Naked Au_{55} Clusters: Dramatic Effect of a Thiol-Terminated Dendrimer

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Abstract: Reaction of the thiol-terminated fourth-generation dendrimer 2-G_4 (96 SH groups) with the gold cluster compound $Au_{55}(PPh_3)_{12}Cl_6$ in a 3:1 molar ratio in dichloromethane results in the formation of bare Au_{55} clusters. The cuboctahedrally shaped Au_{55} particles coalesce to well-formed microcrystals $(Au_{55})_\infty$. The role of the dendrimer is not only to remove the phosphine and chlorine ligands but also to act as an ideal matrix for perfect crystal growth. Transmission electron microscopy (TEM), small- and wide-angle X-ray diffraction (SAXRD and WAXRD) measurements indicate a structure where rows of edge-linked Au_{55} building blocks form a distorted cubic lattice. The X-ray data fit best if a 5% reduction of the Au–Au bond length in the Au_{55} clusters is assumed, in agreement with previous extended X-ray absorption fine structure (EXAFS) measurements. Energy-dispersive X-ray spectroscopy (EDX) analyses and IR investigations show the absence of PPh_3 and Cl in the microcrystals.

Keywords: clusters · dendrimers · gold · superstructures

Introduction

The stabilization of metal clusters by suitable ligand molecules is a necessary and useful way not only to prepare the clusters, but also to make them isolable compounds. The ligand shell prevents coalescence between the metal cores so that their individual characteristics are saved. A ligand-stabilized cluster compound that has been in the center of our research for many years is $Au_{55}(PPh_3)_{12}Cl_6$.[1, 2] As it has been shown by a large number of physical investigations in the course of the last one to two decades, the electronic properties of this cluster are of significance due to its position on the borderline between bulk and molecule. $Au_{55}(PPh_3)_{12}Cl_6$ and a series of derivatives having other ligands instead of PPh_3 show characteristic quantum-size behavior in many respects.[3–7] Most important, it has been shown that they are suited to enable single-electron tunneling (SET) between each other at room temperature.[6] Consequently, these clusters are very promising candidates for future nanoelectronic devices working with quantum dots.

The properties of these clusters are, of course, always linked to the nature of the ligand molecules. We have no information on the electronic behavior of naked Au_{55} clusters. It may be significantly different for cases which lack gold–ligand bonds, since these must influence the electronic life of the cluster core. On the other hand, naked Au_{55} and any other bare clusters will never be available as individual clusters, except in the gas phase. In spite of this it would be highly informative to study the behavior of naked Au_{55} clusters under "realistic conditions" , for example in solution, to learn more about their stability in the uncoated state.

A first hint on the behavior of full-shell clusters was found by us already in 1986, when we succeeded in generating naked Au_{13} clusters by peeling off the outer 42 Au atoms from $Au_{55}(PPh_3)_{12}Cl_6$ together with their ligands by an electrochemical process. Surprisingly we found that Au_{13} nuclei build up superstructures $(Au_{13})_\infty$.[8, 9] Many attempts to remove PPh_3 or other ligands from Au_{55} clusters with conservation of the Au_{55} core have so far failed. Thermal removal, even under high-vacuum conditions, requires temperatures where the clusters decompose. Chemical reactions were accompanied by spontaneous degradation processes.

The known propensity of thiols to form strong bonds with gold has led to several cluster derivatives, where PPh_3 is simply substituted by thiols.[10–12] Now, we tested dendrimers possessing thiol chain ends as stabilizers. It was already reported that organic dendrimers are able to accommodate small copper clusters within the dendrimeric structure,[13] but such experiments have not been carried out yet with regard to the properties of surface functional groups of dendrimers.

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Some of us have reported that the surface of phosphorus-containing dendrimers can be functionalized with a large variety of organic and organometallic groups;[14] thus it was interesting to extend this reactivity to the grafting of thiols. The use of such large ligands leads to the formation of unprecedented and unexpected Au_{55} superstructures.

Results and Discussion

Reaction of the dendrimer 2-G_4, [15] (Figure 1) equipped with 96 SH functions and prepared as shown in Scheme 1, with $Au_{55}(PPh_3)_{12}Cl_6$ in a 3:1 molar ratio, leads to an insoluble black material. The 3:1 ratio turned out to give the best results. Smaller amounts of dendrimer led to less well-developed microcrystals. Transmission electron microscopy (TEM) as well as small- and wide-angle X-ray diffraction (SAXRD, WAXRD) experiments show a very surprising result, namely the formation of superstructures of naked Au_{55} clusters forming perfectly shaped microcrystals $(Au_{55})_\infty$. Figure 2 shows a TEM image of one typical monocrystalline particle.

High-resolution images of very thin crystals and of crystal edges indicate a special ordering of naked Au_{55} clusters. Figure 3 shows a TEM image of a crystal edge with cluster rows of 1.85 nm distance. The image also indicates that the crystal is coated by a thin film which we believe to consist of dendrimer material.

A small and electronically transparent crystal (Figure 4) allowed us the study of the cluster ordering in more detail. It shows the clusters adopt a distorted cubic structure, which can best be matched with an arrangement of Au_{55} clusters as is shown in the sketch in Figure 4. Extended SAXRD and WAXRD measurements confirmed the microscopically sug-

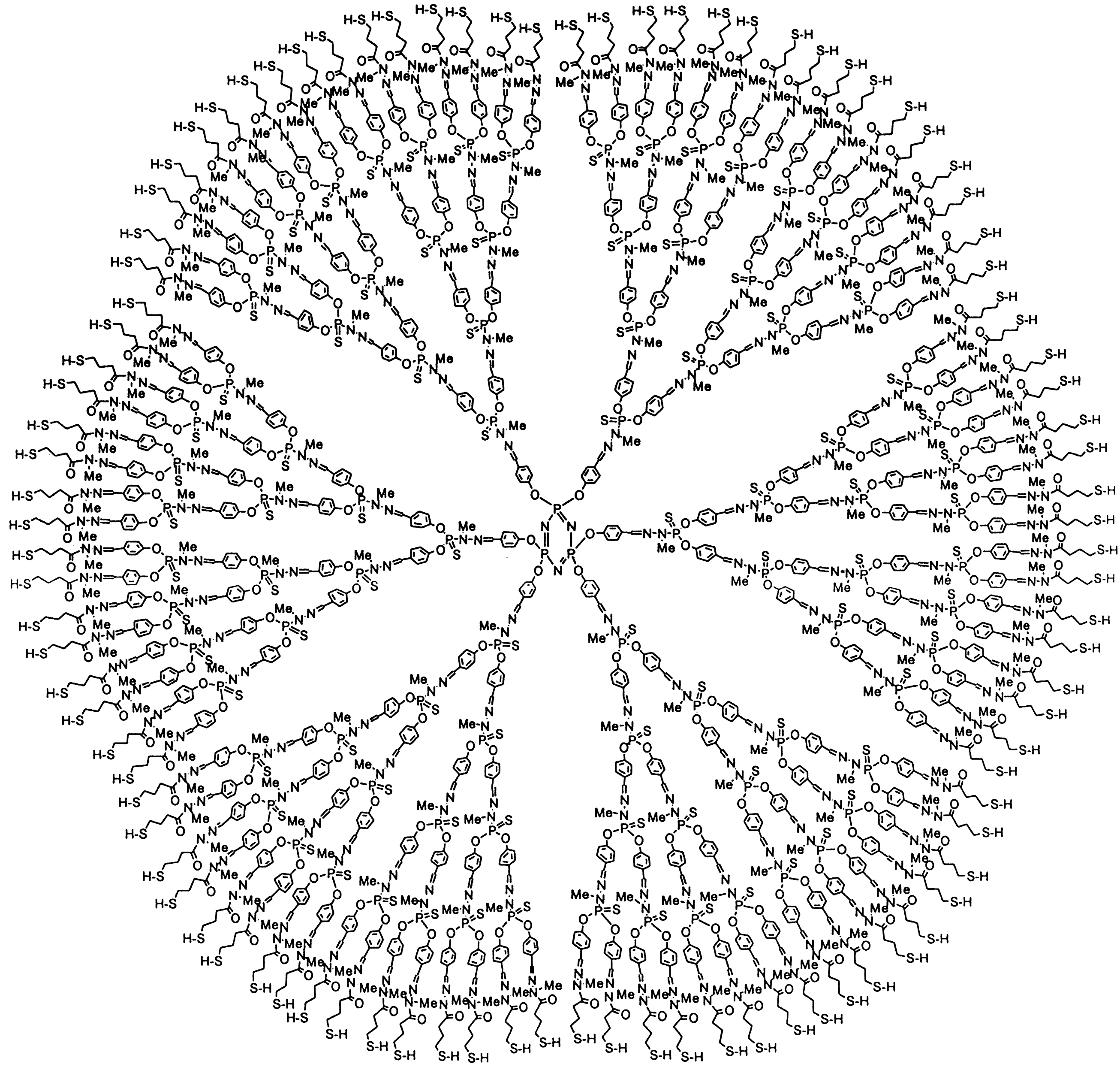

Figure 1. Sketch of the 2-G_4 dendrimer.

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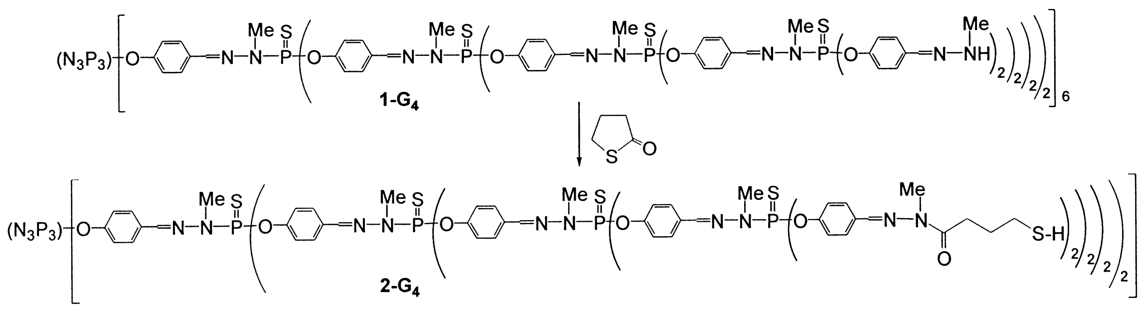

Scheme 1. Formation of the 2-G_4 dendrimer having 96 peripheral SH functions.

gested structure of the bare Au_{55} clusters. As indicated in Figure 4 all reflections can be attributed to that structure principle under one condition: former EXAFS measurements on Au_{55} clusters have shown that the Au–Au distances are about 5 % shorter than those in the bulk.[16] Assuming that this reduction is still valid in the superstructures of Au_{55} the experimental X-ray data fit well to the model.

Table 1 contains the experimental and the calculated X-ray data; the assignments are given Figure 4. First, it should be noted that dendrimer 2-G_4 does not give any X-ray reflection at all, proving that it cannot be part of the crystalline matter, but probably only covers the microcrystals as a thin amorphous layer, as indicated by TEM (see Figure 3). The distances $d^1 = 0.21$ nm and $d^2 = 0.28$ nm correspond to the (111) and the (110) reflections of bulk gold. The identical d^1 values are observed for microcrystalline $Au_{55}(PPh_3)_{12}Cl_6$; thus, the 5 % distance reduction is evidently also valid for the bare clusters, $d^3 = 0.55$ nm, corresponding to half of the cluster diameter, is also observed for the bare as well as for the ligated clusters. The most interesting and, with respect to the superstructure, the most important reflection is $d^4 = 1.98$ nm which is not observed for $Au_{55}(PPh_3)_{12}Cl_6$ microcrystals. It indicates the periodicity typical for the very special cluster arrangement as shown in Figure 4. In contrast to the hexagonal close-packed arrangement of the spherical $Au_{55}(PPh_3)_{12}Cl_6$,[17] the distorted cubic structure of $(Au_{55})_\infty$ is a consequence of the Au–Au contact between naked clusters. They can no longer be considered as spherical but as

Table 1. Experimental and calculated small and wide angle X-ray diffraction data of $(Au_{55})_\infty$.

2θ angle [°]	d (found) [nm]	d (calcd) [nm]
43.02	$d^1 = 0.21$	$1 \times 0.224^{[a]} = 0.224$
31.92	$d^2 = 0.28$	$1 \times 0.274^{[b]} = 0.274$
16.10	$d^3 = 0.55$	$2 \times 0.274^{[b]} = 0.548$
4.46	$d^4 = 1.98$	$7 \times 0.274^{[b]} = 1.918$

[a] hkl (111) = 0.2355 – 5% = 0.224. [b] hkl (110) = 0.2884 – 5% = 0.274.

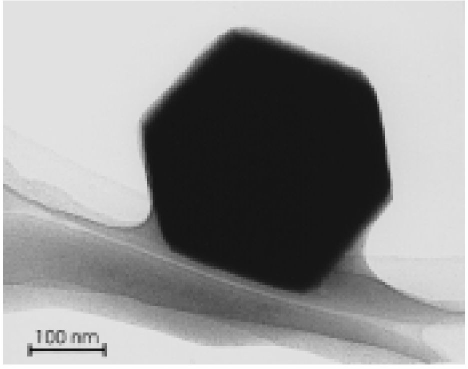

Figure 2. TEM image of a hexagonally shaped microcrystal of $(Au_{55})_\infty$.

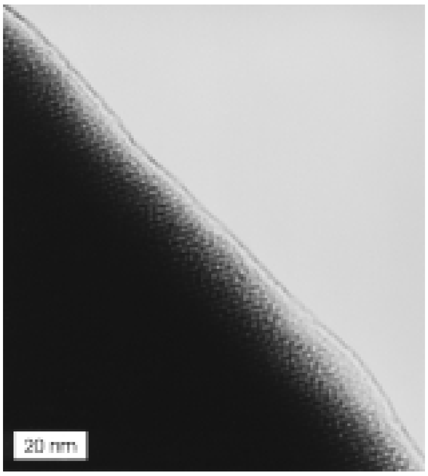

Figure 3. Magnified TEM image of a $(Au_{55})_\infty$ crystal edge showing rows of Au_{55} clusters.

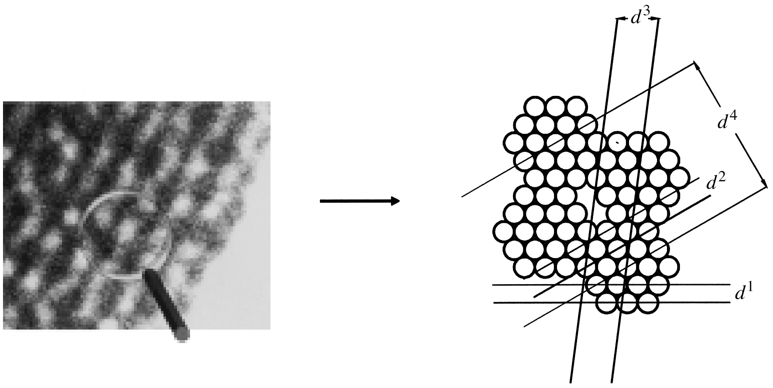

Figure 4. High-resolution TEM image of a cutout of a thin $(Au_{55})_\infty$ microcrystal. The aggregation of the Au_{55} clusters is elucidated in the sketch. The d values indicate the observed X-ray reflections.

regular cuboctahedral particles building up the observed superstructure.

The loss of PPh_3 and Cl as a result of the reaction with 2-G_4 is clearly shown by IR spectroscopy and EDX analysis. $Au_{55}(PPh_3)_{12}Cl_6$ shows a pronounced Au–Cl frequency at 274 cm^{-1}, which has completely disappeared in $(Au_{55})_\infty$. The removal of PPh_3 by 2-G_4 is already indicated by the insolubility of the product in CH_2Cl_2, in contrast to the situation with $Au_{55}(PPh_3)_{12}Cl_6$. The loss is confirmed by IR spectroscopic investigations of the reaction filtrate which shows the typical frequencies of PPh_3 at 3100–2900 (ν(C–H) arom.), 1410–1460 (ν(C=C)arom.), 1038 (ν(C–H) in-plane), and 750 cm^{-1} (ν(C–H) out of plane). Furthermore, an EDX analysis of single microcrystals of $(Au_{55})_\infty$ resulted in a gold content of 90–95%. $Au_{55}(PPh_3)_{12}Cl_6$ has a gold content of only 76%.

Proposal of the microcrystal formation

Good quality $(Au_{55})_\infty$ microcrystals are obtained if a dendrimer:cluster ratio of 3:1 is used. This means that 288 SH groups compete with one Au_{55} cluster. The equivalence of all SH groups obviously does not result in a distinct cluster–dendrimer combination, but instead the bare clusters move on the dendrimer surfaces without being trapped at favored positions. The sketch in Figure 5 illustrates this in a simplified manner. Whenever two or more ligand-free clusters touch each other inside the matrix of dendrimers they can form thermodynamically favored metal–metal bonds.

Thus, crystal "germs" within a shell of dendrimers are generated ending up in microcrystals. Some of the TEM images reveal an amorphous looking shell of material that envelopes the microcrystals. We believe this shell consists of dendrimer material. The chemical fixation of the dendrimers is further supported by the fact that they could not be removed by solvents such as dichloromethane which dissolves free dendrimers to some extent.

Conclusion

In continuation of work since our discovery of $(A_{13})_\infty$ superclusters in 1986, we have now found a way to make bare Au_{55} clusters, which act as building blocks in $(Au_{55})_\infty$ superstructures. These latter have been characterized by TEM, SAXRD, and WAXRD experiments. The PPh_3 ligands and the chlorine atoms of $Au_{55}(PPh_3)_{12}Cl_6$ have been peeled off by the reaction with a fourth-generation dendrimer having 96 peripheral SH groups. They remove the phosphines, but are obviously not able to anchor the Au_{55} clusters in such a way that stable dendrimer/cluster arrangements are formed. Instead, for the lack of energetically preferred positions on the dendrimer surfaces, the bare clusters coalesce to form $(Au_{55})_\infty$ superstructures. These results were unexpected; however, they can be understood in light of what has been observed: it is the route to the energetically most stable product under the experimental conditions.

Experimental Section

General: TEM images were obtained using a Philips CM 200 FEG microscope working with 200 kV accelerating voltage. SAXRD and WAXRD patterns were obtained by using standard Siemens D5000 diffractometers. The X-ray source was equipped with a fine focus tube and a primary monochromator selecting $Cu_{K\alpha}$ wavelength (0.154 nm). The beam was detected by using a scintillographic detector. Exposure times were 72 h. IR spectra were recorded with a Bruker FT-IR IFS 113v spectrometer. For NMR spectra a Bruker AC 200 was used. Elementary analyses were carried out by the Analytical Laboratory of the Fachbereich

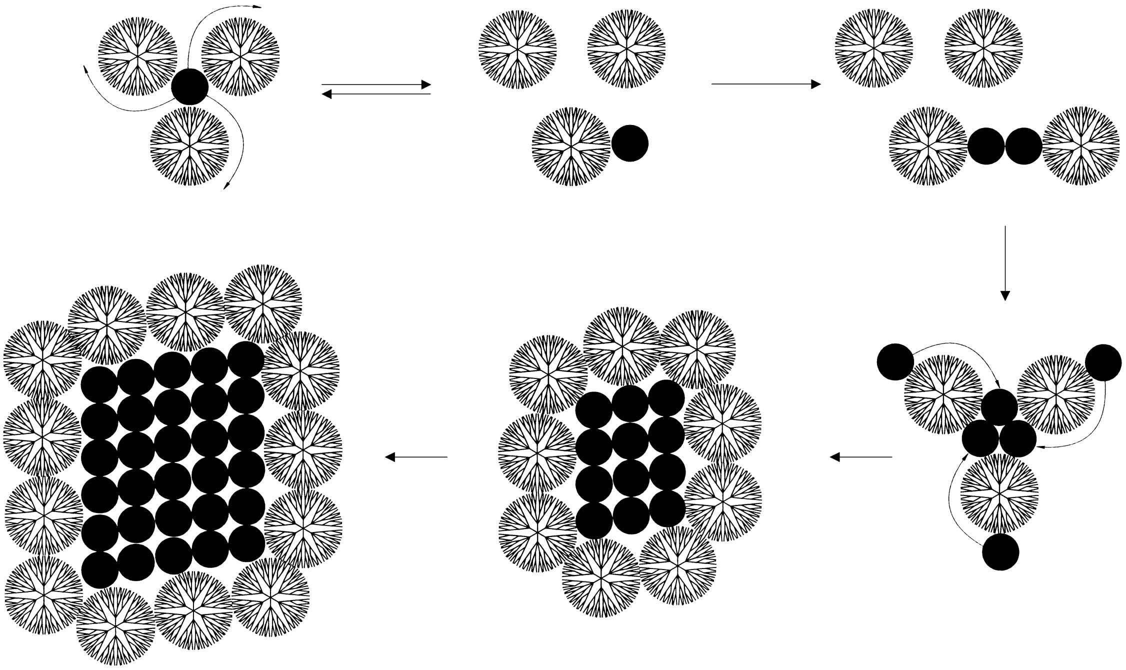

Figure 5. Simplified illustration of the proposed $(Au_{55})_\infty$ superstructure formation in the matrix of excess dendrimers. These peel off the PPh_3 and Cl ligands from $Au_{55}(PPh_3)_{12}Cl_6$ and thus allow cluster–cluster interactions, which subsequently leads to the observed microcrystals.

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Chemie, Universität Essen, and the Laboratoire de Chimie de Coordination in Toulouse.

Dendrimer 2-G_4: 1-G_4 fourth-generation dendrimer with 96 NH end groups (1.000 g)[15] was dissolved in pure γ-thiobutyrolactone (2.5 mL) in a pressure Schlenk. The mixture was kept under stirring at 50 °C for three days. After cooling, the crude material was washed with diethyl ether (3 × 50 mL) to yield quantitatively 2-G_4 as a white powder. $^{31}P\ \{^1H\}$NMR ($CDCl_3$): $\delta = 62.2$ (br.s, P=S) (N_3P_3 not attributed); ^1H NMR ($CDCl_3$): $\delta = 1.31$ (br.s, 96 H, SH), 1.92 (br.s, 192 H, CH_2-$\mathit{CH_2}$-CH_2), 2.52 (br.s, 192 H, $\mathit{CH_2}$-SH), 2.87 (br.s, 192 H, CH_2-CO), 3.23 (br.s, 558 H, N-CH_3), 7.1–7.8 (m, 930 H, C_6H_4, CH=N); $^{13}C\ \{^1H\}$ NMR ($CDCl_3$): $\delta = 24.4$ (s, CH_2), 27.8 (s, CH_2), 29.3 (s, CH_2), 32.0 (s, $\mathit{CH_3}$-N-CO), 33.1 (br.d, $^2J_{C,P} = 13.4$ Hz, P-N-CH_3), 121.8 (br.s, O-C^o), 128.2 (s, O-C^m), 132.2 (s, O-C^p), 137.7 (s, CH=N-N-C), 139.1 (m, CH=N-N-P), 151.3 (br.s, O-C^i), 174.2 (s, C=O); anal. calcd. for $C_{1872}H_{2160}N_{375}O_{282}P_{93}S_{186}$ (43273): C 51.96, H 5.03, N 12.14; found: C 51.68, H 4.97, N 12.01. The irradiation frequency used for MALDI-TOF experiments (337 nm) provokes the degradation of this phosphorus-containing dendrimer. Therefore, this method did not allow us to check rigorously their purity, although the molecular peak could be observed.

$(Au_{55})_\infty$: 2-G_4 (91 mg, 2.104 µmol) was dissolved under a nitrogen atmosphere in dried dichloromethane (10 mL) and placed in a dry 100 mL three-necked round-bottomed flask filled with nitrogen. The flask was topped by a dropping funnel containing $Au_{55}(PPh_3)_{12}Cl_6$ (10 mg, 0.701 µmol) dissolved in dried dichloromethane (40 mL). Under vigorous stirring, the diluted gold cluster solution was added at the rate of one drop per two seconds. After complete addition, the brown solution was stirred for a further 90 min. The solvent was then removed under vacuum and the crude brown product was washed with acetonitrile (50 mL) to remove free triphenylphosphine, filtered, and dried. The resulting filtration pad, which was insoluble in all common organic solvents, was washed with copious amounts of dichloromethane (5 × 25 mL) to remove excess dendrimer and unreacted $Au_{55}(PPh_3)_{12}Cl_6$. The brownish black powder was then dried overnight under vacuum.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 452) and the Fonds der Chemischen Industrie, Frankfurt. We would like to thank Dr. Ulrich Simon, Universität Essen, for helpful discussions. We also gratefully acknowledge Dr. B. Marler, Universität Bochum, for the SAXRD measurements and Dr. P. Sonntag, Universität Essen, for performing the WAXRD investigations. Thanks are also due to D.G.A. for financial support (grant to C.O.T.) and to the Cost D II program from the EC.

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Received: August 30, 1999 [F2010]

0947-6539/00/0609-1697 $ 17.50+.50/0