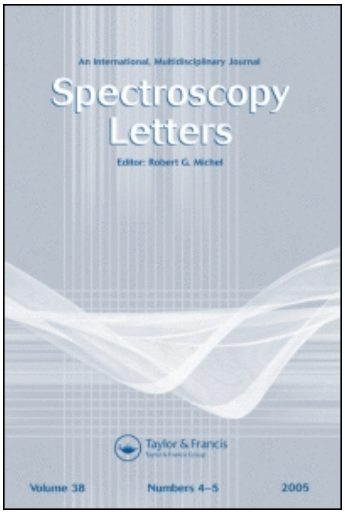

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Precious Metals: A Convenient Recycle Procedure for Laboratory Rejects with Spectroscopic Characterisation of the Products

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PRECIOUS METALS : A CONVENIENT RECYCLE PROCEDURE FOR LABORATORY REJECTS WITH SPECTROSCOPIC CHARACTERISATION OF THE PRODUCTS

Key-words: coordination chemistry, inorganic synthesis, organometallic compounds, transition metals

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ABSTRACT

The recycling process of metals is also a good opportunity to get in touch with the economic and environmental issues involving the routine in the chemistry laboratory. This strategy has been introduced regularly in the laboratory in order to reduce the waste material storage. The recovery process focusing on the precious metals, gold and palladium, gives as a result the phosphine derivatives of these metals, compounds that are extremely useful in

different areas: catalysis, organometallic syntheses, and in medicine (the gold derivatives are used in the treatment of arthritis and neoplasias). $AuPPh_3Cl$ and $Pd(PPh_3)_2Cl_2$ were prepared from rejects stored in the laboratory using a new synthetic route and were characterised by ^{31}P $\{^1H\}$, UV/visible spectra and elemental analysis.

INTRODUCTION

Environmental carelessness concerning waste material deposition can be substantially reduced through routine recycling procedures. Metal recovery preserves limited mineral sources besides saving the energy spent in the extraction of primary resources. The recovery process for the precious metals, gold and palladium, illustrates physical and chemical procedures, in both, implicit application and technological skills.

Otherwise, this recycling process gives, as a result, the isolation of phosphine derivatives of gold that are compounds extremely useful in different areas of Chemistry, e. g., use as precursors in catalysts syntheses *(1)* its application in medicine in the treatment of rheumatoid arthritis, and *(2)* as well as in the treatment of neoplasias as a cytostatic drug (Et_3PAuCl, Me_3PAuCl, PPh_3AuCl) *(3)*.

The compound $AuPPh_3Cl$ and its derivatives are also used as precursors in the synthesis of gold clusters *(4)*. The addition of fragments $[AuPPh_3]^+$ is an

important step in the synthesis of some heterometallic clusters; $AuPPh_3Cl$ and $AuPPh_3NO_3$ are commonly used. These compounds are obtained according to very well established procedures found in the literature *(5,6)*. Their utilisation as precursors is based on the isolobal analogy principle between H^+ and $[AuPPh_3]^+$. Ex : reaction **I***(7)*

$$[HRh(CO)(PPh_3)_2] + AuPPh_3NO_3 \rightarrow [Rh(H)(CO)(PPh_3)_2(AuPPh_3)]^+ \quad \textbf{(I)}$$

In this paper a new synthetic route is presented established for the recovery of gold and palladium as $AuPPh_3Cl$ and $Pd(PPh_3)_2Cl_2$ from the rejects stored in the laboratory. This route is a derivative of the classic method found in the literature *(8)*.

MATERIALS AND METHODS

Triphenylphosphine was purchased from Sigma-Aldrich Chemical Company and ferric sulphate from Synth. The ethanol, methanol, dichloromethane, and acetone were from Merck Chemical Company (analytical grade) and diethyl ether was from Carlo Erba Reagenti.

The laboratory residue is rich gold and palladium and also triphenylphosphine, partially dissolved in a mixture of different solvents (acetone, methanol, ethanol, dichloromethane, diethyl ether) . This mixture is filtered to separate the solid phase, constituted of insoluble by-products of

synthesised compounds (clusters) and other derivatives eventually formed during the storage period.

The filtrate obtained, with intensive yellow colour is distilled. As a consequence, a reasonable amount of $AuPPh_3Cl$ precipitates in the flask (transparent needle crystals).The content of the flask is filtered off under low pressure, washed with diethyl ether and dried.

The evaporation of the solvents obtained from distillation is done under temperature control. The volatile fraction (diethyl ether and dichloromethane) is discarded and the other fraction constituted of higher boiling point solvents, (mostly ethanol and acetone) is stored for further use as cleaning solvents in the laboratory.

The first compound obtained, $AuPPh_3Cl$, is dissolved in CH_2Cl_2, filtrated through diatomaceous earth and crystallised in diethyl ether. After one hour is filtered off, washed with diethyl ether and dried. The reject of this procedure (the filtrate) is collected in a flask and stored regarding further recovering process where the palladium is obtained as $Pd(PPh_3)_2Cl_2$, and gold as a metal. After the residue treatment *(8),* gold is obtained as metallic gold according to reaction **II** using ferric sulphate solution.

$$H[AuCl_4] + 3FeSO_4 \rightarrow Au_{(s)} + Fe_2(SO_4)_3 + FeCl_3 + HCl \quad \textbf{(II)}$$

The gold is collected as a fine powder using a centrifuge and separated from solution. The solution is submitted to a drying process using a heating

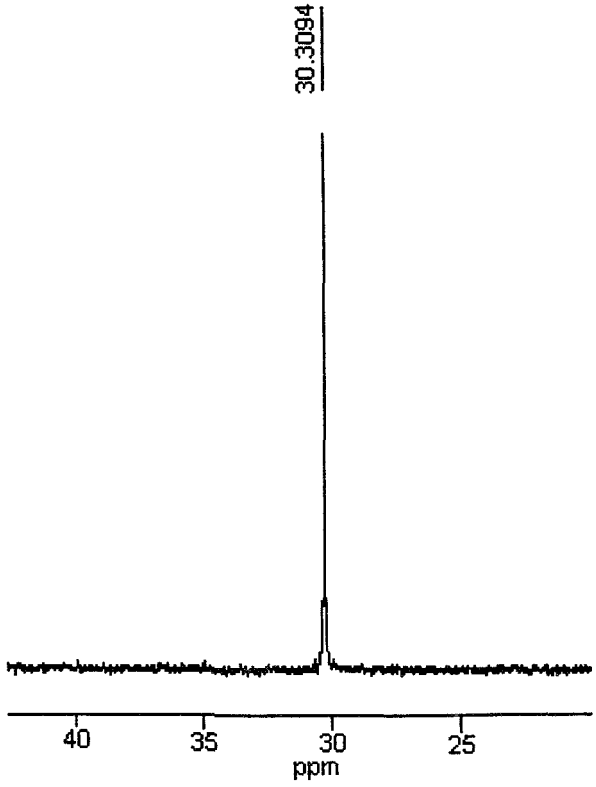

Figure 1: 31P NMR{^{1}H} of $AuPPh_3Cl$

plate. Initially the precipitation of ferric salts occurs which are filtered off carefully. The remaining solution after drying gives the metallic palladium as a fine powder that is weighed and dissolved by heating in aqua regia (approximately 20mL per each gram of metal). The solution is then evaporated near dryness, then HCl concentrated (20mL, 3 times) is added to form H_2PdCl_4. The resulting solution is filtered through diatomaceous earth and stored until

cold. This solution is then added to an emulsion of triphenylphosphine and ethanol and stirred with a magnetic bar. The mixture changes to a yellow colour immediately. After 1 hour stirring, the compound is filtered off, washed with ethanol and diethyl ether and dried.

The proportion used for H_2PdCl_4 and PPh_3 is 1:2 (reactions **III** and **IV**)

$$Pd^{2+} + 4HCl \rightarrow H_2PdCl_4 \textbf{ (III)}$$

$$H_2PdCl_4 + 2PPh_3 \rightarrow Pd(PPh_3)_2Cl_2 + 2Cl^- + 2H^+ \textbf{ (IV)}$$

Figure 2: 31P NMR{^{1}H} of $[Pd(PPh_3)_2Cl_2]$

Table 1: Elemental analysis results of four fractions of the compound $Au(PPh_3)Cl$

Results	% C	% H	% Cl
Theoretical	43.68	3.03	7.18
Fraction 1	43.60	3.03	7.18
Fraction 2	43.63	3.02	7.17
Fraction 3	43.72	3.06	7.15
Fraction 4	43.58	2.99	7.18

Table 2: Elemental analysis results of the compound $[Pd(PPh_3)_2Cl_2]$

Results	% C	% H	% Cl
Theoretical	61.59	4.32	10.10
Experimental	61.61	4.31	10.08

RESULTS

The compounds were characterised by elemental analysis (Perkin-Elmer Elemental Analyzer 2400CHN), NMR $^{31}P\{^1H\}$(Brucker 200MHz), and UV-visible spectroscopy (Hitachi U-300 spectrophotometer) .

The compound $AuPPh_3Cl$ was obtained in four different fractions and each one was characterised through elemental analysis. The results of elemental analysis are shown in Tables 1 and 2.

The NMR ^{31}P {H} spectra of $AuPPh_3Cl$ (in CH_2CL_2, using H_3PO_4 as an external reference at 25°C) shows a single peak at δ 30.3 *(9)* and the spectrum of $[Pd(PPh_3)_2Cl_2]$ using the same conditions showed the characteristic peak of this compound at δ 23.2 (Fig. 1and 2).

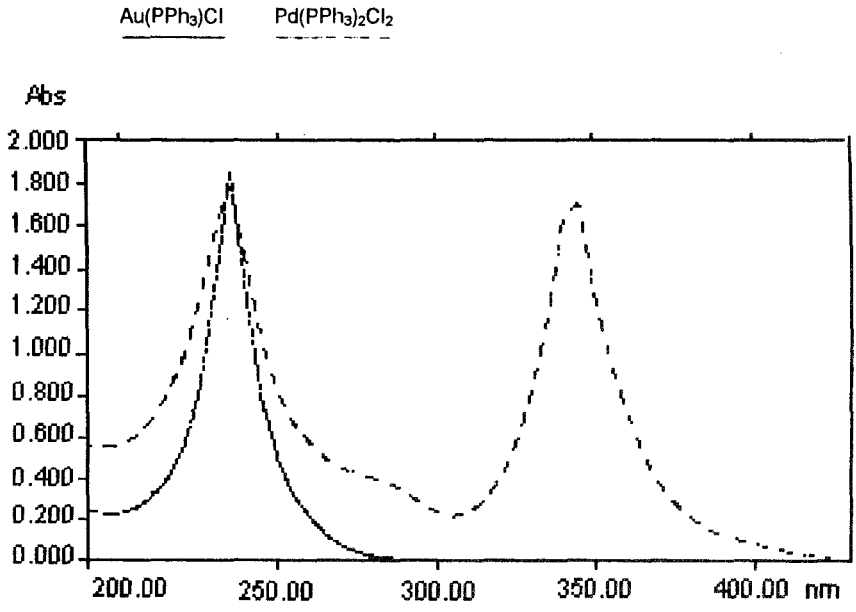

FIG. 3: **UV-visible spectra of the compounds**

The UV/visible spectra of the compounds (Fig. 3) showed bands in the region of 254nm assigned to the PPh_3 aromatic groups, present in both compounds *(10)*.

CONCLUSION

10L of residue has been treated using this route. 12.5g of pure $AuPPh_3Cl$ has been obtained corresponding to 4.9g of metallic gold that were spared. The residue treated using the method found in the literature *(8)* gave 4.98g of pure gold and 10.54g of pure $Pd(PPh_3)_2Cl_2$.

Through this experiment two goals were achieved; first, the pollution can be avoided by recycling chemicals, second, some economic measures are adopted when new synthetic routes are established in order to reduce the hazardous waste material in the laboratory.

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