# Neutral AuCl complexes supported in linear high molecular weight, poly-spirophosphazene-phosphine copolymers and its conversion to nanostructured gold materials

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*Dedicated to Professor Victor Riera, Departamento de Quimica Orgánica e Inorgánica, Universidad de Oviedo, Spain, on the occasion of his 70th birthday.*

## Summary

The reaction under very mild conditions of the polyspirophosphazene copolymer with pendant diphenylphosphine groups $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2]_{0.15}\}_n$ (**I**) ($O_2C_{12}H_8$ = 2,2'-dioxybiphenyl) with [Au(THT)Cl] (THT = tetrahydrothiophene) gives the neutral polymeric complex $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2-AuCl)_2]_{0.15}\}_n$ (**II**). The new material has been characterized by spectrocopic and thermochemical methods (TGA and DSC). Pyrolysis of the Au polymer (**I**) in air at 800°C gave gold nanostructured materials that were characterized by TEM, SEM-EDAX and X-ray diffraction. Nanoparticles in the range of 90 to 130 nm were seen.

## Introduction

Polymers having pendant MLn transition metal complexes coordinated to a ligand that is attached to a polymeric chain by a convenient spacer [1,2] may be useful in the design of new types of catalysts [3,4].

Also these types of polymers are useful as solid state templates for obtaining metallic nanoparticles [2,5,6]. Pyrolysis of polyphosphazenes containing anchored organometallic fragments yields nanostructured materials whose composition depend on the nature of the metal; for instance metal phosphates in which the metal is Mn [5] or metal oxides in which the metal is Cr [6] or W [5]. With noble metals the pyrolysis is expected to afford the nanostructured noble metal. In earlier studies we reported simple synthetic methods to obtain metal complexes based on poly(aryloxy)phosphazene chains $[N=P(OR)_2]_n$ having functionalized repeating units

$[N=P(OR-L-MLn)_2]_n$ with various pendant -OR-L-MLn groups [2,7-14]). The spectroscopic data of all those materials have provided the basis for the unambiguous determination of their chemical formulas, particularly useful for characterizing crosslinked insoluble materials.

In this paper we report the facile synthesis and full characterization of well defined high molecular weight polymeric phosphazene-based complexes of the AuCl fragment attached to the main chain through phosphine ligands and their pyrolytic study in air with the aim to obtain nanostructured noble metal materials.

Few polyphosphazene-containing Au fragments anchored to the polymeric chain have been reported. Allcock referred to a Au phosphazene polymer of the type

$$[N=P(OC_6H_5)_2]_x [N=P(OC_6H_4PPh_2 \bullet AuCl)(OC_6H_5)]_y \text{ [15].}$$
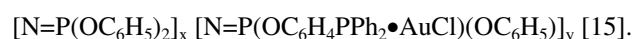
## Experimental

*Materials*

$K_2CO_3$ was dried at 140°C prior to use. The THF was treated with KOH and distilled twice over Na in the presence of benzophenone. Petroleum ether refers to the 60-65ºC fraction. The starting polymer $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2]_{0.15}\}_n$ (**I**) was prepared as described previously for analogues with other compositions [14] (see below). The [Au(THT)Cl] complex was prepared as described in the literature [16]. All the reactions were carried out under dry nitrogen.

*Instruments*

IR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer. Wavenumbers are in cm$^{-1}$. NMR spectra were recorded on Bruker AC-200, AC-300 and DPX-300 instruments. $^1$H and $^{13}$C$\{^1$H$\}$ NMR values are given in δ relative to TMS. $^{31}$P$\{^1$H$\}$ NMR values are given in δ relative to external 85% aqueous $H_3PO_4$. Coupling constants are in Hz. C, H, N analyses were performed with a Perkin Elmer 240 microanalyzer and the calculated data were determined for the ideal formula. GPC were run on Perkin Elmer equipment with a model LC 250 pump, a model LC 290 UV, and a model LC 30 refractive index detector. The samples were eluted with a 0.1 wt% solution of tetra-n-butylammonium bromide in THF through Perkin Elmer PLGel (Guard, $10^5$, $10^4$ and $10^3$ Å) at 30°C. Approximate molecular weight calibration was made using narrow molecular weight distribution polystyrene standards. Tg values were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer. Thermogravimetric analyses were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10°C/min from ambient temperature to 800°C under a constant flow of nitrogen.

The pyrolysis experiments were performed by pouring weighed portions (0.05-0.15 g) of the organometallic polymer into aluminium oxide boats which were placed in a tubular furnace under an air flow using a temperature program. Yields were in the range of 20%.

SEM images were made on a Philips EM 300 apparatus. Energy-dispersive X-ray analyses (EDAX) were performed using a Noran Instruments micro-probe attached to

a JEOL 5410 scanning electron microscope. TEM images were made on a JEOL SX 100 transmission electron microscope. The finely powdered samples were dispersed in water and dropped on a conventional carbon-coated copper grid. X-ray diffraction (XRD) was made on a Siemens D-5000 diffractometer with θ-2θ geometry working at room temperature. The XRD data were collected using Cu-kα radiation (40 kV amd 30 mA) wave.

## Significant data of $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2]_{0.15}\}_n$ (*I*)

The $^{31}P$ NMR spectrum showed bands at –6.6 [$NP(O_2C_{12}H_8)$], –22,3 [$NP(OC_6H_4-)_2$] and –6.2 ($PPh_2$) with the expected intensity ratios for the idealized composition indicated in scheme 1. The spectrum also showed very weak bands at 28.7 (oxidized – $Ph_2P=O$ sites; 5 %) and no signals attributable to $\{[NPCl(OC_6H_4-)]\}$ units, indicating that the oxidized $PPh_2$ groups and the remaining Cl sites are negligible. The $^1H$ NMR showed broad signals at 7.1 and 6.7 for the aromatic rings and the near absence of trapped solvents (about 1.0 wt% as hexanes). Therefore the actual functioanallization degree (mmol of $PPh_2$ ligand per gram of material) of the polymer (that was the one used in the stoichiometric calculations for the preparation of the gold complex) is 0.96, which is very close to the value corresponding to the idealized formula 0.3/284.6 = 1.05. On standing in solution under air, the amount of $POPPh_2$ oxidized sites may be increased, but the process is too slow in the solid state.
Analysis % Calc(found) for $C_{15.6}H_{11}NO_2P_{1.3}$ (M=284.63): 64.3(65.8) C; 3.89(3.82) H; 4.92(5.15) N.
GPC: Mw 160 000, Mw/Mn = 2.7.
TGA: -2.9% (from 20ºC to 300ºC, retained solvents); –43.5 % (from 300ºC to 600ºC, with a strong maximun at 482ºC); -30.5 (from 600ºC to 800ºC). Additional loss 1/2 h. at 800ºC: -14% (not stabilized).
DSC: Tg = 126 ºC ($\Delta Cp$= 0.18 J/gK ).

## Significant data of $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2-AuCl)_2]_{0.15}\}_n$ (*II*)

To a solution of (**I**) (0.25 g, 0.87 mmol was added 0.24 mmol of $PPh_2$) in $CH_2Cl_2$ (20 mL), [Au(THT)Cl] (0.077 g, 0.24 mmol), and the mixture was stirred at room temperature for 30 min. The mixture was filtered, concentrated in vacuo to about 2 ml and poured dropwise into hexane (0.5 L) with stirring. The cream-white precipitate was dried at r.t. under vacuum for 3 days and then another 24 h at 70ºC. Yield 0.25 g. (80%).
Analysis % Calc(found) for $C_{15.6}H_{11}NO_2P_{1.3}Cl_{0.3}Au_{0.3}$ (M=354.45): 52.8(52.9) C; 3.13(3.47) H; 3.95(4.07) N.
IR (KBr pellets) 3062m ($\nu_{CH}$, arenes), 1589w, 1500m, 1478m, 1437m, 1374m.br., 1263s, sh ($\nu_{PO-C}$), 1246vs ($\nu_{NP}$), 1195vs ($\nu_{NP}$), 1096s ($\nu_{P-OC}$), 952vs, br ($\delta_{POC}$), 786s ($\delta_{PNP}$), 752s, 716m, 693s, 609m. 590sh, 542s, br.
$^{31}P\{^1H\}$NMR (CDCl$_3$) δ (ppm): 32.4 [$PPh_2$-Au], -4.9br. [N$P(O_2C_{12}H_8)$], -23.9v.br. [N$P(OC_6H_4PPh_2)_2$].
$^1H$ NMR (CDCl$_3$): δ (ppm): 7.4, 7.2, 6.9 m, br. (arene rings).
TGA: -2.9% (from 20ºC to 300ºC, retained solvents); –43.3% (from 300ºC to 600ºC, with a strong maximun at 487ºC); -9.7 (from 600ºC to 800ºC). Additional loss 1/2 h. at 800ºC: -12% (not stabilized).

## Results and discussion

The addition of [Au(THT)Cl] to a dichloromethane solution of the phosphine functionalized phosphazene polymer $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2]_{0.15}\}_n$ **(I)** $(O_2C_{12}H_8=2,2'$-dioxybiphenyl) with a functionalization degree of FD= 0.96 mmol/g., led to the fast replacement of the labile THT ligand to give the polymer $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2-AuCl)_2]_{0.15}\}_n$ **(II)**, containing the AuCl group linked to the main chain by strong phosphine-Au(I) bonds (Scheme 1).
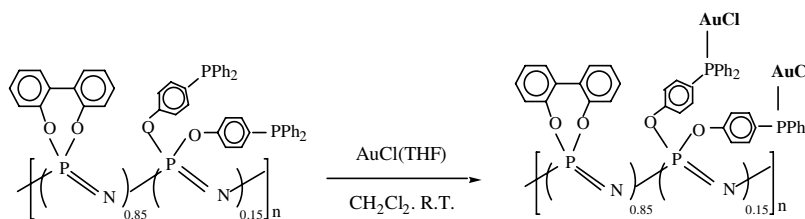


**Scheme 1.** Reaction for the formation of Au-Polymer.

All the analytical and spectroscopic properties were in agreement with the chemical composition of **(II)**. The solid state IR spectra (KBr pellets) showed all the absorptions expected for the starting polyphosphazene ligand $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2]_{0.15}\}_n$ (I) [14], and the only difference was the band at 1437 cm$^{-1}$, which was clearly more intense in the spectrum of the complex, an observation that could be useful in the characterization of related insoluble materials.

The $^{31}$P NMR spectra was especially useful, showing the broad signals of the phosphorus of the $[NP(O_2C_{12}H_8)]$ units (in the region of -7 ppm), those of the $[NP(OC_6H_4PPh_2)]$ units (very broad in the region of -22 ppm), and the sharper signals of the PPh$_2$ ligand (-6.2 ppm), that were very unshielded upon coordination with the Au(I) fragments (32.4 ppm). As in previous examples [7], also the phosphorus bearing the group with the ligand involved in the coordination, i.e. the one in the $[NP(OC_6H_4PPh_2)]$ units, wase also sensitive to the coordination of the gold, shifting slightly to lower frequencies. In all cases, the relative intensities were in agreement with the proposed formula.

The thermal stability of the polymeric complex **(II)** was studied by TGA at a heating rate of 10°C/min (see experimental part). The 43% loss centered at ca. 480°C, is very similar to the observed in the TGA of the free polymeric ligand **(I)** and is probably due to the elimination of organic molecules from the pendant groups. However, the 9.7% loss between 600-800°C, which corresponds to the decomposition of the phosphazene chains to form the final crosslinked pyrolitic residue [17] is much smaller than the observed in the TGA in **(I)** (30.5%). It is therefore clear that, as found in other cases [13], the presence of the metal has a stabilizing effect on the phosphazene pyrolitic residues.

The DSC curve for **(II)**, scanned from –50°C to 250°C, showed no clear heat capacity jump corresponding to a glass transition to measure the Tg. However, because of the presence of the voluminous metal-ligand fragment transition it should be higher [7,18] than that of the free phosphine polymer **(I)**, which has Tg = 126°C.

Solid state pyrolysis of the Au polymer in air at 800°C gave a yellow powder in 20% yield. Characterization of this material by transmission electron microscopy (TEM) indicates the formation of metallic nanoclusters as shown in Fig. 1(a).
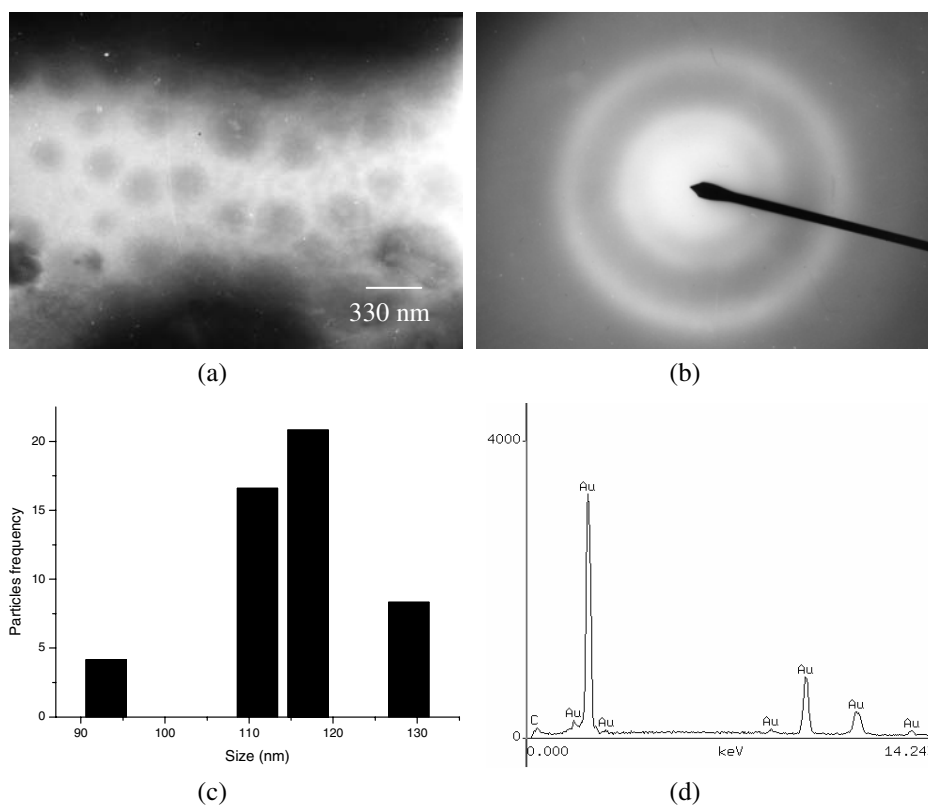


(a)  (b)



(c)  (d)

**Figure 1.** TEM image (a), electron nanodiffraction (b), histogram (c) and EDAX (d) of the nanostructured gold material.

The nanodiffraction patterns of figure 1(b) show a somewhat crystalline material. A histogram of the material indicated some broad size dispersion with nanoclusters mainly in the 90-130 nm range, mostly 117 nm (Fig. 1(c)). As shown in Fig. 1(d), EDAX analysis of the material confirmed the presence of only gold. The XRD patterns of the materials (Fig. 2) can be indexed to cubic Au [19].

The morphology seen on calcination of the organometallic gold polymer was studied by scanning electron microscopy. A porous 2-D shape was found for the Au polymer as shown in figure 3.

Figure 3(d) show a several pore sizes, most of them around 1 $\mu$m.

The possible formation mechanism of gold nanostructures can be proposed considering the general formation mechanism of metallic nanoparticles previously proposed for the formation of metal oxides and metal phosphates [5]. Calcination of the organic matter produces holes in the polymeric matrix. Simultaneously, this process leads to the formation of CO which probably reduces the Au(I), causing the agglomeration of the metallic particles in the holes produced previously. Finally,

oxidation of the P=N of the polymeric chain produces volatile nitrogen oxides and the thermally stable phosphorus oxides which act as a solid state stabilizer for the Au nanoparticles.
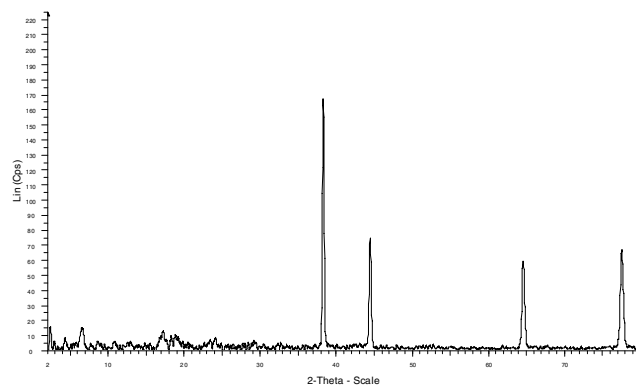


**Figure 2.** X-ray difracction patters of the Au product.
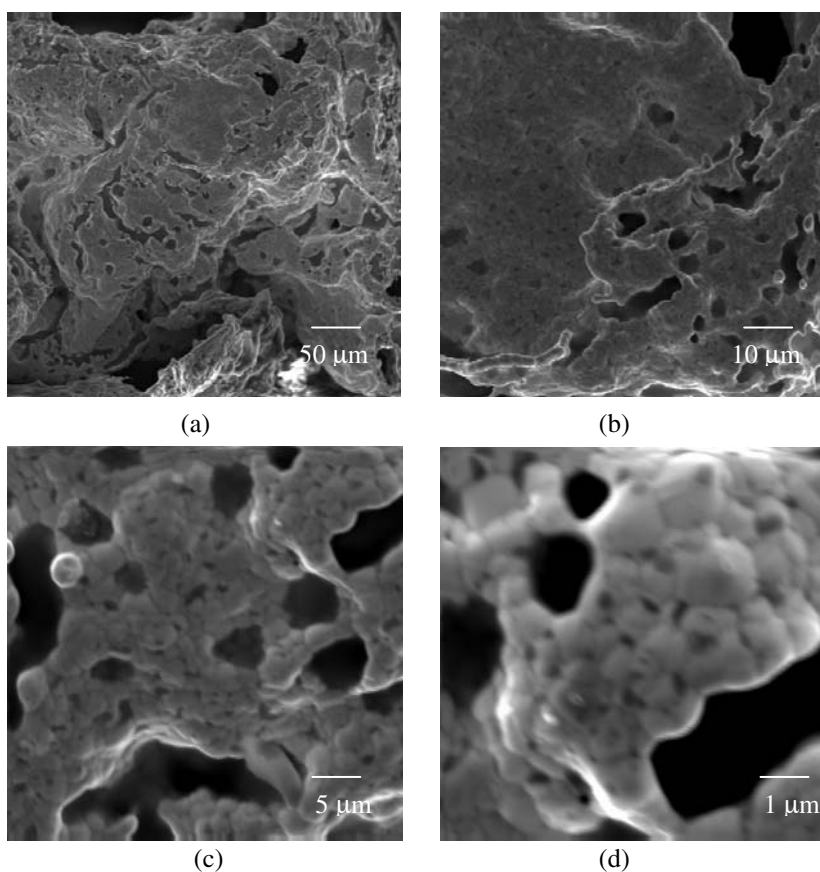


(a)

(b)

(c)

(d)

**Figure 3.** SEM imagen of the Au product at different magnifications.

Materials as the nano-regime as nanoparticles represent an exciting new class of materials [20]. As a consequence of their tiny size, nanomaterials often display unique physical and chemical properties that are atypical of the bulk materials. For instance optical, magnetic and electrical properties are sensitive to size effects. Furthermore, nanosized particles are very efficient in the field of catalysis [21] due to their high surface-to-volume ratio. Consequently, numerous processes for nanomaterial synthesis have been investigated in a attempt to control their size, morphology, structure and chemical composition. Large numbers of studies on the production of nanoparticles have been published [20], almost all in solution. Although gold nanoparticles are one of the most widely studied systems [22], few preparation methods in the solid state have been reported [23-25]. Thus this report is the first to use a phosphonitrilic polymer to obtain nanostructured gold in the solid state. The formation of gold nanoparticles in the solid state by pyrolysis of organometallic copolyphosphazenes opens a potential way for imprinting nanostructured gold on glazes and metal and ceramic surfaces with possible applications in solid state electronic devices [26].

## Conclusion

We have shown that the heat-induced pyrolysis in air of polyphosphazene containing Au fragments anchored to the polymeric chain provides an effective solid state route to gold nanostructured materials.

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