Synthesis and study of the cluster $[Pd(AuPPh_3)_6(HgNO_3)](NO_3)$ by reversed-phase high-performance liquid chromatography, thermoanalysis, infrared, nuclear magnetic resonance, and fast atom bombardment mass spectrometry

Adriana F. Sotelo, Anna Maria P. Felicissimo[*]

Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, 05508-900 São Paulo, Brazil

Abstract

The addition reaction of Hg^0 and Hg_2^{2+} to the bimetallic cluster $[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2$ (**I**) has been studied. The reaction, monitored by HPLC, showed the time elapsed to obtain the pure cluster $[Pd(AuPPh_3)_6(HgNO_3)](NO_3)$ (**II**). The use of $^{31}P\{^1H\}$ NMR, IR spectra, FABMS and thermoanalysis data was very useful for confirming the results. The reaction was monitored by taking five samples after 3, 6, 17, 21 and 24 h. The process was finalised after 24 h and the pure trimetallic cluster **II**, free of the intermediate, appeared in the chromatogram as a large, unique peak. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The synthesis of new cationic mixed gold clusters with transition metals and triphenylphosphine (PPh_3) as ligand [1] is a field of great interest due to their potential utilisation in catalysis [2], both homogeneous and heterogeneous [3,4]. The electron counting model derived from Stone theory [5] can predict the structural properties and reactivity of these clusters. The addition of metals (Ag, Cu, Hg) to the structure of bimetallic clusters M–Au (M=Pt or Pd) usually occurs through the occupation of the metallic atoms in the periphery, so that these atoms in solution can be naked, introducing sites of coordina-

tive insaturation and promoting catalytic synergism [6].

High-performance liquid chromatography (HPLC) has been used for the separation and identification of cluster compounds for the last few years. A wide variety of large cationic metal cluster compounds have been successfully separated by this technique [7,8]. The characterisation of these compounds has been a major problem in this area and, frequently, the use of single crystal X-ray crystallography is required. The recent successful use of FABMS in the characterisation of ionic metal clusters, when combined with NMR data, leads to an accurate determination of the molecular formula [9].

This paper reports the addition reaction of Hg^0 (or Hg_2^{2+}) to the cluster **I,** giving a new trimetallic 16-electron cluster **II**. The reaction was monitored

through HPLC and NMR, IR, thermoanalysis (TG) and FABMS techniques were used to confirm the results.

2. Physical and reagents

2.1. Liquid chromatography system

A Schimadzu equipment (LC 10 AC-pump) was used for high-performance liquid chromatography (HPLC), variable-wavelength detector operated at 254 nm, Rheodyne 7105 injection valve with a 20 μl loop, a stainless-steel C_{18} (25×0.4 cm I.D.) analytical column and a guard column (2×0.2 cm I.D.) filled with C_{18}. Isocratic separations were performed at a flow-rate of 0.3 ml min^{-1} and at ambient temperature. All samples were prepared in ethyl alcohol with concentrations around 1 mg ml^{-1}. The chromatographic runs were performed with product samples obtained by dissolution just before injection on the column.

The mobile phase consisted of NH_4NO_3 (0.075 M) dissolved in ethyl alcohol, and pure ethyl alcohol (80:20). This solution was filtered through a 0.5 μm filter and degassed with ultrasound under reduced pressure.

2.2. Spectroscopy

A Perkin Elmer Model 1750 FT-IR spectrometer with KBr pellets was used for vibrational spectroscopy in the IR region (500–4000 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectra were recorded on a Brucker 200 MHz equipment with H_3PO_4 or TMP (trimethylphosphate) as reference standards and $CDCl_3$ as solvent. A fast atom bombardment (FABMS) – VG Analytical, Ltd. 707E-HF equipment with m-nitrobenzyl alcohol matrix (MNBA) and CsI as reference was used for low resolution mass spectroscopy. Accelerated Xe atoms were used as the fast atom source.

2.3. Thermoanalysis equipment

Thermobalance. A Shimadzu TGA – 50 thermobalance was employed for the TG study. Samples sizes in mass from 4 to 5 mg were pyrolyzed at a

heating rate of 10°C min^{-1} in a dynamic air atmosphere in a circular alumina crucible container [17].

2.4. Atomic absorption

The amounts of metal (Au and Pd) in the samples were determined by atomic absorption with a Varian 1475 spectrometer, with acetylene/compressed air (40/60 proportion) and a hollow cathode lamp.

The sample (10.82 mg) used for this technique was dissolved in 20 ml of hot aqua-regia, then diluted with deionized water to a final volume of 100 ml. From this solution, two samples of 10 and 20 ml, respectively, were used for the Au and Pd analysis. Both were diluted once more to 100 ml with deionized water.

2.5. Solvents and reagents

Solvents were of HPLC grade for high-performance liquid chromatography. The syntheses were carried out according to procedures described in the literature [15] and the solvents of gradient grade (Merck) dried and distilled prior to use.

The compounds were: NH_4NO_3 (Merck), $Hg_2(NO_3)_2 \cdot 2H_2O$ (Aldrich), Hg^0 (CAAL), $PdCl_2$ (Aldrich) and all manipulations were carried out under purified N_2 atmosphere using standard Schlenk techniques.

2.6. Experimental

$[Pd(PPh_3)_2Cl_2]$, $[Au(PPh_3)NO_3]$ and $[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2$ were prepared as described in the literature [10–12].

2.6.1. $[Pd(AuPPh_3)_6(HgNO_3)](NO_3)$ (II) obtained from the nucleophilic addition and substitution reaction between Hg^0 and cluster I:

The mixture of the cluster **I** (73 mg – 0.022 mmol) and Hg^0 (45 mg – 0.23 mmol) was dissolved in acetone (8 ml). The solution was stirred at room temperature in a round 50 ml Schlenk flask for approximately 24 h, at which time the excess of mercury appeared as a black powder. The acetone solution was filtered through diatomaceous earth to remove the excess Hg metal. Diethyl ether (10 ml) was added to the filtrate. After standing overnight, a

precipitate was obtained and separated from the liquid phase. The dark solid was discarded after characterisation through ^{31}P {^1H} NMR and HPLC as a by-product of the synthesis.

The solution was transferred to another flask and more diethyl ether (12 ml) was added. After 72 h a brown reddish precipitate was formed: cluster **II**. This precipitate was collected in a funnel and washed with small portions of diethyl ether and dried in air. The yield was 51%.

Cluster **II** is soluble in dichloromethane, acetonitrile, methanol, and acetone and insoluble in saturated hydrocarbons and diethyl ether.

2.6.2. Synthesis of [Pd(AuPPh$_3$)$_6$(HgNO$_3$)](NO$_3$) (II) using Hg$_2^{2+}$ and the cluster I

The mixture of the cluster **I** (100 mg–0.031 mmol) and Hg$_2$(NO$_3$)$_2$·2H$_2$O (17 mg–0.030 mmol) was dissolved in methanol (8 ml) at 0°C (ice-water bath). The solution was stirred for 25 min and the

solvent then removed under reduced pressure. The brown solid obtained was dissolved in dichloromethane (10 ml) and the mixture filtered through diatomaceous earth on a fritted glass filter flask; the filtrate was evaporated once more at low pressure. The solid was dissolved in methanol (10 ml) and filtered through diatomaceous earth. Diethyl ether (10 ml) was added to the filtrate. After 24 h, a dark solid precipitated was obtained (by-product) and separated from the solution by filtration. The solution was transferred to another small flask and diethyl ether (20 ml) added; finally, a brown solid was formed: cluster **II**, that was collected and washed with small portions of diethyl ether and dried in air. The yield was 30%.

3. Results and discussion

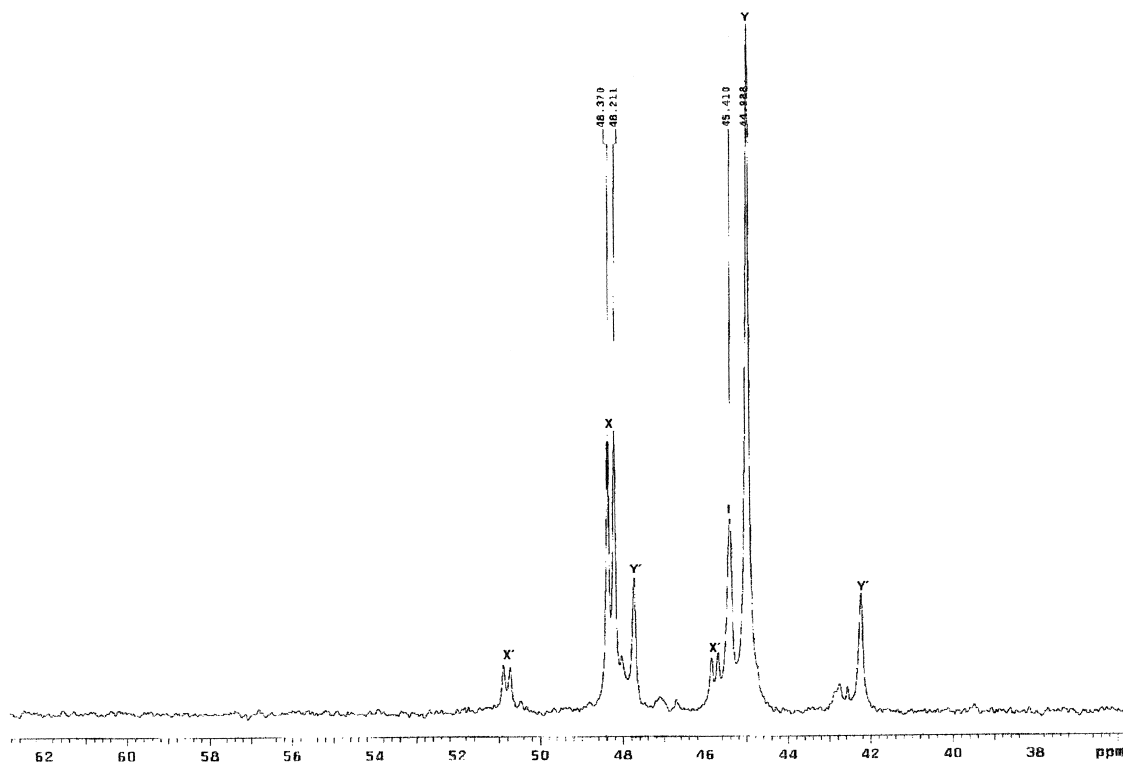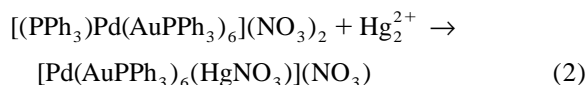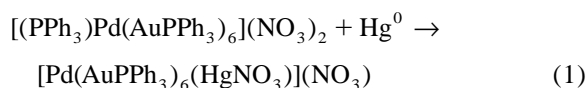The trimetallic cluster **II** was prepared from the

Fig. 1. ^{31}P {^1H} NMR spectrum of the intermediate (peak X), cluster **II** (peak Y) and by-product (peak **I**) in solution recorded at 25°C with the use of CH$_3$OH as solvent (internal standard TMP).

reaction of the bimetallic cluster **I** with either Hg^0 or $Hg_2(NO_3)_2 \cdot 2H_2O$:

$$[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2 + Hg^0 \rightarrow$$
$$[Pd(AuPPh_3)_6(HgNO_3)](NO_3) \qquad (1)$$

$$[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2 + Hg_2^{2+} \rightarrow$$
$$[Pd(AuPPh_3)_6(HgNO_3)](NO_3) \qquad (2)$$

3.1. Spectroscopic methods

The first $^{31}P\{^1H\}$ NMR spectrum of the sample in CH_3OH, collected after 12 h of reaction, showed two peaks at δ 48 and δ 45 (Fig. 1). These peaks were attributed to the presence of two different compounds, the intermediate and the cluster **II** (the final product). The study of the reaction by HPLC was based on this result obtained from NMR.

The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ of another sample collected after stirring overnight (Fig. 2) showed a doublet assigned to the PPh_3 ligands bound to the Pd atom at δ 48 ($^3J_{P-P} = 26$ Hz) with ^{199}Hg satellites ($^3J_{Hg-P} = 640$ Hz). The ^{31}P NMR data suggested that the intermediate might be $[(PPh_3)Pd(AuPPh_3)_6(HgNO_3)](NO_3)$, but the multiplet (septet) that would confirm this suggestion was not observed. The $^{31}P\{^1H\}$ NMR spectrum (Fig. 3) of the cluster **II** presented one single peak at δ 43 with ^{199}Hg satellites ($^3J_{Hg-P} = 690$ Hz) due to the $AuPPh_3$ ligands bound to the Pd atom. This spectrum was taken after 24 h of reaction.

The IR spectra of clusters **I** and **II** (Fig. 4) showed one band attributed to the NO_3^- group at 1384 cm^{-1} (unbound) and another attributed to the $HgNO_3$
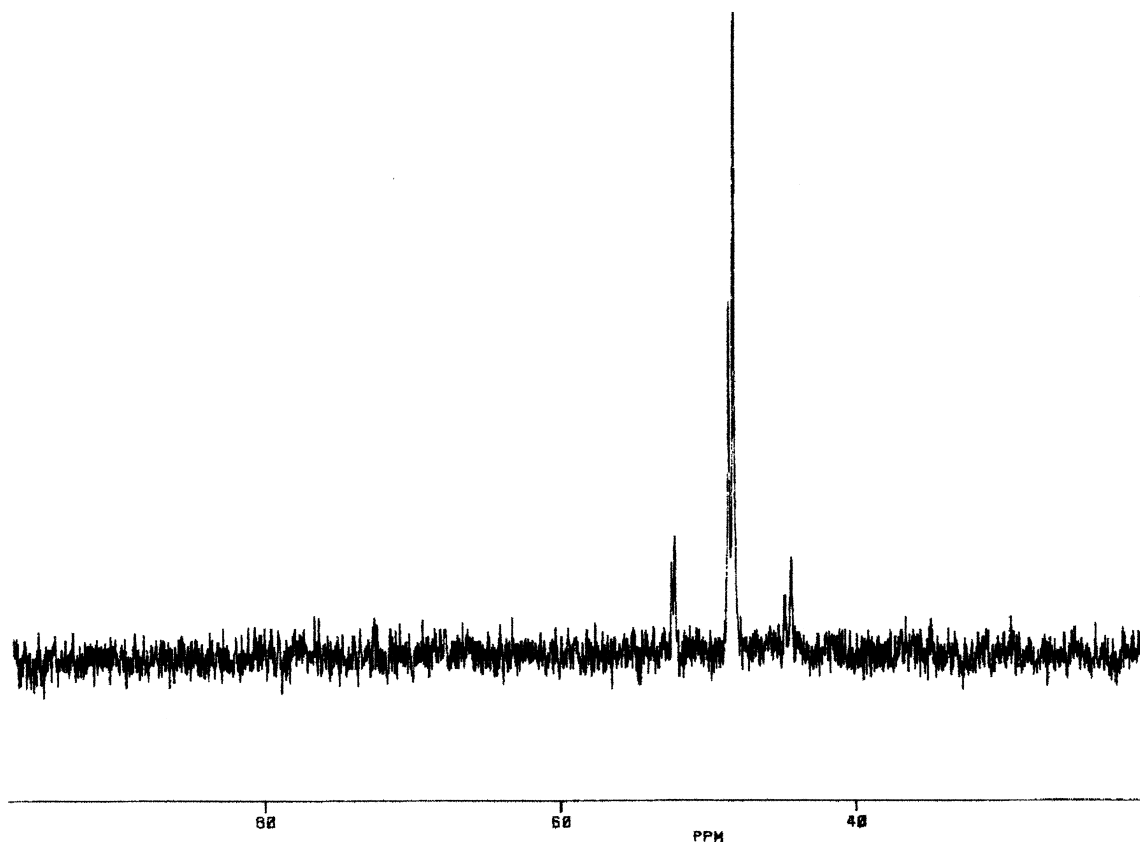

Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of the intermediate in solution recorded at 25°C with the use of $CDCl_3$ as solvent (internal standard H_3PO_4, $\delta = 0$). The central doublet due to the $Au(PPh_3)$ phosphorus and satellites due to the mercury.

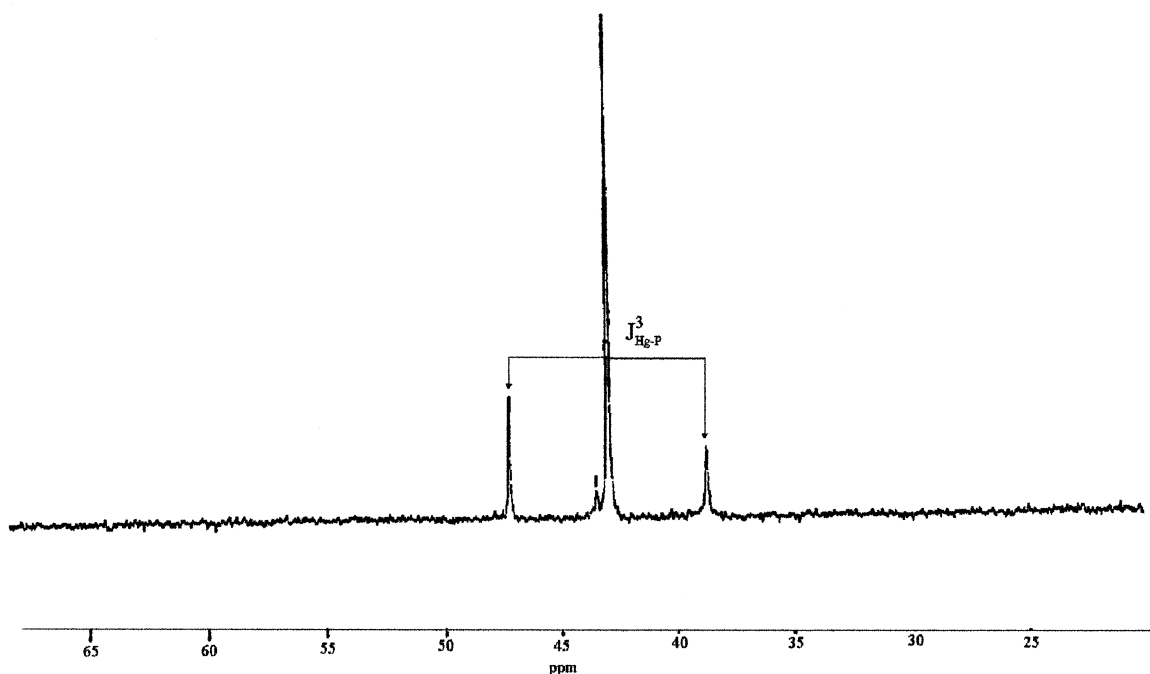Fig. 3. ^{31}P {^{1}H} NMR spectrum of the cluster **II** and by-product (peak **I**) in solution recorded at 25°C with the use of $CDCl_3$ as solvent (internal standard H_3PO_4, $\delta = 0$). The central single peak due to the $Au(PPh_3)$ phosphorus and satellites due to the mercury.
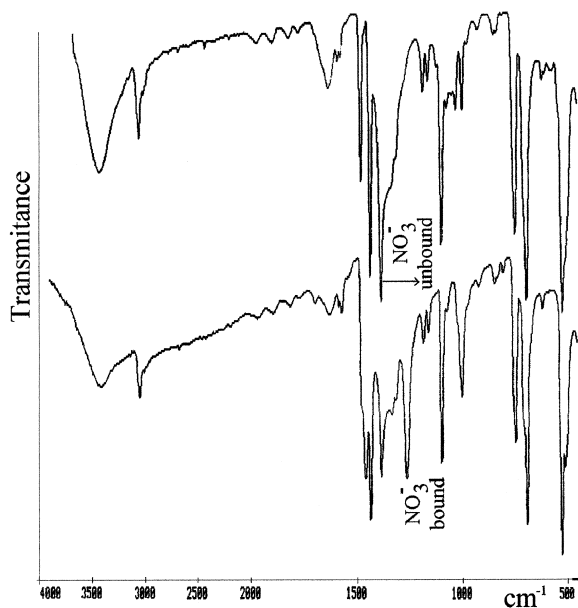

Fig. 4. Spectra in the IR region of the clusters **I** and **II**.

group at 1266 cm^{-1} (bound) only in cluster **II** spectrum [13]. The intense bands exhibited 20% transmittance due to the NO_3^- counter ion and 37% transmittance due to co-ordinated NO_3^-. Crystals were obtained using different solvents, but were inappropriate for X-ray analysis. FABMS, TG and the absorption spectrum were used for the characterisation of the trimetallic cluster **II**. FABMS is an extremely useful technique in the determination of the molecular formula of clusters when X-ray quality crystals are impossible to obtain [2,9].

From the cationic fragments obtained by FABMS (Fig. 5), it was possible to reproduce the molecular weight of the cluster **II.** The highest mass peak was assigned as $M = [Pd(AuPPh_3)_6(HgNO_3)](NO_3)$ where obsv m/e 3182.8 {calc 3183 for M}; 3120.7 {calc 3121 for $[M–NO_3]^+$}; 3057.7 {calc 3059 for $[M-2(NO_3)]^+$}.

3.2. Thermoanalysis

The TG curve of cluster **II** in air indicated thermal decomposition in three steps (Fig. 6). Based on the
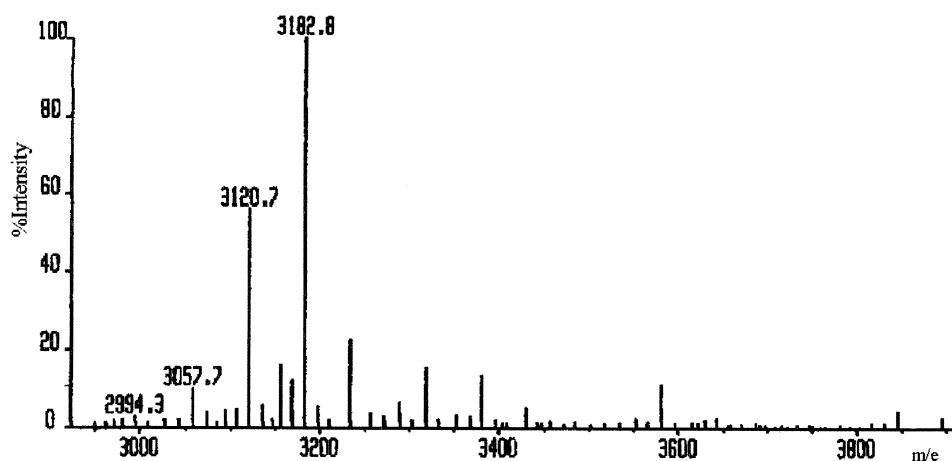
Fig. 5. FABMS of fragments from cluster **II** were calculated for the isotopic combination of metals as Pd = 106 and Hg = 199. FABMS data was recorded in a *meta*-nitrobenzyl alcohol (MNBA) matrix. The highest mass peak was assigned as M = [Pd(AuPPh$_3$)$_6$(HgNO$_3$)](NO$_3$) where obsv *m/z* 3182.8 {calc 3183 for M}; 3120.7 {calc 3121 for [M − NO$_3$]$^+$}; 3057.7 {calc 3059 for [M − 2(NO$_3$)]$^+$}.

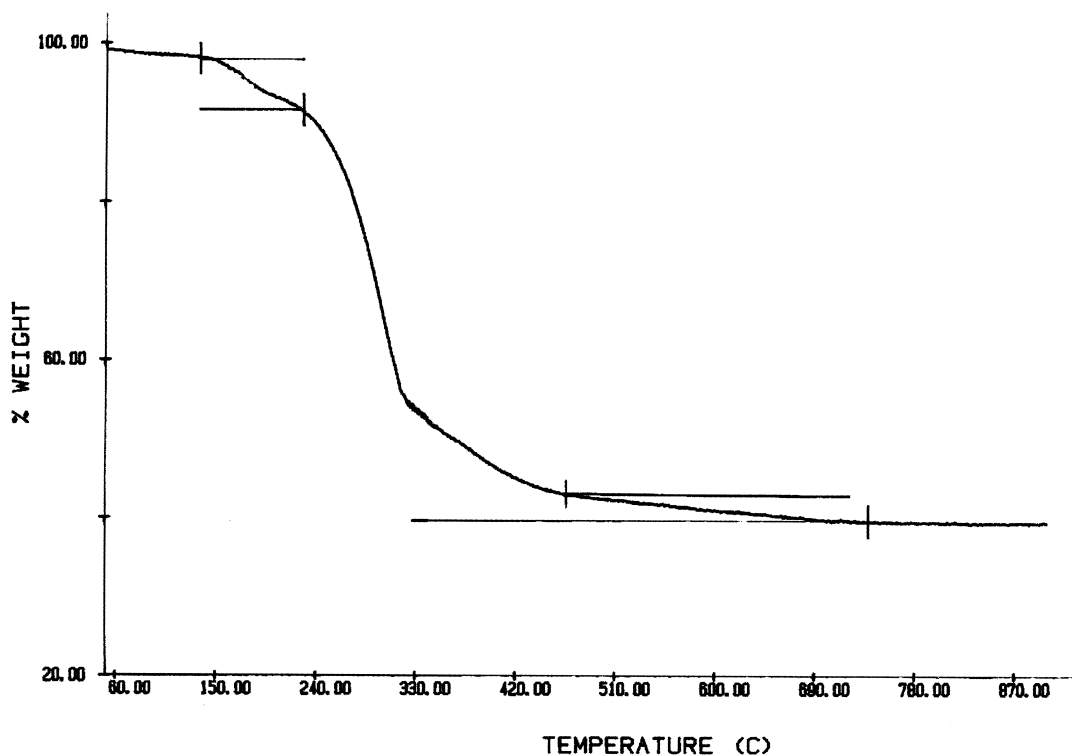

Fig. 6. TG curve of cluster **II** heating rate of 10°C min^{-1} in a dynamic air atmosphere.

Table 1
Thermoanalysis results

| Thermal decomposition steps	% Theoretical	% Experimental	Δm (mg)	ΔT (°C)
HgO e NO (1st step)	6.7	7.7	0.30	93
6PPh$_3$ (2nd step)	48.4	48.5	2.19	235
5O$_2$ (3rd step)	2.5	3.5	0.16	240

TG curve, the thermal decomposition for cluster (II) can be interpreted as follows:

Between 135 and 228°C dissociation of **Hg** and **N,** that separate as oxides and volatilise [17,18]:

$$[(HgNO_3)Pd(AuPPh_3)_6]^+ \rightarrow HgO + NO +$$

$$[Pd(AuPPh_3)_6]^+ \qquad (3)$$
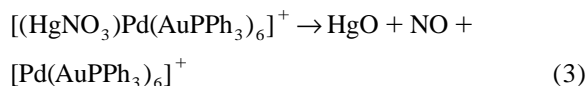
Between 228 and 463°C loss of mass related to liberation of **PPh$_3$** ligands and formation of **Pd** and **Au** oxides:

$$[Pd(AuPPh_3)_6]^+ \rightarrow PdO + 3Au_2O_3 + 6PPh_3 \qquad (4)$$
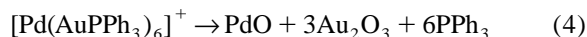
The loss of mass due to the volatilisation of the ligand (triphenylphosphine) occurred in the range between 228 and 463°C. This was confirmed by the attribution of the bands in the IR spectrum of the cluster after the sample was burned at 350°C. The presence of bands characteristic of PPh$_3$ in 616, 696, 908, 1109 and 1440 cm^{-1} in the spectrum confirmed that the organic part of the cluster was completely burned above the temperature of 350°C (Fig. 6).

Between 480 and 720°C the formation of a grey metallic residue:

$$PdO + 3Au_2O_3 \rightarrow Pd + 6Au + 5O_2 \qquad (5)$$

The results of the TG experiments are summarized in Table 1; they were employed to obtain the %P through the value of loss of mass.

3.3. Atomic absorption

The quantitative determination of the metals Pd and Au of the cluster **II** are Calc **1**Pd: **6**Au (Experimental **0.92**Pd: **6.32**Au) [16].

Anal. Calc for II: PdAu$_6$P$_6$C$_{108}$H$_{90}$HgN$_2$O$_6$: Pd = 3.33% Au = 37.12%. (Found: Pd = 3.08% Au = 39.11%).

3.4. Chromatography

Initially, the separation process for clusters and PR$_3$ ligands using chromatography follows the relation between polarity and solubility in both phases (mobile and stationary). The polarity of PPh$_3$ clusters is determined by the cationic charge and to the number of PPh$_3$ groups present [7].

The separation of cluster **I**, the intermediate and cluster **II** was carried out on a C$_{18}$ column (Table 2), with an isocratic mobile phase of ethyl alcohol and NH$_4$NO$_3$ [14] that eluted the compound of lowest polarity first: [Pd(AuPPh$_3$)$_6$(HgNO$_3$)]$^+$ < [(PPh$_3$)-

Table 2
Chromatographic data for gold cluster compounds

Compound	t_R (min)	$N_{\text{theoretical}}$ [a]	Mobile phase
[(PPh$_3$)Pd(AuPPh$_3$)$_6$]$^{2+}$	34.4	1156	80% [EtOH + (0.075 M) NH$_4$NO$_3$] and
[Pd(AuPPh$_3$)$_6$(HgNO$_3$)]$^+$	27.4	2916	20% EtOH

[a] $N_{\text{theoretical}} = 16 (t_R/w_{1/2})^2$ where $w_{1/2}$ is the peak width at half-height and $N_{\text{theoretical}}$ = theoretical plate numbers.

$Pd(AuPPh_3)_6(HgNO_3)]^+ < [(PPh_3)Pd(AuPPh_3)_6]^{2+}$ (elution order in an apolar mobile phase).

The reaction between the cluster **I** and Hg^0 was monitored by HPLC taking five samples after stirring for 3, 6, 17, 21 and 24 h, respectively (Fig. 7).

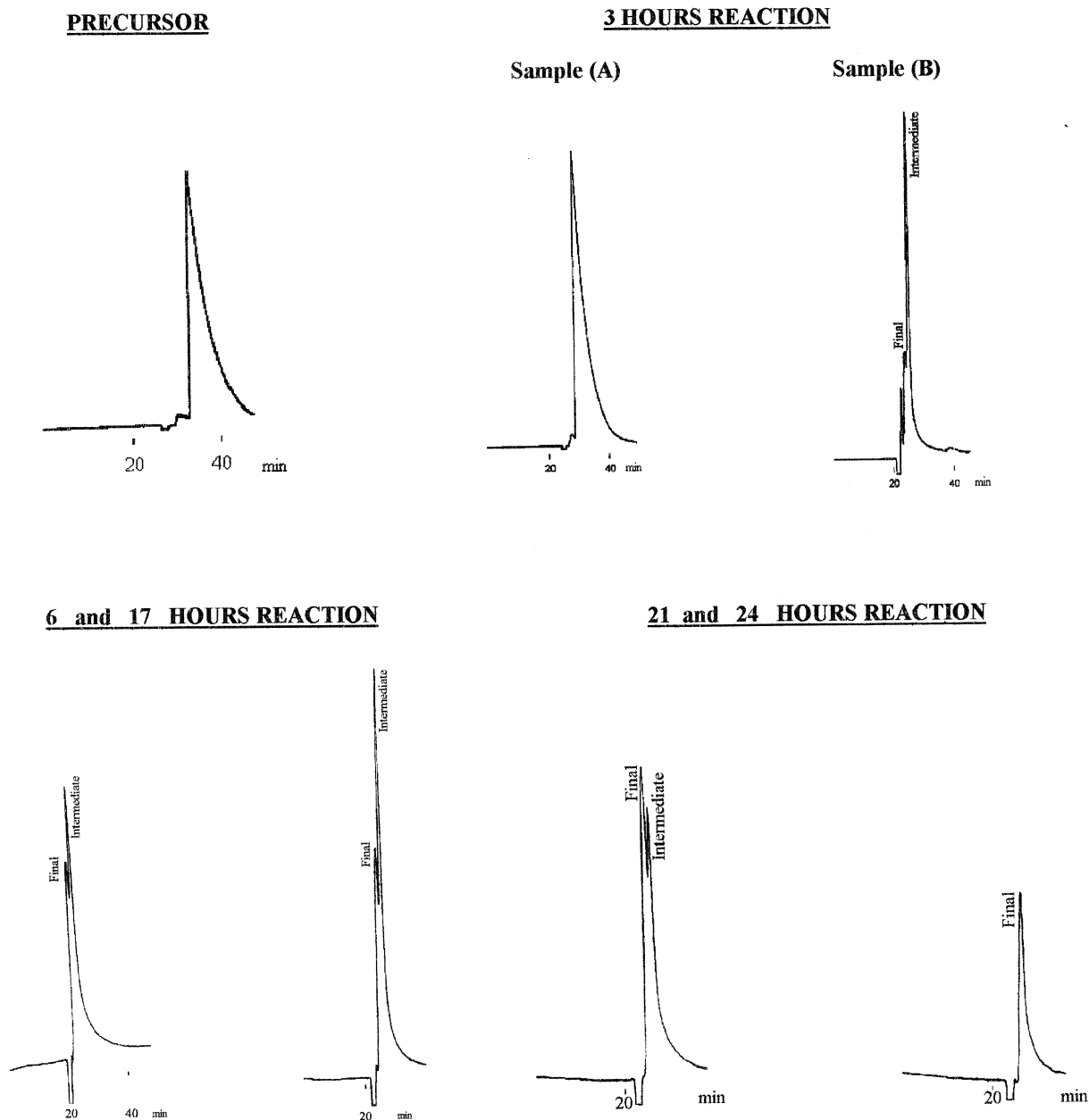*After stirring during 3 h* the solution was filtered

Fig. 7. Chromatograms of the clusters precursor=**I**; intermediate and final=**II**. Column, C_{18}; mobile phase, 0.075 *M* ammonium nitrate–ethanol and ethanol (80:20); flow-rate, 0.3 ml min^{-1}; detector, UV, 254 nm.

through in diatomaceous earth, diethyl ether added to the filtrate and the solid formed collected (sample A)

The sample (A) was dissolved in ethanol and the chromatogram showed a peak similar to that obtained for cluster **I**. Diethyl ether was added to the liquid separated from sample (A) by filtration. After 48 h a solid was formed and separated from the liquid by filtration (sample B). The sample (B) showed new peaks in the chromatogram due to the intermediate and also a small amount of cluster **II**. These results were also confirmed through the IR spectra. In samples (A) and (B) the characteristic bands due to NO_3^- (unbound) was observed and in sample (B) the band due to NO_3^- (bound) as well. $^{31}P\{^1H\}$ NMR spectra also confirmed these results for sample (A) with δ 46.5 and sample (B) with δ 48 and δ 43 attributed to cluster **I**, intermediate and cluster **II**, respectively.

After stirring during 6, 17 and 21 h the solution was filtered through in diatomaceous earth, diethyl ether added to the filtrate and the solid formed collected. The chromatograms showed the same peaks, but in different concentrations: the peak attributed to the intermediate decreased and the peak for cluster **II** increased with time of reaction.

After stirring during 24 h the solution was filtered through diatomaceous earth, and diethyl ether added to the filtrate and the solid formed collected. The chromatogram showed only one peak for cluster **II** and the reaction was considered finished.

4. Conclusion

The results obtained concerning to cluster **II** lead to the following conclusions:

The $^{31}P \{^1H\}$ NMR spectrum showed the presence of ^{199}Hg (active nucleus in NMR with spin number 1/2 and natural abundance of 16.84%) related to the satellites. The removal of one PPh$_3$ ligand linked to Pd could be observed by the presence of a singlet (high intensity band) attributed to one equivalent ^{31}P and, consequently, to a sixteen electron cluster.

The IR data of the cluster showed the bands due to the NO_3^- group (1264 cm^{-1} and 1384 cm^{-1}), confirming that NO_3^- is present in the cluster **II** in two different bond types, one co-ordinated to the Hg and the other as counter ion. The band due to the

HgNO$_3$ group confirmed the change that occurred in the spectrum of the precursor cluster **I** after the reaction with Hg^0.

Mass spectral data using the FABMS technique, TG data and the atomic absorption spectrum led to the percentage of the metallic elements Au, Pd and the number of PPh$_3$ ligands present in the molecular formula of the cluster.

The use of HPLC to monitor the reaction made it possible to estimate the reaction time needed to obtain a pure cluster without the presence of the intermediate.

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