

First Organometallic Compounds with Pt–Au Bonds

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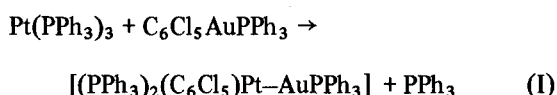
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The synthesis of complexes containing heteronuclear metal–metal bonds without bridging groups has stimulated the interest in the bonding and stereochemistry of these molecules. Their preparation is essentially based on metathesis reactions between a metal carbonyl and a metal halide [1]. Another convenient method to prepare complexes with a metal–metal bond between transition elements is the reaction of a metal compound in a low oxidation state with a complex or halide of the other metal. Thus, addition of HgCl_2 or ClAuPPh_3 to $\text{Pt(PPh}_3)_3$ gives $[(\text{PPh}_3)_2\text{ClPt–HgCl}]$ or $[(\text{PPh}_3)_2\text{ClPt–AuPPh}_3]$, respectively; these were the first bimetallic compounds with Pt–Hg and Pt–Au bonds [2]. Subsequently, organometallic compounds with Pt–Hg bonds were prepared according to this method [3]. The synthesis of the first organometallic compounds with Pt–Au bonds using the same method, is described in this paper.

Results and Discussion

The addition of $\text{C}_6\text{Cl}_5\text{AuPPh}_3$ to a solution of $\text{Pt(PPh}_3)_3$ in benzene leads to (I) according to:

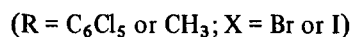
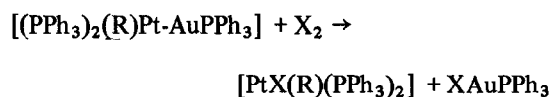


(I) is a white crystalline solid, stable both in the air and in solution. It is soluble in most organic solvents but insoluble in ether and hexane. Orange $[(\text{PPh}_3)_2(\text{CH}_3)\text{Pt–AuPPh}_3]$ (II) is similarly obtained from $\text{CH}_3\text{AuPPh}_3$ and $\text{Pt(PPh}_3)_3$.

The action of heat, Br_2 , I_2 and 1,2- $\text{Br}_2\text{C}_2\text{H}_4$ on the solutions of (I) and (II) was examined in order to study the stability of the Pt–Au bonds. (I) is recovered after refluxing in xylene for 2 h; on the contrary, (II) decomposes under the same conditions. These results agree with an increase in the stability of the Pt–Au bond on increasing the size and electro-negativity of the organic group coordinated to platinum, similarly to that observed in compounds of the type $[(\text{PPh}_3)_2(\text{R})\text{Pt–Hg(R)}]$ where an immediate demercuration occurs for $\text{R} = \text{Ph}$ [4], and isolation

of the bimetallic species is not possible. On the other hand when $\text{R} = \text{C}_6\text{Cl}_5$ the compound is stable and is not decomposed by refluxing in xylene [5].

The addition of Br_2 and I_2 to benzene solutions of (I) and (II) at room temperature results in the cleavage of the Pt–Au bond and the corresponding halogen derivatives are obtained,

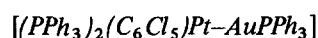


On the other hand, the action of an excess of 1,2- $\text{Br}_2\text{C}_2\text{H}_4$ on benzene solutions of (I) and (II) cleaves the Pt–Au bond only in the latter; this fact agrees with the greater stability of the Pt–Au bond in the presence of a pentachlorophenyl group.

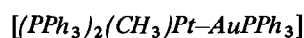
The study of the action of PET_3 , PPhEt_2 and PPh_2Et on the chloroform solutions of (I) shows that replacement of only one triphenylphosphine by a less bulky phosphine occurs, according to the IR and PMR spectra, and elemental analyses of the products obtained. The new compounds should have the formulation $[(\text{PPh}_3)_2(\text{C}_6\text{Cl}_5)\text{Pt–AuPR}_3]$ since we have observed that ClAuPPh_3 easily undergoes replacement of PPh_3 by the phosphines indicated above, and that the compound $[\text{PtCl}(\text{C}_6\text{Cl}_5)(\text{PPh}_3)_2]$ does not undergo such replacements.

Experimental

$\text{Pt(PPh}_3)_3$ and $\text{C}_6\text{Cl}_5\text{AuPPh}_3$ were prepared according to literature methods [6, 7]. $\text{CH}_3\text{AuPPh}_3$ was obtained by treating ClAuPPh_3 with CH_3MgI in THF.



1.0 g of $\text{Pt(PPh}_3)_3$ (1.0 mmol) and 0.7 g of $\text{C}_6\text{Cl}_5\text{AuPPh}_3$ (1.0 mmol) in 20 ml of benzene were stirred under nitrogen at refluxing temperature for 30 min. The resulting solution was evaporated to dryness and the residue washed twice with 20 ml of warm hexane, and recrystallized from dichloromethane–methanol to give a white solid. Yield 65%. M.p.: 275–276 °C (darkening from 200 °C). C_6Cl_5 IR bands: 1320, 1310, 1280, 1265 and 1220 cm^{-1} . Anal. Calcd. for $\text{C}_{60}\text{H}_{45}\text{Cl}_5\text{P}_3\text{AuPt}$: C, 50.4; H, 3.1; Cl, 12.4. Found: C, 50.1; H, 3.2; Cl, 12.3%.



1.0 g of $\text{Pt(PPh}_3)_3$ (1.0 mmol) and 0.48 g of $\text{CH}_3\text{AuPPh}_3$ (1.0 mmol) in 20 ml of benzene were stirred under nitrogen at 50 °C for 30 min. The rest

of the procedure is as above. An orange solid was obtained with 60% yield. M.p.: 204 °C (darkening from 170 °C). *Anal.* Calcd. for $C_{55}H_{48}P_3AuPt$: C, 54.2; H, 4.0. Found: C, 53.5; H, 4.0%. CH_3 IR bands: 2920 and 2860 cm^{-1} . Proton NMR integration, Ph/ CH_3 = 8.82/1.00.

Displacement of phosphines

An excess of the appropriate phosphine (PEt_3 , $PPhEt_2$ or PPh_2Et) was added to a solution of 0.2 g of $[(PPh_3)_2C_6Cl_5]Pt-AuPPh_3$ in 30 ml of chloroform. The solution was stirred under nitrogen at refluxing temperature for 3 h and evaporated to dryness. The rest of the procedure is as above. The yields were almost quantitative. *Anal.* Calcd. for $C_{48}H_{45}Cl_5P_3AuPt$: C, 44.9; H, 3.5; Cl, 13.8. Found: C, 44.7; H, 3.5; Cl, 13.7%. M.p.: 225 °C (d). Proton NMR integration, Ph/Et = 5.87/3.00. *Anal.* Calcd. for $C_{52}H_{45}Cl_5P_3AuPt$: C, 46.9; H, 3.4; Cl, 13.3. Found: C, 46.7; H, 3.8; Cl, 13.2%. M.p.: 228 °C (d). Proton NMR integration, Ph/Et = 6.76/2.00. *Anal.* Calcd. for $C_{54}H_{45}Cl_5P_3AuPt$: C, 48.7; H, 3.3; Cl, 12.8.

Found: C, 48.5; H, 3.3; Cl, 12.9%. M.p.: 231 °C (d). Proton NMR integration: Ph/Et = 7.85/1.00.

C and H determinations were carried out at the Institute of Bio-Organic Chemistry of Catalunya. Halogens were determined by Schöniger's method. Infrared spectra were recorded on a Beckman IR-20 A spectrophotometer. PMR spectra were obtained with a Perkin Elmer R-12 A spectrometer using $CDCl_3$ as solvent and TMS as reference.

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