



Designed synthesis of metal-organic frameworks containing gold(I) cations supported in phosphazene-phosphine polymeric matrices

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ABSTRACT

The reaction of the polyphosphazenes $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2]_x\}_n$, $x = 0.15$ (**1a**), 0.25 (**1b**), 0.35 (**1c**), with $[\text{Au}(\text{THT})\text{Cl}]$ (THT = tetrahydrothiophene) in dichloromethane gave the polymers $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2\text{AuCl})_2]_x\}_n$, $x = 0.15$, (**2a**), 0.25 (**2b**), 0.35 (**2c**), respectively. The reaction of (**1a**) with $[\text{Au}(\text{PPh}_3)_2]\text{PF}_6$ in refluxing THF led to the replacement of the PPh_3 ligands giving a metal-organic framework of idealized formula $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}]_x\}_n$, $x = 0.15$, (**3a**), 0.25 (**3b**) containing cationic $[-\text{Ph}_2\text{P}-\text{Au}^+-\text{PPh}_2-]$ cross-linking sites. The insoluble polymeric matrix (**3a**), having pendant PPh_2 groups, was reacted with $[\text{Au}(\text{THT})\text{Cl}]$ to give the new polymeric framework of composition $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{0.85}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2(\text{AuPF}_6)_{0.5}(\text{AuCl})_{0.15}]\}_n$ (**4**).

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1. Introduction

The polymers having pendant MLn transition metal complexes coordinated to a ligand that is attached to a polymeric chain by an appropriate spacer [1] may be useful to design new catalysts [2]. In this respect, polyphosphazenes [3], that are convenient and versatile materials to support catalysts, have not been sufficiently explored [2a,4]. In earlier studies, we have reported simple synthetic methods to obtain a variety of polyphosphazene random copolymers containing functional repeating units of the types $[\text{N}=\text{P}(\text{OR}-\text{L}-\text{MLn})_2]_n$ carrying transition metal complexes [5a]. In general, the polymeric phosphazene complexes may be prepared by two different routes: (a) the macromolecular-substitution of a labile ligand (S) from a precursor complex MLn(S) using a polymer carrying the coordinating group L; (b) the macromolecular-substitution of Cl from a chlorine containing polyphosphazene with phenolic complexes HO-R-L-MLn in the presence of caesium carbonate [5b]. A variation of the first method may include also not labile ligands taking advantage of the macroligand effect of the polymers to form insoluble cross-linked materials. Examples are the $\text{Ru}(\text{II})(\eta^6\text{-}p\text{-cymene})$ complexes supported on poly(spirophosphazene-pyridine) copolymers [6].

Although several Au(I) complexes have been considered as useful catalysts for a variety of organic reactions [7], the incorporation of Au(I) derivatives to polyphosphazenes, that begun very early [4b], remains insufficiently explored. Therefore, we considered of interest the design of new synthetic methods for soluble or insol-

uble polymeric complexes with Au(I) having well defined compositions and regular structures. Herein we wish to report the preparation of two polymeric matrices containing $-\text{PPh}_2-\text{Au}^+-\text{PPh}_2-$ cationic sites and neutral AuCl groups together with free PPh_2 ligands available for further coordination, that can be included in the coordination polymers category of the general hybrid inorganic-organic framework materials [8].

2. Experimental

2.1. Materials and general techniques

All the reactions were carried out under dry nitrogen. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with boiling point in the range 60–65 °C. KPF_6 (Aldrich) was used as purchased. The complex $[\text{Au}(\text{THT})\text{Cl}]$ (THT = tetrahydrothiophene) was prepared as described in the literature [9]. The well known [10] $[\text{Au}(\text{PPh}_3)_2][\text{PF}_6]$ complex was prepared by a modified method using KPF_6 instead of TlPF_6 as described below. The phenol-phosphine $\text{HO}-\text{C}_6\text{H}_4-\text{PPh}_2$ was synthesized as described elsewhere [5b]. The phosphine containing polyphosphazenes $\{[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]_{1-x}[\text{NP}(\text{OC}_6\text{H}_4\text{PPh}_2)_2]_x\}_n$, $x = 0.15$ (**1a**), 0.25 (**1b**), 0.35 (**1c**) were prepared by the same procedures previously described for the analogous with $x = 0.15$ [11], 0.35 [5b] and 0.4 [12]. Significant data are: ^{31}P NMR (CDCl_3 , ppm): -6.6 $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)]$, -22.3 $[\text{NP}(\text{OC}_6\text{H}_4)_2]$, -6.2 (PPh_2), with the expected intensity ratios. The spectra also showed very weak bands at 28.7 ($\text{Ph}_2\text{P}=\text{O}$ sites) indicating that the fraction of oxidized PPh_2 groups (less than 4%) can be neglected. The ^1H NMR showed broad signals at 7.1 and 6.7 for the

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aromatic rings and the practically absence of trapped solvents (maximum less than 2% in weight). Therefore the functionalization degrees (FD in mmol of PPh₂ ligand per gram of material), used for determining the stoichiometric amounts of reactants, were the calculated for the idealized composition: 0.3/284.6 = 1.05 mmol/g (**1a**), 0.5/322.5 = 1.5 mmol/g (**1b**), and 0.7/358.5 = 1.9 mmol/g (**1c**). The average Mw of **1** could not be accurately measured by GPC, but they were estimated to be of the order of 700000. The glass transition temperatures (by DSC) were $T_g = 126$ °C ($\Delta C_p = 0.18$ J/g K) (**1a**) [11]; 111 °C ($\Delta C_p = 0.22$ J/g K) (**1b**); 109 °C ($\Delta C_p = 0.31$) (**1c**). NOTE: Those values may differ in ca. 10 °C depending on the oxidation degree of the phosphines.

The IR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer. Wavenumbers are in cm⁻¹. NMR spectra were recorded at room temperature on Bruker NAV-400, DPX-300, AV-400 and AV-600 instruments ¹H and ¹³C{¹H} NMR are given in δ relative to TMS. ³¹P{¹H} NMR are given in δ relative to external 85% aqueous H₃PO₄. The C, H, N, analyses were performed with an Elemental Vario Macro. GPC were measured with a 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% by weight solution of tetra-*n*-butylammonium bromide in THF through Perkin-Elmer PLGel (Guard, 10⁵, 10⁴ and 10³ Å) at 30 °C. Approximate molecular weight calibration was obtained using narrow molecular weight distribution polystyrene standards. T_g values were measured with a Mettler DSC Toledo 822 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analysis were performed on a Mettler Toledo TG 50 TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under constant flow of nitrogen.

2.2. Preparation of [Au(PPh₃)₂]PF₆

To a solution of [Au(THT)Cl] (0.3 g, 0.936 mmol) in THF (30 mL), PPh₃ (0.59 g, 2.25 mmol) and KPF₆ (0.69 g, 3.75 mmol) were added and the mixture stirred and refluxed for 2 h. The resulting mixture was filtered and concentrated to 10 mL. The diethyl ether was added with stirring to form [Au(PPh₃)₂][PF₆] as a white precipitate that was washed with ether and dried in vacuo 2 h. Yield: 0.73 g (90%). The compound can be obtained as colourless crystals by slow diffusion of hexane into a very concentrated dichloromethane solution in the dark. This procedure avoids the more hazardous TlPF₆ reagent used previously [10].

2.3. {[NP(O₂C₁₂H₈)]_{1-x}[NP(OC₆H₄PPh₂AuCl)₂]_x]_n, x = 0.15 (**2a**), 0.25 (**2b**), 0.35 (**2c**)

To a solution of **1b** ($x = 0.25$) (1.5 g, 4.65 mmol, 2.3 mmol of PPh₂) in CH₂Cl₂ (60 mL), [Au(THT)Cl] (0.70 g, 2.2 mmol) was added and the mixture was stirred at room temperature for 15 min. The mixture was filtered, concentrated in vacuum to about 5 mL and poured drop wise into hexane (0.5 L) with stirring. The crême-white precipitate was dried at room temperature in the vacuum for 3 days to give **2b**. Yield 2.0 g (98%). NOTE: Attempts of drying at 70 °C may cause the formation of small gold nanoclusters as evidenced by a pink to violet coloration that, occasionally, may be not noticed until the compound is dissolved in chloroform. It was also observed that, as many other Au(I) species, the compound is light sensitive, specially in chloroform solutions. Anal. Calc. for C₁₈H₁₃NP_{1.5}O₂Cl_{0.5}Au_{0.5} (438.7): C, 49.2; H, 2.96; N, 3.41. Found: C, 48.7; H, 3.19; N, 3.11%. IR (in cm⁻¹; KBr pellets) 3057m (ν_{CH} , arenes), 1588w, 1493m, 1478m, 1436s, 1380–1373m.br., 1263s, sh (ν_{PO-C}), 1245vs (ν_{NP}), 1193vs, 1172vs,sh (ν_{NP}), 1096vs (ν_{P-OC}), 1045w, 1014w, 924vs, br (δ_{POC}), 834m, 785s (δ_{PNP}), 750s, 716m, 691s, 608m. 586sh, 541s, br cm⁻¹. ³¹P{¹H}NMR (CDCl₃, δ ppm):

32.7 [PPh₂-Au], -4.8 m [NP(O₂C₁₂H₈), -23.7 m [NP(OC₆H₄PPh₂)₂]. ¹H NMR (CDCl₃, δ ppm): 7.4, 7.2, 6.9 m, br. (arene rings). Solvents retained (as hexanes) were 2–3%. ¹³C{¹H} NMR (CDCl₃, δ ppm): 154, 135, 122, [OC₆H₄P], 134, 132, 130, [PPh₂] 148, 130 (hidden), 126, 122s [O₂C₁₂H₈]. TGA: -3.3% from the beginning up to 270 °C (evaporation of solvents), then a continuous loss with maxima at 400 and 485 °C. Residue at 800 °C 54% (teor. AuCl gold content 26.4%). Further heating for ½ h at 800 °C caused an extra loss of 3.6%. DSC: $T_g = 176$ °C ($\Delta C_p = 0.23$ J/g K). Complexes **2a** and **2c** were similarly obtained in 88% yield. The T_g 's were not clearly observed.

2.4. Preparation of {[NP(O₂C₁₂H₈)]_{1-x}[NP(OC₆H₄PPh₂)₂(AuPF₆)_{0.5}]_x]_n (**3a**, **3b**)

To a solution of **1b** (0.25 g, 0.78 mmol, 0.38 mmol PPh₂) in THF (20 mL), [Au(PPh₃)₂]PF₆ (0.08 g, 0.09 mmol) was added and the mixture was refluxed for 15 h. The solvent was evaporated in vacuum and the residue was washed with diethyl ether (5 × 20 mL) to extract the triphenylphosphine (0.047 g, 0.18 mmol, 98% of the expected value). The residue was dried overnight in vacuum to give a white material with idealized formula {[NP(O₂C₁₂H₈)]_{0.75}[NP(OC₆H₄PPh₂)₂(AuPF₆)_{0.5}]_{0.25}]_n, (**3b**, $x = 0.25$). Yield 0.25 g (88%). Anal. Calc. for C₁₈H₁₃NP_{1.5}O₂(AuPF₆)_{0.12} (363.1): C, 59.5; H, 3.61; N, 3.86. Found: C, 57.6; H, 3.59; N, 3.88%. IR (in cm⁻¹; KBr pellets). Like **2** plus two new bands at 837s, 556m, cm⁻¹ (PF₆⁻). ³¹P{¹H}NMR (gel state in THF) δ (ppm): 42 very broad [PPh₂-Au], -4, -6, -24 broad [NP(O₂C₁₂H₈), and OC₆H₄PPh₂], -144 heptet [PF₆⁻]. Weak sharp signals at ca. 29 were due to the presence of some oxidized [N=P-OC₆H₄P(O)Ph₂] units. Those tend to be much intense with the permanence in solution. TGA: from R.T. to 800 °C a continuous loss (-62%) centred at 433 °C. Residue at 800 °C: 38%. Additional loss 30 min at 800 °C: 1.8%. DSC: $T_g = 159$ °C ($\Delta C_p = 0.14$ J/g K).

The compound **3a** was similarly prepared in a 2 grams scale and 98% yield from the corresponding phosphazene-phosphine (**1a**). Anal. Calc. for C_{15.6}H₁₁NP_{1.38}O₂(AuPF₆)_{0.08} (310.35): C, 60.3; H, 3.54; N, 4.50. Found C, 57.2; H, 3.00; N, 4.36%. TGA: from R.T. to 320 °C a loss of 3% (solvents retained). From 310 to 800 °C a continuous loss (-53%) centered at 464 °C. Residue at 800 °C: 44%. Additional loss 30 min at 800 °C: 4%. DSC: $T_g = 170$ °C ($\Delta C_p = 0.27$ J/g K).

2.5. Preparation of {[NP(O₂C₁₂H₈)]_{0.85}[NP(OC₆H₄PPh₂)₂(AuCl)_{0.5}(AuPF₆)_{0.5}]_{0.15}]_n (**4**)

To a solution of AuCl(THT) (0.039 g, 0.121 mmol) in THF (50 mL), solid **3a** (0.5 g, 1.61 mmol, 0.24 mmol of free PPh₂) and the mixture was stirred at room temperature for 2. The ¹H NMR spectrum of the liquid showed only the presence of un-coordinated THT. The volatiles were evaporated in vacuum for 1 h to give (**4**) as an off-white solid. Yield: 0.52 g (ca. 98%). Anal. Calc. for C_{15.6}H₁₁NP_{1.38}O₂(AuPF₆)_{0.08}(AuCl)_{0.08} (327.8): C, 57.1; H, 3.36; N, 4.27. Found: C, 54.7; H, 3.32; N, 4.04%. IR (in cm⁻¹; KBr pellets). Like **3** including the bands at 837s, 556m, cm⁻¹ (PF₆⁻). ³¹P NMR spectrum (gel-suspension in THF): 42 ppm (cationic -Ph₂P-Au⁺-PPh₂- sites), 29 ppm (PPh₂-AuCl), -10 ppm, -25 ppm (P=N units) and -145 ppm (PF₆⁻).

TGA: from R.T. to 273 °C a loss of 4% (solvents retained). From 273 to 800 °C a continuous loss (-49%) centered at 482 °C. Residue at 800 °C: 47%. Additional loss 30 min at 800 °C: 4%. DSC: $T_g = 176$ °C ($\Delta C_p = 0.26$ J/g K).

3. Results and discussion

The reaction of the polyphosphazenes {[NP(O₂C₁₂H₈)]_{1-x}[NP(OC₆H₄PPh₂)₂]_x]_n, $x = 0.15$ (**1a**), 0.25 (**1b**), 0.35 (**1c**) (O₂C₁₂H₈ = 2,2'-dioxybiphenyl), with [Au(THT)Cl] (THT = tetrahy-

drothiophene) (1 mmol of Au per mmol of available PPh₂ groups) in CH₂Cl₂ at room temperature led to the fast replacement of the labile THT ligand giving the polymers {[NP(O₂C₁₂H₈)]_{1-x}[NP(OC₆H₄PPh₂AuCl)₂]_x]_n (**2a–2c**), containing the AuCl group linked to the main chain by strong phosphine–Au(I) bonds (Scheme 1). The complex **2a** ($x=0.15$) had been previously reported [11].

All the data confirmed the composition of the new polymers. Most significantly, the ³¹P NMR spectra showed, together with the broad signals of the [NP(O₂C₁₂H₈)] units (near –5 ppm), and [NP(OC₆H₄PPh₂)] units (near –24 ppm), the signal of the PPh₂ groups at ca. 33 ppm (that was at –6.6 ppm in the spectra of the un-coordinated phosphine polymers). The ¹³C NMR (Section 2) also showed the coordination of the gold(I) chloride because the peak corresponding to the C₁ carbon of phenyl rings of the PPh₂ fragment appeared at 132 ppm, while in the free ligand **1** their chemical shift is 138 ppm. The presence of the AuCl in the coordinated polymers was also evidenced in the solid state IR spectra (KBr pellets) by a slight but noticeable increase of the intensity of the medium band near 1436 cm⁻¹ relative to that at 1478 cm⁻¹, as compared with the found in the spectra of the polymeric free ligands **1**. The effect can probably be attributed to the influence of the gold atom on the C=C vibrations of the Ph rings of the PPh₂ groups.

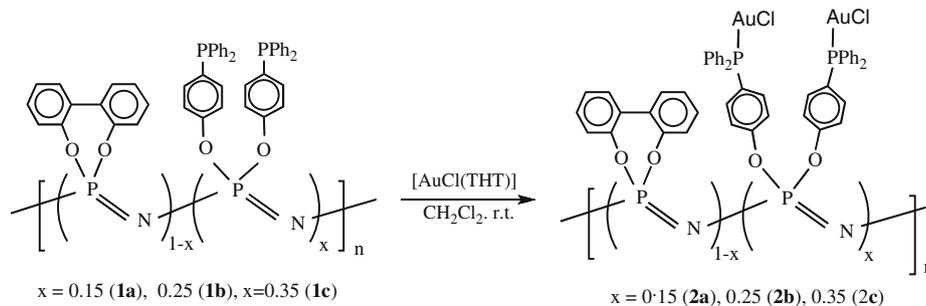
Although the AuCl-supported polymers **2** were rather thermally stable a soft heating at 70 °C under vacuum may cause the formation of small gold nanoclusters, as evidenced by a pink to violet coloration, that occasionally may be unnoticed until the compound is dissolved in chloroform. We observed that the presence of the metallic colloidal gold did not alter significantly the relative inten-

sities of the ³¹P NMR signals and that could be eliminated by stirring a dichloromethane solution of the complex with mercury. It was also noticed that, as many other Au(I) species, the compound is light sensitive, specially in solution, turning pink to violet after some time.

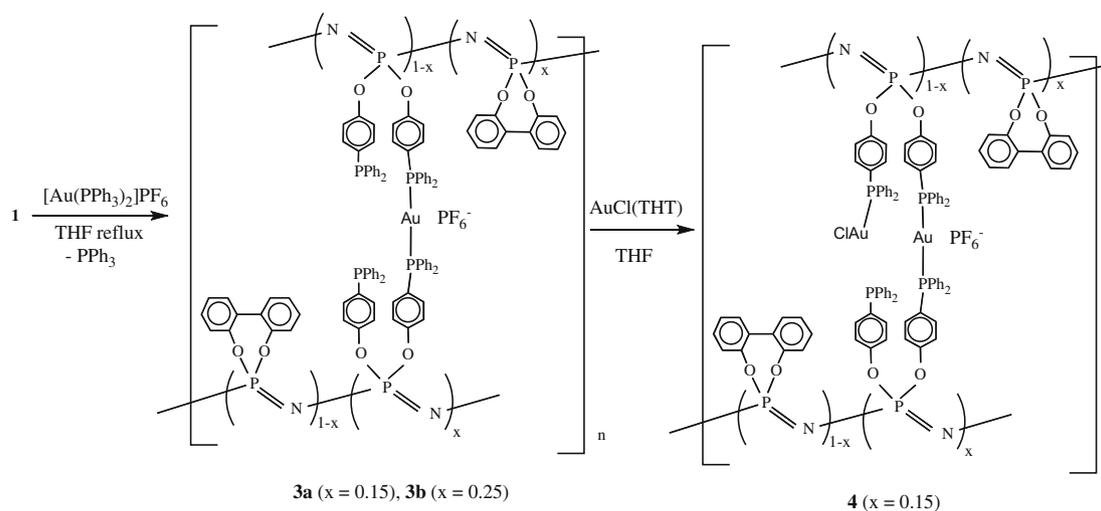
The DSC curves for the polymeric complexes, scanned from 0 °C to 200 °C did not show a distinct heat capacity jump corresponding to a glass transition except for **2b**. As expected, the *T_g* value (176 °C) was higher than those observed for the corresponding un-coordinated phosphine polymer (111 °C).

The use of substoichiometric amounts of [Au(THT)Cl] with respect the PPh₂ contents gave the expected partially loaded products in which both phosphine coordinated AuCl and free PPh₂ sites were present. Stirring a dichloromethane solution of those polymers for 15 min (15 h gave identical results) at room temperature in the presence of KPF₆, lead to the precipitation of insoluble white materials the IR spectra of which showed the strong absorption at 837 cm⁻¹ and the weak to medium band at 556 cm⁻¹, corresponding to the PF₆⁻ anion. This proves the formation of cationic sites –Ph₂P–Au⁺–PPh₂– giving cross-linked polymeric materials. However, the yields of the products finally isolated were rather low (30–50%) and the possibility of incomplete substitution leaving unreacted AuCl sites could not be ruled out. It is very likely, that the replacement of the Cl ligand at the Au(I) centres, that might be favoured by the macroligand effect of the polymeric matrix, might be handicapped by the early precipitation of the product.

Better defined cross-linked polymers with the same cationic –Ph₂P–Au⁺–PPh₂– connections between the chains could be obtained by the direct reaction of **1**, with the gold complex



Scheme 1.



Scheme 2.

[Au(PPh₃)₂]PF₆ (1 mmol per 4 mmol of available PPh₂) in refluxing THF (Scheme 2). This process led to the elimination of the PPh₃ ligands and the formation of insoluble materials that were characterized (Section 2) as the polymeric solid matrices of composition $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(OC_6H_4PPh_2)_2(AuPF_6)_{0.5}]_x\}_n$, $x = 0.15$, (**3a**), 0.25 (**3b**). The idealized structure proposed for **3** (Scheme 2), is based on the regular distribution of the two phosphazenic units present in the starting copolymeric chains of **1**. It has been previously demonstrated that the polymers of this type, resulting from a macromolecular step-wise substitution from $[NPCL_2]_n$, behave as perfectly randomized copolymers and the average chain can be considered as perfectly alternating [13]. As a result, in the average, the cross-linking sites are regularly separated by *circa* 9 units in an open tridimensional matrix that can be included in the coordination polymers category of the general hybrid inorganic–organic framework materials [8].

The IR spectrum confirmed the presence of the PF₆⁻ ion and, even though the ³¹P NMR spectra (measured in a THF saturated gel-suspension state) were not well resolved, the presence of a broad weak signal at ca. 42 ppm, evidenced the cationic –Ph₂P–Au⁺–PPh₂– sites. The other less broad signals observed were the expected ones for the phosphorus of the NP(O₂C₁₂H₈), NP–OC₆H₄– and PPh₂ moieties (–4, –24 and –6 ppm, respectively) and the [PF₆⁻] anion (–144 heptet). It was also noticed that, on standing in solution (but not in the solid state) a sharp signal at 29 ppm appeared due to the formation of the oxidized [N=P–OC₆H₄P(O)Ph₂] units, showing that **3** is rather sensitive to oxygen.

The DSC of **3** exhibited well defined glass transitions at 170 °C (**3a**) and 159 °C (**3b**), showing the expected increase with the fraction of the [NP(O₂C₁₂H₈)] groups ($1 - x = 0.85$ and 0.75, respectively). Also consistently, the T_g's of the solid matrices were higher than those of the starting linear polymeric phosphines (**1a**) (126 °C) and (**1b**) (111 °C) showing the effects of the cationic cross-linking sites.

The reaction leading to **3** is based on the fast free/coordinated phosphine interchange process that the cationic [Au(PR₃)₂]⁺ complexes undergo in the presence of excess PR₃ [14], that, in the case of the polymeric phosphine ligands **2** might be directed to **3** by the precipitation of these insoluble cross-linked materials.

The insoluble polymeric matrix (**3a**), that has free PPh₂ groups available (functionalization degree FD = 0.48 mmol PPh₂/gram), was used to coordinate AuCl groups. Thus, when solid **3a** was added to a solution of [AuCl(THT)] in THF the ¹H NMR spectrum of the liquid revealed the disappearance of the coordinated THT and the presence of only free THT molecules in solution. The new insoluble solid obtained had analytical and IR data consistent with the idealized formula $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2(AuCl)_{0.5}(AuPF_6)_{0.5}]_{0.15}\}_n$ (**4**).

Significantly, the IR spectrum showed that a clear increase of the intensity of the band at 1428 cm⁻¹ relative to that at 1478 cm⁻¹ occurred when **3** was transformed in **4**, paralleling the effect of the transformation of **1** in **2** mentioned above. Also consistently, the ³¹P NMR spectrum (gel-suspension in THF) showed the peaks at 42 ppm (cationic –Ph₂P–Au⁺–PPh₂– sites), 29 ppm (PPh₂–AuCl), –10 ppm and –25 ppm (P=N units) and –145 ppm (PF₆⁻). However, the possibility that some PPh₂ units were oxidized during the process cannot be completely ruled out.

The thermal stability of the new polymeric materials was studied by TGA at a heating rate of 10 °C min⁻¹. A part from a small occasional first loss (2–4%) centred near 250 °C, corresponding to the evaporation of solvents retained, a continuous loss was

observed in all the cases, centred in the region of 450 °C. The final residues at 800 °C (38–47%), that were almost stabilized (further heating for 30 min resulted in small additional losses of ca. 2–4%) changed very slightly with the gold contents. As for many other polyphosphazenes, the main loss is due to the volatilization of organic compounds during the decomposition [15], and, considering earlier results [11], the final residues should contain all the gold as nanoparticles. The high char residues left at 800 °C may also account for the relative low carbon found in some of the experimental analysis, which is not unusual with phosphazene materials.

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