

THE ROLE OF FAST ATOM BOMBARDMENT MASS SPECTROSCOPY (FABMS) IN CLUSTER CHARACTERIZATION

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Fast atom bombardment mass spectroscopy has been used to study a large number of cationic phosphine-containing transition-metal-gold clusters, which ranged in mass from 1000 to 4000. Many of these clusters have been previously characterized and were examined in order to test the usefulness of the FABMS technique. Results showed that FABMS is excellent in giving the correct molecular formula and when combined with NMR, IR, and microanalysis gave a reliable characterization for cationic clusters¹. Recently FABMS has become one of the techniques employed as routine in cluster characterization^{2,3} and also is an effective tool for the structure analysis of large biomolecules⁴. Some results in the present work reinforce the importance of these data in the characterization of clusters in the absence of crystals with quality for X-ray analysis.

Keyword: cluster; gold; palladium.

INTRODUCTION

Although single crystal X-ray crystallography remains the only definitive technique for structural characterization of heteronuclear gold cluster compounds other techniques, and in particular FABMS, have made available valuable information especially concerning the nature of these species in solution³.

The advent of FABMS in which ion generation is achieved by bombardment of the sample by a beam of fast rare gas atoms⁵ resolved the limitation problem that the conventional electron impact mass spectrometry used to have in the characterization of high molecular weight cluster compounds. The FABMS spectra of these species are presented as a number of peaks with well resolved fine structures arising from the various possible isotopic combinations for a given molecular formula.

FABMS is also extremely useful in determining the molecular formula of the parent cluster⁶. Assignments of the clusters fragments provide additional information about cluster composition. As an example the FAB spectrum for the supra cluster [Pt₂(AuPPh₃)₁₀Ag₁₃Cl₇] shows in the 4500 to 7000 range some masses assigned to molecular fragments⁷. In general the most abundant peak in this range is due to the parent cluster molecular ion. In many cases the use of this technique provides the best information about the nature of a new or novel cluster when the X-Ray quality crystals are impossible to obtain. Then, associated to other spectroscopic techniques as NMR, IR and with microanalysis gives a reliable characterization for compounds with high molecular weight. Many examples are given in order to emphasize the power of this technique for cluster characterization.

FABMS and cationic clusters

The synthesis of new cationic mixed gold clusters with transition metals and triphenylphosphine (PPh₃) as ligand is a field of great interest due to their potential utilization in catalysis^{8,9}.

Research involving ligand stabilized metal clusters has increased considerably in the last two decades and great progress has been

achieved in this field. These compounds have gained attention among chemists and physicists due to their fascinating geometries, unique fluxional behavior, catalytic potential and interesting chemical reactivity^{6,10,11}.

Originally the studies of metal clusters dealt primarily with their synthesis and structure determination. More recently efforts have turned towards a systematic study of chemical reactivity and catalytic properties⁶.

The report on the synthesis and characterization including a single crystal X-ray crystallographic analysis of the first cluster compound containing Au-Pd bond was published in 1989¹⁰. Since then only some new and novel clusters of this type have been synthesized and well characterized¹².

The cationic cluster [(PPh₃)Pd(AuPPh₃)₆](NO₃)₂ (**1**), a promising complex for reactivity studies was first isolated by Ito *et al.*¹⁰ as a minor product of the reaction between [Pd(PPh₃)₄] and AuPPh₃NO₃ in CH₃OH/CH₂Cl₂ using inert atmosphere. The minor product of this reaction was identified as (**1**) and separated from the major product [Pd(AuPPh₃)₈]²⁺ by HPLC. The cluster was later prepared with better yield using palladium acetate as precursor¹¹. Another faster synthesis of this cluster has been carried out with Pd(PPh₃)Cl₂ and AuPPh₃NO₃¹³. The addition reaction of NH₄PF₆ salt to the cluster [(PPh₃)Pd(AuPPh₃)₆](NO₃)₂, provided a new cluster with PF₆⁻ as counterion, and the crystal and molecular structure of this compound has been reported¹². The characterization was also made by ³¹P {¹H} NMR, microanalysis, IR and FABMS. The FABMS data are the subject of the present article.

A new phosphine stabilized Au-Pd cluster compound [(dmpi)₂Pd(AuPPh₃)₃](NO₃)₂ was prepared by direct reaction of dmpi (2,6 dimethyl phenyl isonitrile) with the cluster (**1**) under nitrogen atmosphere. The structure for this cluster was obtained¹⁴ in agreement with FAB data (two isonitrile groups substituted the PPh₃ group present in cluster (**1**)).

The addition reaction of Hg⁰ or Hg₂²⁺ to the cluster (**1**) was also reported¹⁵. ³¹P {¹H} NMR, IR, and FAB-MS data were very useful in confirming the structure of this trimetallic cluster.

Another trimetallic cluster containing Au-Pd and Sn, [Pd(AuPPh₃)₆(SnCl₃)₂](NO₃)₂ was prepared from the reaction of (**1**) and SnCl₂·2H₂O under nitrogen atmosphere. This new compound

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has been characterized by $^{31}\text{P}\{^1\text{H}\}$ NMR, IR, FAB-MS and TGA/DTG¹⁶.

This paper reports the results obtained with the use of FABMS, for some Pd-Au clusters emphasizing the utility of this technique in giving the correct molecular formula when combined with NMR, IR and elemental analysis.

EXPERIMENTAL PART

Physical measurements

FABMS experiments were carried out with use of a VG Analytical, Ltd., 7070-HF high resolution double focusing mass spectrometer equipped with VG11-250 data system.

Reagents

All manipulations concerning the syntheses were carried out under a purified N_2 atmosphere with use of standard Schlenk techniques unless otherwise noted. Solvents were dried and distilled prior to use. NaBH_4 was purchased from Aldrich Chemical S. A.

Preparation of the compounds

1. $[(\text{PPh}_3)_2\text{Pd}(\text{AuPPh}_3)_6](\text{PF}_6)_2$ was prepared as described in the literature. The analytical data reported below is for the PF_6^- derivative. ^{31}P NMR (H_3PO_4 , 20 °C): d 50.0 (doublet with $^3J_{\text{P-P}} = 31$ Hz), δ 62.1 (multiplet with $^1J_{\text{P-F}} = 712$ Hz). Anal. Calcd. for $\text{Au}_6\text{Pd}_2\text{P}_9\text{C}_{126}\text{H}_{105}\text{F}_{12}$: C, 44.3; H, 3.08. Found: C, 44.04; H, 3.23. IR (KBr): ν (cm^{-1}) = 840 (PF_6)¹².
2. $[(\text{dmp})_2\text{Pd}(\text{AuPPh}_3)_6](\text{NO}_3)_2$ was prepared as described in literature. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C): AuP δ 45.0 (singlet), IR: ν (CNR) 2093 cm^{-1} . Conductance (CH_3CN solution): 321 S $\text{cm}^2 \text{mol}^{-1}$ (1:2 electrolyte)¹⁴.
3. $[\text{Pd}(\text{AuPPh}_3)_6(\text{HgNO}_3)](\text{NO}_3)$ was obtained from nucleophilic addition and substitution reaction between either Hg^0 or Hg_2^{2+} and cluster (1) as reported in the literature. $^{31}\text{P}\{^1\text{H}\}$ NMR

(CDCl_3 , 25 °C): AuP δ 43.0 (singlet) with ^{199}Hg satellites ($^3J_{\text{Hg-P}} = 690$ Hz) due to the AuPPh_3 ligands bound to Pd atom. The quantitative determination of metals Pd and Au: calc. 1 Pd : 6 Au (0.92 Pd : 6.32 Au). Anal. Calc. $\text{PdAu}_6\text{P}_6\text{C}_{108}\text{H}_{90}\text{HgN}_2\text{O}_6$, Pd = 3.33%, Au = 37.12% (found: Pd = 3.08%, Au = 39.11%)¹⁵.

4. $[\text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2](\text{NO}_3)_2$ was prepared from the substitution reaction (PPh_3 to SnCl_3) between (1) and $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C): AuP δ 49.0 (singlet). IR (KBr): ν (cm^{-1}) = 1186 (NO_3). Raman: ν (cm^{-1}) = 291.6 (SnCl)¹⁶.

RESULTS AND DISCUSSION

The reaction of $[(\text{PPh}_3)_2\text{Pd}(\text{AuPPh}_3)_6](\text{NO}_3)_2$ (1) with excess of NH_4PF_6 gave the cluster compound $[(\text{PPh}_3)_2\text{Pd}(\text{AuPPh}_3)_6](\text{PF}_6)_2$ in 40% yield. The compound has been characterized by NMR, IR, microanalysis, and X-Ray crystal and molecular structure¹².

The molecular composition of PF_6^- derivative was also confirmed by FABMS. These results turned possible the determination of the cluster ion formula despite not related in that publication (previously not available). Positive-ion FABMS analysis (m-nitrobenzyl alcohol matrix) of this cluster gave a spectrum with well-resolved peaks. An analysis of the isotopic distribution pattern for the most abundant mass ion in 3006.4 corresponded to the ion $\{[\text{Pd}(\text{AuPPh}_3)_6](\text{PF}_6)\}^+$. Other results showed fragmentation at: m/z 3413.8 (fragment $[\text{M} + 2\text{X}]^+$, where $\text{M} = [\text{Pd}(\text{AuPPh}_3)_6(\text{PPh}_3)]$ and $\text{X} = \text{PF}_6$); 3269.0 (fragment $[\text{M} + \text{X}]^+$); 2861.5 (fragment $[\text{M} - \text{PPh}_3]^+$); 2664.7 (fragment $[\text{M} - (\text{AuPPh}_3)]^+$); 2547.3 (fragment $[\text{M} - \text{AuPPh}_3 - \text{PPh}_3 + \text{X}]^+$).

Although the FABMS of these mixed metal-gold clusters gave accurate information on the molecular formula, it is also very important to analyze other spectroscopic and analytical data. NMR gives information on the relative number of non-equivalent phosphine ligands. IR assignment confirms the presence of PF_6^- as counterion. A complete analysis of the fragmentation pattern suggested that the neutral compound was $[(\text{PPh}_3)_2\text{Pd}(\text{AuPPh}_3)_6](\text{PF}_6)_2$ (Figure 1). These data can be compared with the analogous cluster

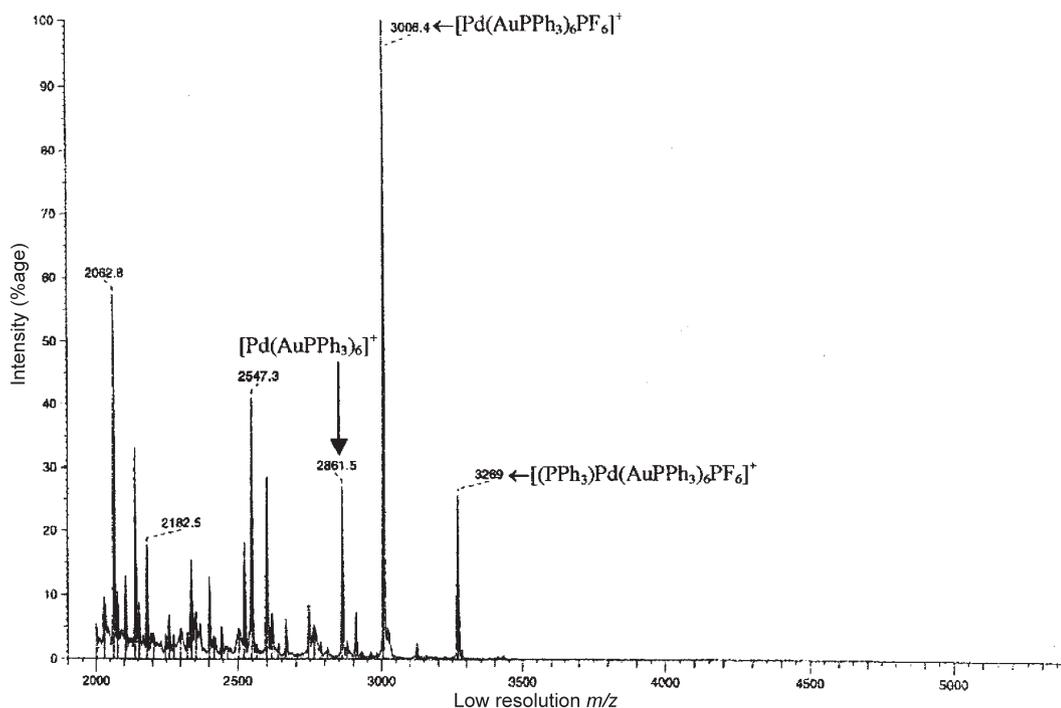


Figure 1. Positive ion FAB-MS of $[(\text{PPh}_3)_2\text{Pd}(\text{AuPPh}_3)_6](\text{PF}_6)_2$ in the m/z range 2000-5600. The major peaks are assigned to molecular fragments as indicated

with NO_3^- as counterion¹¹, and these results shows, once more, the reliability of this technique.

The FABMS analysis of the cluster $[(\text{dmpi})_2\text{Pd}(\text{AuPPh}_3)_6](\text{NO}_3)_2$ gave direct evidence for the new cluster composition. The spectrum presented well-resolved peaks. The $(\text{M} + \text{NO}_3)$ ion pair was the highest mass peak and the loss of dmpi and PPh_3 was noted. The results of FABMS (*m*-nitrobenzyl alcohol matrix) where assigned as follow: m/z 3185.3 (fragment $[\text{M} + \text{NO}_3]^+$, where $\text{M} = [\text{Pd}(\text{AuPPh}_3)_6(\text{dmpi})_2]$); 3056.2 (fragment $[\text{M} + \text{NO}_3 - \text{dmpi}]^+$); 2992.9 (fragment $[\text{M} - \text{dmpi}]^+$); 2924.6 (fragment $[\text{M} + \text{NO}_3 - 2 \text{dmpi}]^+$); 2924.6 (fragment $[\text{M} + \text{NO}_3 - \text{PPh}_3]^+$); 2861.5 (fragment $[\text{M} - 2 \text{dmpi}]^+$); 2861.5 (fragment $[\text{M} - \text{PPh}_3]^+$); 2793.3 (fragment $[\text{M} + \text{NO}_3 - \text{dmpi} - \text{PPh}_3]^+$); 2599.9 (fragment $[\text{M} - 2 \text{dmpi} - \text{PPh}_3]^+$); 2599.9 (fragment $[\text{M} - 2 \text{PPh}_3]^+$). Just every expected peak was present and they were all major peaks. The proposed molecular formula for this cluster was confirmed later by single crystal X-ray structure¹⁴.

High purity crystals of the cluster $[\text{Pd}(\text{AuPPh}_3)_6(\text{HgNO}_3)](\text{NO}_3)$ were obtained but, unfortunately, inappropriate for X-ray analysis. FABMS, in this case, was an extremely useful technique in the determination of the molecular formula. The highest mass peak was assigned as $\text{MX} = [\text{Pd}(\text{AuPPh}_3)_6(\text{HgNO}_3)](\text{NO}_3)$. Other results FABMS (*m*-nitrobenzyl alcohol matrix) are presented: m/z 3182.8 (fragment $[\text{M} + \text{X}]^+$, where $\text{M} = [\text{Pd}(\text{AuPPh}_3)_6(\text{HgNO}_3)]$ and $\text{X} = \text{NO}_3$); 3120.7 (fragment $[\text{M}]^+$); 3057.7 (fragment $[\text{M} - 2 \text{X}]^+$); 2980.9 (fragment $[\text{M} - \text{Hg}]^+$).

The trimetallic cluster $[\text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2](\text{NO}_3)_2$ was obtained in high purity state but the crystals were inappropriate for X-ray analysis. In this case, FABMS and TGA/DTG were techniques extremely useful in the determination of the molecular formula. Positive-ion FABMS analysis of this cluster gave a spectrum with well-resolved peaks. The highest mass peak (FABMS) was assigned as $[\text{M} - \text{Cl}] = [\text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2 - \text{Cl}]$ in m/z 3276.2. All the assignments are presented and results show all the usual fragmentations (Table 1). Other technique used in order to achieve the molecular formula was TGA/DTG.

Table 1. Positive ion FABMS of $[\text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2](\text{NO}_3)_2$ cluster followed by m/z , relative abundance (assignment)^a, $\text{M} = \text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2$; $\text{X} = \text{NO}_3$

Species	Calculated (amu)	Observed (amu)	Relative intensity (%)
$[\text{M} - \text{Cl}]^+$	3276.6	3276.2	10
$[\text{M} - \text{AuPPh}_3 - \text{Cl}]^+$	2817.4	2818.3	40
$[\text{M} - \text{AuPPh}_3 - \text{SnCl}_4]^+$	2592.3	2592.0	60
$[\text{M} - (\text{AuPPh}_3) - \text{SnCl}_4 - \text{PPh}_3]^+$	2330.1	2329.6	35
$[\text{M} - 2 (\text{AuPPh}_3) - \text{SnCl}_4]^+$	2133.5	2133.4	100
$[\text{M} - 2 (\text{AuPPh}_3) - \text{SnCl}_6]^+$	2062.5	2062.6	55

The thermal decomposition process observed in TGA/DTG curves started at 24 °C, was pronounced at 196 °C and finalized at 895 °C. The mass loss was of 56.3% against the theoretical result 55.5% (calculated from the mass of remaining metals). The proposed stoichiometry based on these data is 1Pd: 6 Au: 2 Sn, that reinforces the argument of the molecular formula $[\text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2](\text{NO}_3)_2$ for this cluster.

NMR spectrum of the cluster $[\text{Pd}(\text{AuPPh}_3)_6(\text{SnCl}_3)_2](\text{NO}_3)_2$ showed one peak at 49 ppm (singlet), interpreted as due to the presence of equivalent phosphorus atoms linked to the gold atoms (P-Au). The absence of other couplings in the spectrum confirms that there are no phosphorus atoms linked to palladium, as it occurred with the precursor cluster $[\text{Pd}(\text{AuPPh}_3)_6(\text{PPh}_3)](\text{NO}_3)_2$. The presence of Sn and of NO_3^- as counterion in this compound was respectively confirmed by Raman and IR spectra.

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