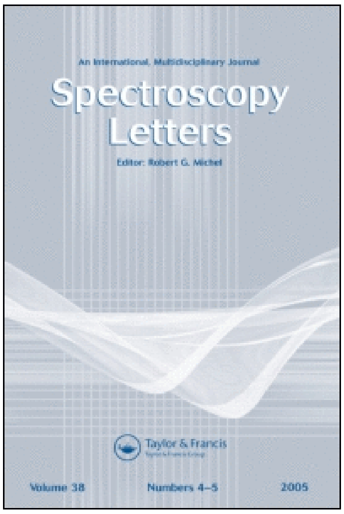

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A New Synthesis, Properties and Spectroscopic Characterization of $[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2$

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COMMUNICATION

A NEW SYNTHESIS, PROPERTIES AND SPECTROSCOPIC CHARACTERIZATION OF $[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2$

Key words: cluster, phosphine, gold compounds, palladium compounds, heterometallic compounds.

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ABSTRACT

$[(PPh_3)Pd(Au(PPH_3)_6](NO_3)_2$ is synthetised from $[PdCl_2(PPh_3)_2$ and $AuPPh_3NO_3$. This alternative method is very convenient compared to others performed previously for the synthesis of this cluster.

INTODUCTION

The synthesis of cluster compounds of late transition metals such as gold, palladium and platinum is very rich and

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varied. The research involving these elements is concerned with synthesis and reactivity of ligand stabilized cluster compounds that could bridge the gap between the molecular and solid state levels [1].

The synthesis that is reported in this paper appears to be quite simple when compared to previous ways used to prepare this 16 electron cluster that, according to electron count, is predicted to be very reactive [2].

The 16 electron clusters undergo electrophilic reactions as well as nucleophilic addition reaction yielding 16 and 18 electron cluster respectively. Oxidative addition reactions giving 18 electron clusters are also observed. Another important aspect about mixed-metal-gold cluster is their application to catalysis.

Catalytic properties of Pd-Au and Pt-Au cluster compounds have been studied under homogeneous and heterogeneous conditions in the solution phase at room temperature and atmosferic pressure. The best results have been achieved with the largest clusters that have the highest Au/Pt ratio, such as $[Pt(AuPPh_3)_8](NO_3)_2$ and $[Pt(PPh_3)_8CuCl](NO_3)_2$ [3].

Besides these chemical reactivities, a number of 16 electron cluster compounds have shown interesting electrochemical behaviour. Ex.: $[Pd(PPh_3)_8]^{2+}$ could be reduced in two consecutive one electron steps, yielding 18 electron clusters [4].

The electron count is also related to geometry and 18 electron clusters have spherical geometries called spheroidal and 16 electron clusters have toroidal geometries[5,6,7].

$[PPh_3]Pd(AuPPh_3)_6]^{2+}$ as the isoelectronic and isostructural $[(PPh_3)Pt(AuPPh_3)_6]^{2+}$ [8] is a promising complex for reactivity studies and, according to the way introduced here, can be synthetised under mild conditions with no need of any special atmosfere most of the time, since this compound and also the starting material used, are air stable.

$[(PPh_3)Pd(AuPPh_3)_6]^{2+}$ was first isolated by Ito et al.[9] as a by product, through the reaction of a CH_2Cl_2 solution of $Pd(PPh_3)_4$ and $AuPPh_3NO_3$, using inert atmosfere. The minor product of this reaction, was identified as $[(PPh_3)Pd(AuPPh_3)_6(NO_3)_2$ and was separated by HPLC , from the major product, $[Pd(AuPPh_3)_8(NO_3)_2$, using an 85% ethanol/% 15 0.125 M NH_4NO_3 isocratic elution.

This cluster was later prepared by Ito et al.[4] with much better yield and not requiring the use of HPLC. This procedure was until now the one of choice: $[(PPh_3)Pd(AuPPh_3)_6]^{2+}$ was prepared by dissolving $Pd(acetate)_2$ and PPh_3AuNO_3 in CH_2Cl_2 and magnetically stirring the solution under 1 atm of H_2, during 17 hours. After this period of time and using Schlenk technics, the product was isolated in a good yield.

EXPERIMENTAL:

Solvents were distilled before use. Starting materials: $PdCl_2$ P.A., NaCl P.A. and Triphenylphosphine P.A. were from Aldrich.

IR was recorded on a Perkin Elmer-FTIR and ^{31}P NMR was recorded on a Brucker 200 Mhz instrument.

$[PdCl_2(PPh_3)_2]$: 0.235g (0.33 mmol, obtained following Massabni et al method[10], from NaCl, $PdCl_2$ and triphenylphosphine) was placed in a wide mouth 100 ml Schlenk flask with $AuPPh_3NO_3$; 0.843g (1.6mmol) and a magnetic stir bar. Dichloromethane was added (40ml) to the reaction vessel and a dark red coloured homogeneous solution resulted. A methanol solution of $NaBH_4$ (30ml, 0.60g, 1.6mmol) was added to the magnetically stirred reaction mixture. The dark brown coloured solution was stirred at room temperature during 10 minutes, then destilled water (0.10ml) was added, to quench the reaction. The solvents were removed under vacuum. Methanol was added to the flask and the crude mixture filtered through diatomaceous earth to remove the the precipitate. The dark brown coloured filtrate was reduced to dryness and acetone (20ml) was added to dissolve the dark purple solid, then the dark brown solution was filtered again through diatomaceous earth. The dark brown filtrate was, once more, evaporate to dryness, then 5ml of methanol was added to dissolve the solid that remained and 40ml of diethylether was added by liquid diffusion to obtain a brown, microcristaline, solid. The

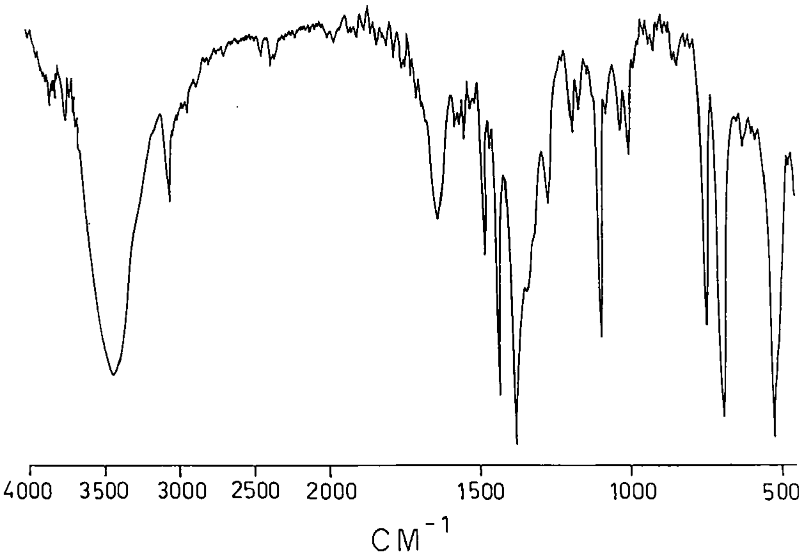

FIGURE 1 - Infra-red spectrum of $[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2$

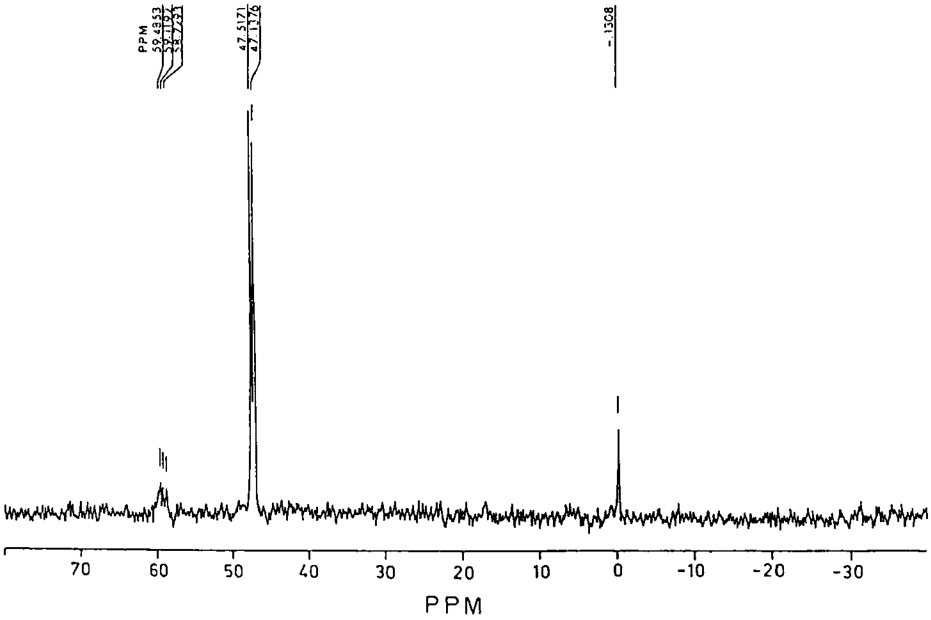

FIGURE 2 - ^{31}P NMR of $[(PPh_3)Pd(AuPPh_3)_6](NO_3)_2$

solid was isolated on a fritted filter, washed with diethylether and dried under vacuum. The yield was 69% based on gold.

IR spectrum showed the presence of the counterion $[(NO_3)]$ υ = 1343cm^{-1} (FIGURE 1).

^{31}P NMR (CD_2Cl_2) (FIGURE 2)

δ = 59.8 ppm (septet 3 Jp-p = 31 Hz int = 1)

δ = 47.5 ppm (d 3 Jp-p = 31 Hz int = 6).

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