



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 Ru(II)(η^6 -p-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 HO-C₆H₄-PPh₂ 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: ³¹P NMR (CDCl₃, 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 (PPh₂), with the expected intensity ratios. The spectra also showed very weak bands at 28.7 (Ph₂P=O sites) indicating that the fraction of oxidized PPh₂ 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 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-

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