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Preparation of $[(PPh_3)_2ClPt(\mu\text{-}3,4,5,6\text{-}C_6Cl_4)\text{-}AuPPh_3]$

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The first organometallic compounds with Pt–Au bonds, $[(PPh_3)_2XPt\text{–}AuPPh_3]$ (X = Cl, Br), were obtained by Nyholm [1] by reacting $XAuPPh_3$ with $Pt(PPh_3)_3$ in warm benzene.

Using the same method we have recently reported analogous organometallic compounds with X = C_6Cl_5 or CH_3 [2].

It was not possible to obtain crystals of $[(PPh_3)_2(CH_3)Pt\text{–}AuPPh_3]$, but X-ray structure determination of the compound with X = C_6Cl_5 [3] has revealed that no direct bond exists between the platinum and gold atoms. These atoms are bonded through a bridging tetrachlorophenyl group (Pt–Au distance, 3.26 Å). The Pt atom has a planar, four-coordination, with the triphenylphosphine groups in the *trans* position. The Au atom exhibits a distorted linear coordination due to the steric effects between the phenyl groups (P–Au–C angle, 173.2°). The tetrachorophenyl group is planar, within experimental error.

TABLE I. Selected Interatomic Distances (A).

Au–C	2.062(9)
Au–P	2.295(3)
Pt–C	2.013(8)
Pt–Cl	2.406(2)
Pt–P(4)	2.330(3)
Pt–P(42)	2.310(3)

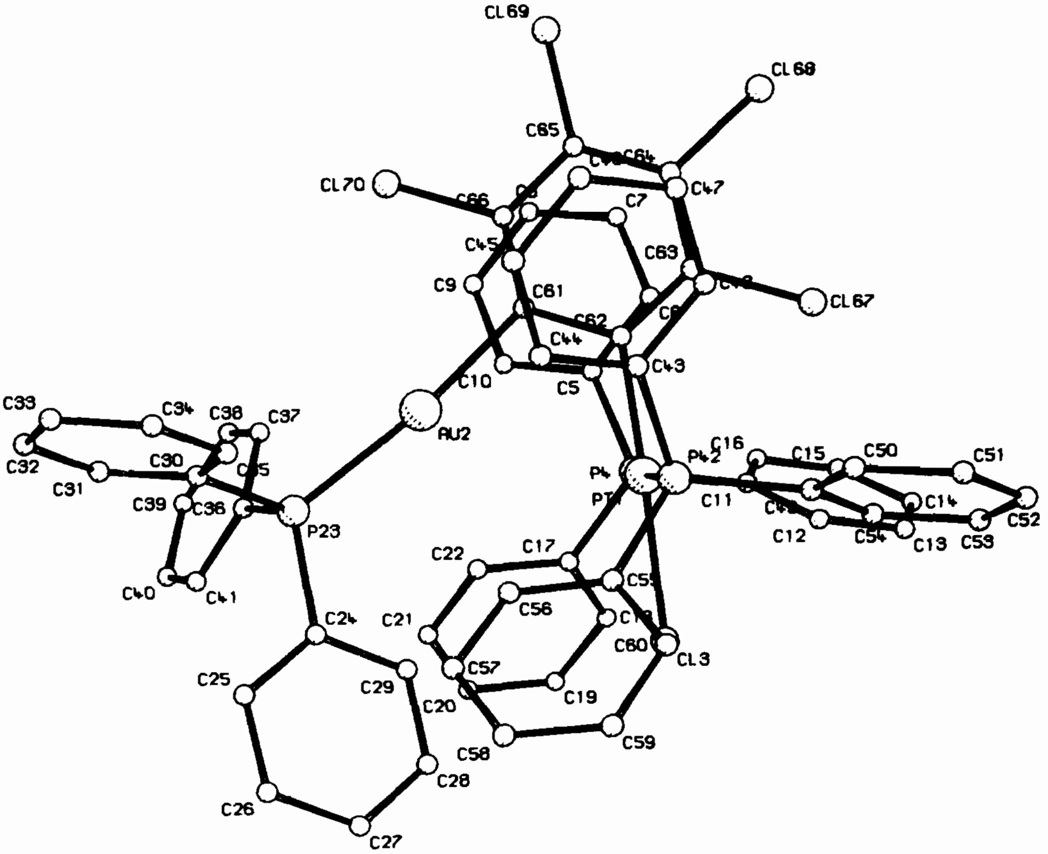

Fig. 1. X-ray structure of the title compound.

Formation of [$(PPh_3)_2ClPt(\mu$-3,4,5,6-$C_6Cl_4)AuPPh_3$]* from $C_6Cl_5AuPPh_3$ and $Pt(PPh_3)_3$ must proceed through a mechanism involving oxidative addition of $C_6Cl_5AuPPh_3$ to $Pt(PPh_3)_3$. This reaction is unusual since the oxidative additions of aryl chlorides to platinum(0) complexes are not common. Thus, $Pt(PPh_3)_4$ reacts easily with iodobenzene in benzene solution at 50–60 °C, giving [$PtI(C_6H_5)(PPh_3)_2$] but not bromobenzene or chlorobenzene, even at higher temperatures [4]. On the other hand we have observed that hexachlorobenzene does not react with $Pt(PPh_3)_3$.

Thus, it may be concluded that during the formation of [$(PPh_3)_2ClPt(\mu$-3,4,5,6-$C_6Cl_4)AuPPh_3$] the $AuPPh_3$ group activates an *ortho* C–Cl pentachlorophenyl bond, thereby facilitating the addition on $Pt(PPh_3)_3$.

We are currently working with other organogold compounds in order to study the factors which govern this reaction.

References

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*Selected interatomic distances are listed in Table I.