic properties on the way from the bulk to the nanosized species. By reducing the size of a three-dimensional metal particle, initially having bulk properties, to a zero-dimensional arrangement containing dozens or a few hundreds of atoms, a dramatic change in the electronic properties is observed. The electrons, which are free in all three dimensions, now behave like electrons in a box and the continuous density of states is replaced by a more discrete energy level structure. This band-gap structure can be considered as an intermediate between the typical band structure in the bulk and the bonding and antibonding system in a molecular state. In this way, if a metal cluster has a diameter in the order of the de Broglie wavelength of the valence electrons, the metal core could be regarded as a zero-dimensional quantum dot.

For the two-shell cluster $(PPh_3)_{12}Au_{55}Cl_6$, physical investigations have clearly indicated the existence of Quantum Size Effects.[2][3] Electronic inter-cluster tunneling processes through the ligand shell have been observed and are caused by an electron jump from one metal island to the other.

This class of small metal particle needs a protective ligand shell to prevent uncontrolled growth and the formation of macroscopic metal particles. It therefore seemed interesting to modify the nature and the size of this ligand shell in order to evaluate the influence of the latter on the chemical, physical, and electronic properties. Our investigations are based principally on functionalized organosilsesquioxane ligands (OSS) for several reasons. Firstly, it is likely that they should represent a satisfactory class of spacers to obtain well-separated ligand-stabilized quantum dots. On the other hand, the incomplete T_7-OSS (**1**; T = number of $RSiO_{3/2}$ units), which is used as a precursor in the synthesis of different functionalized OSS, has been subject to great attention since this molecule has a close similarity with the β-cristobalite form of silica.[4]

Figure 1. Formalized structure of the incompletely condensed silsesquioxane (cyclopentyl)$_7$Si$_7$O$_9$(OH)$_3$ (**1**)



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During the last few years, Feher et al. have focused a great deal of effort to describe a new approach for modeling the chemistry of silica-supported transition-metal complexes.[5][6] After corner-capping reactions with metal complexes, they obtained representative models for catalysts supported on hydroxylated silica. It appears fundamental to try to adapt this approach to cluster chemistry. Previous work with the functionalized T_8-OSS−ethyldiphenylphosphane ligand has already given good precursors to achieve gold clusters but has never led to the isolation of such materials.[7] We have therefore extended these studies with SH-functionalized OSS. We describe here the synthesis of a new thiol-substituted OSS that is obtained by treating 3-mercaptopropyltrimethoxysilane with the incompletely condensed $(cyclopentyl)_7Si_7O_9(OH)_3$. Subsequent use of this functionalized OSS as a protective ligand has allowed us to isolate a new Au_{55} cluster whose numerous advantages are reported.

Results and Discussion

Trichloro(cyclopentyl)silane, $(cyclopentyl)SiCl_3$, is obtained by hydrosilylation of cyclopentene and trichlorosilane in the presence of H_2PtCl_6 as catalyst.[8] The hydrolysis of $(cyclopentyl)SiCl_3$ in a mixture of water/acetone leads to the incompletely condensed $(cyclopentyl)_7Si_7O_9(OH)_3$ (**1**) after two weeks. The reaction between **1** and the (3-mercaptopropyl)trimethoxysilane allows the isolation of the thiol-substituted OSS **2**, whose elemental analysis, IR, ^{1}H-, $^{13}C\{^1H\}$-, and $^{29}Si\{^1H\}$-NMR data are given in the Experimental Section.

Marsmann et al. have already reported the synthesis of a similar thiol-functionalized OSS by co-hydrolysis of trichloro(*n*-propyl)silane with the (3-mercaptopropyl)trimethoxysilane in a 7:1 ratio.[9][10] In the case reported here, we have preferred to perform two successive hydrolyses in order to avoid the statistically possible formation of polythiol-functionalized OSS as products of a competitive reaction.

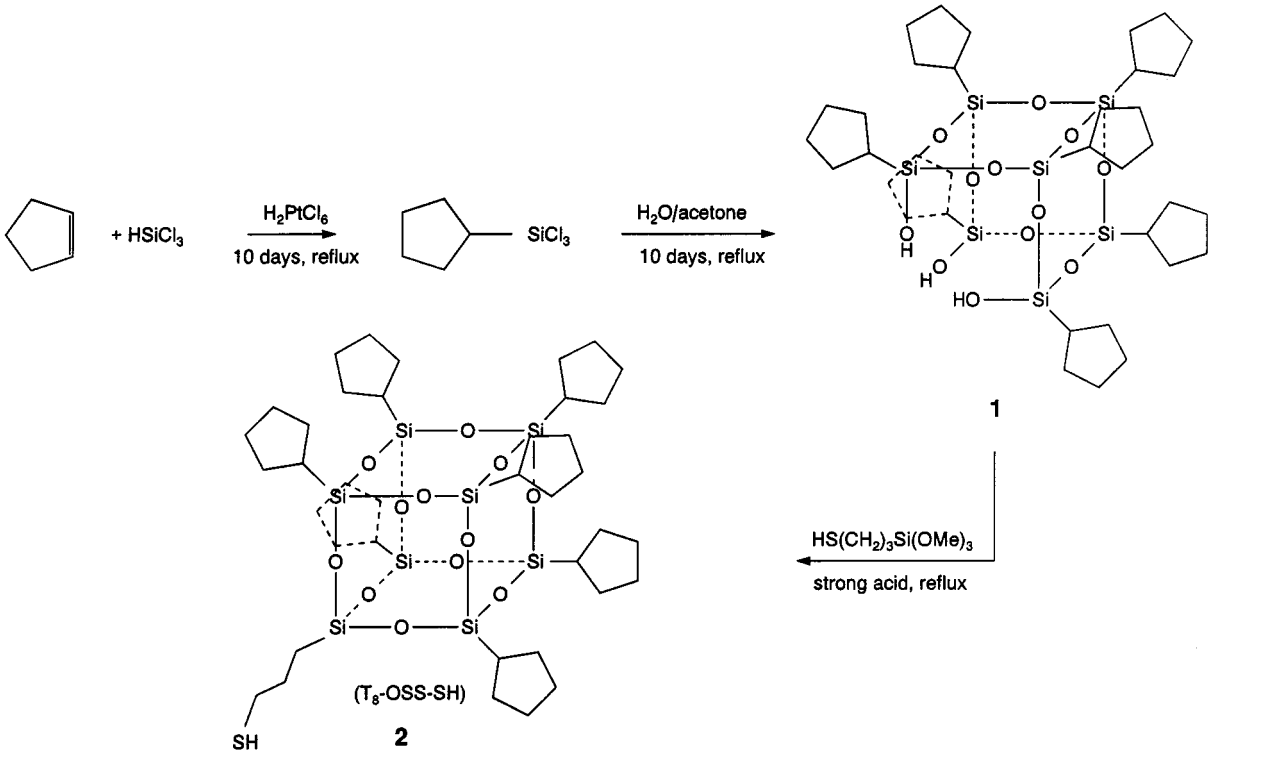
Although it is difficult to evaluate the exact size of **2** due to the flexibility of the propyl chain, the total diagonal length of this ligand should be in a range of 1.4−1.5 nm. As explained in the introduction, this size allows one to predict the possibility of obtaining well-separated quantum dots.

In previous works we described the exchange of the PPh_3 ligand shell in $(PPh_3)_{12}Au_{55}Cl_6$ by $Ph_2PC_6H_4SO_3Na$ in a phase-transfer reaction to give a water-soluble gold cluster.[11] Owing to the well-known affinity of thiol functions to gold atoms[12] and the labile nature of the phosphane ligands bound to the surface gold atoms,[13] we tried to use this method to synthesize thiol-functionalized OSS gold clusters (Equation 1).

$$(PPh_3)_{12}Au_{55}Cl_6 + 12\ T_8\text{-OSS}-SH \rightarrow (T_8\text{-OSS}-SH)_{12}Au_{55}Cl_6\ (\mathbf{3}) + 12\ PPh_3 \quad (1)$$

This approach has been successfully applied and allowed us to obtain the expected cluster in almost quantitative yield. However, to prevent coalescence special precautions should be taken (see Experimental Section). ^{1}H-, $^{31}P\{^1H\}$-NMR spectroscopy, and elemental analysis prove that all

Scheme 1. Synthesis of the silsequioxane ligand $(cyclopentyl)_7Si_8O_{12}[CH_2]_3SH$ (T_8-OSS−SH) (**2**)



twelve phosphane ligands are replaced by thiol-functionalized oligosilsesquioxanes.

The most remarkable changes in behavior are found in the solubility and in the stability of this new cluster. It is soluble in pentane as well as in dichloromethane and the solutions are stable over several months. This behavior is in contrast to the very labile $(PPh_3)_{12}Au_{55}Cl_6$ cluster which degrades, if dissolved, in the course of hours. Transmission electron microscopy (TEM) investigations show monodisperse particles (Figure 2).

Figure 2. Transmission electron microscopy image of a ca. 145 × 200 nm area of randomly oriented $(T_8\text{-OSS}-SH)_{12}Au_{55}Cl_6$ clusters

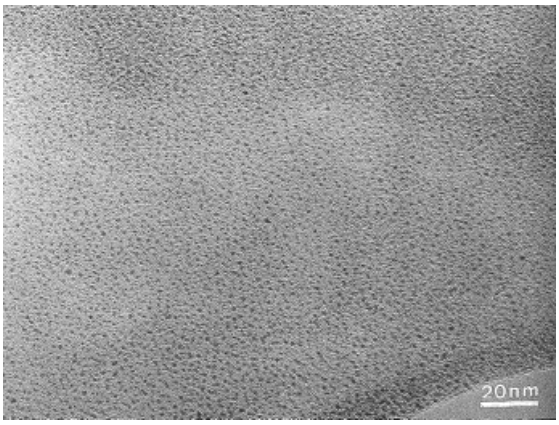
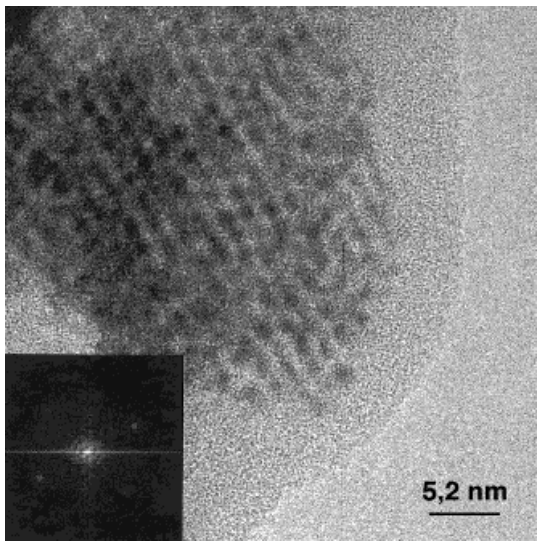


Figure 3 shows a high resolution electron microscopy (HRTEM) image of an area of a well-ordered two-dimensional arrangement of $(T_8\text{-OSS}-SH)_{12}Au_{55}Cl_6$ (**3**) clusters. The formation of ordered monolayers of nanosized metal particles has been observed previously.[14] Ordering seems to happen preferentially if clusters can arrange from solution on a support without chemical interactions between each other and the surface. In this way ideal arrangements may occur owing to the mobility of the clusters. If strong chemical interaction between cluster and surface is provoked organization is clearly hindered, as has been shown in numerous studies of cluster assemblies on chemically modified surfaces.[15] The quality of the ordered area in Figure 3 also becomes visible from a Fourier transform (insert in Figure 3). The angle between the visible peaks can be measured as ca. 75°. The size of the individual clusters can be determined as 1.4 ± 0.1 nm, a value that is in good agreement with the calculated value (1.4 nm). HRTEM results of this quality with other Au_{55} clusters, e.g. $(PPh_3)_{12}Au_{55}Cl_6$, have not been obtained in the past due to very fast coalescence and aggregation processes occurring under the influence of the electron beam[16] and so have led to misinterpretation of HRTEM work by other groups.[17]

The increase in the thickness of the ligand shell on changing from PPh_3 to T_8-OSS−SH, i.e. from 2.1 to ca. 4.4 nm for the total size of the cluster, leads to considerable changes in the interelectronic relation between neighboring clusters. Recently, we determined the activation energy for electron-tunneling processes in densely packed Au_{55} cluster pellets containing different ligand shells or spacer molecules,[18] and this resulted in a linear relation between cluster spacing and activation energy. $(T_8\text{-OSS}-SH)_{12}Au_{55}Cl_6$ fits well into this series and shows a Coulomb gap of 0.26 eV, corresponding to a distance of the cluster nuclei of ca. 3 nm, a value that is in agreement with the theoretical value of 4.4 nm − 1.4 nm = 3.0 nm.[19]

Figure 3. High resolution transmission electron microscopy image of a 52 × 52 nm area of oriented $Au_{55}(T_8\text{-OSS}-SH)_{12}Cl_6$ clusters; the insert shows the Fourier transform of that area



These results impressively show that a change in the nature of the ligand molecules causes drastic effects in the physical properties. The solubility in pentane is explained by the presence of many non-polar cyclopentyl groups on the ligand. To understand the unusual stability we should consider the total cluster diameter including the metal gold core and the ligand shell. The diameter is close to 4.4 nm [2.1 nm for $(PPh_3)_{12}Au_{55}Cl_6$] and this is probably the main reason that agglomeration among clusters is efficiently prevented. However, this phenomenon is also due to the good affinity of thiols for gold atoms, even if at present we cannot assert anything about the nature of the sulfur−gold bond. Indeed two approaches can be considered. The first involves an elimination or migration of hydrogen and the formation of a covalent bond between gold and the ligand. The second is to consider an interaction of intact thiol with gold atoms and the formation of a dative bond.

Theoretically, there is also one other way that should allow us to synthesize this new cluster by a phase-transfer reaction, according to Equation 2.

$$(PPh_2C_6H_4SO_3Na)_{12}Au_{55}Cl_6 + 12\ T_8\text{-OSS}-SH \rightarrow (T_8\text{-OSS}-SH)_{12}Au_{55}Cl_6 + 12\ PPh_2C_6H_4SO_3Na \quad (2)$$

However, we did not observe any exchange of $PPh_2C_6H_4SO_3Na$ by T_8-OSS−SH. Despite this failure we do not believe that $PPh_2C_6H_4SO_3Na$ ligands have better affinity to gold atoms than T_8-OSS−SH. One hypothesis could be to consider that non-polar thiol-functionalized OSS encounters difficulties in crossing the water phase and the water layer surrounding the water-soluble gold cluster. The fact that no phase-transfer reaction is observed be-

tween $(T_8\text{-OSS}-SH)_{12}Au_{55}Cl_6$, dissolved in dichloromethane, and $PPh_2C_6H_4SO_3Na$, dissolved in water, supports this assumption and indicates clearly that we cannot have any doubts about the affinity of thiol groups for gold atoms.

Following this synthetic work, a number of investigations were undertaken to assess physical properties and applications.

In nanoporous membranes science, the size and the high stability of this newly synthesized gold cluster turned out to be very advantageous. Recent works have shown that in alumina membrane pores near 7 nm in diameter can be filled with this new Au_{55} cluster, leading to a monodisperse helical arrangement.[20] These results are very promising in terms of the elaboration of 1D quantum wires and are all the more interesting since it is still difficult, in practice, to make smaller pores near 3 nm in order to fill them with usual $(PR_3)_{12}Au_{55}Cl_6$ clusters, the size of which does not exceed 2.1−2.2 nm.

Conclusions

The 3-propylthiol-substituted T_8-OSS (T_8-OSS−SH) has allowed us to synthesize, for the first time and in very high yield, a new Au_{55} cluster stabilized with thiol-functionalized OSS ligands.

This work clearly demonstrates the dramatic influence of this new ligand on the cluster properties. Among these properties, the size and the high stability are the greatest advantages for future physical investigations and applications.

This newly synthesized Au_{55} cluster can also be considered as a valuable model for transition-metal complexes or clusters supported on silica surface since OSS show great similarities with the cristobalite form of silica.

Following these first results many future possibilities can be suggested. It should first be possible to modify the length of the functionalized OSS carbon chain to investigate inter-tunnel conductivity and quantum-size effects. Moreover, the functional group could also be changed to synthesize other ligands to stabilize different metal centers in clusters or colloids. In this way the trisilanol part of the incompletely condensed $(cyclopentyl)_7T_7(OH)_3$ allowed us to complex nickel clusters.[21]

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Experimental Section

All reactions using air-sensitive reagents and products were performed under nitrogen using standard Schlenk techniques. In the work described here only the (3-mercaptopropyl)trimethoxysilane is highly sensitive in the presence of water and humidity. All solvents were dried and purified using standard procedures. − NMR spectra were recorded with a Bruker DPX working at 300 MHz for ^1H, 75.5 MHz for $^{13}C\{^1H\}$, 121.5 MHz for $^{31}P\{^1H\}$ and 59.6 MHz for $^{29}Si\{^1H\}$. − Infrared spectra were recorded with a Perkin-Elmer FT-IR 1600 spectrometer. − TEM images were recorded using Philips FEG-CM 200 and JEM-4000 EX machines working with 200 and 400 kV accelerating voltages, respectively. − Elemental analyses were carried out by the Analytical Laboratory of the Chemistry Department of the University of Essen.

(Cyclopentyl)SiCl$_3$ and (Cyclopentyl)$_7$T$_7$(OH)$_3$ (**1**): (Cyclopentyl)$SiCl_3$ and **1** were synthesized by well-known literature procedures. **1** was obtained with yields as high as 80% and the purity of this product was assessed by comparison of the NMR and IR data and elemental analysis. − IR: ν = 3200 cm^{-1} m ν(OH), 2949 s, 2865 s, ν(alkyl), 1452 m, 1250 s, δ(C−H), 1120 vs ν_{asym}(Si−O−Si), 498 m ν_{sym}(Si−O−Si). − ^1H NMR ($CDCl_3$): δ = 0.95−1.2 (m, 7 H, CH pentyl), 1.45−1.95 (m, 56 H, CH_2 pentyl), 6.10 (br., 3 H, OH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.97, 22.10, 22.48 (s, CH, pentyl), 26.72, 26.75, 26.78 (s, CH_2), 26.99, 27.01, 27.02 (s, CH_2). $C_{35}H_{66}O_{12}Si_7$ (875.5): calcd. C 48.02, H 7.60; found C 47.98, H 7.68.

(Cyclopentyl)$_7$T$_8$(CH$_2$)$_3$SH (**2**): 272 mg (1.39 mmol) of $HS(CH_2)_3Si(OMe)_3$ was placed in a dry 100-ml three-necked round-bottomed flask filled with nitrogen. 30 ml of dried benzene and, with vigorous stirring, 1.2 g (1.39 mmol) of **1** and 10 mg of *p*-toluenesulfonic acid, diluted in few ml of dried acetone, were added. The solution was stirred for 20 h under reflux, then cooled with an ice bath, concentrated to 10 ml and carefully layered with 60 ml of acetonitrile whereupon **2** precipitated. In order to simplify the filtration, the resulting white solid was allowed to stand overnight in a cold place. After filtration and washing with acetonitrile, pure **2** was dried under vacuum. Yield 1.03 g (78%). − IR: ν = 2950 cm^{-1} s ν(alkyl), 2866 s, 2590 w ν(S−H), 1452 m δ(C−H), 1250 s, 1121 vs, ν_{asym}(Si−O−Si), 733 w ν(Si−CH_2), 693 w, 507 m ν_{sym}(Si−O−Si). − ^1H NMR (C_6D_6): δ = 0.75 (t, 2 H, CH_2−Si), 1.10 (t, 1 H, SH), 1.18−1.28 (m, 7 H, CH-pentyl), 1.45−1.90 (m, 56 H, CH_2-pentyl, m, 2 H, $CH_2-CH_2-CH_2SH$), 2.27 (m, 2 H, CH_2−SH). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 11.38 (d, CH_2−Si), 22.70, 22.71, 22.73 (s, CH-pentyl, 3:3:1), 27.35 (s, CH_2−SH), 27.43, 27.45, 27.46, 27.83, 27.85, 27.86 (s, CH_2-pentyl, 3:3:1:3:1:3), 28.24 (s, CH_2-CH_2SH). − $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = −66.56 (Si−cyclopentyl, 3), −66.59 (Si−cyclopentyl, 1), −66.62 (Si−cyclopentyl, 3), −66.96 ($SiCH_2$, 1). − $C_{38}H_{70}O_{12}SSi_8$ (975.7): calcd. C 46.77, H 7.23; found C 46.35, H 7.32.

(T$_8$-OSS-SH)$_{12}$Au$_{55}$Cl$_6$ (**3**): 20 mg (1.41 μmol) of $(PPh_3)_{12}Au_{55}Cl_6$ and 16.5 mg (16.9 μmol) of **2** were placed in a dry 100-ml three-necked round-bottomed flask filled with nitrogen. 50 ml of dried benzene and, a few minutes later, 5 × 10 ml of dried dichloromethane were added with vigorous stirring. After evaporation of the solvents, the brown product was extracted with 50 ml of pentane and filtered through an ANOTOP® filter (20 nm). The pentane was removed under vacuum and the new gold cluster was precipitated with 30 ml of acetonitrile and filtered. The filtration pad was washed with copious amounts of acetonitrile in order to remove triphenylphosphane and dried overnight under vacuum. At this stage, the black powder obtained still contained an excess of T_8-OSS−SH due to a slight amount of decomposition during the ligand-exchange reaction. Usual purification methods such as extraction, recrystallisation or chromatography did not allow the isolation of the pure gold cluster and mainly led to progressive decomposition. The best way to purify **3** was found to be ultra-fast centrifuging. This method was successfully applied with a concentrated pentane solution with 28000 rpm (34000 *g*) over 24 h. Yield: 20−30 mg (60−90%). − The spectroscopic data (IR, ^1H, $^{13}C\{^1H\}$ NMR) are the same as for the free ligand (see above). ^{31}P-NMR signals could no longer be observed. − $C_{456}H_{840}Au_{55}Cl_6O_{144}S_{12}Si_{96}$ (22754.5): calcd. C 24.07, H 3.72, S 1.69; found C 25.36, H 3.81, S 1.53. − The slight excess of carbon and hydrogen, as well as the

low value for sulphur, can be explained by the presence of solvent molecules on the cluster surface. Indeed, if this cluster is sterically well covered and protected by functionalized OSS there would still be enough space in between to trap a few solvent molecules.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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