^{252}Cf-Plasma Desorption Mass Spectrometry of Gold Clusters: Fragmentation Patterns in Small Clusters and Differences in Sample Composition in Large Clusters

C. J. McNeal,*,[†] R. E. P. Winpenny,[§] J. M. Hughes,[†] R. D. Macfarlane,[†] L. H. Pignolet,[‡] L. T. J. Nelson,[‡] T. G. Gardner,[†] L. H. Irgens,[†] G. Vigh,[†] and J. P. Fackler, Jr.*,[†]

Departments of Chemistry, Texas A&M University, College Station, Texas 77843, University of Minnesota, Minneapolis, Minnesota 55455, and The University of Edinburgh, Edinburgh, Scotland

Received December 9, 1992[⊗]

A series of small gold phosphine clusters, including $[Au_6(PPh_3)_6](NO_3)_2$ (**1**), $[Au_6(PPh_3)_8](NO_3)_2$ (**2**), $[Au_9(PPh_3)_8](NO_3)_3$ (**3**), $[Au_{11}(PPh_3)_8Cl_2]Cl$ (**4**), $[Au_{13}(PPh_2Me)_8I_4]I$ (**5**), and $[CAu_6(PPh_3)_6](BF_4)_2$ (**6**), have been studied using ^{252}-Cf-plasma desorption mass spectrometry (^{252}Cf-PDMS). This series of well-characterized clusters was studied to develop an understanding of ^{252}Cf-PDMS as applied to gold clusters and, hence, use ^{252}Cf-PDMS to study much larger gold clusters. The study of small gold clusters indicates that extensive fragmentation occurs. Oligomerization of these clusters, or cluster fragments, is uncommon, and even when it occurs it is limited. These results allow us to estimate the molecular mass of much larger clusters, on the basis of the highest observed fragment ion, and not the centroid of peak distributions as suggested previously. The study of the large clusters, moderated by our knowledge of the spectra of small clusters, indicates that a large gold cluster, formulated by Schmid as $Au_{55}(PPh_3)_{12}Cl_6$, gives spectra that indicate that sample composition varies dependent on a number of factors. These factors include the source of the sample, the age of the sample, and the temperature at which the sample is stored. It is also possible that the sample is inhomogenous as prepared; it is probable that aged samples are inhomogeneous and contain at least three clusters of molecular weight *ca.* 9500, 14 000, and 20 000 mu (mass units).

Introduction

The synthesis of a very large gold cluster, reported by Schmid and co-workers,[1] has stimulated interest in the structure and properties of high-nuclearity clusters. A structure, of formula $Au_{55}(PPh_3)_{12}Cl_6$, has been proposed for this cluster on the basis of the data obtained from a very large number of techniques,[2] including sedimentation equilibria, elemental analysis, Mössbauer spectroscopy, ^{31}P-NMR, EXAFS, high resolution transmission electron microscopy (HRTEM), and scanning-tunneling microscopy (STM). While all of the data collected can be interpreted to support the model structure proposed, even the combination of all of these techniques has not provided the indisputable confirmation of the structure that might be obtained from X-ray crystallographic analysis. Unfortunately single crystals of the cluster have not been obtained.

The structure proposed[1,2] is a two-layer cuboctahedron, composed of a centered Au_{13} cuboctahedron surrounded by a further 42 gold atoms in a cubic close-packed (ccp) array. Twelve triphenylphosphine ligands are assumed to be attached to the vertices of the outer cuboctahedron with six Cl^- anions attached to the center of each square face. This structure, and the formulation as $Au_{55}(PPh_3)_{12}Cl_6$, has gained widespread acceptance, despite the lack of conclusive proof of its validity and despite some theoretical objections to such a model. Sphere-packing calculations,[3] valence bond,[4] and molecular orbital calculations[5] for gold clusters suggest that icosahedral symmetry may be preferred to ccp arrangements for small gold clusters, despite the fact that gold is ccp in the bulk state. Until very recently all X-ray crystallographic studies of small clusters of the coinage group metals also supported this contention that icosahedral symmetry should be predominant.[6] The largest such cluster analyzed is an M_{46} cluster prepared by Teo and co-workers[7] and consists of four icosahedra sharing six vertices. However recently Teo has reported an Au_{39} cluster[8] which does *not* have a structure based in any way on icosahedra; rather it is a 1:9:9:1:9:9:1 layered hexagonal close-packed arrangement of gold atoms. This structure was completely unexpected: it does not correspond to the structures of similar sized mixed Au–Ag clusters[7] nor to the structure of Au in the bulk state. This report[8] illustrates very well the dangers of predicting structures of high-nuclearity clusters on the basis of theory or "sporting" techniques.

We have used ^{252}Cf-plasma desorption mass spectrometry (^{252}Cf-PDMS) to attempt to verify the formulation of the $Au_{55}(PPh_3)_{12}Cl_6$ cluster. Our preliminary communication[9] reported spectra recorded on samples obtained from two different laboratories, but both were prepared using a procedure outlined by Schmid and co-workers.[10] The results we obtained did not seem to us consistent with Schmid's formulation, and we proposed a different model for the structure of this cluster—a model based on vertex-sharing icosahedra. Of more immediate concern was the observation that the samples obtained from two different laboratories did not give the same spectrum. Both samples gave spectra containing three broad, high-mass zones with the zones occurring at the same place in each spectrum but with the relative intensities of the zones differing between samples. We suggested that each of the zones was caused by fragmentation of one cluster, and therefore, as each spectrum contained three zones, each sample contained three different, large gold clusters with the relative mole ratios of the three clusters varying between samples.

The reformulation of the cluster and the contention that the sample contains three different clusters have been disputed by

---

[†] Texas A&M University.

[‡] University of Minnesota.

[§] The University of Edinburgh.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Schmid, G.; Pfeil, R.; Boese, R.; Bandermann, F.; Meyer, S.; Calis, G. H. N.; van der Velden, J. A. M. *Chem. Ber.* **1981**, *114*, 3634.

(2) Schmid, G. *Struct. Bonding* **1985**, *62*, 51. Schmid, G. *Chem. Rev.* **1992**, *92*, 1709 and references cited therein.

(3) Allpress, J. G.; Sanders, J. V. *Aust. J. Phys.* **1970**, *23*, 23.

(4) McAdon, M. H.; Goddard, W. A., III. *J. Phys. Chem.* **1987**, *91*, 2607.

(5) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1976**, *1163*.

(6) Hall, K. P.; Mingos, D. M. P. *Prog. Inorg. Chem.* **1984**, *32*, 237 and references therein. The authors thank Professor D. M. P. Mingos for samples of some related gold clusters.

(7) Teo, B. K.; Shi, X.; Zhang, H. *Chem. Eng. News* **1989**, *67*, 6.

(8) Teo, B. K.; Shi, X.; Zhang, H. *J. Am. Chem. Soc.* **1992**, *114*, 2743.

(9) Fackler, J. P., Jr.; McNeal, C. J.; Pignolet, L. H.; Winpenny, R. E. P. *J. Am. Chem. Soc.* **1989**, *111*, 6434.

(10) Schmid, G. *Inorg. Synth.* **1990**, *27*, 214.

0020-1669/93/1332-5582$04.00/0

Benninghoven, Schmid, *et al.*,[11] on the basis of results obtained using ^{252}Cf-PDMS and secondary ion mass spectroscopy (SIMS). They argue that the mass spectra they obtained are consistent with the original formulation and that the presence of several high-mass zones of high intensity are caused by degradation of Au_{55} units to give Au_{13} clusters which then oligomerize. While oligomerization of metal clusters during mass spectroscopic studies is not unique, e.g. platinum carbonyl clusters show just such an oligomerization when studied by ^{252}Cf-PDMS,[12] the decomposition of an Au_{55} cluster to give specifically the central Au_{13} cuboctahedron which then oligomerizes does seem unlikely. The formation of oligomers of fragment ions would be a unique process and has no precedent in the literature. In any case a gold cluster based on vertex-sharing Au_{13} icosahedra might equally well break down to give Au_{13} icosahedra which in turn might then oligomerize. The SIMS results do not prove the original Schmid formulation, nor do they invalidate our original data.

These reports[9,11] assume that new mass spectroscopic techniques (^{252}Cf-PDMS, SIMS) are well established as tools for elucidating the structures of organometallic, as opposed to inorganic, clusters. This is far from the case; our report[9] was the first of such a study using ^{252}Cf-PDMS, although the use of FABMS is well-known.[13–15] No study of fully-characterized organometallic clusters using SIMS has appeared. Therefore there was a need to establish the ^{252}Cf-PDMS technique, before making any further comment on the likely formulation and structure of the Schmid cluster. This has been partly done by studies of platinum carbonyl clusters.[12] Herein we report our studies of small gold clusters, followed by further studies of samples of "Au_{55}" obtained from four different laboratories.

Experimental Section

Samples. Five small gold clusters were synthesized by previously reported methods.[16–20] These were $[Au_6(PPh_3)_6](NO_3)_2$ (**1**),[16] $[Au_8(PPh_3)_8](NO_3)_2$ (**2**),[17] $[Au_9(PPh_3)_8](NO_3)_3$ (**3**),[18] $[Au_{11}(PPh_3)_8Cl_2]Cl$ (**4**),[19] and $[Au_{13}(PPh_2Me)_8I_4]I$ (**5**).[6] In addition a sample of $[CAu_6(PPh_3)_6](BF_4)_2$ (**6**) was generously provided by Prof. H. Schmidbaur (Technischen Universität, München, Germany). The synthesis and complete characterization of this complex have been described.[20]

Samples of large gold clusters were obtained from four different research groups (L.H.P., M. Andrews, F. Furuya, and G. Schmid). All samples were made by the standard literature procedure[10] involving reduction of Ph_3PAuCl by B_2H_6 in benzene, with the exception of the sample prepared by F. Furuya which used $THF{\cdot}BH_3$ as the reducing agents. Samples were purified on a Celite column.

Separation Procedure. Further separations of the large gold clusters were carried out on 4.0–6.25-cm columns of Celite (Aldrich Chemical, 16743–6; high-purity, analytical grade), prepared in a Pasteur pipet from a slurry in CH_2Cl_2. The samples (5–7 mg) were added as saturated solutions in Ch_2Cl_2 and eluted with CH_2Cl_2. Pyridine was added gradually to increase the polarity of the eluant. For all samples two bands were eluted from the column—the first with approximately 9:1 CH_2Cl_2/pyridine and the second with pure pyridine. The first band, on evaporation to dryness under reduced pressure at room temperature, gave a brown/black residue which redissolved in CH_2Cl_2. The second band, on evaporation, gave a black solid which did not dissolve in CH_2Cl_2 or any common organic solvent. Material retained on the column became purple within a period of 1 h.

Mass Spectral Analysis. All samples were dissolved in dichloromethane, except for a small number of experiments performed in 95:5 tetrahydrofuran:water (see Results and Discussion). The solution concentrations for the small clusters were 5 mg/mL. For the large clusters sample concentrations were normally ca. 10 mg/mL (i.e. approx 10^{-3} M). Spectra at a range of lower concentrations (*ca.* 10^{-6} M as minimum) were also recorded on a sample of the large cluster made in the L.H.P. laboratories. Samples were prepared for analysis either by electrospraying[21] or spin casting[22] 25–50 μL of each solution onto 1.5-μm aluminized Mylar foils (Atlan-Tol) which had been sputter coated with 50 nm of gold (Hummer X, Technics). This gold coating eliminates interfering aluminum oxide peaks from the mass spectrum. Mass spectra of the foils, prior to sample deposition, exhibit only low mas ions, primarily below m/z 250 (m/Z = mass/charge). The ^{252}Cf-plasma desorption mass spectra were obtained on an instrument fabricated at Texas A&M. A description of the design and data acquisition and analysis has been reported.[23,24] The 5-μCi ^{252}Cf source (Isotope Products) and fission fragment detector were situated on a removable probe that could be placed within 4 mm of the sample foil. The fission fragment flux through the sample foil was *ca.* 1800 s^{-1}. Secondary ions produced by the interaction of the ^{252}Cf fission fragment with the sample film were accelerated and mass-analyzed by their time-of-flight and subsequently detected by a secondary ion detector. The flight path for the small clusters, and for spectrum A, was 50 cm; for the remaining large clusters the flight path was 32 cm. The acceleration voltage used was +12 or −10 kV. The mass resolution ($M/\Delta M$) was estimated to be 500. Data were accumulated for 60 min and analyzed at 6.25 ns/channel unless otherwise stated.

Results and Discussion

(a) Outline of Project. The discussion which follows is long and complex, and therefore it is necessary to first outline the structure of this discussion. It can be split into two sections.

First, results of the mass spectral study of small gold clusters of known composition are presented. This work establishes the potential and limitations of ^{252}Cf-PDMS with regard to gold phosphine clusters. Specific questions about the technique, as applied to gold clusters, have been answered. These include: How reproducible are the spectra? Is there a well-defined molecular ion in each spectrum? Are peaks observed at masses above the molecular ion in any spectrum, indicating some form of oligomerization? Is fragmentation extensive, and is the resulting fragmentation pattern interpretable? Are spectra sufficiently diagnostic to enable us to recognize known gold clusters and, hence, to predict the formulas of unknown gold clusters from mass spectrocopy alone?

Second, results of an extended study of the large gold clusters first synthesized by Schmid *et al.*[1] are presented. As the reliability and limitations of ^{252}Cf-PDMS as applied to this class of compounds are known from the first second of the project, the conclusions reached about the large gold clusters, while possibly less radical than our previous suggestions,[9] should be less open to contradiction.

(b) ^{252}Cf-PDMS of Small Gold Clusters. Six gold phosphine clusters, $[Au_6(PPh_3)_6](NO_3)_2$ (**1**),[16] $[Au_8(PPh_3)_8](NO_3)_2$ (**2**),[17] $[Au_9(PPh_3)_8](NO_3)_3$ (**3**),[18] $[Au_{11}(PPh_3)_8Cl_2]Cl$ (**4**),[19] $[Au_{13}(PPh_2Me)_8I_4]I$ (**5**),[6] and $[CAu_6(PPh_3)_6](BF_4)_2$ (**6**)[20] were studied. All have been fully characterized previously by X-ray crystallography. $[Au_6(PPh_3)_6](NO_3)_2$ (**1**) contains an edge-sharing bitetrahedron of gold atoms. $[Au_8(PPh_3)_8](NO_3)_2$ (**2**), $[Au_9(PPh_3)_8](NO_3)_3$ (**3**), and $[Au_{11}(PPh_3)_8Cl_2]Cl$ (**4**) all contain a central gold atom bound to the remaining, peripheral golds. Their structures can

---

[11] Feld, H.; Leute, A.; Rading, D.; Benninghoven, A.; Schmid, G. *J. Am. Chem. Soc.* **1990**, *112*, 8166. Feld, H.; Leute, A.; Rading, D.; Benninghoven, A.; Schmid, G. *Z. Phys. D.* **1990**, *17*, 73.

[12] McNeal, C. J.; Hughes, J. M.; Lewis, G. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 372.

[13] Miller, J. M. *Mass Spec. Rev.* **1989**, *9*, 319.

[14] Lidell, M. J.; Bruce, M. I. *Appl. Organomet. Chem.* **1987**, *1*, 191.

[15] Boyle, P. D.; Johnson, B. J.; Alexander, B. D.; Casalnuovo, J. A.; Gannon, P. R.; Johnson, S. M.; Larka, E. A.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1987**, *26*, 1346.

[16] Briant, C. E.; Hall, K. P.; Mingos, D. M. P. *J. Organomet. chem.* **1983**, *254*, C18. Mingos, D. M. P. *Gold Bull.* **1984**, *17*, 1.

[17] Manassero, M.; Naldini, L.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1979**, 385. Vollenbroek, F. A.; Bosman, W. P.; Bour, J. J.; Noordik, J. H.; Beurskens, P. T.; *J. Chem. Soc., Chem. Commun.* **1979**, 387.

[18] Naldini, L.; Cariati, F. *J. Chem. Soc., Dalton Trans.* **1972**, 2286.

[19] Vollenbroek, F. A.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 137.

[20] Scherbaum, F.; Grohmann, A.; Huber, B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544. Schmidbaur, H. *Gold Bull.* **1990**, *23*, 1.

[21] McNeal, C. J.; Macfarlane, R. D.; Thurston, E. L. *Anal. Chem.* **1979**, *108*, 2036.

[22] Meyerhofer, D. J. *J. Appl. Phys.* **1978**, *49*, 3993.

[23] Macfarlane, R. D. *Anal. Chem.* **1983**, *55*, 1247A.

[24] Sundqvist, B.; Macfarlane, R. D. *Mass Spec. Rev.* **1985**, *4*, 421.

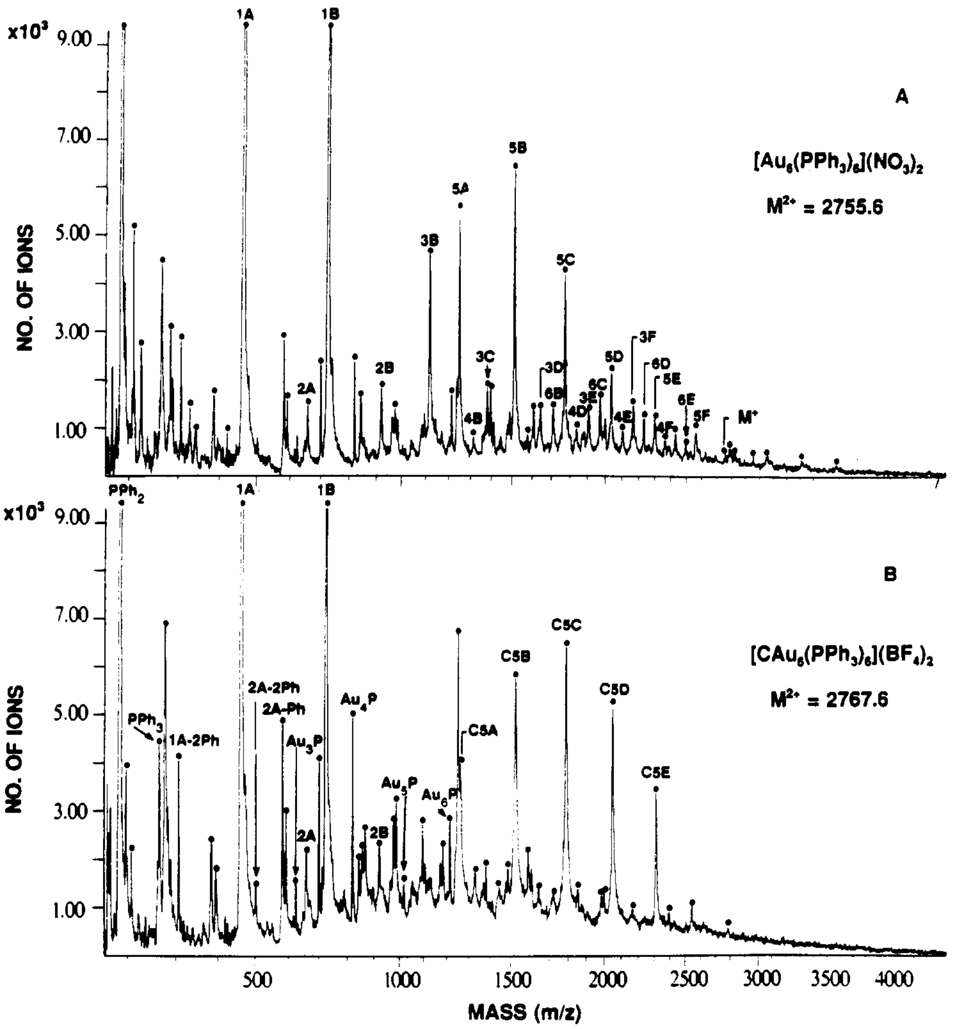

Figure 1. (A) ^{252}Cf-PD positive ion mass spectrum of $[Au_6(PPh_3)_6](NO_3)_2$ (**1**) from *m/z* 160–4500. (B) ^{252}Cf-PD positive ion mass spectrum of $[CAu_6(PPh_3)_6](BF_4)_2$ (**6**) from *m/z* 160–4500. The peaks are identified by an alphanumeric combination corresponding to the number of gold atoms and triphenylphosphine ligands. The former is specified by the number, and the latter by a letter following the number. One ligand is represented by A, two ligands by B, and so forth. In spectrum **B** the letter C before the number indicates the presence of the central C atom; i.e., C5C indicates five golds and three phosphines attached to the central carbon.

Table I. Observed Fragment Ions of Type $[Au_xL_y]^+$ ($L = PPh_3$)

cluster	AuL_y	Au_2L_y	Au_3L_y	Au_4L_y	Au_5L_y	Au_6L_y	Au_7L_y	Au_8L_y	Au_9L_y	$Au_{10}L_y$
1	$1 \le y \le 2$	$1 \le y \le 2$	$2 \le y \le 6$	$2 \le y \le 6$	$1 \le y \le 6$	$2 \le y \le 6$				
2	$y = 1, 2, 4$	$y = 1, 2$	$2 \le y \le 6$	$y = 5, 6$	$2 \le y \le 6$	$y = 2, 3$	$2 \le y \le 4$	$2 \le y \le 4$		
3	$1 \le y \le 3$	$1 \le y \le 4$	$2 \le y \le 6$	$3 \le y \le 7$	$1 \le y \le 7$	$2 \le y \le 6$	$1 \le y \le 8$	$2 \le y \le 7$	$y = 4, 6, 8$	
4	$1 \le y \le 4$	$1 \le y \le 4$	$2 \le y \le 7$	$3 \le y \le 7$	$2 \le y \le 7$	$1 \le y \le 6$	$2 \le y \le 5$	$2 \le y \le 5$	$2 \le y < 4$	

be rationalized as based on fragments of centered Au_{13} icosahedra. $[Au_{13}(PPh_2Me)_8I_4]I$ (**5**) has a complete, centered icosahedral array of gold atoms. $[CAu_6(PPh_3)_6](BF_4)_2$ (**6**) contains an octahedron of gold atoms, all bound to a central, six-coordinate carbon atom.

(i) Positive Ion Spectra. ^{252}Cf-PDMS study of these clusters gave reproducible positive ion spectra which contain several general features. For each cluster a very large amount of fragmentation was observed. The majority of fragment peaks could be assigned in each case. **1**–**3** give very similar spectra. The exact details of the fragmentation differs slightly for **4**, which contains a halide ion bound to the gold cluster. **5** and **6** give quite different fragment ions.

For compounds **1**–**4** fragment ions are seen for a wide range of $[Au_x(PPh_3)_y]^+$ species. For example, the spectrum of **1** (Figure 1A) contains peaks for fragments $Au_6(PPh_3)_y$, $2 \leqslant y \leqslant 6$; $Au_5(PPh_3)_y$, $1 \leqslant y \leqslant 6$; $Au_4(PPh_3)_y$, $2 \leqslant y \leqslant 6$; $Au_3(PPh_3)_y$, $2 \leqslant y \leqslant 6$; $Au_2(PPh_3)_y$, $1 \leqslant y \leqslant 2$; and $Au(PPh_3)_y$, $1 \leqslant y \leqslant 2$. A complication arises from the fact that four times the mass of Au is 788 mu, which is also three times the mass of PPh_3. Thus given the resolution of the spectrometer, several possible ions cannot be distinguished, e.g. $[Au_6(PPh_3)]^+$ cannot be differentiated from $[Au_2(PPh_3)_4]^+$. Chemical considerations can be applied to rule out some formulations; e.g., $[Au(PPh_3)_5]^+$ would clearly be impossible because of steric considerations. Unfortunately more general considerations baesd on solution chemistry cannot be applied, as the requirements for the observation of a fragment ion in a mass spectrometer are not related to the stability of a cluster in solution. Therefore although species such as $[Au_6(PPh_3)_2]^+$ would not exist in solution, thee is no reason to assume they cannot exist as fragments in a mass spectrometer.

For **2**–**4** additional $[Au_x(PPh_3)_y]^+$ fragments are seen at higher mass compared to those observed for **1**. This is consistent with **2**–**4** being larger clusters. A full list of $[Au_x(PPh_3)_y]^+$ fragments observed is given in Table I. It is apparent from this listing that each cluster undergoes extensive fragmentation. Similar fragments occur in each spectrum, with the larger clusters merely gaining a few new fragments at the high-mass end. The molecular ion is only observed for **1** and, with very low intensity, for **4**. Not

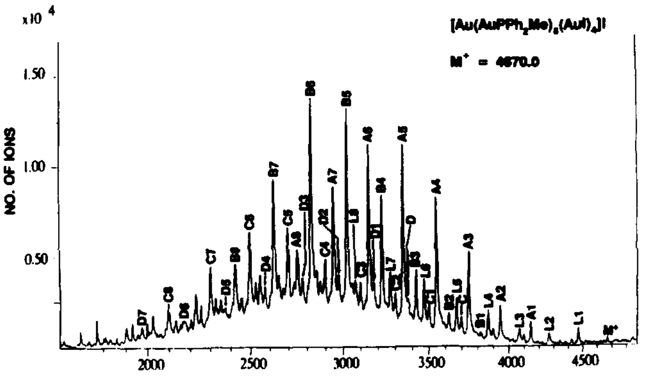

Figure 2. ^{252}Cf-PD positive ion mass spectrum of $[Au(AuPPh_2Me)_8(AuI)_4]I$ (**5**) from *m/z* 1600–4900. The peaks are designated by a letter corresponding to the number of AuI units lost from the molecular ion (L = 0, A = 1, B = 2, C = 3, D = 4) and a number corresponding to the number of PPh_2Me ligands lost.

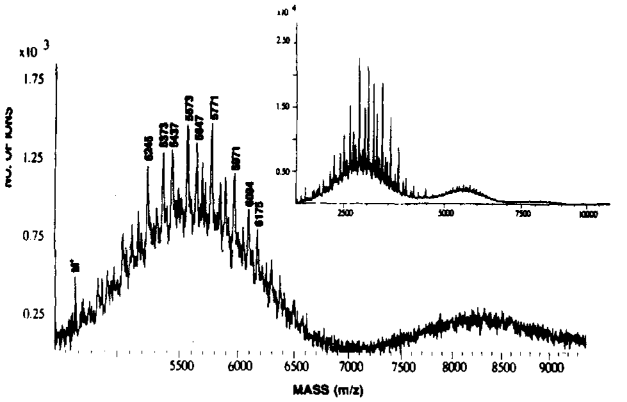

Figure 3. High-mass region in the ^{252}Cf-PD positive ion mass spectrum of **5**. The intensity of these distributions relative to the primary distribution is shown in the inset. The possible assignment of the peaks is discussed in the text.

all possible $[Au_x(PPh_3)_y]^+$ fragments are observed in any of the spectra, and it is unclear why specific fragments are sometimes missing.

Fragments of the type $[Au_x(PPh_3)_y]^+$ do not account for all the peaks seen. Many peaks are seen which can be attributed to the fragmentation of the PPh_3 ligand, while still attached to a gold cluster. This is unsurprising given that the mass spectrum of PPh_3 itself contains very strong peaks for P^+, PPh^+, and PPh_2^+. Thus fragments of the type $[Au_x(PPh_3)_y(PPh_2)_z]^+$ are seen for **1**–**4**. Related to these fragments are two peaks seen in all these spectra at 819 and 1213 mu. The first of these can only be assigned as $[Au_4P]^+$, and the second could then be $[Au_6P]^+$ [although alternative formulations for this peak e.g. $Au_2(PPh_3)_2(PPh_2)(PPh)^+$ are clearly possible; peaks which can be assigned as $[Au_3P]^+$ and $[Au_5P]$ are also found in the spectra of **1** and **6**]. Again, although such species appear very exotic in terms of solution chemistry, this does not rule them out as possible fragment ions.

The fragmentation extends even beyond the simple loss of phenyl groups from the PPh_3 ligand. Peaks are observed which do not correspond to either of the two types of fragments discussed above. These peaks could be due to still further fragmentation of the organic ligands. In all these positive ion spectra none of the many peaks can be assigned to doubly charged ions. Such peaks would be distinctive as previous studies indicate that doubly charged ions give much narrower peaks than singly charged ions.

One additional series of fragments is observed for cluster **4**. The series $[Au_{10}(PPh_3)_yCl]^+$, $2 \le y \le 7$, is seen. This reflects the fact that in **4** Cl^- is bound directly to the gold cluster, which might be more accurately formulated $[Au(AuPPh_3)_8(AuCl)_2]^+$. No peaks in the spectra of compounds **2** or **3** correspond to incorporation of the counterion. In the spectrum of **1** a peak is seen above the mass of the molecular ion which corresponds to $[Au_6(PPh_3)_6(NO_3)]^+$. Therefore the presence of fragments containing Cl^- in **4** is significant, indicating that only when a ligand or anion is bound to the cluster will fragment ions containing that ligand be seen.

Cluster **5** fragments in a quite different way to compounds **1**–**4** (Figure 2). **5** is a centered icosahedra and is perhaps best formulated as $[Au(AuPPh_2Me)_8(AuI)_4]I$. The molecular ion is seen for **5**, and five series of fragments are also seen. These five series are as follows: $[Au_9(PPh_2Me)_y(AuI)_4]^+$, $0 \leqslant y \leqslant 8$; $[Au_9(PPh_2Me)_y(AuI)_4]^+$, $0 \leqslant y \leqslant 8$; $[Au_9(PPh_2Me)_y(AuI)_3]^+$, $0 \leqslant y \leqslant 7$; $[Au_9(PPh_2Me)_y(AuI)_2]^+$, $0 \leqslant y \leqslant 7$; $[Au_9(PPh_2Me)_y(AuI)]^+$, $0 \leqslant y \leqslant 8$; $[Au_9(PPh_2Me)_y]^+$, $0 \leqslant y \leqslant 7$. [The presence of a different phosphine in **5** makes interpretation more straightforward as there is now no problem of the mass of four Au equaling the mass of three ligands. It is possible that for a high-mass cluster the mass of one Au would not be distinguishable from the mass of one PPh_2Me (200 mu); however, the mass of two golds would be distinguishable from the mass of two PPh_2Me.] These results are surprising in that the lowest member of each series contains *no* phosphine in fragments such as $[Au_{13}I_4]^+$, $[Au_{12}I_3]^+$, $[Au_{11}I_2]^+$, $[Au_{10}I]^+$, and $[Au_9]^+$, respectively. Fragments of the type $[Au_x(PPh_2Me)_y]^+$ are not seen with any great intensity, except for $x = 9$ as listed above.

An additional feature is also seen in the spectrum of **5** which is not seen for clusters **1**–**4**. Peaks are seen at *above* the mass of the molecular ion (4670 mu) (Figure 3). Broad distributions are seen between *m/z* 4000 and 7300 and between *m/z* 7300 and 9750. If data are accumulated for a much longer period, then a third distribution between *m/z* 9750 and 12 000 becomes apparent. In the first of these regions sharp, assignable peaks can be seen. These include peaks at *m/z* 5245, which can be assigned as $[Au_{26}I]^+$ (calc 5249); at 5373, $[Au_{26}I_2]^+$ (calc 5376); 5437, $[Au_{24}(PPh_2Me)I_4]^+$ (calc 5436); 5573, $[Au_{27}I_2]^+$ (calc 5574); 5647, $[Au_{27}(PPh_2Me)I]^+$ (calc 5646); 5771, $[Au_{28}I_2]^+$ (calc 5770); 5971, $[Au_{28}(PPh_2Me)I_2]^+$ (calc 5970); 6094, $[Au_{29}I_3]^+$ (calc 6094); and 6175, $[Au_{26}(PPh_2Me)I_4]^+$ (calc 6176). Each peak could be assigned slightly differently; e.g., one Au could always be changed for one PPh_2Me in each formula. What is clear is that oligomerization of the original Au_{13} cluster is occurring. The three distributions observed can be assigned as due to a dimer, trimer, and tetramer of the original cluster. However this dimerization is not clean; e.g., peaks are seen for both more and less than 26 gold atoms in the dimer distribution. Also it appears it is the metal core which is dimerizing and not the complete cluster. The metal:ligand ratio is much higher for the oligomers than it is for the Au_{13} cluster itself. The oligomerization observed is limited; only units up to $(Au_{13})_4$ are seen.

We can contrast this oligomerization with that observed in the ^{252}Cf-PDMS of platinum carbonyl clusters.[12] There the oligomerization was very extensive—a dodecamer of a Pt_{26} cluster was osberved, and the distributions were sharp—indicating that there was no fragmentation of the metallic core. The only common feature is that the metal:ligand ratio is higher for the oligomers than for the original cluster in both the gold phosphine and platinum carbonyl clusters.

The final cluster studied, **6**, is different in that it has a central carbon atom. Fragmentation is again quite different from that seen for **1**–**5**. The positive ion spectrum is dominated by peaks due to fragments of the type $[CAu_5(PPh_3)_y]^+$, $1 \leqslant y \leqslant 5$ (Figure 1B). The molecular ion is seen but only as a very weak peak. Again strong peaks due to $[Au_xP]^+$ fragments are seen for $3 \leqslant x \leqslant 6$. $[Au_x(PPh_3)_y]^+$ fragment ions, which are so noticeable in the spectra of **1**–**4**, are largely absent except for ions containing Au and Au_2.

The discussion has concentrated thus far only on the presence or absence of peaks; little has been said about the relative intensities. For all samples the most intense peaks are due to very small fragments such as $[PPh_2]^+$, $[PPh_3]^+$, $[AuPPh_3]^+$, and $[Au(PPh_3)_2]^+$. This is predictable given the very large amount of fragmentation observed.

What is less predictable, and hence more important, is that there is a distinct shape to the distributions of peaks containing polynuclear gold fragments. It is more noticeable for compound **5** (Figure 2). The peaks for the smallest polymetallic fragments observed are *less* intense than the peaks for middle-mass fragments, with a further diminution in intensity for the highest mass fragments. Thus for **5** the most intense peaks of this type occur for $[Au_9(PPh_2Me)_3(AuI)_2]^+$, $[Au_9(PPh_2Me)_2(AuI)_2]^+$, $[Au_9(PPh_2Me)_3(AuI)_3]^+$, and $[Au_9(PPh_2Me)_2(AuI)_3]^+$ and not for smaller polynuclear fragments nor for fragments close to the molecular ion. It is observed for **5** that the series $[Au_9(PPh_2Me)_y(AuI)_2]^+$ and $[Au_9(PPh_2Me)_y(AuI)_3]^+$ are more intense than the other three series observed. Similarly for **1** the series $[Au_5(PPh_3)_y]^+$ gives much the strongest peaks, and as stated above for **6**, fragments of the type $[CAu_5(PPh_3)_y]^+$ are predominant (Figure 1). The picture is not so clear for **2**–**4**, but even for these compounds there is a distinct "hump" of the most intense peaks near the middle of the distributions due to polynuclear compounds. It appears therefore that the most abundant fragment ions are not those due to complete disintegration of the metallic core of the cluster but those due to the loss of only one or two gold atoms from the core plus a larger number of phosphine ligands.

(ii) Negative Ion Spectra. The negative ion spectra do not contain any peaks characteristic of the structural framework of the compounds. In some cases the counterion is observed strongly, e.g. for **2** the nitrate ion is highly abundant, but this is not a reliable guide as frequently Cl^- is observed which was only present as part of the dichloromethane solvent.

The most interesting feature of the negative ion spectrum of clusters **1**–**4** and **6** is the presence of a series of "naked" gold cluster ions (Au_x^-), which extend far beyond the size of the parent cluster. The odd number peaks are more intense than the even number peaks. Peaks for fragments up to $[Au_{17}]^-$ are observed.

As with the positive ion spectra, **5** gives a different pattern compared to that of the other clusters. Fragments of the type $[Au_xI_z]^-$ are observed for $1 \leqslant x \leq 13$ and $1 \leqslant z \leq 3$. Additional peaks for $[Au_xI_zP]^-$ fragments are seen. No discrete peaks can be identified which contain more than 13 gold atoms. However there is some evidence for oligomerization with a broad unresolvable distribution between *m/z* 4500 and 6400. The center of this distribution is close to the mass of $[Au_{26}I_3]^-$.

(iii) Conclusions Based on the ^{252}Cf-PDMS Study of Small Gold Clusters. The first point to make is that fragmentation of the clusters is so extensive that it is impossible to be confident in assigning a structure or formulation to a cluster on the basis of the mass spectral evidence. In particular compounds **2**–**4** gave very similar positive ion spectra with peaks seen for most chemically conceivable fragments. The negative ion spectra were even less informative. The mass spectra therefore tend to exaggerate similarities between clusters rather than emphasising differences in structure.

The second point to make is that resolvable peaks do not extend beyond the mass of the molecular ion unless oligomerization occurs. Therefore the highest mass peak observed in the lowest mass distributions is either the molecular ion or a fragment thereof. This does give some information; the molecular weight of the cluster is not going to be overestimated on the basis of the mass spectral evidence, and the probability is that the mass of the cluster is close to, but slightly above, the mass of the highest peaks seen in a distribution of peaks.

The third point is that the spectrum of **5**, the Au_{13} cluster, is quite different from that observed for the other, smaller clusters. It is the only cluster for which oligomerization is observed in the positive ion spectrum. Second, the amount of fragmentation is much less severe—fragments containing between nine and two gold atoms are much less abundant than the fragments containing eleven or twelve gold atoms. Three distributions can be observed which appear to be due to oligomers. Therefore although oligomerization of an Au_{13} cluster is seen, in ^{252}Cf-PDMS the oligomerization of this cluster is limited, with nothing beyond a tetramer of Au_{13} seen. This point will become important in the discussion of the results of SIMS[11] and ^{252}Cf-PDMS studies of the much larger gold clusters made by Schmid and co-workers.[1]

A fourth point is that the presence of halide ions attached to the cluster is reflected in the fragment ions seen. Thus for **4** and **5** peaks are seen for ions containing Cl^- and I^-, respectively. Therefore mass spectra should be able to show whether halides are attached to clusters or present as counterions.

(c) ^{252}Cf-PDMS of Large Gold Clusters. Our initial studies of the cluster originally synthesized by Schmid *et al.*[1] were aimed at arriving at a definite confirmation of the structure.[9] This was overambitious. In this report we will concentrate on three points. The first is whether the samples produced in different laboratories by different groups of workers give the same, or even similar, spectra. This should establish whether the synthesis of the "Au_{55}" cluster is reproducible in different hands. The second is whether the samples change with time and in what manner they change dependent on how they are stored. Finally, the third is whether the spectra observed are consistent with one cluster being present, an homogeneous sample, or several different clusters. The studies of small gold clusters have established that ^{252}Cf-PDMS can answer all of these questions. The question of heterogeneity of sample would be difficult to answer if two very similar clusters were present as the technique exaggerates similarities between clusters; it is unlikely that ^{252}Cf-PDMS would make the converse mistake, of making an homogeneous sample look heterogenous.

These three points are the most important in this area, for samples of this large gold clusters[1] are being heavily studied as a possible link between small metal clusters and colloids.[2] These physical studies are of interest, whatever the structure of the cluster, if the same compound is being studied every time and if the sample is homogenous. They are much less valuable if the sample is inhomogeneous or if its constitution is inconsistent. Compared with these questions, the structure of the cluster is of secondary importance.

(i) Sample Dependence On Age. The first question to deal with is whether the samples change with age and, if they do, whether the aging is dependent on how the sample is stored. Figure 4 shows four positive ion spectra recorded on samples synthesized in the L.H.P. laboratory. Spectrum A is that which we originally reported,[9] spectrum **B** is of a second sample which had been treated in exactly the same way as the first, i.e. stored at 0 °C and studied after a period of 1–2 months; spectrum C is of a sample studied immediately after synthesis; spectrum D is of the sample used for spectrum C but after it had been stored for several months at room temperature (*ca.* 18 °C).

Spectra A and B are very similar (some of the apparent difference is due to a change in instrumentation since our original report: see Experimental Section). In these two spectra there are three distributions centered at *m/z* 8200, 12 800, and 16 800. Spectrum B also has an additional, low-intensity distribution centered at *m/z* 21 800. The ratios of the intensities of these distributions is also fairly constant, with the lowest mass distribution being very slightly weaker in spectrum B than in spectrum A. Spectrum C contains exactly the same distributions as spectrum B but here the comparative intensities are more radically changed. Now the distribution centered at *m/z* 16 800 is the most intense. The comparative intensities of the distributions is quite unlike that observed for oligomers of clusters.[11,12] If higher mass zones are caused by oligomers of clusters, then they

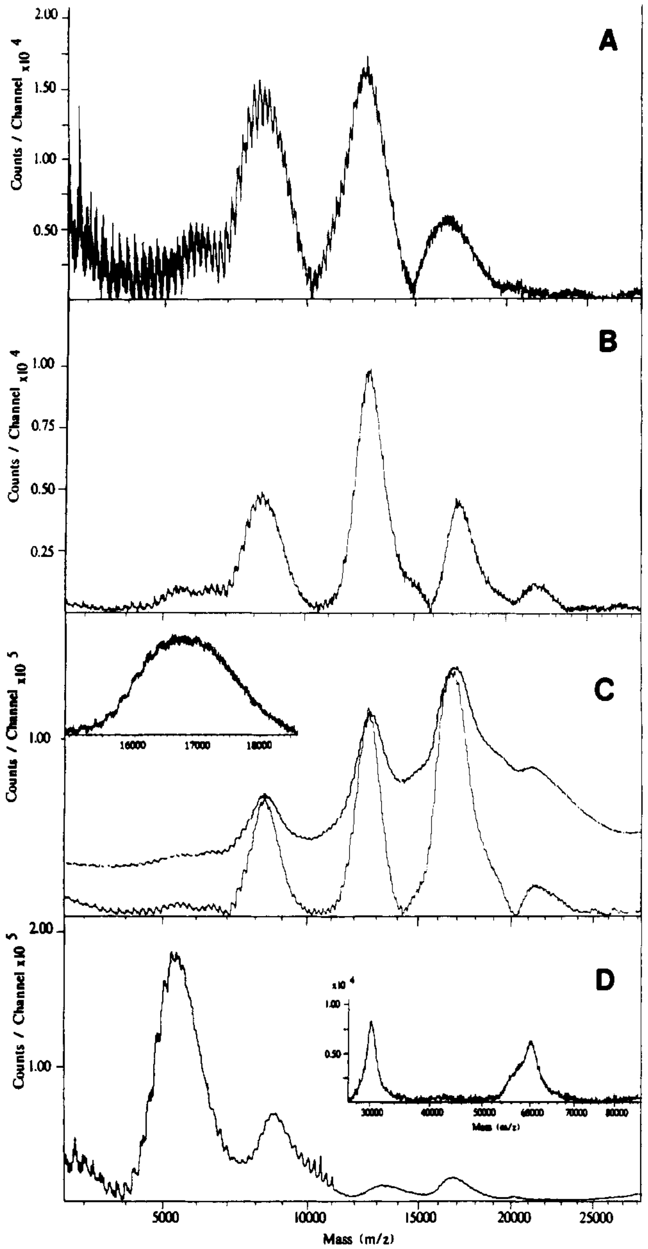

Figure 4. ^{252}Cf-PD positive ion mass spectra of four samples of the "Au$_{55}$" synthesized in the L.H.P. laboratory corresponding to (A) the original sample reported in ref 9, (B) a sample synthesized later and treated identically to the first, i.e. analyzed after 1–2 months storage in air at 0 °C, (C) sample analyzed immediately after synthesis, and (D) the same sample as in (C) but left at room temperature for several months. All spectra have been plotted after background subtraction. The top trace in (C) is the raw data before background subtraction. the inset of (C) is an expansion of the third distribution. In each spectrum data were accumulated for 10 h and are plotted at 32 ns/channel.

are always *less* intense than the zone due to the cluster-monomer. Thus it is extremely unlikely that the zone at *m*/*z* 16 800 could be due to oligomerization of a cluster of lower mass.

Spectrum D is quite different from the other three spectra. The major distributions are now centered at *m*/*z* 5300, 8600, 13 200, 16 800, 30 000, and 60 000. The distributions at *m*/*z* 5300 and 8600 are very close in mass to the distributions seen for oligomers of the Au$_{13}$ cluster (**5**) discussed above. The *m*/*z* 5300 distribution is the most intense in the spectrum, followed by the distribution at *m*/*z* 8600. No intense distribution is seen for Au$_{13}$ itself however, unlike for **5**. The intensities of the distributions in spectrum D do bear some resemblance to the intensities in mass spectra which contain oligomers, in that the lowest mass zones are the most intense.

Table II. High Mass Resolved Peaks in Spectrum D and Possible Assignments

peak (*m*/*z*)	possible assgnt (calc mass, mu)	
10 992	$Au_{39}(PPh_3)_{11}Cl_{12}$ (10 993)	
10 959	$Au_{39}(PPh_3)_{11}Cl_{11}$ (10 958)	
10 730	$Au_{39}(PPh_3)_{10}Cl_{12}$ (10 731)	
10 695	$Au_{39}(PPh_3)_{10}Cl_{11}$ (10 696)	
10 495	$Au_{38}(PPh_3)_{10}Cl_{11}$ (10 497)	
10 467	$Au_{39}(PPh_3)_9Cl_{12}$ (10 468)	
10 232	$Au_{38}(PPh_3)_9Cl_{11}$ (10 233)	
10 198	$Au_{38}(PPh_3)_9Cl_{10}$ (10 198)	
10 005	$Au_{37}(PPh_3)_9Cl_{10}$ (10 002)	$Au_{38}(PPh_3)_8Cl_{12}$ (10 009)
9 972	$Au_{37}(PPh_3)_9Cl_9$ (9 968)	$Au_{38}(PPh_3)_8Cl_{11}$ (9 973)
9 744	$Au_{37}(PPh_3)_8Cl_{10}$ (9 740)	$Au_{38}(PPh_3)_7Cl_{12}$ (9 747)
9 710	$Au_{37}(PPh_3)_8Cl_9$ (9 705)	$Au_{38}(PPh_3)_7Cl_{11}$ (9 712)
9 480	$Au_{37}(PPh_3)_7Cl_{10}$ (9 478)	$Au_{38}(PPh_3)_6Cl_{12}$ (9 484)
9 445	$Au_{37}(PPh_3)_7Cl_9$ (9 443)	$Au_{38}(PPh_3)_6Cl_{11}$ (9 449)

To try to disrupt any oligomerization, the samples were prepared in a more polar solvent (95% THF/H$_2$O). Spectra B and C were unchanged, but in spectrum D the distributions at *m*/*z* 16 800, 30 000, and 60 000 disappeared. This supports the contention that these distributions at *m*/*z* 16 800, 30 000, and 60 000 are due to oligomers of the clusters which are causing the zones at lower mass.

Whatever the explanation of the highest mass distributions in spectrum D the important conclusion is that the sample, if stored at room temperature, *does* change. This is in agreement with the eventual conversion of the cluster to gold colloids or metallic gold if heated.

A feature observed in spectrum D, but not in the other three spectra, is a series of resolvable peaks on the high-mass end of the distribution of *m*/*z* 8600. These appear as seven sets of "doublets", which the two peaks in each "doublet" separated by 35 mu. The doublets are then separated from each other by either 262 or 197 mu. These peaks are listed, with possible assignments in Table II. Other assignments are possible; e.g., four golds can always be replaced by three phosphine ligands, but it does appear that sensible assignments of this region are restricted to clusters with between 37 and 46 gold atoms. It is tempting to associate these fragments with the $Au_{39}(PPh_3)_{14}Cl_8$ cluster reported by Teo and co-workers.[8]

An additional change observed in spectrum D was in the relative intensity of the low-mass ions. In spectra B and C peaks due to PPh$_3$ and PPh$_2$ were more intense than peaks due to Au(PPh$_3$) and Au$_2$(PPh$_3$). In spectrum D this pattern is reversed. The pattern in the SIMS spectrum observed by Benninghoven, Schmid, and co-workers,[11] in the low-mass region, bore much more similarity to the pattern we observe for spectrum D, the aged sample.

These spectra differ fundamentally from the spectra reported by Benninghoven, Schmid, and co-workers.[11] SIMS causes very extensive oligomerization of the cluster or a fragment thereof. ^{252}Cf-PDMS does not cause such extensive oligomerization of these compounds. This suggests that the two techniques are complementary, giving different information about the behavior of this cluster. SIMS indicates that the cluster has a tendency to oligomerize, an observation confirmed by HRTEM[2] and indeed by the gold mirror rapidly formed when a solution of the cluster is warmed. ^{252}Cf-PDMS appears to be a "more gentle" technique than SIMS for these clusters; we believe we are not seeing the result of a massive reorganization of the cluster, as proposed for the SIMS spectra, but spectra more immediately related to the structure of the cluster itself.

(ii) Sample Dependence on Different Sources. In our original report[9] we studied samples supplied by two different groups. We found that the spectra recorded on the two samples differed significantly. The great interest in the work of Schmid had led to many other groups also making samples of this cluster. Therefore, we have been able to obtain further samples, made by

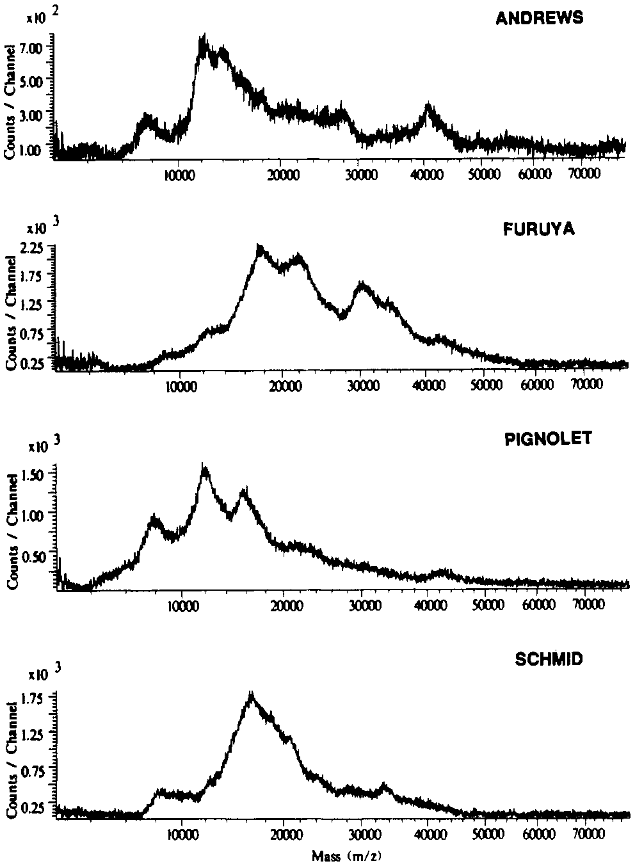

Figure 5. ^{252}Cf-PD positive ion mass spectra of "Au_{55}" clusters synthesized by four different laboratories. The same L.H.P. sample was used to obtain the spectrum shown in this figure as that used for Figure 4B. Data were acquired for 1 h and are plotted at 32 ns/channel.

still other hands. We felt it was of considerable importance to establish whether there was a great difference between the samples prepared by different workers.

Four samples were studied, all synthesized by the Schmid procedure.[10] These clusters were prepared by M. P. Andrews (Bell Labs) and F. Furuya (Brookhaven Laboratories), in addition to a sample prepared in the L.H.P. laboratory and an orginal sample obtained from the Schmid laboratory. The last sample is important as it is much older (*ca.* 1 year older) than the samples from the other three sources. The spectra are shown in Figure 5, with minimal data manipulation e.g. background subtraction. Clearly the spectra are different, and therefore, assuming the technique gives reproducible results, the samples made in the different laboratories are also nonidentical. The dissimilarities are numerous, though one could say that some of the same distributions of peaks are present in each sample.

The last stage of the synthetic procedure described by Schmid[10] involves a filtration of a dichloromethane solution of the sample through Celite. We felt it was worth attempting to repeat this purification step on the four samples studied. The purification step involved eluting the sample through a 4–6-cm column of Celite using a solution of the samples in CH_2Cl_2, gradually increasing the polarity of the eluant by adding pyridine. Two bands came through, the first in 9:1 CH_2Cl_2/pyridine. This could be evaporated to dryness and redissolved in CH_2Cl_2. The second band could only be eluted with pure pyridine. This band, on evaporation, gave a black solid, which did not redissolve in any common solvent. A large amount of material was left on the column, which became purple within 1 h. This "purification" probably causes some decomposition of the cluster, and we believe both band two and the residue are probably gold colloids rather than gold phosphine clusters. These colloids are probably the result of the purification, rather than components of the original sample.

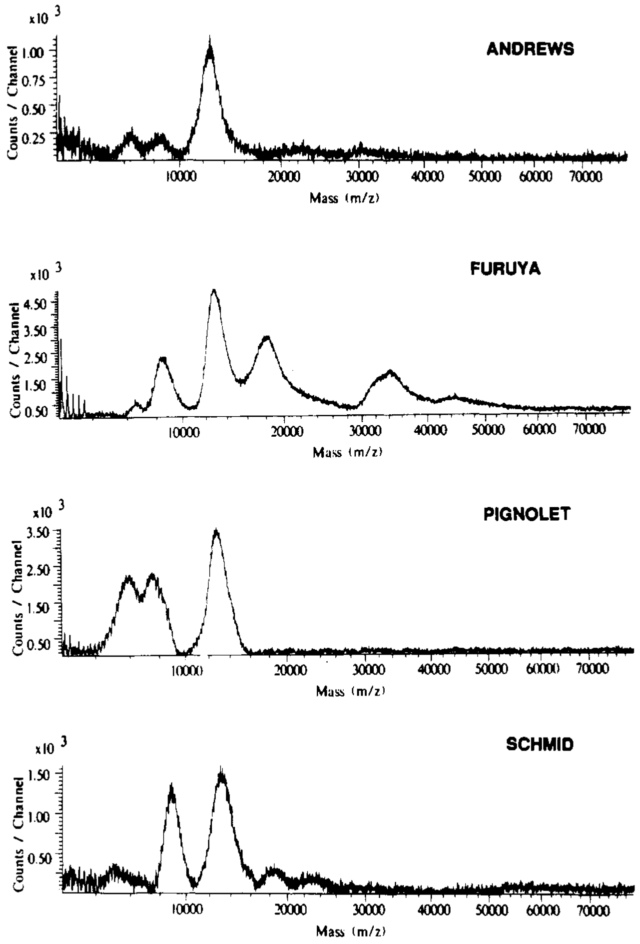

Figure 6. ^{252}Cf-PD positive ion mass spectra of the cluster products after chromatography through Celite. Data were acquired for 1 h.

Mass spectral analysis of the compounds in the first band was interesting, and the spectra are shown in Figure 6. The similarities between the four spectra are now much more pronounced. In each the most prominent distribution is now centered at m/z 12 870 ± 50. With the exception of the Furuya sample all the higher mass distributions have been eliminated. These high mass distributions were also much more evident in the Furuya sample before purification (Figure 5). Additionally in the chromatographed samples two zones are observed at lower mass, and they are at the same position in each spectrum, although their relative intensities differ greatly between samples. These spectra indicate that the similarity of the samples can be improved considerably by a second separation step. Attempts to devise a less crude separation procedure have thus far been unsuccessful.

These results strongly suggest that the samples prepared by different research groups are nonidentical, despite all groups intending to follow the same procedure. This procedure[10] involves several steps which might cause subtle differences in the sample produced. For example, we have shown that the compound changes depending on the temperature at which it is stored. The preparation requires reduction of $Au(PPh_3)Cl$, starting at room temperature, followed by raising the temperature to 50 °C. It is unlikely that all the groups kept to precisely the same temperature regime. The reduction is carried out for "~40 minutes". Later in the synthetic procedure pentane is added over a period of "~2 hours" to precipitate the compound. Rapid precipitation is said to produce different products,[10] and a variation in the rate at this stage by the different groups might again produce a different product. Therefore, the implications from the spectra are quite reasonable. The synthetic procedure is open to a variety of minor changes, and it appears that the resulting compound is sensitive to these minor changes.

(iii) Homogeneity of Samples. We have shown that the compound changes with time and that the synthetic procedure in different hands gives different products. There remains the question of whether the samples prepared are homogeneous, i.e. contain just one cluster, or whether they contain mixtures of several different high-nuclearity clusters. The crude chromatographic procedure described above may appear to indicate that we can separate out different fractions, but the likelihood of sample decomposition and of interference from the polar component of the solvent system does not make this a decisive test. The spectra of the compounds as prepared have to be considered. For this purpose therefore the spectra B–D are most important (Figure 4), as here we have a series of spectra recorded on samples synthesized by one group.

In each of these spectra we see several zones of high-mass peaks. There are four possible explanations for the presence of such peaks. The first is that the technique is entirely unreliable and that we might see zones anywhere regardless of sample composition. All the experiments we have tried on small gold phosphine clusters and on platinum carbonyl clusters[12] suggest this is an incorrect proposition. The similarity of spectra A and B also rule against this being a serious alternative.

The second possibility is that the various distributions are caused by oligomerization of one cluster. In the spectrum of **5**, the Au_{13} cluster, we did see four zones, despite it being a pure, crystallographically characterized compound. Benninghoven, Schmid, and co-workers have interpreted SIMS results[11] as due to oligomerization of Au_{13}. We can rule this out for spectra B and C. These spectra are not due to oligomerization of Au_{13} units; we know what such a ^{252}Cf-PDMS spectrum would look like as we have studied an Au_{13} cluster. The spectrum of 5 does not resemble spectrum B or C. To reiterate, the oligomer distributions would be expected to have lower intensity than the monomer distribution. In spectrum C the zone at *m/z* 16 800 is the most intense. This implies that it cannot be due to an oligomer of either of the lower mass zones. Spectrum C is simply not consistent with any spectrum seen for oligomerization of any organometallic cluster. On the other hand, in spectrum D it is possible that all the higher mass zones are due to oligomerization of one cluster and that cluster would be that which gives rise to the high intensity distribution centered at *m/z* 5300. Oligomerization should also lead to concentration-dependent spectra—peaks due to oligomers should decrease more rapidly in intensity as the concentration is lowered than peaks due to monomers. In spectra recorded on the sample used for spectrum B, all zones diminished in intensity at the same rate as the concentration of the solution was lowered from *ca.* 10^{-3} to 10^{-6} M. Therefore, we can exclude the presence of four zones being due to oligomers.

The third possibility is that the distributions are due to fragmentation of one cluster. Considering spectrum C, the zones centered at *m/Z* 8200 and 12 800 would then be due to fragments of the cluster giving rise to the zone centered at *m/z* 16 800. (NB.: the low intensity zone at higher mass *could* be due to an oligomer as it is of such low intensity.) This alternative cannot be easily dismissed. In terms of the chemistry of the system, this would mean that fragmentation of the parent cluster would cause the zone at *m/z* 16 800, while fragmentation of daughter clusters would cause the zones at *m/z* 8200 and 12 800. In such a case the parent cluster would have to give two daughter clusters of special stability. Several different possible models could be proposed to account for this. For example, if we consider the 39 gold atom cluster characterized by Teo, it contains 1:9:9:1:9:9:1 Au atom layers. It has the correct mass to be the daughter cluster giving rise to the zone centered at *m/z* 8200. Adding on another three layers, to give 1:9:9:1:9:9:1:9:9:1, would give a 58 atom cluster, which would explain the zone at *m/z* 12 800. The parent cluster would then be a 1:9:9:1:9:9:1:9:9:1:9:9:1 77 atom cluster.

We are not proposing this model as an explanation, merely using it as an illustration of the type of process which would give rise to the spectrum seen, assuming the spectrum is due to fragmentation of one parent cluster and two daughters. A layered cuboctahedral model such as that proposed by Schmid[2] might also explain the pattern. Vertex-sharing icosahedra, as proposed previously,[9] would explain how one parent would give two daughter clusters. Deciding between these, and other, models is impossible on the basis of the evidence, through some models may appear inherently more probable than others.

The question is whether the fragmentation of one parent into two different daughters explains all spectra. Spectrum B differs from spectrum C merely in the comparative intensities of the various distributions. Assuming that the fragmentation explanation is correct, then we have to assume that the aging of sample C to give sample B has not changed the composition of sample B but merely changed the degree to which it fragments. For spectrum C, the parent cluster is the most abundant in the spectrum, but for spectrum B one of the daughter clusters is more numerous. This seems an unlikely scenario but possible. A more probable explanation is that the sample which gave rise to spectrum B already contained the two daughter clusters in addition to the parent. In other words, the aging process at 0 °C (which gave sample B) and the fragmentation process seen in spectrum C are proceeding *via* the same path.

If we take this one step further, we can see how this would explain spectrum D. Aging the sample at room temperature leads to still further fragmentation of the cluster to give yet smaller daughter clusters—the most abundant being that which gives the zone centered at *m/z* 5300. The final step in the decomposition to the metallic state is oligomerization of the daughter seen in spectrum D or perhaps a yet smaller daughter. This process would then be in complete agreement with the model proposed by Benninghoven, Schmid, and co-workers to explain their SIMS results,[11] the difference being that using ^{252}Cf-PDMS we have observed the intermediate clusters before oligomerization, whereas SIMS shows the oligomerization process itself.

The final possible explanation of the presence of several distributions in each spectrum is that the sample is inhomogenous. The previous explanation involved assuming that sample B was inhomogeneous after aging. It is also possible that the sample as prepared is inhomogeneous and does not contain only one cluster. This explains all the spectra observed without difficulty, the only difference from the fragmentation explanation is that it assumes the parent and daughter clusters are "born" at the same time. Deciding between these last two possible explanations is not possible from the mass spectral evidence. We are unaware of any previous studies which would support either explanation; e.g., HRTEM[2] might decide between a 500 atom cluster and a 50 atom cluster, but it is not a suitable technique for ruling out the presence of a 40 atom cluster in a sample of a 55 atom cluster.

(iv) Possible Model Structures. In our preliminary communication on this work[9] we suggested that the Schmid cluster be reformulated as $Au_{67}(PPh_3)_{14}Cl_8$—a cluster consisting of six icosahedra sharing six vertices. This was based on a mistake: we assumed that the center of each zone most accurately reflected the mass of the cluster. We now realize, from our studies of small gold phosphine clusters, that it is the upper-edge of each zone that most accurately reflects the mass of the cluster giving rise to the zone. The upper edges for the three intense zones in spectra B and C are at *ca. m/z* 9500, 14 000, and 20 000. The prominent distribution in the chromatographed samples also has an upper-edge of *ca. m/z* 14 000.

We could explain these distributions in terms of various possible series of related clusters; however we realize that our evidence is inconclusive and that any number of models are equally believable. The structure of Au_{39} reported by Teo has lent support to the view that predicting the structures of such high-nuclearity clusters is a hazardous undertaking. However, we do feel that any others who wish to propose structural models for the Schmid cluster are obliged to explain the apparent stability of clusters of mass *ca.* 9500, 14 000 and 20 000 mu. On this subject it is worth stating that the formulation $Au_{55}(PPh_3)_{12}Cl_6$ (MW = 14 195) would explain the middle zone, and this is also the most prominent zone for the chromatographed samples. The most abundant cluster in the freshly synthesized sample appears to be of higher mass than "Au_{55}".

Conclusions

In the discussion above we have attempted to describe the potential and limitations of ^{252}Cf-PDMS as applied to small gold phosphine clusters and then use this technique to study the very large gold cluster first synthesized by Schmid and co-workers.[1]

^{252}Cf-PDMS has previously been shown[12] to give interesting and unusual results with platinum carbonyl clusters. These clusters are considerably more robust than the gold phosphine clusters studied here. Our results indicate that the small gold clusters undergo extensive fragmentation and that although this fragmentation does indicate that a polynuclear gold cluster is present, it is not diagnostic for a particular formula for the cluster. Our studies indicate that the molecular weight of the cluster is close to, but above, the mass of the highest fragment seen. Thus ^{252}Cf-PDMS will enable prediction of the *lowest possible value for the molecular mass of a cluster.*

We have also shown that an Au_{13} cluster gives different spectra from smaller clusters. The spectrum of **5** contains quite different fragment ions and distributions of peaks consistent with oligomerization of the metallic core of the cluster. The most abundant fragments contain either 11 or 12 gold atoms, indicating that fragmentation is limited; the oligomers extend only as far as a very weak distribution for a tetramer of Au_{13}. This oligomerization is quite unlike that observed for platinum carbonyl clusters.[12]

For clusters containing only 6–13 metal atoms such results are disappointing and no better than those obtained by FABMS. It would not be possible to predict a molecular formula based on these results. For high-nuclearity clusters there are other questions to be answered, such as whether large clusters decompose with time and whether syntheses in different hands produce the same result. ^{252}Cf-PDMS can answer these questions.

The studies on four samples of the Schmid cluster lead to the following conclusions: 1. The samples synthesized by different groups of workers *are* different. The synthesis appears to be open to interpretation, leading to different clusters being formed in different laboratories. 2. The samples change with time, slightly if stored at 0 °C and markedly if stored at room temperature. 3. Part of the aging process is that the sample becomes inhomogeneous. The relative intensities of the several zones observed in the spectrum change as the sample is aged. This is consistent with the original cluster breaking down to give daughter clusters; presumably these daughter clusters have structures related to that of the parent. 4. Distributions are seen in the spectrum of a freshly prepared sample which have to be assigned as due to three different clusters. Therefore, the sample as synthesized is either inhomogenous, i.e. contains more than one cluster, or fragments to give two stable daughter clusters in addition to the parent. 5. Whether the sample is inhomogeneous or not, whichever model is used in the future for the Schmid cluster will have to account for the stability of three clusters with molecular weights close to, but possibly slightly above, 9500, 14 000, or 20 000 mu.

The ^{252}Cf-PDMS results are quite different from those obtained by Benninghoven, Schmid, and co-workers[11] using SIMS. SIMS gave spectra containing distributions of peaks with masses up to 139 000 mu. There is no doubt that these distributions reflect oligomerization of some cluster or cluster fragment, but it is still debatable what that cluster is.[25] It is well documented[26] that much larger cluster ions of metals and ionic solids (e.g. CsI) are observed by SIMS than by ^{252}Cf-PDMS. It is therefore not unreasonable that in the SIMS spectra oligomers of "Au_{55}" are observed, whereas in the superior, merely that they are different. All results (e.g. concentration dependence, relative intensities of distributions, dependence on solvent polarity) indicate that the ^{252}Cf-PDMS spectra of freshly prepared "Au_{55}" does not contain oligomers.

The explanation of the spectra in terms of structural models for the cluster or clusters in the sample is controversial, and currently insufficient evidence exists to prove any particular structure. What is unarguable, given the spectra discussed above, is that the synthesis of the compound is not completely reproducible between different research groups and that the sample changes with time. It is entirely possible, though not proven, that all samples are inhomogeneous.

Three points are of great importance to all workers studying these fascinating compounds. The structure is *not proven.* The constitution may not be monodispersed. The results of physical studies of these clusters must be reconsidered in the light of these facts.

Acknowledgment. We thank Prof. G. Schmid (University of Essen) and Drs. F. Furuya (Brookhaven National Laboratory) and M. P. Andrews (Bell Lab) for samples of the large gold clusters synthesized in their laboratories. J.M.H. was supported by a National Merit Minority Grant. The work was also supported by National Science Foundation grants awarded to C.J.M. (CHE 9101855), L.H.P. (CHE 8818187), J.P.F. (CHE 8708625), and G.V. (CHE 8919151). A Robert A. Welch Foundation grant (A-0960) awarded to J.P.F. also supported R.E.P.W. R.D.M. acknowledges support from the Robert A. Welch Foundation (A-258) and the National Institutes of Health (GM26096). Helpful suggestions from Prof. L. F. Dahl are also gratefully acknowledged.

---

(25) It is proposed[11] that the monomer is Au_{13}. Three spectra are reported, with the thickness of the layer of sample varied between each spectrum. The only oligomers found are $(Au_{13})_n$ with $n = 7, 15, 23, 31, 39, 47$, and 55 or $n = 5, 9, 17$, and 33 or n = 3, 7, and 13 depending on the exact conditions of the experiment—the thicker the layer, the greater the degree of oligomerization. No reason is given why these oligomers, and no others, are seen. The most extended SIMS spectrum consists of a series of broad distributiosn separated by *ca.* 20 000 mu (e.g. centered at 17 900, 38 400, 58 900, 79 400, 99 500, 119 000, and 139 000). This separation happens to be close to the mass of $(Au_{13})_8$. It is, of course, also close to the mass of *any* gold cluster which contains around 100 atoms. It is also close to the mass of the largest distribution we observed by ^{252}Cf-PDMS. Indeed, this spectrum reported by Benninghoven, Schmid, and co-workers is entirely consistent with the oligomerization of a cluster of mass 20 000 mu. The distribution for the monomer would be *centered* near 17 000–18 000 mu (as for spectrum C above) but would have an upper-edge at *ca.* 20 000 mu. As we have shown, it is the upper-edge value which is important, not the mass at the center of the distribution. Oligomerization of such a cluster would give zones separated by 20 000 mu. Such an oligomerization would be precedented in the literature,[12] while the proposed oligomerization[11] of a fragment (Au_{13}) of a cluster (Au_{55}) has no precedent. Whether the SIMS results are interpreted as originally proposed, or reconsidered, they remain quite different from the ^{252}Cf-PDMS results.

(26) Colton, R. J.; Kidwell, D. A.; Ross, M. M. In *Mass Spectrometry in the Analysis of Large Molecules*; McNeal, C. J., Ed.; John Wiley & Sons: Chichester, U.K., 1986; p 13.